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GCE A/L CHEMISTRY A+

ENGLISH MEDIUM

FAST TRACK
WORK PACKAGE

- CONCEPT FOCUSED
- EXAM ORIENTED
- PRACTICE DRIVEN

Prepared under the guidance of
Dr. Muthunu Akurugodagama

GCE A/L Chemistry

English Medium · Fast Track Work Package · A+

Prepared under the guidance of Dr. Muthunu Akurugodagama
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Open the interactive edition

Start here

How to use this publication

Choose a syllabus unit from Short notes, read its linked NIE Resource Book pages, and attempt the model questions before revealing the answers. Practise past-paper MCQs, structured essays and essays using the year selector. Mark units as revised and follow the 12-week A+ planner; progress is saved on this device.

Know the paper

Exam blueprint

Taken from the paper covers and the "Distribution of Marks" page of the marking schemes (2019–2025).

Paper I · 2 hours

- 50 multiple-choice questions, all compulsory, 1 mark each (1 × 50 = 50).
- **Q1–30**: choose the single best answer from five options.
- **Q31–40**: decide which of four responses (a)–(d) are correct and mark a code.
- **Q41–50**: judge a pair of statements and mark a code.
- A periodic table and constants (R, N_A, h, c) are given. **Calculators are not allowed.**

Paper II · 3 hours + 10 minutes reading

- **Part A**: four structured questions (Q1–4), all compulsory, answered on the paper, 100 marks each.
- **Part B**: answer two of Q5–7, 150 marks each.
- **Part C**: answer two of Q8–10, 150 marks each.
- 400 + 300 + 300 = 1000 marks, reported as a Paper II mark out of 100.
- Use the 10 minutes of reading time to choose your Part B and C questions.

Response codes for Q31–40

Code	Meaning
(1)	only (a) and (b) are correct
(2)	only (b) and (c) are correct
(3)	only (c) and (d) are correct
(4)	only (d) and (a) are correct
(5)	any other number or combination is correct

Statement-pair codes for Q41–50

Code	Statement 1	Statement 2
(1)	True	True, and correctly explains statement 1
(2)	True	True, but does not explain statement 1
(3)	True	False
(4)	False	True
(5)	False	False

Analysis of 2019–2026 papers

Where the marks are

Every MCQ in the seven current-syllabus papers we have in English (2019, 2020, 2021(22), 2022(23), 2024, 2025, 2026) was assigned to the one unit it mainly tests. Paper II questions were mapped to all the units they draw on. The 2023(24) Paper I is not in the collection.

350

MCQs analysed

58

Equilibrium MCQs

138

Physical Chemistry MCQs

72

Organic Chemistry MCQs

36

Industry & Environment MCQs

MCQs per unit, per paper

Unit	2019	2020	2021(22)	2022(23)	2024	2025	2026	MCQs, all years	Paper II Qs
1 Atomic structure	3	6	3	3	3	4	3	25	9
2 Bonding	6	3	3	3	3	4	1	23	7
3 Calculations	4	3	4	3	4	3	3	24	8
4 Gases	2	3	3	2	1	·	1	12	5
5 Energetics	6	3	2	2	4	5	6	28	8
6 s, p, d block	2	3	5	5	5	4	8	32	23
7 Organic basics	2	2	1	2	2	1	2	12	4
8 Hydrocarbons	5	2	3	4	4	3	4	25	14
9 O-compounds	3	5	4	3	4	4	4	27	14
10 N-compounds	1	1	3	1	·	2	·	8	4
11 Kinetics	1	3	4	3	4	2	3	20	6
12 Equilibrium	7	9	7	10	8	10	7	58	19
13 Electrochemistry	3	3	2	3	3	3	3	20	8
14 Industry & environment	5	4	6	6	5	5	5	36	10

MCQs per paper:

Hover or tap a cell for the exact count. The bar column totals all seven papers; the last column counts Paper II questions since 2019 that test the unit. The biggest MCQ shares: Unit 12 Equilibrium (58), Unit 14 Industry & environment (36), Unit 6 s, p, d block (32).

What each Paper II question slot usually tests

Question	Part	Units it tested, 2019–2026 (papers in which it did)
Q1	A	U1 Atomic structure **7/7** U2 Bonding **7/7** U6 s, p, d block **1/7**
Q2	A	U6 s, p, d block **7/7** U1 Atomic structure **2/7** U14 Industry & environment **1/7**
Q3	A	U12 Equilibrium **5/7** U4 Gases **1/7** U11 Kinetics **1/7**
Q4	A	U8 Hydrocarbons **6/7** U9 O-compounds **6/7** U7 Organic basics **4/7**
Q5	B	U5 Energetics **7/8** U12 Equilibrium **7/8** U4 Gases **2/8**
Q6	B	U12 Equilibrium **7/8** U11 Kinetics **5/8** U4 Gases **2/8**
Q7	B	U13 Electrochemistry **8/8** U6 s, p, d block **7/8**
Q8	C	U8 Hydrocarbons **8/8** U9 O-compounds **8/8** U10 N-compounds **4/8**
Q9	C	U6 s, p, d block **8/8** U3 Calculations **6/8**
Q10	C	U14 Industry & environment **8/8**

The slot pattern has held since 2019. Q2 and Q9 always test s, p and d-block identification, and Q10 is always industrial and environmental chemistry. So you can choose your Part C questions in advance.

Structured revision

12-week fast-track plan

Eleven weeks of unit work in syllabus order, then a week of timed full papers. Each week names three recent Paper II questions to practise; the full MCQ lists are on each unit page.

Week	Units	Focus and practice	Done
Week 1	U1 Atomic structure U2 Bonding	Atomic structure and bonding: quantum numbers, trends, Lewis structures, VSEPRRead the cited Resource Book sections → notes → all unit MCQs from 2019–2026 → Paper II: 2026 Q1, 2025 Q1, 2024 Q1	
Week 2	U3 Calculations U4 Gases	Moles, titrations and redox balancing; gas laws and kinetic theoryRead the cited Resource Book sections → notes → all unit MCQs from 2019–2026 → Paper II: 2026 Q9, 2025 Q9, 2021(22) Q5	
Week 3	U5 Energetics	Hess's law, Born–Haber cycles, $\Delta G = \Delta H - T\Delta S$Read the cited Resource Book sections → notes → all unit MCQs from 2019–2026 → Paper II: 2026 Q5, 2025 Q5, 2024 Q5	
Week 4	U6 s, p, d block	s- and p-block chemistry, period 3 trends, element identification (Paper II Q2)Read the cited Resource Book sections → notes → all unit MCQs from 2019–2026 → Paper II: 2026 Q2, 2025 Q2, 2024 Q2	
Week 5	U6 s, p, d block	d-block, complexes and naming, cation/anion tests (Paper II Q9)Read the cited Resource Book sections → notes → all unit MCQs from 2019–2026 → Paper II: 2026 Q9, 2025 Q7, 2024 Q9	
Week 6	U7 Organic basics U8 Hydrocarbons	IUPAC names, isomerism, hydrocarbon and halide reactions with mechanismsRead the cited Resource Book sections → notes → all unit MCQs from 2019–2026 → Paper II: 2026 Q4, 2025 Q4, 2022(23) Q4	
Week 7	U9 O-compounds U10 N-compounds	Alcohols to acid derivatives; amines and diazonium salts; conversionsRead the cited Resource Book sections → notes → all unit MCQs from 2019–2026 → Paper II: 2026 Q8, 2025 Q8, 2024 Q4	
Week 8	U11 Kinetics	Rate laws, half-life, mechanisms and energy profilesRead the cited Resource Book sections → notes → all unit MCQs from 2019–2026 → Paper II: 2026 Q6, 2025 Q6, 2020 Q6	
Week 9	U12 Equilibrium	Equilibrium constants, Le Chatelier, acids, bases, pH and buffersRead the cited Resource Book sections → notes → all unit MCQs from 2019–2026 → Paper II: 2026 Q3, 2025 Q3, 2024 Q3	
Week 10	U12 Equilibrium U13 Electrochemistry	K_{sp}, phase diagrams, liquid mixtures, partition; cells and electrolysisRead the cited Resource Book sections → notes → all unit MCQs from 2019–2026 → Paper II: 2025 Q5, 2024 Q6, 2026 Q7	
Week 11	U14 Industry & environment	Industrial processes as flow charts; polymers; air and water pollutionRead the cited Resource Book sections → notes → all unit MCQs from 2019–2026 → Paper II: 2026 Q10, 2025 Q10, 2024 Q10	
Week 12	All units	Timed full papers: 2026, 2025, 2024, 2022(23), then review your error logPaper I in 2 h, Paper II in 3 h + 10 min reading, marked against the scheme	

Unit

Grade 12 · 25 MCQs in 7 papers · 9 Paper II questions since 2019

Atomic structure

How we know atoms have a nucleus and electrons, how electrons are arranged in energy levels, and why properties repeat across the Periodic Table. Every Paper I opens with two or three questions from here, and Paper II Q1 nearly always does too.

Read alongside: NIE Resource Book, Vol. 1 (Grade 12, 2018), Unit 1, pp. 1–42

Evidence for subatomic particles

RB §1.1 · p. 2

- **Cathode rays** (Thomson): streams of negative particles, identical whatever the gas or electrode metal. They travel in straight lines, carry momentum and are deflected by electric and magnetic fields towards the positive plate.
- **Positive rays** (canal rays): their charge-to-mass ratio depends on the gas in the tube. The lightest, from hydrogen, is the proton.
- **Rutherford's gold-foil experiment**: most α-particles pass straight through, a few are deflected strongly. So the atom is mostly empty space, with a tiny, dense, positive nucleus.
- **Radioactivity** was discovered by Becquerel. Neutrons were identified later (Chadwick).

Atomic number, isotopes and relative atomic mass

RB §1.1 · p. 2

Z = number of protons, and A = protons + neutrons. Isotopes have the same Z but different A. The atomic mass unit is 1/12 of the mass of a ^{12}C atom. Relative atomic mass is the abundance-weighted mean of the isotope masses.

Light and quantisation

RB §1.2 · p. 13

Light behaves as a wave ($c = \nu\lambda$) and as a stream of photons ($E = h\nu$). Matter also has wave character: $\lambda = h/mv$ (de Broglie). Energy in atoms is **quantised**, so electrons can only occupy fixed energy levels.

The hydrogen spectrum

RB §1.3 · p. 17

Each line comes from an electron falling from a higher level to a lower one: $\Delta E = h\nu$. The **Lyman** series ends on n = 1 (ultraviolet). The **Balmer** series ends on n = 2 (visible). The **Paschen** series ends on n = 3 (infrared). Lines crowd together at high frequency because the levels converge.

Quantum numbers and orbitals

RB §1.3 · p. 17

Quantum number	Allowed values	Describes
n (principal)	1, 2, 3 …	shell, energy and size
l (azimuthal)	0 … n−1 (s, p, d, f)	sub-shell and orbital **shape**
m_l (magnetic)	−l … +l	orientation of the orbital
m_s (spin)	+½ or −½	electron spin

A sub-shell has 2l + 1 orbitals. A shell holds up to $2n^2$ electrons. Each orbital holds at most two electrons, with opposite spins.

Electron configuration

RB §1.4 · p. 23

The **Aufbau principle** fills orbitals from lowest energy upwards: 1s 2s 2p 3s 3p 4s 3d 4p. The **Pauli principle** allows no two electrons the same four quantum numbers. **Hund's rule** puts one electron in each orbital of a sub-shell, with parallel spins, before any pairing.

Learn the exceptions: Cr is $[Ar]3d^5 4s^1$ and Cu is $[Ar]3d^{10} 4s^1$. Transition metals lose their 4s electrons **before** 3d electrons when they form ions (Fe^{3+} = $[Ar]3d^5$).

Periodic trends (s and p block)

RB §1.6 · p. 32

- **Atomic radius** decreases across a period, because effective nuclear charge rises while shielding barely changes. It increases down a group.
- **Isoelectronic ions**: the more protons, the smaller the ion. So $O^{2-} > F^- > Na^+ > Mg^{2+}$.
- **First ionization energy** rises across a period, but dips at Group 13 (a 2p electron is higher in energy) and at Group 16 (repulsion between paired electrons).
- **Successive ionization energies** jump sharply when an electron must come from a new, inner shell. The jump tells you the group.
- **Electron gain energy** becomes more negative across a period. Cl is more negative than F because F is small and crowded. N and the noble gases have positive or near-zero values.
- **Electronegativity** increases across a period and decreases down a group. F is the highest.

Key equations

Wave speed $c = \nu\lambda$

Photon energy $E = h\nu = hc/\lambda$

de Broglie $\lambda = h/(mv) = h/\sqrt{(2mE_k)}$

Electrons in a shell $2n^2$

Orbitals in a sub-shell $2l + 1$

Exam traps

- The Balmer series ends on n = 2, it does not start there. 'n = 3 → n = 2' is visible; 'n = 2 → n = 1' is ultraviolet.
- "Number of electrons with n = 4 and l = 2" means the whole 4d sub-shell: 5 orbitals × 2 = 10.
- For a second ionization energy, compare the configuration of the ion being ionized (for example B^+ is $2s^2$), not the neutral atom.
- Cations are always smaller than their parent atoms and anions always larger. Across a period, compare isoelectronic series separately.

A+ moves

- Plot successive ionization energies as a log graph in your head. The first big jump marks the group number.
- Keep a one-page table of the d-block configurations (Sc → Zn) and the configurations of their common ions.

Past paper practice for Unit 1

Paper I · 25 MCQs (2019–2026)

- 2026 Q 1, 2, 3
- 2025 Q 1, 2, 6, 41
- 2024 Q 2, 3, 4
- 2022(23) Q 1, 2, 3
- 2021(22) Q 1, 2, 3
- 2020 Q 1, 2, 3, 6, 18, 22
- 2019 Q 1, 2, 5

Paper II · 11 questions (2016–2026)

- 2026 Q2 — Identify p-block elements from allotropes (O, C) and an s-block metal from successive ionization energies; an oxoacid formed from CO_2 and water
- 2026 Q1 — Atomic/ionic properties from a species list; Lewis and resonance structures; σ/π bonds from orbital overlap; ordering properties (incl. carbonate decomposition temperature)
- 2025 Q1 — True/false on shapes and periodic properties; Lewis structure of $ClSO_2F$ with oxidation state and resonance; successive ionization energies of a period 3 element
- 2024 Q1 — True/false on shapes and ionization energy; Lewis structure of ISO_2F and oxidation numbers; ordering electronegativity and other properties
- 2022(23) Q1 — True/false on line spectra and atomic structure; Lewis structure of an N–F–S molecule; ordering ionic character of CaX_2
- 2021(22) Q1 — True/false on polarizing power and bonding; Lewis structure of Cl_2O_3 and oxidation states
- 2020 Q1 — Ionic radii and periodic properties; Lewis structures and shapes
- 2019 Q2 — An s-block element identified from successive ionization energies (Mg) and its compounds
- 2019 Q1 — Properties of second-row elements; Lewis structures and shapes
- 2018 Q1 old syllabus — Lewis structures and shapes; ordering properties
- 2017 Q1 old syllabus — Formal charge in Lewis structures; quantum numbers of sub-shells

Model questions (original, in past-paper style)

M1.1

Single answer · like Q1–30

Which electronic transition in a hydrogen atom emits a photon in the **visible** region?

- (1)n = 2 → n = 1
- (2)n = 3 → n = 2
- (3)n = 4 → n = 3
- (4)n = 5 → n = 3
- (5)n = 1 → n = 2

Show model answer

Answer (2). Visible lines belong to the Balmer series, which ends on n = 2. Option 5 is an absorption, not an emission.

M1.2

Single answer · like Q1–30

The first four ionization energies of an element are 578, 1817, 2745 and 11 577 kJ mol^{-1}. The element belongs to

- (1)Group 1
- (2)Group 2
- (3)Group 13
- (4)Group 14
- (5)Group 15

Show model answer

Answer (3). The large jump comes after the third electron, so there are three valence electrons: Group 13. These are aluminium's values.

M1.3

Single answer · like Q1–30

How many orbitals in an atom can have n = 3 and $m_l = -1$?

- (1)1
- (2)2
- (3)3
- (4)4
- (5)6

Show model answer

Answer (2). For n = 3, l can be 0, 1 or 2. $m_l = -1$ is possible only for l = 1 (one 3p orbital) and l = 2 (one 3d orbital).

M1.4

Structured · like Paper II

(a) Arrange O^{2-}, F^-, Na^+ and Mg^{2+} in increasing order of radius and explain your order. (b) Give the complete electron configurations of Cr and Cr^{3+}.

Show model answer

(a) $Mg^{2+} < Na^+ < F^- < O^{2-}$. All four ions have 10 electrons (isoelectronic). Nuclear charge falls from 12 to 8, so the same electron cloud is pulled in less strongly and the radius increases. (b) Cr: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$. Cr^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$. The 4s electron is lost first, then two 3d electrons.

Unit

Grade 12 · 23 MCQs in 7 papers · 7 Paper II questions since 2019

Structure and bonding

Lewis structures, shapes, hybridization, resonance and the forces between particles. These ideas run through every other unit, and Paper II Q1 always asks you to draw a 'most acceptable' Lewis structure.

Read alongside: NIE Resource Book, Vol. 1 (Grade 12, 2018), Unit 2, pp. 43–84

Lewis structures and formal charge

RB §2.1 · p. 44

Count all the valence electrons, add one for each negative charge and remove one for each positive charge. Join the atoms with single bonds, complete the octets of the outer atoms, then put any remaining electrons on the central atom. Period 3 and heavier central atoms (P, S, Cl, Xe) can exceed an octet. B and Be can have fewer than eight.

Formal charge = (valence electrons) − (non-bonding electrons) − ½(bonding electrons). The **most acceptable** structure has the smallest formal charges, puts any negative formal charge on the more electronegative atom, and avoids like charges on neighbouring atoms.

Dative covalent bonds

RB §2.2 · p. 51

Both bonding electrons come from one atom, for example NH_4^+, H_3O^+, $H_3N{\rightarrow}BF_3$ and CO. Once a dative bond has formed, it is identical to any other covalent bond.

VSEPR: electron-pair geometry vs shape

RB §2.3 · p. 52

Electron pairs	Pair geometry	Shape for 0 / 1 / 2 / 3 lone pairs
2	linear	linear
3	trigonal planar	trigonal planar / angular
4	tetrahedral	tetrahedral / trigonal pyramidal / angular
5	trigonal bipyramidal	trigonal bipyramidal / see-saw / T-shaped / linear
6	octahedral	octahedral / square pyramidal / square planar

Repulsion decreases in the order lone pair–lone pair > lone pair–bond pair > bond pair–bond pair, so lone pairs squeeze bond angles (CH_4 109.5°, NH_3 107°, H_2O 104.5°). NF_3 has a smaller angle than NH_3 because the bonding pairs are pulled out towards F. In a trigonal bipyramid, lone pairs sit in the equatorial positions.

Hybridization, σ and π bonds

RB §2.3 · p. 52

sp (180°), sp^2 (120°), sp^3 (109.5°), sp^3d (trigonal bipyramidal) and sp^3d^2 (octahedral). A double bond is one σ bond plus one π bond. A triple bond is one σ plus two π. σ bonds form from end-on overlap (s–s, s–hybrid, hybrid–hybrid). π bonds form from sideways overlap of p orbitals. Paper II often asks which orbitals overlap to form a named bond.

Resonance

RB §2.3 · p. 52

When one Lewis structure cannot describe a species, the real structure is a **resonance hybrid** of several contributing structures (NO_3^-, CO_3^{2-}, O_3, C_6H_6, carboxylate ions). The bonds are equal in length and intermediate between single and double. Only electrons move between resonance structures, never atoms. The most stable contributors have complete octets, fewer separated charges and negative charge on the more electronegative atom.

Polarity and electronegativity

RB §2.3 · p. 52

A polar bond does not guarantee a polar molecule. The bond dipoles may cancel by symmetry (CO_2, BF_3, CCl_4 and SF_6 are non-polar; SO_2, NF_3 and SF_4 are polar). The electronegativity of an atom also depends on its hybridization (sp C > sp^2 C > sp^3 C) and on its oxidation state and charge. A carbon bonded to more electronegative atoms is itself more electronegative.

Ionic, metallic and secondary interactions

RB §2.4 · p. 75

- **Covalent character in ionic compounds** increases with the polarizing power of the cation (small and highly charged) and the polarizability of the anion (large).
- **Metallic bonding** becomes stronger with more delocalised electrons per atom and smaller atoms. Group 2 metals have stronger bonding than Group 1.
- **Secondary interactions** include ion–dipole, dipole–dipole, hydrogen bonding (H on N, O or F) and London dispersion forces, which grow with molar mass and surface area. They control boiling points and solubility.

Key equations

Formal charge$FC = V - N - \frac{1}{2}B$

Bond order (simple)σ + π count between two atoms

Electron pairs on central atom(valence e^- of centre + e^- from ligands ± charge) ÷ 2

Exam traps

- Always state both the electron-pair geometry and the shape when asked. SF_4 has a trigonal bipyramidal pair geometry and a see-saw shape.
- Do not draw resonance structures that move atoms or break the octet rule for second-period atoms.
- Hydrogen bonding needs H bonded directly to N, O or F. H_2S has no hydrogen bonding, which is why it boils far lower than H_2O.
- Examiners note that candidates lose marks for missing lone pairs and formal charges on Lewis structures (Evaluation Report 2016).

A+ moves

- Practise the four-step routine for Lewis structures: count electrons, build the skeleton, complete the octets, then minimise formal charges.
- Memorise the VSEPR table as a grid. Most shape MCQs then take about 30 seconds.

Past paper practice for Unit 2

Paper I · 23 MCQs (2019–2026)

- 2026 Q 45
- 2025 Q 3, 4, 11, 44

- 2024 Q 1, 7, 8
- 2022(23) Q 4, 7, 9
- 2021(22) Q 4, 6, 8
- 2020 Q 4, 12, 32
- 2019 Q 3, 6, 11, 14, 31, 41

Paper II · 10 questions (2016–2026)

- 2026 Q1 — Atomic/ionic properties from a species list; Lewis and resonance structures; σ/π bonds from orbital overlap; ordering properties (incl. carbonate decomposition temperature)
- 2025 Q1 — True/false on shapes and periodic properties; Lewis structure of $ClSO_2F$ with oxidation state and resonance; successive ionization energies of a period 3 element
- 2024 Q1 — True/false on shapes and ionization energy; Lewis structure of ISO_2F and oxidation numbers; ordering electronegativity and other properties
- 2022(23) Q1 — True/false on line spectra and atomic structure; Lewis structure of an N–F–S molecule; ordering ionic character of CaX_2
- 2021(22) Q1 — True/false on polarizing power and bonding; Lewis structure of Cl_2O_3 and oxidation states
- 2020 Q1 — Ionic radii and periodic properties; Lewis structures and shapes
- 2019 Q1 — Properties of second-row elements; Lewis structures and shapes
- 2018 Q1 old syllabus — Lewis structures and shapes; ordering properties
- 2017 Q1 old syllabus — Formal charge in Lewis structures; quantum numbers of sub-shells
- 2016 Q1 old syllabus — p-block elements from a list; Lewis structure of CN_2-type molecule

Model questions (original, in past-paper style)

M2.1

Single answer · like Q1–30

Which molecule is **polar**?

- (1)CO_2
- (2)BF_3
- (3)SF_6
- (4)PCl_5
- (5)SF_4

Show model answer

Answer (5). SF_4 has one lone pair on S and a see-saw shape, so its bond dipoles do not cancel. The other four are symmetrical.

M2.2

Single answer · like Q1–30

The shapes of XeF_4, ClF_3 and I_3^- are respectively

- (1)tetrahedral, trigonal planar, linear
- (2)square planar, T-shaped, linear

- (3)square planar, trigonal pyramidal, angular
- (4)see-saw, T-shaped, angular
- (5)octahedral, trigonal planar, linear

Show model answer

Answer (2). XeF_4 has 6 pairs with 2 lone, so it is square planar. ClF_3 has 5 pairs with 2 lone, so it is T-shaped. I_3^- has 5 pairs with 3 lone, so it is linear.

M2.3

Statement pair · like Q41–50

Statement 1: The bond angle in NF_3 is smaller than in NH_3. **Statement 2:** F is more electronegative than H, so the bonding pairs in NF_3 lie further from N and repel each other less.

Answer with the statement-pair code (1)–(5) from the code table.

Show model answer

Answer (1). Both statements are true, and statement 2 correctly explains statement 1.

M2.4

Structured · like Paper II

For the nitrate ion, NO_3^-: (a) draw the resonance structures, (b) state the hybridization of N and the O–N–O bond angle, (c) explain why all three N–O bonds are the same length.

Show model answer

(a) Three equivalent structures, each with one N=O and two N–O^-. N carries a formal charge of +1 and the double bond moves around the three O atoms. (b) N is sp^2 hybridized and the angle is 120° (trigonal planar). (c) The real ion is a resonance hybrid. The π electrons are delocalised over all three N–O bonds, so each bond has a bond order of 1⅓ and the bonds are identical.

Unit

Grade 12 · 24 MCQs in 7 papers · 8 Paper II questions since 2019

Chemical calculations

Oxidation numbers, moles, concentrations, balancing and stoichiometry. Calculators are not allowed, so the skill is setting up the ratio correctly and simplifying the arithmetic. Unit 3 also supports the quantitative analysis part of Paper II Q9 every year.

Read alongside: NIE Resource Book, Vol. 1 (Grade 12, 2018), Unit 3, pp. 87–120

Oxidation numbers and redox

RB §3.1 · p. 88

Elements are 0. O is usually −2 (−1 in peroxides). H is +1 (−1 in metal hydrides). F is always −1. The oxidation numbers in a species add up to its charge. Oxidation is an increase in oxidation number (loss of electrons) and reduction is a decrease. In a **disproportionation**, one element is oxidized and reduced at the same time (for example $Cl_2 + H_2O$).

Naming inorganic compounds

RB §3.2 · p. 93

Use Stock notation for variable valency, such as iron(III) chloride. Learn the polyatomic ions: NO_3^-, NO_2^-, SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, CO_3^{2-}, HCO_3^-, PO_4^{3-}, MnO_4^-, CrO_4^{2-}, $Cr_2O_7^{2-}$, ClO^-, ClO_3^- and ClO_4^-.

The mole

RB §3.3 · p. 97

$n = m/M$ and $N = n \times N_A$ (6.022×10^{23} mol^{-1}). An empirical formula comes from the mole ratio of the elements. The molecular formula = (empirical formula) × (M ÷ empirical formula mass).

Composition of mixtures

RB §3.5 · p. 102

- Mass fraction, %(w/w), %(w/v) and mole fraction $x_i = n_i/n_{total}$.
- **Molarity** is mol dm^{-3} of solution. **Molality** is mol kg^{-1} of solvent. **ppm** is mg kg^{-1} (≈ mg dm^{-3} for dilute water).
- Concentration of a commercial acid: $c = (1000 \times d \times w\%) \div (100 \times M)$, with d in g cm^{-3}.

Balancing equations

RB §3.6 · p. 105

Simple equations can be balanced by inspection. For redox equations, balance the electron change: write the oxidation and reduction half-equations, balance O with H_2O and H with H^+, then the charge with electrons, and combine. Nuclear equations must balance mass number and atomic number.

Solutions and stoichiometry

RB §3.7 · p. 113

Dilution: $c_1V_1 = c_2V_2$. Use a primary standard to make a standard solution. Limiting reagent, percentage yield, gas volumes and titrations (acid–base, $KMnO_4$, $K_2Cr_2O_7$, iodometric with $Na_2S_2O_3$) all come back to the mole ratio in the balanced equation.

Key equations

Molesn = m/M = cV

Dilution$c_1V_1 = c_2V_2$

Mole fraction$x_A = n_A / n_{total}$

Electrons per oxidant (acid)MnO_4^- 5 e^- · $Cr_2O_7^{2-}$ 6 e^-

Iodometry$IO_3^- \rightarrow 3I_2 \rightarrow 6S_2O_3^{2-}$

Exam traps

- Convert cm^3 to dm^3 (÷1000) before using c = n/V.
- Iron(II) oxalate, FeC_2O_4, gives **3** electrons per formula unit (1 from Fe^{2+} and 2 from $C_2O_4^{2-}$). So 5 FeC_2O_4 react with 3 MnO_4^-.
- In iodometric titrations, $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$. The average oxidation number of S in $S_4O_6^{2-}$ is +2.5.
- Examiners reward correctly balanced equations with physical states, and correct units with correct conversions (Evaluation Report 2016).

A+ moves

- Write the mole ratio as a fraction before doing any arithmetic, then cancel. Papers set numbers that simplify neatly.
- Build a small table of molar masses you use often: $KMnO_4$ 158, $K_2Cr_2O_7$ 294, $Na_2S_2O_3 \cdot 5H_2O$ 248, KIO_3 214.

Past paper practice for Unit 3

Paper I · 24 MCQs (2019–2026)

- 2026 Q 11, 29, 30
- 2025 Q 8, 12, 28
- 2024 Q 11, 15, 27, 29
- 2022(23) Q 13, 26, 27
- 2021(22) Q 12, 18, 22, 27
- 2020 Q 8, 14, 24
- 2019 Q 8, 18, 24, 25

Paper II · 10 questions (2016–2026)

- 2026 Q9 — Identify four water-soluble inorganic compounds (two with d-block ions); quantitative analysis of a Cu–Zn–Sn alloy
- 2025 Q9 — Qualitative analysis of four cations in solution Y; quantitative analysis of siderite ($FeCO_3$)
- 2024 Q9 — Qualitative analysis of four cations; sulfur content of iron pyrite (FeS_2)
- 2023(24) Q9 — Identify five solutions by mixing; analysis of a solid containing iron oxides
- 2021(22) Q9 — Qualitative analysis of four cations; analysis of an Al_2S_3/Fe_2S_3 mixture
- 2021(22) Q5 — Combustion of a gas mixture in a rigid container (gas laws); enthalpy by a thermochemical cycle
- 2021(22) Q3 — Temperature–composition diagram of an ideal solution; titration of acetic acid

- 2019 Q9 — Qualitative analysis of four cations; quantitative analysis of anions in a water sample
- 2018 Q3 old syllabus — Kinetics/equilibrium of A + B ⇌ 2C + D; analysis of Pb and Cu in a sample
- 2017 Q8 old syllabus — Qualitative analysis of three cations; ammonium salts by quantitative analysis

Model questions (original, in past-paper style)

M3.1

Single answer · like Q1–30

25.00 cm^3 of 0.020 mol dm^{-3} acidified $KMnO_4$ reacts exactly with $Fe^{2+}(aq)$. The amount of Fe^{2+} oxidized is

- (1)5.0×10^{-4} mol
- (2)1.0×10^{-3} mol
- (3)2.5×10^{-3} mol
- (4)5.0×10^{-3} mol
- (5)1.0×10^{-4} mol

Show model answer

Answer (3). $n(MnO_4^-) = 0.020 \times 0.025 = 5.0 \times 10^{-4}$ mol, and each MnO_4^- accepts 5 e^-. So $n(Fe^{2+}) = 5 \times 5.0 \times 10^{-4} = 2.5 \times 10^{-3}$ mol.

M3.2

Single answer · like Q1–30

Concentrated H_2SO_4 is 98% (w/w) with a density of 1.84 g cm^{-3} (H_2SO_4 = 98). The volume needed to make 500 cm^3 of 1.0 mol dm^{-3} H_2SO_4 is about

- (1)13.6 cm^3
- (2)18.4 cm^3
- (3)27.2 cm^3
- (4)50.0 cm^3
- (5)54.3 cm^3

Show model answer

Answer (3). c = (1000 × 1.84 × 98) ÷ (100 × 98) = 18.4 mol dm^{-3}. V = 0.50 mol ÷ 18.4 mol dm^{-3} = 0.0272 dm^3 = 27.2 cm^3.

M3.3

Structured · like Paper II

0.214 g of pure KIO_3 (M = 214) was dissolved in water and treated with excess KI and dilute acid. The liberated iodine needed 24.00 cm^3 of $Na_2S_2O_3$ solution. (a) Write balanced ionic equations for both reactions. (b) Calculate the thiosulfate concentration.

Show model answer

(a) $IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \rightarrow 3I_2(aq) + 3H_2O(l)$, and $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$. (b) $n(KIO_3) = 1.00 \times 10^{-3}$ mol, so $n(I_2) = 3.00 \times 10^{-3}$ mol and $n(S_2O_3^{2-}) = 6.00 \times 10^{-3}$ mol. c = $6.00 \times 10^{-3} \div 0.02400 = 0.250$ mol dm^{-3}.

Unit

Grade 12 · 12 MCQs in 7 papers · 5 Paper II questions since 2019

Gaseous state of matter

The gas laws, partial pressures, the kinetic theory and how real gases differ from ideal ones. These calculations also feed into equilibrium (Kp) and kinetics questions in rigid containers.

Read alongside: NIE Resource Book, Vol. 2 (Grade 12, 2018), Unit 4, pp. 1–29

Gas laws and the ideal gas equation

RB §1.2 · p. 5

Boyle's law: PV is constant (fixed n and T). Charles's law: $V \propto T$ (fixed n and P). Avogadro's law: $V \propto n$. Together these give **PV = nRT**, with P in Pa, V in m^3, T in K and R = 8.314 J K^{-1} mol^{-1}. The molar volume of any ideal gas at 273 K and 1 atm is 22.4 dm^3 mol^{-1}. Rearranging gives $M = \rho RT/P$.

Dalton's law of partial pressures

RB §1.3 · p. 16

$P_{total} = P_A + P_B + \ldots$, and each partial pressure $P_A = x_A P_{total}$. In a **rigid** container V is fixed, so the pressure is proportional to nT. Watch the total number of gas moles change as a reaction goes on.

Kinetic molecular theory

RB §1.4 · p. 19

The model assumes negligible molecular volume, no intermolecular forces, elastic collisions and random motion. It gives $PV = \frac{1}{3}Nmc^2$, where c^2 is the mean square speed. The average kinetic energy depends **only on temperature**: any two gases at the same T have the same average kinetic energy. $c_{rms} = \sqrt{(3RT/M)}$, so lighter molecules move faster.

Maxwell–Boltzmann distribution

RB §1.4 · p. 19

Raising the temperature flattens and broadens the curve and moves the peak to higher speed. The area under the curve, which is the number of molecules, stays the same. More molecules now exceed any chosen energy, and this links straight to reaction rates in Unit 11.

Real gases

RB §1.5 · p. 24

Real gases deviate from ideal behaviour at **high pressure** (molecular volume matters) and **low temperature** (attractions matter). Gases are most nearly ideal at low pressure and high temperature. The compressibility factor $Z = PV/nRT$. The van der Waals equation is $(P + an^2/V^2)(V - nb) = nRT$. Above its **critical temperature**, a gas cannot be liquefied by pressure alone.

Key equations

Ideal gas $PV = nRT$

Partial pressure $P_A = x_A P_{total}$

Kinetic theory $PV = \frac{1}{3} N m c^2$

rms speed $c_{rms} = \sqrt{(3RT/M)}$

van der Waals $(P + an^2/V^2)(V - nb) = nRT$

Exam traps

- Always use kelvin. 1 $dm^3 = 10^{-3}$ m^3, and 1 $cm^3 = 10^{-6}$ m^3.
- 'Same mean square speed' means T/M is the same. H_2 at T matches N_2 at 14T.
- A rigid container has a fixed volume, so any pressure change must come from a change in n or T.
- Real-gas questions are often worded as 'lower pressure than calculated' (attractions dominate) or 'higher than calculated' (molecular volume dominates).

A+ moves

- Papers often give a convenient value such as RT = 2500 J mol^{-1} at 300 K. Look for it before multiplying out 8.314 × T.
- Learn the three Maxwell–Boltzmann sketches (two temperatures, a catalyst's Ea line, and the area under the curve).

Past paper practice for Unit 4

Paper I · 12 MCQs (2019–2026)

- 2026 Q 38
- 2024 Q 24
- 2022(23) Q 21, 22
- 2021(22) Q 21, 23, 38
- 2020 Q 7, 39, 44
- 2019 Q 9, 49

Paper II · 5 questions (2016–2026)

- 2025 Q6 — Initial-rate method for 2NO + Cl_2; gas from Cu + HNO_3 (gas laws); vapour pressure of water vs glycerol solution; ideal binary liquid mixture
- 2025 Q5 — N_2 + 3H_2 ⇌ 2NH_3: Kc, partial pressures and Kp; effect of temperature using ΔH° and ΔS°; normal boiling point and vaporization of CCl_4
- 2024 Q6 — Kinetic molecular theory of gases; elementary reactions and molecularity; iodine partition between water and CCl_4
- 2022(23) Q3 — Ideal gas laws in a piston container; Cl-catalysed ozone depletion mechanism
- 2021(22) Q5 — Combustion of a gas mixture in a rigid container (gas laws); enthalpy by a thermochemical cycle

Model questions (original, in past-paper style)

M4.1

Single answer · like Q1–30

At what temperature does helium (M = 4) have the same rms speed as O_2 (M = 32) at 400 K?

- (1)25 K
- (2)50 K
- (3)100 K
- (4)800 K
- (5)3200 K

Show model answer

Answer (2). $c_{rms}^2 \propto T/M$, so $400/32 = T/4$ and $T = 50$ K.

M4.2

Single answer · like Q1–30

A rigid 2.0 dm^3 container holds 0.10 mol N_2 and 0.30 mol H_2 at 300 K (take $RT = 2500$ J mol^{-1}). The partial pressure of H_2 is

- (1)1.25×10^5 Pa
- (2)2.50×10^5 Pa
- (3)3.75×10^5 Pa
- (4)5.00×10^5 Pa
- (5)7.50×10^5 Pa

Show model answer

Answer (3). $P_{total} = nRT/V = 0.40 \times 2500 \div (2.0 \times 10^{-3}) = 5.0 \times 10^5$ Pa. $P(H_2) = 0.75 \times 5.0 \times 10^5 = 3.75 \times 10^5$ Pa.

M4.3

Statement pair · like Q41–50

Statement 1: At the same temperature, H_2 and CO_2 molecules have the same average kinetic energy.
Statement 2: The average kinetic energy of gas molecules depends only on absolute temperature.

Answer with the statement-pair code (1)–(5) from the code table.

Show model answer

Answer (1). Both statements are true, and the second explains the first.

M4.4

Structured · like Paper II

(a) State two assumptions of the kinetic theory that fail for real gases at high pressure and low temperature. (b) Explain how the terms a and b in the van der Waals equation correct for each failure.

Show model answer

(a) The volume of the molecules is negligible compared with the container volume, and there are no forces between molecules. (b) The term $(V - nb)$ subtracts the volume taken up by the molecules themselves. The term an^2/V^2 is added to the measured pressure because attractions pull molecules back from the walls, so the measured pressure is lower than the ideal pressure.

Unit

Grade 12 · 28 MCQs in 7 papers · 8 Paper II questions since 2019

Energetics

Enthalpy changes, Hess's law, Born–Haber cycles, entropy and Gibbs energy. Paper I carries four or five questions from here every year, and Part B essays usually combine ΔH°, ΔS° and ΔG° with an equilibrium.

Read alongside: NIE Resource Book, Vol. 2 (Grade 12, 2018), Unit 5, pp. 30–58

Systems and state functions

RB §2.1 · p. 31

A system can be **open** (exchanges matter and energy), **closed** (exchanges energy only) or **isolated** (exchanges neither). Enthalpy H, entropy S and Gibbs energy G are **state functions**: a change in any of them depends only on the initial and final states, not on the route.

Enthalpy changes

RB §2.2 · p. 36

ΔH is the heat change at constant pressure. Exothermic means ΔH < 0 and endothermic means ΔH > 0. Learn the standard enthalpies of formation, combustion, neutralization, solution, hydration, atomization, bond dissociation, ionization and electron gain. Each definition names the substance, the amount (1 mol) and the physical states.

Hess's law: the total enthalpy change is the same whatever route is taken. Calorimetry gives q = mcΔT, and ΔH = −q/n.

Three ways to calculate ΔH

RB §2.2 · p. 36

- From formation data: $\Delta H_r = \Sigma\Delta H_f(\text{products}) - \Sigma\Delta H_f(\text{reactants})$.
- From combustion data: $\Delta H_r = \Sigma\Delta H_c(\text{reactants}) - \Sigma\Delta H_c(\text{products})$.
- From bond enthalpies (gases only): $\Delta H_r = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds formed})$.

Born–Haber cycle and lattice enthalpy

RB §2.3 · p. 51

$\Delta H_f(MX) = \Delta H_{atom}(M) + IE + \Delta H_{atom}(X)$ + electron gain energy + lattice enthalpy (the formation of the solid lattice from gaseous ions, which is negative). The magnitude of the lattice enthalpy increases with higher ionic charges and smaller ions. Enthalpy of solution = (lattice dissociation enthalpy) + Σ(hydration enthalpies of the ions).

Entropy and spontaneity

RB §2.4 · p. 53

Entropy measures how widely energy and matter are dispersed: S(solid) < S(liquid) < S(gas). Entropy increases when a gas forms, when moles of gas increase, when a solid dissolves, and when temperature rises. For the surroundings, $\Delta S_{surr} = -\Delta H/T$.

ΔG = ΔH − TΔS. A process is spontaneous when ΔG < 0. At a phase change, ΔG = 0, so T = ΔH/ΔS (for example, the boiling point is $\Delta H_{vap}/\Delta S_{vap}$).

ΔH	ΔS	Spontaneous?
−	+	at all temperatures

ΔH	ΔS	Spontaneous?
+	−	never
−	−	at low T only
+	+	at high T only

Key equations

Calorimetry $q = mc\Delta T$; $\Delta H = -q/n$

Formation route $\Delta H_r = \Sigma \Delta H_f(P) - \Sigma \Delta H_f(R)$

Bond enthalpy route $\Delta H_r = \Sigma$ broken $- \Sigma$ formed

Gibbs energy $\Delta G = \Delta H - T\Delta S$

Phase change $T = \Delta H / \Delta S$

Surroundings $\Delta S_{surr} = -\Delta H/T$

Exam traps

- Convert ΔS from J K^{-1} to kJ K^{-1} before combining it with ΔH in kJ.
- Bond enthalpies apply only to gaseous species. Include enthalpies of vaporization if the data involve liquids.
- The free expansion of an ideal gas into a vacuum has $\Delta H = 0$, $\Delta S > 0$ and $\Delta G < 0$.
- Not every spontaneous reaction is exothermic. Endothermic reactions are spontaneous when $T\Delta S > \Delta H$ (for example, NH_4Cl dissolving in water).

A+ moves

- Draw every Hess cycle or Born–Haber cycle as a labelled diagram before writing numbers. Examiners give method marks for a correct cycle.
- When a question links ΔG° and an equilibrium constant, think ahead to Unit 12: a negative ΔG° means $K > 1$.

Past paper practice for Unit 5

Paper I · 28 MCQs (2019–2026)

- 2026 Q 10, 13, 16, 18, 21, 46
- 2025 Q 13, 18, 21, 38, 46
- 2024 Q 12, 17, 18, 20
- 2022(23) Q 18, 23
- 2021(22) Q 19, 42
- 2020 Q 13, 17, 21
- 2019 Q 16, 26, 30, 33, 42, 44

Paper II · 11 questions (2016–2026)

- 2026 Q5 — $Fe_2O_3 + 3CO$: ΔH°, ΔS°, ΔG° and spontaneity; Ag_2CrO_4 solubility product
- 2025 Q5 — $N_2 + 3H_2 \rightleftharpoons 2NH_3$: Kc, partial pressures and Kp; effect of temperature using ΔH° and ΔS°; normal boiling point and vaporization of CCl_4

- 2024 Q5 — NO + O_2 equilibrium in a rigid container; Hess's law with NO, NO_2 and N_2O_4
- 2023(24) Q5 — CaO + water thermochemistry; $Ca(OH)_2 \rightleftharpoons CaO + H_2O(g)$ heterogeneous equilibrium and Kp
- 2022(23) Q5 — Combining Kc values (H_2/S_2 and H_2/I_2 equilibria); ΔH°, ΔS°, ΔG° for $H_2 + I_2$; Cl^-/CrO_4^{2-} precipitation with Ag^+
- 2021(22) Q5 — Combustion of a gas mixture in a rigid container (gas laws); enthalpy by a thermochemical cycle
- 2020 Q5 — Gas-phase dissociation equilibrium XY_2Z_2 and Kp; Gibbs energies and spontaneity
- 2019 Q3 — Calorimetry: enthalpy of dissolution of a salt
- 2018 Q5 old syllabus — Gas-phase equilibrium and Kp at 800 K; thermochemical cycles
- 2017 Q5 old syllabus — Thermal decomposition of $NaHCO_3$: equilibrium and ΔH° by experiment
- 2016 Q5 old syllabus — Partition coefficient of butanedioic acid; ΔH, ΔS and spontaneity

Model questions (original, in past-paper style)

M5.1

Single answer · like Q1–30

Given $\Delta H_f^\circ(CO_2,g) = -393$, $\Delta H_f^\circ(H_2O,l) = -286$ and $\Delta H_c^\circ(CH_4,g) = -890$ kJ mol^{-1}, $\Delta H_f^\circ(CH_4,g)$ in kJ mol^{-1} is

- (1)−965
- (2)−211
- (3)−75
- (4)+75
- (5)+211

Show model answer

Answer (3). $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$. $-890 = [-393 + 2(-286)] - \Delta H_f(CH_4)$, so $\Delta H_f(CH_4) = -965 + 890 = -75$ kJ mol^{-1}.

M5.2

Single answer · like Q1–30

For a reaction, ΔH° = +40 kJ mol^{-1} and ΔS° = +100 J K^{-1} mol^{-1}. Assuming both are independent of temperature, the reaction is spontaneous

- (1)at all temperatures
- (2)at no temperature
- (3)only below 400 K
- (4)only above 400 K
- (5)only above 4000 K

Show model answer

Answer (4). T = ΔH/ΔS = 40 000 ÷ 100 = 400 K. Above this, TΔS exceeds ΔH and ΔG becomes negative.

M5.3

Statement pair · like Q41–50

Statement 1: All spontaneous reactions are exothermic. **Statement 2:** For any reaction, ΔG = ΔH − TΔS.

Answer with the statement-pair code (1)–(5) from the code table.

Show model answer

Answer (4). Statement 1 is false (endothermic reactions can be spontaneous). Statement 2 is true.

M5.4

Structured · like Paper II

Use the data to calculate the lattice enthalpy of MgO (kJ mol^{-1}): ΔH_f(MgO) = −602; ΔH_{atom}(Mg) = +148; IE_1 = +738; IE_2 = +1451; ½ bond enthalpy of O_2 = +249; first electron gain energy of O = −141; second = +798. Explain why the second electron gain energy is positive.

Show model answer

Lattice enthalpy = −602 − (148 + 738 + 1451 + 249 − 141 + 798) = −602 − 3243 = −3845 kJ mol^{-1}. The second electron is added to a negative O^- ion, so energy must be supplied to overcome the repulsion.

Unit

Grade 12 · 32 MCQs in 7 papers · 23 Paper II questions since 2019

Chemistry of s, p and d block elements

The largest descriptive unit. It feeds Paper II Q2 (identifying elements and compounds), Q7(b) (complexes) and Q9 (qualitative analysis), as well as about five MCQs a year. Learn it as patterns and tests, not lists.

Read alongside: NIE Resource Book, Vol. 3 (Grade 12, 2018), Unit 6, pp. 121–176

Group 1

RB §4.1 · p. 122

Reactivity increases down the group. $2M + 2H_2O \rightarrow 2MOH + H_2$. On burning in air, Li forms Li_2O, Na forms Na_2O_2 (peroxide) and K forms KO_2 (superoxide). Li is the only Group 1 metal that forms a nitride (Li_3N). $LiNO_3$ and Li_2CO_3 decompose like Group 2 salts (diagonal relationship with Mg). Other Group 1 carbonates are stable, and their nitrates give the nitrite plus O_2. Almost all Group 1 salts are soluble. Flame colours: Li crimson, Na yellow, K lilac.

Group 2

RB §4.2 · p. 126

Be is amphoteric. Mg reacts with steam, while Ca, Sr and Ba react with cold water. When burnt in air they also form nitrides (Mg_3N_2). The **thermal stability** of carbonates and nitrates increases down the group, because the polarizing power of the cation decreases. Hydroxides become more soluble down the group, and sulfates become less soluble ($BaSO_4$ is insoluble). Flame colours: Ca brick-red, Sr crimson, Ba apple-green. Mg gives no flame colour.

Groups 13 and 14

RB §4.3 · p. 131

Al: Al_2O_3 and $Al(OH)_3$ are amphoteric and dissolve in excess NaOH as $[Al(OH)_4]^-$. $AlCl_3$ is covalent, forms the dimer Al_2Cl_6, acts as a Lewis acid (as in Friedel–Crafts) and hydrolyses to give an acidic solution. Concentrated HNO_3 makes Al passive. **C**: diamond (sp^3, hard, an insulator) and graphite (sp^2 layers, conducts). CO is a neutral, toxic reducing agent. CO_2 is acidic and forms H_2CO_3 in water.

Group 15

RB §4.5 · p. 136

N_2 is unreactive because of its strong triple bond. NH_3 is basic, acts as a ligand and is made by the Haber process. Ammonium salts release NH_3 when warmed with NaOH. On heating: $NH_4NO_3 \rightarrow N_2O + 2H_2O$, $NH_4NO_2 \rightarrow N_2 + 2H_2O$, $(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3 + 4H_2O$. HNO_3 is an oxidizing acid: concentrated acid with Cu gives NO_2, dilute acid gives NO. Concentrated HNO_3 is kept in brown bottles because light decomposes it to NO_2.

Group 16

RB §4.6 · p. 141

The allotropes are O_2 and O_3 (ozone has a pungent smell). H_2O boils far higher than H_2S because of hydrogen bonding. **H_2O_2** can act as an oxidizing agent or a reducing agent (it reduces MnO_4^-), and it decomposes to $H_2O + O_2$, catalysed by MnO_2. Rhombic sulfur is the stable allotrope at room temperature. SO_2 is a reducing agent: it turns acidified $Cr_2O_7^{2-}$ from orange to green and decolourises MnO_4^-. Concentrated H_2SO_4 is both a dehydrating agent and an oxidizing agent. $S_2O_3^{2-} + 2H^+ \rightarrow S + SO_2 + H_2O$.

Group 17 and 18

RB §4.7 · p. 149

Oxidizing power: F_2 > Cl_2 > Br_2 > I_2. In water, HF is a weak acid, while HCl, HBr and HI are strong. Acid strength increases from HCl to HI as the H–X bond weakens. HF has the highest boiling point of the hydrogen halides (hydrogen bonding). $Cl_2 + H_2O \rightarrow HCl + HOCl$ is a disproportionation. With cold dilute NaOH, Cl_2 gives NaCl + NaOCl. With hot concentrated NaOH, it gives NaCl + $NaClO_3$. Acid strength of the chlorine oxoacids increases from HOCl to $HClO_4$. Xenon compounds: XeF_2 (linear), XeF_4 (square planar), XeO_3 (trigonal pyramidal).

Period 3 trends

RB §4.9 · p. 155

Oxides go from basic (Na_2O, MgO) through amphoteric (Al_2O_3) to acidic (SiO_2, P_4O_{10}, SO_3, Cl_2O_7). NaCl and $MgCl_2$ are ionic. $AlCl_3$, $SiCl_4$ and PCl_5 hydrolyse in water to give acidic solutions.

Transition (3d) elements

RB §4.10 · p. 160

They show variable oxidation states, coloured ions (from d–d transitions in partly filled d orbitals), catalytic activity (Fe in the Haber process, V_2O_5 in the Contact process, Ni in hydrogenation) and complex formation. Sc^{3+} (d^0) and Zn^{2+} (d^{10}) are colourless, and Zn has the lowest melting point in the 3d series. Oxides become more acidic as the oxidation state rises: CrO is basic, Cr_2O_3 amphoteric and CrO_3 acidic; MnO is basic and Mn_2O_7 acidic. $2CrO_4^{2-}$ (yellow) + $2H^+ \rightleftharpoons Cr_2O_7^{2-}$ (orange) + H_2O. MnO_4^- is reduced to Mn^{2+} in acid, MnO_2 in neutral solution and MnO_4^{2-} (green) in strong alkali.

Complexes and their names

RB §4.10.6 · p. 169

Name the ligands in alphabetical order (ammine, aqua, chlorido, cyanido, hydroxido), with di-, tri-, tetra- and so on. Then name the metal with its oxidation state in Roman numerals, using the **-ate** ending for an anionic complex. For example: $[Cu(NH_3)_4]^{2+}$ is tetraamminecopper(II); $K_3[Fe(CN)_6]$ is potassium hexacyanidoferrate(III); $[Co(NH_3)_6]Cl_3$ is hexaamminecobalt(III) chloride. The colour depends on the metal, its oxidation state and the ligands. Fe^{3+} with SCN^- gives a blood-red colour.

Reaction pathways and tests

Cation tests: dilute NaOH(aq) and NH_3(aq), added slowly then in excess

Ion	NaOH(aq)	NH_3(aq)
Al^{3+}	white ppt, dissolves in excess	white ppt, insoluble in excess
Zn^{2+}	white ppt, dissolves in excess	white ppt, dissolves in excess
Pb^{2+}	white ppt, dissolves in excess	white ppt, insoluble in excess
Mg^{2+}	white ppt, insoluble	white ppt, insoluble
Cu^{2+}	blue ppt, insoluble	blue ppt, dissolves in excess to a deep blue solution
Ni^{2+}	green ppt, insoluble	green ppt, dissolves in excess to a blue-violet solution
Fe^{2+}	dirty green ppt, turns brown in air	dirty green ppt, turns brown in air
Fe^{3+}	red-brown ppt, insoluble	red-brown ppt, insoluble
Mn^{2+}	off-white ppt, turns brown in air	off-white ppt, turns brown in air
Cr^{3+}	grey-green ppt, dissolves in excess (green)	grey-green ppt
Ag^{+}	brown ppt (Ag_2O)	brown ppt, dissolves in excess ($[Ag(NH_3)_2]^+$)
NH_4^{+}	NH_3 on warming (damp red litmus turns blue)	—

Group separation used in Paper II

dil. HCl → AgCl, $PbCl_2$ (white)H_2S in acid → CuS, PbS (black)NH_4Cl / NH_3 → $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$$H_2S$ in base → ZnS (white), MnS (pink-buff), NiS, CoS (black)$(NH_4)_2CO_3$ → $CaCO_3$, $SrCO_3$, $BaCO_3$

Oxidize Fe^{2+} to Fe^{3+} (for example with concentrated HNO_3) before the NH_4Cl/NH_3 step. Sulfides that precipitate in acid have the smallest K_{sp} values (see Unit 12).

Anion tests

- CO_3^{2-}: dilute acid gives CO_2, which turns lime water milky.
- SO_4^{2-}: $BaCl_2$ gives a white ppt that is insoluble in dilute HCl. SO_3^{2-} gives a white ppt that dissolves, and SO_2 turns acidified dichromate green.
- S^{2-}: dilute acid gives H_2S, which blackens lead acetate paper. $S_2O_3^{2-}$: dilute acid gives a yellow S precipitate and SO_2.
- Cl^-, Br^-, I^- with $AgNO_3/HNO_3$: AgCl is white and dissolves in dilute NH_3. AgBr is cream and dissolves in concentrated NH_3. AgI is yellow and insoluble.
- NO_3^-: brown ring test, or Devarda's alloy with NaOH gives NH_3.

Key equations

Thermal stability (Group 2)$MgCO_3$ < $CaCO_3$ < $SrCO_3$ < $BaCO_3$

Solubility (Group 2)OH^- salts ↑ down · SO_4^{2-} salts ↓ down

Chromate ⇌ dichromate$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$

Permanganate (acid)$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Exam traps

- Learn the colours exactly. Pale yellow (AgBr) and yellow (AgI) are marked differently.
- Zn^{2+} dissolves in excess of both reagents, Al^{3+} only in excess NaOH, and Cu^{2+} only in excess NH_3. These three are tested very often.
- Write balanced equations for identification reactions as well as observations (Evaluation Report 2016).
- In complex names, spelling counts. One scheme notes: 'If spelling is incorrect do not award marks' (2018 marking scheme).

A+ moves

- Make a one-page colour chart of ions, precipitates and complexes and test yourself on it every day in the final month.
- For element-identification questions (Paper II Q2), use the clues in order: atomic number < 20, allotropes, ionization energy jumps, then reactions with water, acids and NaOH.

Past paper practice for Unit 6

Paper I · 32 MCQs (2019–2026)

- 2026 Q 4, 6, 12, 19, 34, 40, 42, 50
- 2025 Q 19, 34, 39, 50
- 2024 Q 34, 39, 41, 44, 47
- 2022(23) Q 16, 34, 36, 41, 42
- 2021(22) Q 26, 29, 37, 41, 43
- 2020 Q 31, 37, 41
- 2019 Q 23, 37

Paper II · 33 questions (2016–2026)

- 2026 Q9 — Identify four water-soluble inorganic compounds (two with d-block ions); quantitative analysis of a Cu–Zn–Sn alloy
- 2026 Q7 — Reduction potentials, cell diagrams and E°cell; a 4th-period d-block element with an amphoteric oxide
- 2026 Q2 — Identify p-block elements from allotropes (O, C) and an s-block metal from successive ionization energies; an oxoacid formed from CO_2 and water
- 2026 Q1 — Atomic/ionic properties from a species list; Lewis and resonance structures; σ/π bonds from orbital overlap; ordering properties (incl. carbonate decomposition temperature)
- 2025 Q9 — Qualitative analysis of four cations in solution Y; quantitative analysis of siderite ($FeCO_3$)
- 2025 Q7 — Electrochemical cell for $3Cu^+ + Au^{3+}$; octahedral coordination compounds
- 2025 Q2 — Identify s/p-block compounds from composition and reactions; thermal decomposition equations; the industrial process for one product
- 2024 Q9 — Qualitative analysis of four cations; sulfur content of iron pyrite (FeS_2)
- 2024 Q2 — Identify an orange ionic compound from composition; identify eight unlabelled solutions by mixing
- 2023(24) Q9 — Identify five solutions by mixing; analysis of a solid containing iron oxides

- 2023(24) Q7 — Daniell cell; octahedral coordination compounds of iron
- 2022(23) Q9 — Identify a coloured and a colourless compound from their reactions
- 2022(23) Q7 — Galvanic cell with the O_2/OH^- electrode; a 4th-period d-block element
- 2022(23) Q2 — Identify an ionic compound and its reaction products; balanced equations and oxidizing/reducing roles
- 2021(22) Q9 — Qualitative analysis of four cations; analysis of an Al_2S_3/Fe_2S_3 mixture
- 2021(22) Q7 — Displacement among metals L, M, N and cell emf; chemistry of manganese
- 2021(22) Q2 — Identify an s-block element and a p-block anion and their reactions
- 2020 Q9 — Identify substances in an inorganic flow chart
- 2020 Q7 — Electrolytic vs galvanic cells; a coloured complex ion of a 3d metal
- 2020 Q2 — Chlorides of p-block elements and their hydrolysis products; identify six unlabelled solutions
- 2019 Q9 — Qualitative analysis of four cations; quantitative analysis of anions in a water sample
- 2019 Q7 — Electrolysis to find the relative atomic mass of a metal; octahedral coordination compounds
- 2019 Q2 — An s-block element identified from successive ionization energies (Mg) and its compounds
- 2018 Q10 old syllabus — Complexes of manganese; Ag/AgCl electrode and electrolysis of $CaBr_2$(aq)
- 2018 Q8 old syllabus — Identify two cations and two anions in solution P
- 2018 Q2 old syllabus — A diatomic p-block element X and its hydride and oxo-acid; compounds of two elements of the same group
- 2017 Q10 old syllabus — Coordination compounds of titanium; a cell with Ag/AgCl and calomel electrodes
- 2017 Q8 old syllabus — Qualitative analysis of three cations; ammonium salts by quantitative analysis
- 2017 Q2 old syllabus — Elements of one group in successive periods; identify three anions
- 2016 Q10 old syllabus — Octahedral coordination compounds; electrochemistry
- 2016 Q8 old syllabus — A 3d-block complex and its reactions; identify three metal ions
- 2016 Q2 old syllabus — Two s-block elements and their hydroxides
- 2016 Q1 old syllabus — p-block elements from a list; Lewis structure of CN_2-type molecule

Model questions (original, in past-paper style)

M6.1

Single answer · like Q1–30

An aqueous solution gives a white precipitate with both NaOH(aq) and NH_3(aq). The precipitate dissolves in excess of each reagent. The cation is

- (1)Al^{3+}
- (2)Mg^{2+}
- (3)Zn^{2+}
- (4)Pb^{2+}
- (5)Ca^{2+}

Show model answer

Answer (3). $Zn(OH)_2$ is amphoteric (it dissolves in excess OH^-) and also forms $[Zn(NH_3)_4]^{2+}$ in excess ammonia.

M6.2

Multiple response · like Q31–40

Which statement(s) about Group 2 elements and their compounds is/are correct? (a) The thermal stability of the carbonates increases down the group. (b) The solubility of the sulfates increases down the group. (c) Mg burns in air to form MgO and Mg_3N_2. (d) BeO is a basic oxide.

Answer with the response code (1)–(5) from the code table.

Show model answer

Answer (5). Only (a) and (c) are correct. (b) is wrong because sulfate solubility decreases, and (d) is wrong because BeO is amphoteric. The pair (a)+(c) is not one of the coded pairs, so the answer is (5).

M6.3

Single answer · like Q1–30

The correct IUPAC name of $[Co(NH_3)_5Cl]Cl_2$ is

- (1)pentaamminechloridocobalt(III) chloride
- (2)chloridopentaamminecobalt(II) chloride
- (3)pentaamminechloridocobaltate(III) chloride
- (4)pentaamminechlorocobalt(II) dichloride
- (5)chloridopentaamminecobalt(III) dichloride

Show model answer

Answer (1). Ligands go in alphabetical order (ammine before chlorido). Co is +3 because NH_3 is neutral and there are three Cl^- in total (1 inside, 2 outside). The complex is a cation, so there is no -ate ending.

M6.4

Structured · like Paper II

Solution S contains two cations. (i) With dilute HCl, nothing happens. (ii) H_2S passed through the acidified solution gives a black precipitate. (iii) The filtrate, boiled and treated with NH_4Cl/NH_3, gives a white gelatinous precipitate that dissolves in NaOH(aq). Identify the two cations and write an equation for each test.

Show model answer

(ii) shows Cu^{2+}: $Cu^{2+}(aq) + H_2S(g) \rightarrow CuS(s) + 2H^+(aq)$. Pb^{2+} is ruled out because no $PbCl_2$ formed in (i). (iii) shows Al^{3+}: $Al^{3+}(aq) + 3OH^-(aq) \rightarrow Al(OH)_3(s)$, and then $Al(OH)_3(s) + OH^-(aq) \rightarrow [Al(OH)_4]^-(aq)$.

Unit

Grade 12 · 12 MCQs in 7 papers · 4 Paper II questions since 2019

Basic concepts of organic chemistry

Functional groups, IUPAC names and isomerism. Every Paper I asks you to name a compound (usually around Q5) and to judge a stereoisomerism statement. Paper II Q4 starts from isomers of a molecular formula.

Read alongside: NIE Resource Book, Vol. 4 (Grade 12, 2019), Unit 7, pp. 1–25

Why carbon forms so many compounds

RB §1.1 · p. 2

Carbon is tetravalent and can form stable chains and rings (catenation) as well as single, double and triple bonds, so it builds a huge variety of structures.

Functional groups

RB §1.2 · p. 3

The classes to know are alcohols, ethers, aldehydes, ketones, alkyl halides, carboxylic acids, acid halides, esters, amides, amines and nitriles, plus alkenes and alkynes. When a compound has several groups, the principal (suffix) group follows the priority **carboxylic acid > ester > acid halide > amide > aldehyde > ketone > alcohol > amine**. Halo- and nitro- groups are always prefixes.

IUPAC naming routine

RB §1.3 · p. 7

- Find the principal group.
- Choose the main chain that contains it (and any C=C or C≡C).
- Number the chain from the end that gives the principal group the lowest number, then the multiple bonds, then the substituents.
- Put the prefixes in alphabetical order (bromo, chloro, ethyl, formyl, hydroxy, methyl, oxo …).
- Build the name: prefixes + parent chain + -en-/-yn- + suffix.

Examples: $HOCH_2CH_2CHO$ is 3-hydroxypropanal, and $CH_3CH(Br)CH{=}CHCOOH$ is 4-bromopent-2-enoic acid.

Isomerism

RB §1.4 · p. 21

Constitutional isomers differ in the chain, the position of a group or the functional group. **Stereoisomers** have the same connectivity but a different arrangement in space:

- **Geometric (cis/trans)**: needs restricted rotation (C=C) and two different groups on each doubly bonded carbon.
- **Optical**: needs a chiral carbon (four different groups). Enantiomers are non-superimposable mirror images that rotate plane-polarised light equally in opposite directions. A racemic mixture is optically inactive.
- **Diastereoisomers** are stereoisomers that are not mirror images. Cis and trans isomers are diastereoisomers.

Key equations

Degree of unsaturation$(2C + 2 + N - H - X) \div 2$

Chiral centreC with four different groups

Geometric isomerismC=C with two different groups on each carbon

Exam traps

- Not every compound with a C=C shows geometric isomerism. But-1-ene and 2-methylbut-2-ene do not.
- A chiral carbon must carry four different groups. Count CH_2CH_3 and CH_3 as different, but two CH_3 groups as identical.
- CHO on a ring or side chain is named with the prefix 'formyl' when it is not the principal group.
- The examiners asked for clear understanding of 'enantiomer' versus 'diastereomer', with examples (Evaluation Report 2016).

A+ moves

- Draw out every structural isomer of C_4H_9Br, $C_4H_{10}O$ and C_5H_{10} once. These formulas recur in Paper II Q4.
- Calculate the degree of unsaturation first. It tells you straight away whether a ring or a double bond is present.

Past paper practice for Unit 7

Paper I · 12 MCQs (2019–2026)

- 2026 Q 9, 48
- 2025 Q 7
- 2024 Q 5, 42
- 2022(23) Q 5, 8
- 2021(22) Q 5
- 2020 Q 5, 45
- 2019 Q 4, 40

Paper II · 7 questions (2016–2026)

- 2025 Q4 — Reaction scheme from C_5H_{10} to an optically active product; classify reaction types; Friedel–Crafts alkylation mechanism
- 2022(23) Q4 — Identify C_5H_{10} isomers; products of alkyl halide and alcohol reactions
- 2021(22) Q4 — C_4H_9Br isomers with optical isomerism; Grignard products; Br_2 addition to but-2-ene mechanism
- 2020 Q4 — Identify C_5H_{10} structural isomers from their reactions
- 2018 Q4 old syllabus — Structural isomers and their reactions
- 2017 Q4 old syllabus — $C_4H_{10}O$ alcohol isomers and optical isomerism; diazonium reaction schemes
- 2016 Q4 old syllabus — $C_4H_{10}O$ isomers; products of organic reactions

Model questions (original, in past-paper style)

M7.1

Single answer · like Q1–30

How many structural isomers have the formula C_4H_9Br, and how many of them are chiral?

- (1)3 and 0
- (2)4 and 1

- (3)4 and 2
- (4)5 and 1
- (5)5 and 2

Show model answer

Answer (2). The four isomers are 1-bromobutane, 2-bromobutane, 1-bromo-2-methylpropane and 2-bromo-2-methylpropane. Only 2-bromobutane has a chiral carbon.

M7.2

Single answer · like Q1–30

Which compound shows geometric isomerism?

- (1)but-1-ene
- (2)2-methylbut-2-ene
- (3)pent-2-ene
- (4)cyclohexene
- (5)propene

Show model answer

Answer (3). In pent-2-ene, C2 carries H and CH_3 and C3 carries H and C_2H_5, so each carbon has two different groups.

M7.3

Statement pair · like Q41–50

Statement 1: cis-But-2-ene and trans-but-2-ene are diastereoisomers. **Statement 2:** Stereoisomers that are not mirror images of each other are diastereoisomers.

Answer with the statement-pair code (1)–(5) from the code table.

Show model answer

Answer (1). Both statements are true, and the second explains the first.

M7.4

Structured · like Paper II

Give the IUPAC names of (a) $CH_3CH(OH)CH_2CHO$, (b) $CH_3COCH_2CH(CH_3)_2$, (c) $HC{\equiv}CCH_2CH(Cl)CH_3$.

Show model answer

(a) 3-hydroxybutanal. (b) 4-methylpentan-2-one. (c) 4-chloropent-1-yne.

Unit

Grade 12 · 25 MCQs in 7 papers · 14 Paper II questions since 2019

Hydrocarbons and halohydrocarbons

Alkanes, alkenes, alkynes, benzene and alkyl halides: their reactions and mechanisms. Paper II Q4 and Q8 almost always ask for one full mechanism, either electrophilic addition, electrophilic substitution on benzene, or nucleophilic substitution.

Read alongside: NIE Resource Book, Vol. 4 (Grade 12, 2019), Unit 8, pp. 26–52

Alkanes: free-radical substitution

RB §2.2 · p. 33

In light, $Cl_2 \rightarrow 2Cl\bullet$ (initiation). Then $Cl\bullet + CH_4 \rightarrow \bullet CH_3 + HCl$ and $\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\bullet$ (propagation). Two radicals combining is termination, for example $\bullet CH_3 + \bullet CH_3 \rightarrow C_2H_6$. This is why ethane appears as a by-product. The reaction gives a mixture of substituted products.

Alkenes: electrophilic addition

RB §2.2 · p. 33

- **HX**: H^+ adds first to give the more stable carbocation (3° > 2° > 1°), so H goes to the carbon that already has more H (Markovnikov's rule). With peroxides, HBr adds the opposite way.
- **Br_2** (in water or CCl_4): the bromine colour disappears, which is the test for C=C. The reaction goes through a cyclic bromonium ion.
- **Concentrated H_2SO_4, then water**: gives an alcohol (Markovnikov orientation).
- **H_2 with Ni or Pd**: gives the alkane. **Cold, dilute alkaline $KMnO_4$**: gives a diol, and the purple colour turns to a brown MnO_2 precipitate.

Alkynes

RB §2.2 · p. 33

Alkynes add Br_2 and HX twice. With Hg^{2+} and dilute H_2SO_4, water adds to give an enol, which rearranges to a carbonyl compound (ethyne gives ethanal). H_2 with Lindlar's catalyst ($Pd/BaSO_4$/quinoline) stops at the cis-alkene. A **terminal alkyne** has an acidic C–H. It gives a precipitate with ammoniacal $AgNO_3$ (white) or ammoniacal CuCl (red), and reacts with CH_3MgBr to give $RC{\equiv}CMgBr + CH_4$.

Benzene: structure and electrophilic substitution

RB §2.4 · p. 44

Benzene is a resonance hybrid with six delocalised π electrons. All C–C bonds are equal (between single and double), and the ring is far more stable than a 'cyclohexatriene' would be. Benzene therefore undergoes **substitution, not addition**. Nitration uses concentrated HNO_3 and concentrated H_2SO_4 (electrophile NO_2^+). Halogenation uses $Cl_2/FeCl_3$ or $Br_2/FeBr_3$. Friedel–Crafts alkylation uses $RCl/AlCl_3$, and acylation uses $RCOCl/AlCl_3$. The mechanism: the electrophile attacks, forming a resonance-stabilised carbocation (arenium ion), which then loses H^+. The ring resists oxidation, but alkyl side chains are oxidized to –COOH by $KMnO_4$.

Directing effects

RB §2.5 · p. 49

ortho/para directors: –OH, $–NH_2$, –OR and alkyl groups (activating), and halogens (deactivating). **meta directors**: $–NO_2$, –CHO, –COR, –COOH, –CN and $–CO_2R$ (deactivating). In a synthesis, the order of steps decides which isomer you get.

Alkyl halides

RB §2.6 · p. 49

The C–X bond is polar, so the carbon is attacked by nucleophiles. Aqueous NaOH gives an alcohol. KCN gives a nitrile (one carbon longer). RO^- gives an ether. NH_3 gives amines. Alcoholic KOH causes **elimination** to the more substituted alkene. Tertiary halides react by S_{N1} (carbocation, rate = k[RX]), primary halides by S_{N2} (one step, back-side attack, rate = k[RX][Nu^-]). With Mg in dry ether, RX gives the Grignard reagent RMgX, which water destroys (giving RH). Aryl halides such as C_6H_5Cl do **not** undergo nucleophilic substitution easily.

Reaction pathways and tests

Hydrocarbon map

alkyne + H_2 (Lindlar) → cis-alkenealkene + HBr → bromoalkane (Markovnikov)bromoalkane + aq. NaOH → alcoholbromoalkane + alc. KOH → alkenebromoalkane + KCN → nitrile (+1 C)bromoalkane + Mg (dry ether) → RMgBr

Benzene map

C_6H_6 + HNO_3/H_2SO_4 → $C_6H_5NO_2C_6H_6$ + $Br_2/FeBr_3$ → $C_6H_5BrC_6H_6$ + $CH_3Cl/AlCl_3$ → $C_6H_5CH_3C_6H_6$ + $CH_3COCl/AlCl_3$ → $C_6H_5COCH_3C_6H_5CH_3$ + $KMnO_4$ → C_6H_5COOH

Key equations

Carbocation stability3° > 2° > 1° > CH_3^+

S_{N1} raterate = k[RX]

S_{N2} raterate = k[RX][Nu^-]

Exam traps

- Curly arrows start at a lone pair or a bond and point to where the electrons go. A missing charge on an intermediate costs marks.
- m-Bromonitrobenzene needs nitration first (–NO_2 directs meta). Brominating first gives the o- and p-isomers.
- Benzene does not decolourise bromine water. That difference from an alkene is a common statement question.
- Compare Grignard reagents with alkynes that have acidic hydrogen. The examiners flagged this (Evaluation Report 2016).

A+ moves

- Write each mechanism once a week until you can do all three (addition, aromatic substitution, S_N) without notes.
- For synthesis questions, work backwards from the target and count steps. Papers set a maximum (often 3–5).

Past paper practice for Unit 8

Paper I · 25 MCQs (2019–2026)

- 2026 Q 15, 23, 36, 41
- 2025 Q 9, 15, 31
- 2024 Q 14, 21, 32, 45

- 2022(23) Q 20, 24, 32, 44
- 2021(22) Q 20, 31, 45
- 2020 Q 16, 46
- 2019 Q 7, 20, 32, 35, 46

Paper II · 18 questions (2016–2026)

- 2026 Q8 — Ester → Grignard reaction scheme; substitution vs elimination of 1-bromopropane with ethoxide (mechanisms); resonance and basicity of aniline vs ethylamine; conversions
- 2026 Q4 — Identify C_5 chloro-compound A and its products; classify reaction types; Br_2 addition to an alkene with mechanism
- 2025 Q8 — Scheme from 2-methylpropanamide; Markovnikov addition of HBr to 2-methylbut-2-ene; acidity of phenol vs acetic acid; a five-step conversion
- 2025 Q4 — Reaction scheme from C_5H_{10} to an optically active product; classify reaction types; Friedel–Crafts alkylation mechanism
- 2024 Q8 — Reaction scheme from ethanol; conversions incl. an azo dye from aniline; bromination of benzene: mechanism and resonance
- 2023(24) Q8 — Scheme from $(CH_3)_2CHCO_2H$; synthesis from benzene; nitration of benzene mechanism
- 2022(23) Q8 — Synthesis from propyne; four-step transformations; a mechanism with NaOH
- 2022(23) Q4 — Identify C_5H_{10} isomers; products of alkyl halide and alcohol reactions
- 2021(22) Q8 — Multi-step conversion from an amine; nitration route to nitrobenzoic acids; stability of benzene
- 2021(22) Q4 — C_4H_9Br isomers with optical isomerism; Grignard products; Br_2 addition to but-2-ene mechanism
- 2020 Q8 — Organic reaction scheme and conversions
- 2020 Q4 — Identify C_5H_{10} structural isomers from their reactions
- 2019 Q8 — Synthesis using methyl benzoate as the only organic starting material
- 2019 Q4 — $C_5H_{10}O$ carbonyl compounds with 2,4-DNP; reaction sequences with Grignard and Lindlar reagents
- 2018 Q7 old syllabus — Conversions using a given list of chemicals; completing a reaction scheme
- 2017 Q7 old syllabus — Conversions in limited steps and reaction schemes
- 2016 Q7 old syllabus — Conversions using a list of chemicals; completing a reaction scheme
- 2016 Q4 old syllabus — $C_4H_{10}O$ isomers; products of organic reactions

Model questions (original, in past-paper style)

M8.1

Single answer · like Q1–30

The major product when 2-methylpropene reacts with HBr (no peroxide) is

- (1)1-bromo-2-methylpropane
- (2)2-bromo-2-methylpropane
- (3)1-bromobutane
- (4)2-bromobutane

- (5)1,2-dibromo-2-methylpropane

Show model answer

Answer (2). H^+ adds to CH_2 and forms the tertiary carbocation $(CH_3)_3C^+$, which Br^- then attacks.

M8.2

Single answer · like Q1–30

Which reagent sequence converts benzene into m-bromonitrobenzene?

- (1)Br_2/$FeBr_3$, then HNO_3/H_2SO_4
- (2)HNO_3/H_2SO_4, then Br_2/$FeBr_3$
- (3)Br_2 (aq), then HNO_3
- (4)HNO_3/H_2SO_4, then HBr
- (5)Br_2/hν, then HNO_3/H_2SO_4

Show model answer

Answer (2). –NO_2 is a meta director, so it must be put on first. The bromine then enters at the meta position.

M8.3

Multiple response · like Q31–40

Which statement(s) about 2-bromo-2-methylpropane is/are correct? (a) With aqueous NaOH it reacts mainly by S_{N1}. (b) Its reaction rate with OH^- is first order overall. (c) With alcoholic KOH it gives 2-methylpropene. (d) It reacts with Mg in water to give a Grignard reagent.

Answer with the response code (1)–(5) from the code table.

Show model answer

Answer (5). (a), (b) and (c) are correct. (d) is wrong because a Grignard reagent needs dry ether, and water destroys it. Three correct responses is not one of the coded pairs, so the answer is (5).

M8.4

Structured · like Paper II

Write the mechanism for the reaction of propene with HBr. Explain why 2-bromopropane is the major product.

Show model answer

Step 1: the π electrons of C=C attack H of H–Br, and the H–Br bond electrons move to Br, giving Br^- and the carbocation $CH_3C^+HCH_3$. Step 2: Br^- attacks C^+ to give $CH_3CHBrCH_3$. The secondary carbocation is more stable than the primary $CH_3CH_2CH_2^+$ because two alkyl groups release electrons towards it, so the reaction goes mainly through the secondary ion.

Unit

Grade 12 · 27 MCQs in 7 papers · 14 Paper II questions since 2019

Oxygen containing organic compounds

Alcohols, phenols, aldehydes, ketones, carboxylic acids and their derivatives. This is the most heavily tested organic unit in Paper I, and the starting point for most Paper II reaction schemes.

Read alongside: NIE Resource Book, Vol. 4 (Grade 12, 2019), Unit 9, pp. 53–73

Alcohols

RB §3.1 · p. 54

Alcohols are classified as 1°, 2° or 3° by the carbon carrying –OH. Hydrogen bonding gives them high boiling points, and their water solubility falls as the chain grows. Breaking O–H: $2ROH + 2Na \rightarrow 2RONa + H_2$. Breaking C–O: PCl_5, PCl_3 or HX gives RX. Lucas reagent ($ZnCl_2$/conc. HCl) goes cloudy at once with 3°, after a few minutes with 2°, and not at room temperature with 1°. Concentrated H_2SO_4 and heat (or Al_2O_3) dehydrate an alcohol to an alkene. **Oxidation**: 1° → aldehyde (with PCC) → carboxylic acid (with acidified $K_2Cr_2O_7$ or $KMnO_4$); 2° → ketone; 3° → no reaction. Dichromate turns from orange to green.

Phenols

RB §3.2 · p. 58

Phenol is more acidic than an alcohol (the phenoxide ion is stabilised by resonance) but weaker than a carboxylic acid. It reacts with NaOH but **not** with $NaHCO_3$ (no CO_2). Its C–O bond does not undergo nucleophilic substitution. The ring is strongly activated: Br_2(aq) gives a white precipitate of 2,4,6-tribromophenol without a catalyst, and dilute HNO_3 nitrates it. $FeCl_3$ gives a violet colour.

Aldehydes and ketones

RB §3.4 · p. 60

The polar C=O group undergoes **nucleophilic addition**. HCN gives a cyanohydrin. A Grignard reagent gives an alcohol after hydrolysis (HCHO gives 1°, other RCHO give 2°, ketones give 3°). 2,4-DNP (Brady's reagent) gives an orange-red precipitate, which is the test for C=O. Dilute NaOH causes **aldol** condensation when the compound has an α-H. $LiAlH_4$ or $NaBH_4$ reduce them to alcohols, and Zn(Hg)/conc. HCl (Clemmensen) reduces C=O to CH_2. Only aldehydes are oxidized by Tollens' reagent (silver mirror), Fehling's solution (red Cu_2O) and acidified dichromate.

Carboxylic acids

RB §3.5 · p. 66

Hydrogen-bonded dimers give them higher boiling points than alcohols of similar mass. They liberate CO_2 from $NaHCO_3$. Electron-withdrawing groups make the acid stronger ($ClCH_2COOH > CH_3COOH$). PCl_5 gives the acid chloride. An alcohol with concentrated H_2SO_4 gives an ester (reversible). NH_3 gives the ammonium salt, which becomes an amide on heating. $LiAlH_4$ reduces the acid to a 1° alcohol. With a Grignard reagent, the acidic H gives an alkane.

Acid derivatives

RB §3.6 · p. 70

Reactivity: acid chloride > ester > amide. Acid chlorides react with water (giving the acid), alcohols and phenols (esters), NH_3 or amines (amides) and NaOH (the carboxylate), through a tetrahedral intermediate. Esters hydrolyse in acid (reversible) or base (saponification). With excess Grignard reagent they give 3° alcohols, because the ketone formed first reacts faster than the ester. $LiAlH_4$ gives two alcohols. Amides hydrolyse in acid or base, and $LiAlH_4$ reduces them to amines.

Reaction pathways and tests

Oxidation ladder

RCH_2OH (1°)→ RCHO (PCC)→ RCOOH ($H^+/Cr_2O_7^{2-}$)→ RCOCl (PCl_5)→ RCOOR' / $RCONH_2$

Reductions to compare

$NaBH_4$ reduces aldehydes and ketones only. $LiAlH_4$ also reduces acids, esters and amides (and nitriles to amines). The examiners asked candidates to compare these reagents (Evaluation Report 2016).

Key equations

Acidity$ROH < H_2O <$ phenol $<$ RCOOH $< ClCH_2COOH$

Grignard + C=ORMgX + R'CHO → RR'CHOH (after H_3O^+)

Esterification$RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O$

Exam traps

- 'HCN with any aldehyde gives a chiral product' is false. Methanal's cyanohydrin, $HOCH_2CN$, has no chiral carbon.
- Tollens' and Fehling's tests separate aldehydes from ketones. 2,4-DNP does not, because both give a precipitate.
- Phenol does not release CO_2 from $NaHCO_3$, so this test separates phenols from carboxylic acids.
- For ketone + Grignard, you must show the hydrolysis step (H^+/H_2O) to get the alcohol.

A+ moves

- Build one master reaction grid: rows for each functional group, columns for Na, NaOH, $NaHCO_3$, PCl_5, 2,4-DNP, Tollens'/Fehling's, $LiAlH_4$, $NaBH_4$ and RMgX. Fill in product or 'no reaction'.
- Most Paper II schemes give molecular formulas. Track how the formula changes at each step.

Past paper practice for Unit 9

Paper I · 27 MCQs (2019–2026)

- 2026 Q 7, 20, 27, 32
- 2025 Q 20, 27, 42, 47
- 2024 Q 9, 23, 28, 33
- 2022(23) Q 10, 29, 35
- 2021(22) Q 9, 30, 34, 46
- 2020 Q 9, 11, 20, 30, 34
- 2019 Q 13, 45, 48

Paper II · 20 questions (2016–2026)

- 2026 Q8 — Ester → Grignard reaction scheme; substitution vs elimination of 1-bromopropane with ethoxide (mechanisms); resonance and basicity of aniline vs ethylamine; conversions
- 2026 Q4 — Identify C_5 chloro-compound A and its products; classify reaction types; Br_2 addition to an alkene with mechanism
- 2025 Q8 — Scheme from 2-methylpropanamide; Markovnikov addition of HBr to 2-methylbut-2-ene; acidity of phenol vs acetic acid; a five-step conversion

- 2025 Q4 — Reaction scheme from C_5H_{10} to an optically active product; classify reaction types; Friedel–Crafts alkylation mechanism
- 2024 Q8 — Reaction scheme from ethanol; conversions incl. an azo dye from aniline; bromination of benzene: mechanism and resonance
- 2024 Q4 — Identify a carboxylic acid via PCl_5 product mass; products of acetone with NaOH and other reagents; HCN addition mechanism
- 2023(24) Q8 — Scheme from $(CH_3)_2CHCO_2H$; synthesis from benzene; nitration of benzene mechanism
- 2022(23) Q8 — Synthesis from propyne; four-step transformations; a mechanism with NaOH
- 2022(23) Q4 — Identify C_5H_{10} isomers; products of alkyl halide and alcohol reactions
- 2021(22) Q8 — Multi-step conversion from an amine; nitration route to nitrobenzoic acids; stability of benzene
- 2021(22) Q4 — C_4H_9Br isomers with optical isomerism; Grignard products; Br_2 addition to but-2-ene mechanism
- 2020 Q8 — Organic reaction scheme and conversions
- 2019 Q8 — Synthesis using methyl benzoate as the only organic starting material
- 2019 Q4 — $C_5H_{10}O$ carbonyl compounds with 2,4-DNP; reaction sequences with Grignard and Lindlar reagents
- 2018 Q7 old syllabus — Conversions using a given list of chemicals; completing a reaction scheme
- 2018 Q4 old syllabus — Structural isomers and their reactions
- 2017 Q7 old syllabus — Conversions in limited steps and reaction schemes
- 2017 Q4 old syllabus — $C_4H_{10}O$ alcohol isomers and optical isomerism; diazonium reaction schemes
- 2016 Q7 old syllabus — Conversions using a list of chemicals; completing a reaction scheme
- 2016 Q4 old syllabus — $C_4H_{10}O$ isomers; products of organic reactions

Model questions (original, in past-paper style)

M9.1

Single answer · like Q1–30

Propanone reacts with CH_3MgBr in dry ether and the product is hydrolysed. The final organic product is

- (1)propan-2-ol
- (2)2-methylpropan-2-ol
- (3)butan-2-ol
- (4)2-methylpropan-1-ol
- (5)butanone

Show model answer

Answer (2). CH_3 adds to the carbonyl carbon, giving $(CH_3)_3COMgBr$. Hydrolysis gives the tertiary alcohol $(CH_3)_3COH$.

M9.2

Single answer · like Q1–30

Which reagent distinguishes propanal from propanone?

- (1)2,4-DNP
- (2)Na metal
- (3)Fehling's solution
- (4)Br_2/CCl_4
- (5)$NaBH_4$

Show model answer

Answer (3). Only the aldehyde is oxidized and gives red Cu_2O. Both compounds react with 2,4-DNP and $NaBH_4$.

M9.3

Multiple response · like Q31–40

Which statement(s) about phenol is/are correct? (a) It liberates CO_2 from aqueous $NaHCO_3$. (b) It reacts with aqueous NaOH. (c) It gives a white precipitate with bromine water. (d) Its –OH can be replaced by Cl using HCl.

Answer with the response code (1)–(5) from the code table.

Show model answer

Answer (2). Only (b) and (c) are correct, which is code (2). Phenol is too weak an acid for (a), and its C–O bond does not break as in (d).

M9.4

Structured · like Paper II

Compound A (C_3H_6O) gives an orange precipitate with 2,4-DNP and a silver mirror with Tollens' reagent. A is reduced by $NaBH_4$ to B. B reacts with ethanoic acid (concentrated H_2SO_4 catalyst) to give C. Identify A, B and C, and write the equation for the formation of C.

Show model answer

A is propanal, CH_3CH_2CHO (an aldehyde: 2,4-DNP positive, Tollens' positive). B is propan-1-ol, $CH_3CH_2CH_2OH$. C is propyl ethanoate: $CH_3COOH + CH_3CH_2CH_2OH \rightleftharpoons CH_3COOCH_2CH_2CH_3 + H_2O$.

Unit

Grade 12 · 8 MCQs in 7 papers · 4 Paper II questions since 2019

Nitrogen containing organic compounds

Amines, amides and diazonium salts. The unit is short, but it is tested every year, usually through basicity order, the reaction with nitrous acid, and azo-dye coupling inside Paper II synthesis routes.

Read alongside: NIE Resource Book, Vol. 4 (Grade 12, 2019), Unit 10, pp. 74–80

Amines and basicity

RB §4.2 · p. 77

The lone pair on N accepts H^+. Aliphatic amines are stronger bases than NH_3 because alkyl groups release electrons. Aniline is a much weaker base because its lone pair is delocalised into the ring. Amides are practically neutral because the lone pair is delocalised onto C=O. Amines are more basic than alcohols because N is less electronegative than O. Order: ethylamine > NH_3 > aniline > ethanamide.

Reactions of primary amines

RB §4.1 · p. 75

- With alkyl halides: a mixture of 2° and 3° amines and the quaternary ammonium salt.
- With aldehydes and ketones: an imine (C=N), formed by condensation.
- With acid chlorides: an N-substituted amide.
- With nitrous acid ($NaNO_2$/HCl): an aliphatic 1° amine gives an alcohol plus N_2 gas. Aniline at 0–5 °C gives benzenediazonium chloride.
- Aniline's ring is strongly activated: Br_2(aq) gives a white precipitate of 2,4,6-tribromoaniline.

Diazonium salts

RB §4.3 · p. 78

$C_6H_5N_2^+Cl^-$ is stable only below about 5 °C. **Replacement reactions** (N_2 is released): warm water gives phenol; H_3PO_2 gives benzene; CuCl or CuBr gives chloro- or bromobenzene; CuCN gives benzonitrile (which hydrolyses to benzoic acid); KI gives iodobenzene. **As an electrophile**, it couples with phenol in alkaline solution to give an orange-red azo dye, and also couples with aromatic amines.

Reaction pathways and tests

Aromatic nitrogen map

C_6H_6 → $C_6H_5NO_2$ (HNO_3/H_2SO_4)→ $C_6H_5NH_2$ (Sn/conc. HCl, then NaOH)→ $C_6H_5N_2^+Cl^-$ ($NaNO_2$/HCl, 0–5 °C)→ C_6H_5OH, C_6H_5Cl, C_6H_5CN, C_6H_5I or an azo dye

Key equations

Basicity order$C_2H_5NH_2$ > NH_3 > $C_6H_5NH_2$ > CH_3CONH_2

Diazotisation$C_6H_5NH_2 + HNO_2 + HCl \rightarrow C_6H_5N_2^+Cl^- + 2H_2O$ (0–5 °C)

Exam traps

- Keep the diazotisation temperature at 0–5 °C, and say so in synthesis answers. Above this, the salt decomposes.
- An aliphatic 1° amine with HNO_2 gives N_2 bubbles and an alcohol, not a stable diazonium salt.
- $LiAlH_4$ reduces an amide or nitrile to an amine. $NaBH_4$ does not.

- The coupling with phenol needs alkaline conditions (phenoxide ion). The colour is orange-red.

A+ moves

- Learn the diazonium replacements as a star diagram with $C_6H_5N_2^+$ at the centre. They open short routes in Paper II conversions.
- For basicity questions, ask 'Is the lone pair free or delocalised?' before anything else.

Past paper practice for Unit 10

Paper I · 8 MCQs (2019–2026)

- 2025 Q 23, 35
- 2022(23) Q 45
- 2021(22) Q 11, 16, 48
- 2020 Q 48
- 2019 Q 17

Paper II · 8 questions (2016–2026)

- 2026 Q8 — Ester → Grignard reaction scheme; substitution vs elimination of 1-bromopropane with ethoxide (mechanisms); resonance and basicity of aniline vs ethylamine; conversions
- 2025 Q8 — Scheme from 2-methylpropanamide; Markovnikov addition of HBr to 2-methylbut-2-ene; acidity of phenol vs acetic acid; a five-step conversion
- 2024 Q8 — Reaction scheme from ethanol; conversions incl. an azo dye from aniline; bromination of benzene: mechanism and resonance
- 2021(22) Q8 — Multi-step conversion from an amine; nitration route to nitrobenzoic acids; stability of benzene
- 2018 Q7 old syllabus — Conversions using a given list of chemicals; completing a reaction scheme
- 2017 Q7 old syllabus — Conversions in limited steps and reaction schemes
- 2017 Q4 old syllabus — $C_4H_{10}O$ alcohol isomers and optical isomerism; diazonium reaction schemes
- 2016 Q7 old syllabus — Conversions using a list of chemicals; completing a reaction scheme

Model questions (original, in past-paper style)

M10.1

Single answer · like Q1–30

Which of the following is the strongest base in water?

- (1)aniline
- (2)ethanamide
- (3)ethylamine
- (4)ammonia
- (5)phenol

Show model answer

Answer (3). The ethyl group releases electrons and makes the N lone pair more available. Aniline's and ethanamide's lone pairs are delocalised, and phenol is acidic.

M10.2

Single answer · like Q1–30

Benzenediazonium chloride is warmed with water. The organic product and the gas formed are

- (1)benzene and N_2
- (2)phenol and N_2
- (3)aniline and N_2
- (4)chlorobenzene and N_2
- (5)phenol and NH_3

Show model answer

Answer (2). $C_6H_5N_2^+ + H_2O \rightarrow C_6H_5OH + N_2 + H^+$.

M10.3

Statement pair · like Q41–50

Statement 1: Aniline is a weaker base than ethylamine. **Statement 2:** The lone pair on the nitrogen of aniline is delocalised into the benzene ring.

Answer with the statement-pair code (1)–(5) from the code table.

Show model answer

Answer (1). Both statements are true, and the second explains the first.

M10.4

Structured · like Paper II

Show how to convert benzene into phenol in four steps, giving the reagents and conditions for each step.

Show model answer

1. Concentrated HNO_3 / concentrated H_2SO_4 (about 50 °C) → nitrobenzene. 2. Sn / concentrated HCl, then NaOH → aniline. 3. $NaNO_2$ / dilute HCl at 0–5 °C → benzenediazonium chloride. 4. Warm with water → phenol (+ N_2).

Unit

Grade 13 · 20 MCQs in 7 papers · 6 Paper II questions since 2019

Chemical kinetics

Rates, rate laws, orders, half-lives, mechanisms and energy profiles. About three MCQs a year, plus a Part B question (Q6) that usually combines kinetics with another physical topic.

Read alongside: NIE Resource Book, Vol. 5 (Grade 13, 2019), Unit 11, pp. 1–74

Rate and stoichiometry

RB §1.3 · p. 9

Rate is the change in concentration per unit time. It can be an average, instantaneous or initial rate. For aA + bB → cC, rate = $-(1/a)\Delta[A]/\Delta t = -(1/b)\Delta[B]/\Delta t = (1/c)\Delta[C]/\Delta t$. So in $O_2 + 2H_2 \rightarrow 2H_2O$, $[H_2]$ falls twice as fast as $[O_2]$.

Measuring rates

RB §1.4 · p. 14

Rates are followed by gas volume, pressure in a rigid container, colour (colorimetry), conductivity, or titration of quenched samples. 'Clock' reactions, such as thiosulfate with acid, measure the time to reach a fixed point. Keep the temperature constant, because rate depends strongly on T.

Collision theory and factors

RB §1.5 · p. 15

For a reaction to happen, particles must collide with energy ≥ E_a and with the correct orientation. Concentration and pressure raise the collision frequency. Temperature mainly raises the **fraction of collisions with E ≥ E_a** (the Maxwell–Boltzmann tail). Surface area and light also matter.

Rate laws and order

RB §1.5 · p. 15

rate = $k[A]^m[B]^n$. The orders m and n are found by **experiment**, not from the balanced equation. The units of k are mol dm^{-3} s^{-1} (zero order), s^{-1} (first order) and mol^{-1} dm^3 s^{-1} (second order). Initial-rate method: change one concentration at a time. If doubling [A] doubles the rate, the order is 1. If it quadruples the rate, the order is 2. If the rate is unchanged, the order is 0.

Zero order: [A] against t is a straight line, and $t_{½} = [A]_0/2k$. **First order**: ln[A] against t is a straight line, and $t_{½} = 0.693/k$, independent of $[A]_0$. After n half-lives, $(½)^n$ remains, so 87.5% has reacted after 3 half-lives. When one reactant is in large excess, the reaction behaves as **pseudo-first-order**.

Catalysts

RB §1.9 · p. 54

A catalyst provides an alternative pathway with a lower E_a. It speeds up the forward and reverse reactions equally. It changes neither ΔH nor the position of equilibrium, and it is regenerated at the end. Catalysts can be homogeneous or heterogeneous.

Mechanisms and energy profiles

RB §1.10 · p. 57

An **elementary** step's molecularity (1, 2 or 3) equals its order. The slowest step determines the rate. Intermediates are formed in one step and used up in a later one, whereas a catalyst is used up first and regenerated. When a fast pre-equilibrium comes before a slow step, substitute K for the intermediate: for I_2 ⇌

2I (fast) followed by H_2 + 2I → 2HI (slow), rate = k[H_2][I_2]. An energy profile shows E_a, ΔH, transition states and any intermediates, and has one hump for each step.

Key equations

Rate lawrate = $k[A]^m[B]^n$

First-order half-life$t_{½}$ = 0.693 / k

Zero-order half-life$t_{½}$ = $[A]_0$ / 2k

Fraction left$(½)^n$ after n half-lives

Stoichiometric rates$-(1/a)\Delta[A]/\Delta t = (1/c)\Delta[C]/\Delta t$

Exam traps

- Do not read orders from coefficients unless the question says the reaction is elementary.
- Halving the volume of a gas-phase elementary reaction 2X + Y doubles both concentrations, so the rate rises $2^2 \times 2 = 8$ times.
- A catalyst does not shift an equilibrium. 'A catalyst always increases the rate of the forward reaction only' is false.
- Raising the temperature increases k. The big effect comes from more molecules exceeding E_a, not just more collisions.

A+ moves

- Set out initial-rate tables as ratios: $rate_2/rate_1 = ([A]_2/[A]_1)^m$. One line per order.
- Sketch the energy profile whenever a mechanism is given. Number of humps = number of steps, and the highest hump is the slow step.

Past paper practice for Unit 11

Paper I · 20 MCQs (2019–2026)

- 2026 Q 5, 17, 24
- 2025 Q 10, 16
- 2024 Q 10, 16, 22, 31
- 2022(23) Q 12, 31, 48
- 2021(22) Q 10, 13, 14, 44
- 2020 Q 28, 29, 49
- 2019 Q 27

Paper II · 9 questions (2016–2026)

- 2026 Q6 — First-order kinetics and half-life; boiling point of a non-ideal liquid mixture; partition coefficient experiment
- 2025 Q6 — Initial-rate method for 2NO + Cl_2; gas from Cu + HNO_3 (gas laws); vapour pressure of water vs glycerol solution; ideal binary liquid mixture
- 2024 Q6 — Kinetic molecular theory of gases; elementary reactions and molecularity; iodine partition between water and CCl_4
- 2022(23) Q3 — Ideal gas laws in a piston container; Cl-catalysed ozone depletion mechanism

- 2021(22) Q6 — Rate constants and equilibrium constant of reversible elementary reactions; energy profile, ΔH and Ea
- 2020 Q6 — Rate expressions and kinetics of $2N_2O_5 \rightarrow 4NO_2 + O_2$
- 2018 Q3 old syllabus — Kinetics/equilibrium of A + B ⇌ 2C + D; analysis of Pb and Cu in a sample
- 2017 Q6 old syllabus — Factors affecting reaction rate and kinetics
- 2016 Q3 old syllabus — Kinetics of catalysed gas decomposition

Model questions (original, in past-paper style)

M11.1

Single answer · like Q1–30

A first-order reaction has a half-life of 20 min. The fraction of the reactant remaining after 60 min is

- (1)1/2
- (2)1/3
- (3)1/4
- (4)1/6
- (5)1/8

Show model answer

Answer (5). 60 min is 3 half-lives, so $(½)^3$ = 1/8 remains.

M11.2

Single answer · like Q1–30

For the elementary reaction 2X(g) + Y(g) → Z(g), the concentrations of X and Y are both tripled. The rate increases by a factor of

- (1)3
- (2)6
- (3)9
- (4)18
- (5)27

Show model answer

Answer (5). rate = $k[X]^2[Y]$, so the factor is $3^2 \times 3 = 27$.

M11.3

Structured · like Paper II

Initial-rate data for A + B → products at 25 °C: Exp 1 [A] = 0.10, [B] = 0.10, rate = 2.0×10^{-4}; Exp 2 [A] = 0.20, [B] = 0.10, rate = 8.0×10^{-4}; Exp 3 [A] = 0.10, [B] = 0.20, rate = 2.0×10^{-4} (concentrations in mol dm^{-3}, rates in mol dm^{-3} s^{-1}). Find the rate law and the value and units of k.

Show model answer

Exp 1 → 2: [A] doubles and the rate is ×4, so the order in A is 2. Exp 1 → 3: [B] doubles and the rate is unchanged, so the order in B is 0. rate = $k[A]^2$. $k = 2.0 \times 10^{-4} \div (0.10)^2 = 2.0 \times 10^{-2}$ mol^{-1} dm^3 s^{-1}.

Unit

Grade 13 · 58 MCQs in 7 papers · 19 Paper II questions since 2019

Chemical equilibrium

The single most tested unit: about eight MCQs a year and part of most Part B questions. It covers K_c and K_p, Le Chatelier, acids and bases, buffers, K_{sp}, phase diagrams, liquid mixtures and partition. Give it the most revision time.

Read alongside: NIE Resource Book, Vol. 5 (Grade 13, 2019), Unit 12, pp. 75–232

Equilibrium constants

RB §2.1 · p. 76

K_c uses equilibrium concentrations. K_p uses partial pressures. $K_p = K_c(RT)^{\Delta n}$, where Δn is the change in moles of gas. Pure solids and liquids are left out ($CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ gives $K_p = P_{CO2}$). Reversing an equation gives 1/K. Multiplying an equation by n gives K^n. Adding equations multiplies their K values. If Q < K the reaction moves forward, and if Q > K it moves backward.

Le Chatelier's principle

RB §2.1 · p. 76

Adding a reactant or removing a product shifts the equilibrium to the right. Raising the pressure by reducing the volume favours the side with fewer moles of gas. Raising the temperature favours the endothermic direction, and **only temperature changes K**. A catalyst does not shift the equilibrium. An inert gas added at constant volume has no effect. At constant pressure it favours the side with more moles of gas.

Acids, bases and pH

RB §2.2 · p. 118

Brønsted–Lowry acids donate protons and bases accept them, forming conjugate pairs. $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$ at 25 °C, so pH + pOH = 14. K_w increases with temperature: pure water at a higher temperature has pH < 7 but is still neutral. For a weak acid: $K_a = [H^+][A^-]/[HA]$, $[H^+] \approx \sqrt{(K_a\ c)}$, and the degree of dissociation $\alpha \approx \sqrt{(K_a/c)}$, which increases on dilution. For a conjugate pair, $K_a \times K_b = K_w$.

Salt hydrolysis and titrations

RB §2.2 · p. 118

A salt of a weak acid and strong base is basic (CH_3COONa). A salt of a weak base and strong acid is acidic (NH_4Cl). At the equivalence point: strong acid with strong base gives pH 7; weak acid with strong base gives pH > 7 (use phenolphthalein); weak base with strong acid gives pH < 7 (use methyl orange). At half-equivalence in a weak-acid titration, $pH = pK_a$. For a diprotic acid such as H_2CO_3, $K_{a1} \gg K_{a2}$.

Buffers

RB §2.3 · p. 167

A buffer is a weak acid with its salt, or a weak base with its salt. $pH = pK_a + \log([A^-]/[HA])$. Added H^+ is removed by A^-, and added OH^- is removed by HA. The buffer works best when $[A^-] = [HA]$, where $pH = pK_a$.

Solubility equilibria

RB §2.4 · p. 175

For AB, $K_{sp} = s^2$. For AB_2 or A_2B, $K_{sp} = 4s^3$. A precipitate forms when the ionic product exceeds K_{sp}. A common ion lowers solubility. Salts whose anion is a weak base (OH^-, CO_3^{2-}, $C_2O_4^{2-}$, S^{2-}) are **more soluble in acid**. When two precipitates are possible, the one whose K_{sp} is reached first forms first, which is

the basis of selective precipitation and of H_2S group separation (Unit 6). AgBr turns into AgI when I^- is added, because AgI has the smaller K_{sp}.

Phase equilibria

RB §2.5 · p. 199

The saturated vapour pressure depends only on temperature, not on the amount of liquid or the volume. A liquid boils when its vapour pressure equals the external pressure, so water boils below 100 °C at low pressure. In a phase diagram, know the triple point and the critical point. Water's solid–liquid line slopes backwards, so ice melts under pressure. CO_2's triple point is above 1 atm, so dry ice sublimes.

Liquid mixtures and partition

RB §2.6 · p. 216

Raoult's law: $P_A = x_A\,P_A^\circ$. An **ideal** mixture has $\Delta H_{mix} = 0$ and $\Delta V_{mix} = 0$, because A–B forces equal the A–A and B–B forces. The vapour is richer in the more volatile component, which is the basis of fractional distillation. Positive deviation gives a minimum-boiling azeotrope, and negative deviation a maximum-boiling one. **Immiscible** liquids each exert their full vapour pressure, so the mixture boils below either pure liquid: this is steam distillation (used for essential oils). **Partition coefficient** $K_D = [X]_{org}/[X]_{aq}$ at a fixed temperature, for the same molecular form. Several small extractions remove more than one large one.

Key equations

K_p and $K_c$$K_p = K_c\,(RT)^{\Delta n}$

Water$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$ (25 °C)

Weak acid$[H^+] = \sqrt{(K_a\,c)}$

Buffer$pH = pK_a + \log([A^-]/[HA])$

SolubilityAB: $K_{sp} = s^2$ · AB_2: $K_{sp} = 4s^3$

Raoult$P_A = x_A\,P_A^\circ$

Partition$K_D = [X]_{org} / [X]_{aq}$

Exam traps

- Never put solids or pure liquids in K expressions. This is the commonest error in Part B equilibrium answers.
- Use partial pressures in Pa or atm consistently for K_p. In a rigid container, $P \propto n$ at fixed T.
- Adding water to a saturated solution in contact with excess solid does not change the concentrations. It changes the amount dissolved.
- The 2025 marking scheme states 'PHYSICAL STATES ARE NECESSARY' for equilibrium equations in Part B. Always write (g), (aq), (s) and (l).

A+ moves

- Use an ICE (initial / change / equilibrium) table for every K calculation. It earns method marks even when the arithmetic slips.
- Learn log 2 = 0.30 and log 3 = 0.48. Most pH answers without a calculator need nothing else.

Past paper practice for Unit 12

Paper I · 58 MCQs (2019–2026)

- 2026 Q 8, 14, 25, 26, 28, 43, 47

- 2025 Q 5, 14, 17, 24, 29, 30, 32, 36, 43, 48
- 2024 Q 6, 13, 19, 26, 30, 35, 43, 48
- 2022(23) Q 6, 11, 14, 15, 17, 25, 30, 33, 38, 46
- 2021(22) Q 7, 15, 17, 24, 28, 39, 49
- 2020 Q 10, 15, 23, 25, 27, 33, 35, 42, 43
- 2019 Q 12, 19, 21, 22, 28, 34, 38

Paper II · 26 questions (2016–2026)

- 2026 Q6 — First-order kinetics and half-life; boiling point of a non-ideal liquid mixture; partition coefficient experiment
- 2026 Q5 — Fe_2O_3 + 3CO: ΔH°, ΔS°, ΔG° and spontaneity; Ag_2CrO_4 solubility product
- 2026 Q3 — Weak acid HA titrated with KOH: pH at stages of the titration
- 2025 Q6 — Initial-rate method for 2NO + Cl_2; gas from Cu + HNO_3 (gas laws); vapour pressure of water vs glycerol solution; ideal binary liquid mixture
- 2025 Q5 — N_2 + 3H_2 ⇌ 2NH_3: Kc, partial pressures and Kp; effect of temperature using ΔH° and ΔS°; normal boiling point and vaporization of CCl_4
- 2025 Q3 — Weak acid HX (pKa 4): pH and titration; MgF_2 solubility in a common-ion solution
- 2024 Q6 — Kinetic molecular theory of gases; elementary reactions and molecularity; iodine partition between water and CCl_4
- 2024 Q5 — NO + O_2 equilibrium in a rigid container; Hess's law with NO, NO_2 and N_2O_4
- 2024 Q3 — H_2CO_3 dissociation constants and pH; selective precipitation from Al^{3+}/Ag^+ solution
- 2023(24) Q6 — Hydrolysis of methanoate ion and pH; mixtures of two miscible liquids
- 2023(24) Q5 — CaO + water thermochemistry; $Ca(OH)_2$ ⇌ CaO + H_2O(g) heterogeneous equilibrium and Kp
- 2022(23) Q6 — Hydrolysis of sodium acetate and pH; ideal binary liquid mixture
- 2022(23) Q5 — Combining Kc values (H_2/S_2 and H_2/I_2 equilibria); ΔH°, ΔS°, ΔG° for H_2 + I_2; Cl^-/CrO_4^{2-} precipitation with Ag^+
- 2021(22) Q6 — Rate constants and equilibrium constant of reversible elementary reactions; energy profile, ΔH and Ea
- 2021(22) Q3 — Temperature–composition diagram of an ideal solution; titration of acetic acid
- 2020 Q5 — Gas-phase dissociation equilibrium XY_2Z_2 and Kp; Gibbs energies and spontaneity
- 2020 Q3 — Solubility product of a sparingly soluble salt AB_2
- 2019 Q6 — Partition coefficient between an organic solvent and water
- 2019 Q5 — Titration of a weak base with HCl: pH and indicator choice
- 2018 Q6 old syllabus — Partition coefficient of iodine
- 2018 Q5 old syllabus — Gas-phase equilibrium and Kp at 800 K; thermochemical cycles
- 2018 Q3 old syllabus — Kinetics/equilibrium of A + B ⇌ 2C + D; analysis of Pb and Cu in a sample
- 2017 Q5 old syllabus — Thermal decomposition of $NaHCO_3$: equilibrium and ΔH° by experiment
- 2017 Q3 old syllabus — Methylamine as a weak base: Kb and pH
- 2016 Q6 old syllabus — Weak acid HA: dissociation and pH

- 2016 Q5 old syllabus — Partition coefficient of butanedioic acid; ΔH, ΔS and spontaneity

Model questions (original, in past-paper style)

M12.1

Single answer · like Q1–30

For $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, $K_c = K$. For $SO_3(g) \rightleftharpoons SO_2(g) + ½O_2(g)$, K_c is

- (1)K
- (2)1/K
- (3)$K^{½}$
- (4)$K^{-½}$
- (5)−K/2

Show model answer

Answer (4). Reverse the equation (giving 1/K) and halve it (taking the square root), so $K_c = K^{-½}$.

M12.2

Single answer · like Q1–30

A 0.10 mol dm^{-3} solution of a weak acid HA ($K_a = 1.0 \times 10^{-5}$ mol dm^{-3}) at 25 °C has a pH of

- (1)1.0
- (2)2.0
- (3)3.0
- (4)5.0
- (5)6.0

Show model answer

Answer (3). $[H^+] = \sqrt{(1.0 \times 10^{-5} \times 0.10)} = 1.0 \times 10^{-3}$ mol dm^{-3}, so pH = 3.0.

M12.3

Single answer · like Q1–30

The K_{sp} of AB_2 is 4.0×10^{-12} mol^3 dm^{-9} at 25 °C. Its solubility in mol dm^{-3} is

- (1)2.0×10^{-6}
- (2)1.0×10^{-4}
- (3)2.0×10^{-4}
- (4)1.6×10^{-4}
- (5)4.0×10^{-6}

Show model answer

Answer (2). $K_{sp} = 4s^3$, so $s^3 = 1.0 \times 10^{-12}$ and $s = 1.0 \times 10^{-4}$ mol dm^{-3}.

M12.4

Structured · like Paper II

A buffer contains 0.10 mol HA and 0.10 mol NaA in 1.00 dm^3 ($K_a = 1.0 \times 10^{-5}$ mol dm^{-3}). (a) Find its pH. (b) Find the pH after adding 0.020 mol HCl, with no change in volume (log 2 = 0.30, log 3 = 0.48).

Show model answer

(a) pH = pK_a + log(0.10/0.10) = 5.00. (b) A^- + H^+ → HA, so HA = 0.12 mol and A^- = 0.08 mol. pH = 5.00 + log(0.08/0.12) = 5.00 + log(2/3) = 5.00 + (0.30 − 0.48) = 4.82. The pH falls by only 0.18, which shows the buffer action.

Unit

Grade 13 · 20 MCQs in 7 papers · 8 Paper II questions since 2019

Electrochemistry

Conductivity, electrodes, galvanic cells and electrolysis. About three MCQs a year, and Part B Q7(a) is usually a full cell or electrolysis problem.

Read alongside: NIE Resource Book, Vol. 5 (Grade 13, 2019), Unit 13, pp. 233–270

Conductivity

RB §3.1 · p. 234

Electrolyte solutions conduct through moving ions. Conductivity rises with ionic charge, ion mobility (H^+ and OH^- are exceptionally mobile), concentration and temperature. Molar conductivity $\Lambda_m = \kappa/c$. For a strong electrolyte it falls slightly as concentration rises. For a weak electrolyte it rises sharply on dilution, because the degree of dissociation increases.

Electrodes in equilibrium

RB §3.2 · p. 238

- Metal / metal ion, such as $Zn^{2+}(aq)/Zn(s)$.
- Metal / insoluble salt, such as $Ag(s)/AgCl(s)/Cl^-(aq)$ and calomel $Hg(l)/Hg_2Cl_2(s)/Cl^-(aq)$. Their potential depends on $[Cl^-]$.
- Gas electrode: the standard hydrogen electrode (Pt, H_2 at 1 atm, $[H^+] = 1$ mol dm^{-3}, 25 °C) is defined as $E° = 0.00$ V.
- Redox electrode: Pt in Fe^{3+}/Fe^{2+}, or in $MnO_4^-/Mn^{2+}/H^+$.

The electrode potential depends on concentration and temperature (and on pressure for gas electrodes), but not on electrode size or solution volume.

Galvanic cells

RB §3.3 · p. 250

The **anode** is where oxidation happens (the negative electrode). The **cathode** is where reduction happens (positive). Electrons flow through the wire from anode to cathode, and the salt bridge completes the circuit and keeps both solutions neutral. Cell notation: $Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s)$. $E°_{cell} = E°_{cathode} - E°_{anode}$ (right minus left). The cell reaction is spontaneous when $E°_{cell} > 0$, because $\Delta G° = -nFE°$. The more positive $E°$, the stronger the oxidizing agent in that couple.

Electrolysis

RB §3.4 · p. 261

In an electrolytic cell the anode is positive (oxidation) and the cathode is negative (reduction).

- Molten NaCl gives Na and Cl_2.
- NaCl(aq) with inert electrodes gives H_2 at the cathode, and Cl_2 at the anode (O_2 if the solution is very dilute).
- $CuSO_4$(aq) with inert electrodes gives Cu at the cathode and O_2 at the anode, and the solution turns acidic. With Cu electrodes, the anode dissolves and Cu is deposited on the cathode (used to purify copper).

Faraday: $Q = It$, $n(e^-) = Q/F$ ($F = 96\,500$ C mol^{-1}), and moles of product $= n(e^-)/z$.

Key equations

Cell emf $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

Gibbs link $\Delta G^\circ = -nFE^\circ_{cell}$

Charge $Q = It$

Faraday $n(e^-) = Q / F$

Molar conductivity $\Lambda_m = \kappa / c$

Exam traps

- In a galvanic cell the anode is negative. In an electrolytic cell the anode is positive. In both, oxidation happens at the anode.
- Do not multiply E° values by the coefficients when you balance a half-equation.
- Pt is used only when neither half of the couple is a conducting solid. Do not write Pt for Zn^{2+}/Zn.
- Compare galvanic and electrolytic cells in a table (sign, energy change, spontaneity). Paper II asked for exactly this in 2020.

A+ moves

- Write both half-equations, then add them, then calculate E°_{cell}. This fixed order prevents sign errors.
- Use F = 96 500 C mol^{-1} and look for currents and times that give simple charges (such as 0.965 A × 10 000 s = 9650 C).

Past paper practice for Unit 13

Paper I · 20 MCQs (2019–2026)

- 2026 Q 22, 31, 35
- 2025 Q 22, 25, 26
- 2024 Q 25, 38, 46
- 2022(23) Q 19, 28, 43
- 2021(22) Q 33, 35
- 2020 Q 19, 26, 38
- 2019 Q 10, 15, 39

Paper II · 11 questions (2016–2026)

- 2026 Q7 — Reduction potentials, cell diagrams and E°cell; a 4th-period d-block element with an amphoteric oxide
- 2025 Q7 — Electrochemical cell for $3Cu^+ + Au^{3+}$; octahedral coordination compounds
- 2024 Q7 — Electrolysis of molten $MgCl_2$ and Faraday calculations
- 2023(24) Q7 — Daniell cell; octahedral coordination compounds of iron
- 2022(23) Q7 — Galvanic cell with the O_2/OH^- electrode; a 4th-period d-block element
- 2021(22) Q7 — Displacement among metals L, M, N and cell emf; chemistry of manganese
- 2020 Q7 — Electrolytic vs galvanic cells; a coloured complex ion of a 3d metal
- 2019 Q7 — Electrolysis to find the relative atomic mass of a metal; octahedral coordination compounds
- 2018 Q10 old syllabus — Complexes of manganese; Ag/AgCl electrode and electrolysis of $CaBr_2$(aq)

- 2017 Q10 old syllabus — Coordination compounds of titanium; a cell with Ag/AgCl and calomel electrodes
- 2016 Q10 old syllabus — Octahedral coordination compounds; electrochemistry

Model questions (original, in past-paper style)

M13.1

Single answer · like Q1–30

$E°(Cu^{2+}/Cu) = +0.34$ V and $E°(Zn^{2+}/Zn) = -0.76$ V. For the cell made from these half-cells, which statement is correct?

- (1)$E°_{cell} = -0.42$ V and Zn is the cathode
- (2)$E°_{cell} = +0.42$ V and Cu is the anode
- (3)$E°_{cell} = +1.10$ V and electrons flow from Zn to Cu
- (4)$E°_{cell} = +1.10$ V and electrons flow from Cu to Zn
- (5)$E°_{cell} = -1.10$ V and the reaction is not spontaneous

Show model answer

Answer (3). Zn is oxidized (anode) and Cu^{2+} is reduced (cathode). $E°_{cell} = 0.34 - (-0.76) = +1.10$ V, and electrons flow through the wire from Zn to Cu.

M13.2

Single answer · like Q1–30

A current of 0.965 A passes through $CuSO_4(aq)$ for 10 000 s (Cu = 63.5, F = 96 500 C mol^{-1}). The mass of copper deposited is about

- (1)0.32 g
- (2)1.59 g
- (3)3.18 g
- (4)6.35 g
- (5)12.7 g

Show model answer

Answer (3). Q = 9650 C = 0.100 mol of electrons. $Cu^{2+} + 2e^- \rightarrow Cu$, so 0.050 mol Cu = 3.18 g.

M13.3

Multiple response · like Q31–40

Which factor(s) affect the electrode potential of the $M^{2+}(aq)/M(s)$ electrode? (a) the surface area of M(s) (b) the concentration of $M^{2+}(aq)$ (c) the temperature (d) the volume of $M^{2+}(aq)$ solution

Answer with the response code (1)–(5) from the code table.

Show model answer

Answer (2). Only (b) and (c) are correct, which is code (2). Surface area and volume do not change the potential.

M13.4

Structured · like Paper II

Molten $MgCl_2$ is electrolysed between inert electrodes. (a) Write the electrode reactions and state which electrode is positive. (b) How long would a 9650 A current take to produce 24.3 kg of Mg (Mg = 24.3)?

Show model answer

(a) Cathode (negative): $Mg^{2+}(l) + 2e^- \rightarrow Mg(l)$. Anode (positive): $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$. (b) n(Mg) = 1000 mol, so $n(e^-) = 2000$ mol and $Q = 2000 \times 96\,500 = 1.93 \times 10^8$ C. $t = Q/I = 1.93 \times 10^8 \div 9650 = 2.0 \times 10^4$ s (about 5.6 hours).

Unit

Grade 13 · 36 MCQs in 7 papers · 10 Paper II questions since 2019

Industrial chemistry and environmental pollution

Nine manufacturing processes, polymers, products from plants, and air and water pollution. This unit holds the whole of Paper II Q10 and about five MCQs a year. Examiners have noted that achievement in the last units is relatively low, which makes it the easiest place to gain marks.

Read alongside: NIE Resource Book, Vol. 6 (Grade 13, 2019), Unit 14, pp. 1–96

Principles of a chemical industry

RB §1.1 · p. 2

Raw materials, energy, water, transport, waste disposal, safety and the environment all decide where a plant is built. Recurring ideas: **recycling** unreacted materials, the **counter-current principle** (gas and liquid flow in opposite directions for efficient transfer, as in HNO_3 absorption) and catalysts.

Mg (Dow process) and NaOH (membrane cell)

RB §1.2 · p. 6

Dow: seawater with $Ca(OH)_2$ (made from shells or limestone) precipitates $Mg(OH)_2$. Add HCl to get $MgCl_2$, dry it, and electrolyse the molten salt (700–800 °C). Mg forms at the cathode and Cl_2 at the anode, and the Cl_2 is recycled to make HCl. **Membrane cell**: brine is electrolysed. Cl_2 forms at the anode, and H_2 plus OH^- at the cathode. Only Na^+ can pass the cation-exchange membrane, so the products are NaOH, Cl_2 and H_2.

Soap and biodiesel

RB §1.4 · p. 14

Saponification: fat or oil (a triglyceride) + NaOH → soap (sodium salts of fatty acids) + glycerol. Adding NaCl 'salts out' the soap. In hard water, Ca^{2+} and Mg^{2+} form insoluble scum, which lowers cleaning efficiency. Biodiesel is made by transesterifying a triglyceride with methanol (NaOH catalyst), giving methyl esters and glycerol.

Na_2CO_3 (Solvay process)

RB §1.5 · p. 18

The raw materials are brine, limestone and ammonia (recycled). The brine is ammoniated first, then carbonated: $NaCl + NH_3 + CO_2 + H_2O \rightarrow NaHCO_3(s) + NH_4Cl$. Heating gives $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$. NH_3 is recovered with $2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3 + 2H_2O$. The main by-product is **$CaCl_2$**.

NH_3, HNO_3 and H_2SO_4

RB §1.6 · p. 21

- **Haber–Bosch**: $N_2 + 3H_2 \rightleftharpoons 2NH_3$, an exothermic reaction. The Resource Book gives 450–500 °C, 250–300 atm, an iron catalyst and K_2O/Al_2O_3 promoters. The temperature is a compromise between rate and yield, and unreacted gases are recycled.
- **Ostwald**: $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$ (Pt/Rh catalyst). The NO is cooled to about 150 °C: $2NO + O_2 \rightarrow 2NO_2$. Then $4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3$ is absorbed counter-currently at 5–10 atm.
- **Contact process**: $S + O_2 \rightarrow SO_2$, then $2SO_2 + O_2 \rightleftharpoons 2SO_3$ (V_2O_5, about 450 °C, about 1 atm, with excess air). SO_3 is absorbed into concentrated H_2SO_4 to give oleum ($H_2S_2O_7$), which is then diluted. SO_3 is not added directly to water because it forms an acid mist.

TiO_2 and iron

RB §1.9 · p. 31

TiO_2 (chloride process): rutile + coke + Cl_2 at about 950 °C gives $TiCl_4$, which is purified by distillation and then oxidized with O_2 to pure TiO_2, regenerating Cl_2. TiO_2 is used as a white pigment. **Blast furnace**: the raw materials are haematite, coke, limestone and hot air. $C + O_2 \rightarrow CO_2$; $CO_2 + C \rightarrow 2CO$; $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$; $CaCO_3 \rightarrow CaO + CO_2$; $CaO + SiO_2 \rightarrow CaSiO_3$ (slag).

Polymers

RB §1.11 · p. 37

Addition polymers include polyethene, PVC, polystyrene, polypropene and Teflon. **Condensation** polymers include nylon-6,6, polyesters and Bakelite (phenol + methanal). **Thermoplastics** soften on heating. **Thermosets** have a cross-linked 3-D network and do not soften. **Natural rubber** is cis-polyisoprene (from 2-methylbuta-1,3-diene). Latex is coagulated with acetic or formic acid. **Vulcanization** with 1–3% sulfur forms S cross-links, making rubber stronger and more elastic. Ozone attacks the C=C bonds in rubber.

Products from plants

RB §1.12 · p. 48

Ethanol by fermentation: $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$ (yeast enzymes). **Vinegar**: ethanol is oxidized to ethanoic acid by Acetobacter, for example from coconut toddy. **Essential oils** are extracted by steam distillation, solvent extraction or pressing. Examples: citronella (geraniol), cinnamon leaf (eugenol).

Air pollution

RB §1.13 · p. 58

- **Acid rain**: SO_2 and NO_x form H_2SO_4 and HNO_3. Unpolluted rain is already about pH 5.6 because of CO_2.
- **Global warming**: CO_2, CH_4, N_2O, CFCs and water vapour absorb infrared radiation.
- **Ozone layer**: $O_2 + UV \rightarrow 2O$, then $O + O_2 \rightarrow O_3$. CFCs release Cl• in the stratosphere: $Cl• + O_3 \rightarrow ClO• + O_2$, then $ClO• + O \rightarrow Cl• + O_2$. HFCs contain no Cl, so they do not destroy ozone, but they are greenhouse gases.
- **Photochemical smog**: NO_x + volatile hydrocarbons + sunlight give O_3 and PAN. It is worst on sunny days with heavy traffic.

Water pollution

RB §1.14 · p. 80

Water-quality parameters include dissolved oxygen (DO falls as temperature rises), BOD, COD, pH, conductivity, turbidity, hardness, nitrate and phosphate (which cause eutrophication) and heavy metals. Know which parameters matter for waste-water discharge.

Key equations

Haber$N_2 + 3H_2 \rightleftharpoons 2NH_3$ ($\Delta H < 0$)

Contact$2SO_2 + O_2 \rightleftharpoons 2SO_3$ (V_2O_5)

Solvay key step$NaCl + NH_3 + CO_2 + H_2O \rightarrow NaHCO_3 + NH_4Cl$

Ozone depletion$Cl• + O_3 \rightarrow ClO• + O_2$

Exam traps

- Marking schemes accept condition ranges, but you must state the catalyst and the promoters (Haber) or the catalyst (Contact, Ostwald) correctly.

- The 2018 scheme notes that physical states are not required in industrial equations, but correct balancing is. Check each question's wording.
- CFCs and HFCs: both are greenhouse gases, but only CFCs (which contain chlorine) deplete ozone.
- Bakelite is a condensation polymer and a thermoset, not an addition polymer.

A+ moves

- Draw each process as a flow chart (raw materials → steps with conditions → product → by-product → recycling). Paper II Q10(a) gives exactly such charts with symbols to identify.
- Keep a list of the environmental 'cause → chemistry → effect' chains and practise writing them as balanced equations.

Past paper practice for Unit 14

Paper I · 36 MCQs (2019–2026)

- 2026 Q 33, 37, 39, 44, 49
- 2025 Q 33, 37, 40, 45, 49
- 2024 Q 36, 37, 40, 49, 50
- 2022(23) Q 37, 39, 40, 47, 49, 50
- 2021(22) Q 25, 32, 36, 40, 47, 50
- 2020 Q 36, 40, 47, 50
- 2019 Q 29, 36, 43, 47, 50

Paper II · 13 questions (2016–2026)

- 2026 Q10 — Industrial extraction/manufacture flow chart; coconut toddy fermentation to vinegar
- 2025 Q10 — Manufacture of TiO_2 from rutile; pollutants and environmental problems; polymer classification and structures
- 2025 Q2 — Identify s/p-block compounds from composition and reactions; thermal decomposition equations; the industrial process for one product
- 2024 Q10 — Solvay process; causes of global warming; vinegar production
- 2023(24) Q10 — Dow process for Mg; atmospheric pollutants; polymerization reactions
- 2022(23) Q10 — Contact process; C, N and S gaseous pollutants; products from plant sources
- 2022(23) Q3 — Ideal gas laws in a piston container; Cl-catalysed ozone depletion mechanism
- 2021(22) Q10 — Industrial production flow chart; photochemical smog and water pollution; natural rubber and polymer additives
- 2020 Q10 — TiO_2 manufacture by the chloride process; environment and polymers
- 2019 Q10 — Dow process for magnesium; related industrial and environmental questions
- 2018 Q9 old syllabus — Environment and related issues
- 2017 Q9 old syllabus — Industrial processes (bleaching powder, calcium carbide, urea and others)
- 2016 Q9 old syllabus — Planning a chemical industry; atmospheric pollutants

Model questions (original, in past-paper style)

M14.1

Single answer · like Q1–30

The main by-product of the Solvay process is

- (1)NH_4Cl
- (2)$CaCl_2$
- (3)$NaHCO_3$
- (4)CaO
- (5)CO_2

Show model answer

Answer (2). NH_4Cl is recycled to NH_3 using $Ca(OH)_2$, which leaves $CaCl_2$ as the by-product.

M14.2

Multiple response · like Q31–40

Which statement(s) is/are correct? (a) Vulcanization forms sulfur cross-links between rubber chains. (b) Bakelite is an addition polymer. (c) CFCs release chlorine atoms in the stratosphere under UV light. (d) HFCs are the main cause of ozone depletion.

Answer with the response code (1)–(5) from the code table.

Show model answer

Answer (5). Only (a) and (c) are correct. That pair is not one of the coded pairs, so the answer is (5).

M14.3

Statement pair · like Q41–50

Statement 1: In the Contact process, SO_3 is absorbed into concentrated H_2SO_4 rather than water.
Statement 2: SO_3 reacts with water very exothermically, forming an acid mist that is hard to condense.

Answer with the statement-pair code (1)–(5) from the code table.

Show model answer

Answer (1). Both statements are true, and the second explains the first.

M14.4

Structured · like Paper II

For the Haber process: (a) write the equation with ΔH sign, (b) state the conditions given in the Resource Book, (c) explain why a moderate temperature is used even though a lower temperature gives a higher yield, (d) state two uses of ammonia.

Show model answer

(a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta H < 0$. (b) 450–500 °C, 250–300 atm, an iron catalyst with K_2O/Al_2O_3 promoters. (c) At low temperature the rate is too slow, even with a catalyst. A compromise temperature gives an acceptable yield fast enough, and the unreacted gases are recycled. (d) Making fertilisers (urea, ammonium salts) and nitric acid (Ostwald process).

Equations and key relationships

Formula bank

Every key equation from the units on one page, for the last week before the exam.

U1 · Atomic structure

Wave speed $c = \nu\lambda$

Photon energy $E = h\nu = hc/\lambda$

de Broglie $\lambda = h/(mv) = h/\sqrt{(2mE_k)}$

Electrons in a shell $2n^2$

Orbitals in a sub-shell $2l + 1$

U2 · Structure and bonding

Formal charge $FC = V - N - \frac{1}{2}B$

Bond order (simple) σ + π count between two atoms

Electron pairs on central atom (valence e^- of centre + e^- from ligands ± charge) ÷ 2

U3 · Chemical calculations

Moles $n = m/M = cV$

Dilution $c_1V_1 = c_2V_2$

Mole fraction $x_A = n_A / n_{total}$

Electrons per oxidant (acid) MnO_4^- 5 e^- · $Cr_2O_7^{2-}$ 6 e^-

Iodometry $IO_3^- \rightarrow 3I_2 \rightarrow 6S_2O_3^{2-}$

U4 · Gaseous state of matter

Ideal gas $PV = nRT$

Partial pressure $P_A = x_A\, P_{total}$

Kinetic theory $PV = \frac{1}{3}\, N\, m\, c^2$

rms speed $c_{rms} = \sqrt{(3RT/M)}$

van der Waals $(P + an^2/V^2)(V - nb) = nRT$

U5 · Energetics

Calorimetry $q = mc\Delta T$; $\Delta H = -q/n$

Formation route $\Delta H_r = \Sigma\Delta H_f(P) - \Sigma\Delta H_f(R)$

Bond enthalpy route $\Delta H_r = \Sigma$ broken $-\ \Sigma$ formed

Gibbs energy $\Delta G = \Delta H - T\Delta S$

Phase change $T = \Delta H / \Delta S$

Surroundings $\Delta S_{surr} = -\Delta H/T$

U6 · Chemistry of s, p and d block elements

Thermal stability (Group 2) $MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$

Solubility (Group 2)OH^- salts ↑ down · SO_4^{2-} salts ↓ down

Chromate ⇌ dichromate$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$

Permanganate (acid)$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

U7 · Basic concepts of organic chemistry

Degree of unsaturation$(2C + 2 + N - H - X) \div 2$

Chiral centreC with four different groups

Geometric isomerismC=C with two different groups on each carbon

U8 · Hydrocarbons and halohydrocarbons

Carbocation stability$3° > 2° > 1° > CH_3^+$

S_{N1} raterate = k[RX]

S_{N2} raterate = k[RX][Nu^-]

U9 · Oxygen containing organic compounds

Acidity$ROH < H_2O <$ phenol $< RCOOH < ClCH_2COOH$

Grignard + C=ORMgX + R'CHO → RR'CHOH (after H_3O^+)

Esterification$RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O$

U10 · Nitrogen containing organic compounds

Basicity order$C_2H_5NH_2 > NH_3 > C_6H_5NH_2 > CH_3CONH_2$

Diazotisation$C_6H_5NH_2 + HNO_2 + HCl \rightarrow C_6H_5N_2^+Cl^- + 2H_2O$ (0–5 °C)

U11 · Chemical kinetics

Rate lawrate = $k[A]^m[B]^n$

First-order half-life$t_{½} = 0.693 / k$

Zero-order half-life$t_{½} = [A]_0 / 2k$

Fraction left$(½)^n$ after n half-lives

Stoichiometric rates$-(1/a)\Delta[A]/\Delta t = (1/c)\Delta[C]/\Delta t$

U12 · Chemical equilibrium

K_p and $K_c$$K_p = K_c (RT)^{\Delta n}$

Water$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$ (25 °C)

Weak acid$[H^+] = \sqrt{(K_a\ c)}$

Buffer$pH = pK_a + \log([A^-]/[HA])$

Solubility$AB: K_{sp} = s^2 \cdot AB_2: K_{sp} = 4s^3$

Raoult$P_A = x_A\ P_A^\circ$

Partition$K_D = [X]_{org} / [X]_{aq}$

U13 · Electrochemistry

Cell emf$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

Gibbs link$\Delta G^\circ = -nFE^\circ_{cell}$

Charge$Q = It$

Faraday$n(e^-) = Q / F$

Molar conductivity$\Lambda_m = \kappa / c$

U14 · Industrial chemistry and environmental pollution

Haber$N_2 + 3H_2 \rightleftharpoons 2NH_3$ ($\Delta H < 0$)

Contact$2SO_2 + O_2 \rightleftharpoons 2SO_3$ (V_2O_5)

Solvay key step$NaCl + NH_3 + CO_2 + H_2O \rightarrow NaHCO_3 + NH_4Cl$

Ozone depletion$Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$

Practice-focused with past paper style

Past paper hub

Digital Past Papers: all questions retyped with answers and reviews, sorted by year (newest first).

All English-medium question papers in the collection, with the matching marking scheme and the page where its MCQ key sits. Years are the Department of Examinations' labels; 2021(22) means the 2021 examination held in 2022.

Exam	Syllabus	Question paper (English)	Marking scheme	MCQ key
2026	Current	Open paper Complete	Not in the collection	—
2025	Current	Open paper Complete	Open scheme English · partial (MCQ key + Part A only)	PDF p. 2
2024	Current	Open paper Complete	Open scheme English	PDF p. 5
2023(24)	Current	Open paper Paper II Parts B & C only	Open scheme Sinhala medium only	PDF p. 1
2022(23)	Current	Open paper Complete	Not in the collection	—
2021(22)	Current	Open paper Complete	Open scheme English	PDF p. 12
2020	Current	Open paper Complete	Open scheme English	PDF p. 13
2019	Current	Open paper Complete	Open scheme English	PDF p. 12
2018	Old syllabus	Open paper Paper I complete · Paper II incomplete	Open scheme English	PDF p. 14
2017	Old syllabus	Open paper Complete	Open scheme Sinhala medium only	PDF p. 2
2016	Old syllabus	Open paper Complete	Open scheme English · official Evaluation Report (answers, mark scheme, performance data)	PDF p. 24

Strategies and guidance towards an A+

Exam technique

Paper I

- About 2 minutes 20 seconds per question. Do Q41–50 (statement pairs) carefully: decide each statement on its own before judging the "explains" link.
- For Q31–40, mark each of (a)–(d) true or false in the margin, then convert to the code. Three correct responses always means code (5).
- No calculators: look for numbers designed to cancel, such as RT = 2500 J mol^{-1} or 96 500 C mol^{-1} with 0.965 A.

Paper II

- Choose Part B and C questions during the reading time, using the slot pattern above.
- Start every new question on a new page and number parts exactly as printed.
- Show the working: ICE tables, Hess cycles and mole ratios earn marks even if the final number slips.
- Give the length the question asks for. Short, precise answers where "state" or "identify" is used; reasoning where "explain" is used.

Rules seen in the marking schemes

- "PHYSICAL STATES ARE NECESSARY" for equilibrium and thermochemistry answers in Part B (2025 scheme).
- "Physical states are not required" for some industrial equations, but balancing always is (2018 scheme).
- "If spelling is incorrect do not award marks" for names of complexes (2018 scheme).
- "If name is given instead of symbols do not award marks" where symbols are asked for (2019 scheme).

What the examiners asked candidates to do (Evaluation Report 2016, Part III)

- Read the instructions: how many questions in each part, which are compulsory, and the marks available.
- Answer the easier questions first to manage time.
- In organic chemistry: compare the products of $LiAlH_4$ and $NaBH_4$; compare Grignard reactions of esters with those of alkynes with acidic hydrogen; know enantiomers versus diastereomers; and write equations, not only observations, for Brady's, Fehling's and Tollens' tests.
- Understand mechanisms through electron movement rather than learning them by heart.
- In physical chemistry: balance equations to the correct ratio and include physical states; always state and convert units; practise problems with symbols and with logarithms.
- Connect principles: equilibrium with rates; ΔH, ΔS, ΔG with spontaneity; reactions with phase equilibria; Le Chatelier with applications.
- In inorganic chemistry: link colours, complexes and oxidation numbers; draw Lewis and resonance structures with lone pairs and formal charges; explain bond-angle differences (NH_3 vs NF_3, H_2O vs H_2S).
- Give more attention to the last units of the syllabus, where achievement has been relatively low.

Paraphrased from Department of Examinations (2016), Evaluation Report, 02 – Chemistry, pp. 68–71. Open the report.

2026 · Chemistry Digital Paper

50 questions · 2 hours

MCQ · Paper I

Question 1 · Q1–30 · single answer

The lines in the Balmer series of the hydrogen emission spectrum result from transitions of electrons denoted by the energy levels (n = principal quantum number)

- (1)n > 1 to n = 1
- (2)n = 2 to n > 2
- (3)n > 3 to n = 3
- (4)n > 2 to n = 2
- (5)n < 2 to n = 2

Answer and review

Answer **(4)** Prepared answer (no official scheme available)

Emission means an electron falls to a lower level. The Balmer series is the set of lines for electrons falling from any level above n = 2 down to n = 2; these lines are in the visible region. Falls to n = 1 give the Lyman series (ultraviolet) and falls to n = 3 the Paschen series (infrared).

RB U1 §1.3 · p. 17

Question 2 · Q1–30 · single answer

The outermost p electrons of a nitrogen atom in ground state can be denoted by the quantum numbers n = 2 and l = 1. According to Hund's rule the m_l and m_s quantum numbers of two of these electrons can be

- (1)electron 1: $m_l = +1$, $m_s = +½$ and electron 2: $m_l = +1$, $m_s = +½$
- (2)electron 1: $m_l = +1$, $m_s = +½$ and electron 2: $m_l = −1$, $m_s = −½$
- (3)electron 1: $m_l = 0$, $m_s = +½$ and electron 2: $m_l = +1$, $m_s = +½$
- (4)electron 1: $m_l = 0$, $m_s = +½$ and electron 2: $m_l = −1$, $m_s = −½$
- (5)electron 1: $m_l = +1$, $m_s = −½$ and electron 2: $m_l = 0$, $m_s = +½$

Answer and review

Answer **(3)** Prepared answer (no official scheme available)

Nitrogen is $2p^3$. Hund's rule puts the three p electrons in different orbitals (different m_l) with parallel spins (same m_s). Option (1) breaks the Pauli principle (identical quantum numbers); options (2), (4) and (5) give opposite spins. Only (3) has different m_l values and the same m_s.

RB U1 §1.4 · p. 23

Question 3 · Q1–30 · single answer

Consider the species $Cl^−$, Ar and K^+. Which statement is true regarding these species?

- (1)They have the same atomic/ionic mass.

- (2)They have the same atomic/ionic radius.
- (3)They have the same atomic number.
- (4)The effective nuclear charge felt by an outermost electron of each species is the same.
- (5)They have the same number of p electrons.

Answer and review

Answer **(5)** Prepared answer (no official scheme available)

All three are isoelectronic ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$), so each has 12 p electrons. Their nuclear charges are 17, 18 and 19, so their radii and the effective nuclear charge felt by the outer electrons differ (K^+ is smallest).

RB U1 §1.6 · p. 32

Question 4 · Q1–30 · single answer

Which of the following statements is **false** with regard to Xe and its compounds?

- (1)Xe has the highest boiling point among the elements He to Xe in group 18 of the Periodic Table.
- (2)Xe has the highest first ionization energy among the group 18 elements of the Periodic Table.
- (3)The oxidation numbers of Xe in XeF_4 and XeF_6 are +4 and +6 respectively.
- (4)XeF_2 shows a trigonal bipyramidal electron pair geometry.
- (5)The atomic radius of Xe is the highest among the first five elements of group 18 of the Periodic Table.

Answer and review

Answer **(2)** Prepared answer (no official scheme available)

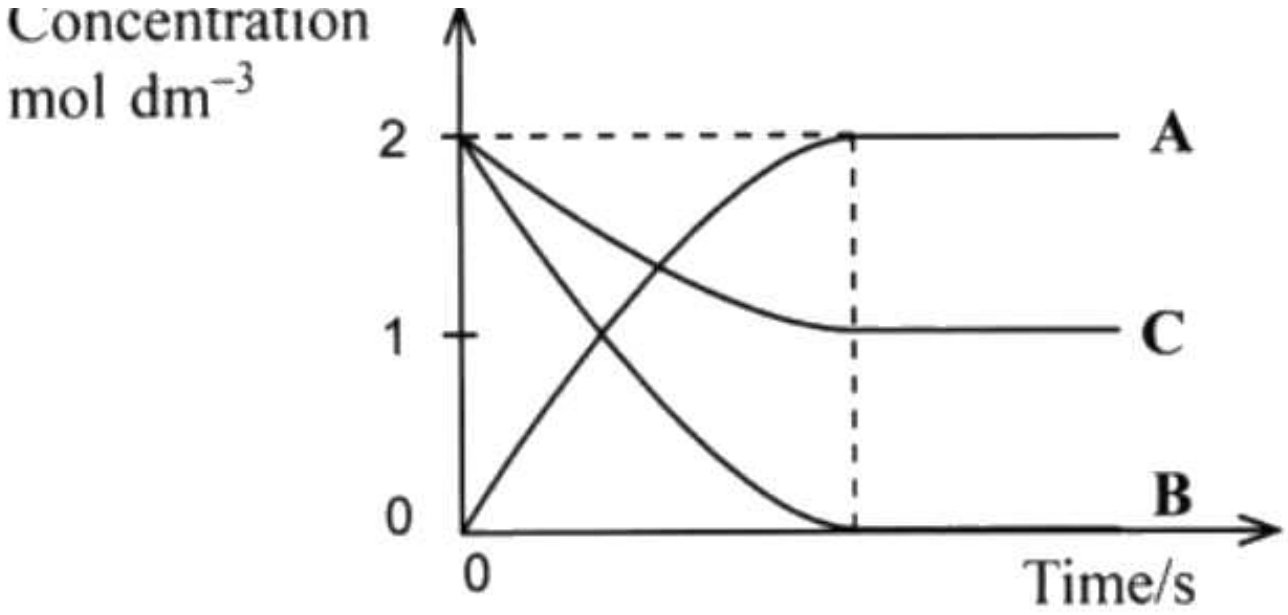
First ionization energy falls down a group, so He (not Xe) has the highest value in group 18. London forces grow down the group, so Xe has the highest boiling point of He–Xe. XeF_2 has 5 electron pairs on Xe (2 bonding, 3 lone), giving a trigonal bipyramidal pair geometry and a linear shape.

RB U6 §4.8 · p. 152 RB U1 §1.6 · p. 32

Question 5 · Q1–30 · single answer

The curves A, B and C given in the diagram show the variations in the concentrations of species that exist in a closed system when the following gas phase reaction takes place.
$O_2(g) + 2H_2(g) \rightarrow 2H_2O(g)$

The correct representation of the species $O_2(g)$, $H_2(g)$ and $H_2O(g)$ respectively, is



- (1)A, B, C
- (2)B, A, C
- (3)B, C, A
- (4)C, A, B
- (5)C, B, A

Answer and review

Answer **(5)** Prepared answer (no official scheme available)

Both reactants start at 2 mol dm^{-3}. H_2 is used twice as fast as O_2, so H_2 falls from 2 to 0 (curve B) while O_2 falls only from 2 to 1 (curve C). H_2O forms at the same rate as H_2 is used, rising from 0 to 2 (curve A). Rates are linked by the stoichiometry: $-\Delta[O_2]/\Delta t = -\frac{1}{2}\Delta[H_2]/\Delta t = \frac{1}{2}\Delta[H_2O]/\Delta t$.

RB U11 §1.3 · p. 9

Question 6 · Q1–30 · single answer

Which of the following statements is correct about sodium and potassium?

- (1)When burnt in air, both sodium and potassium form their peroxides as the main product.
- (2)The reaction of both sodium and potassium with water is exothermic.
- (3)Both sodium and potassium react with H_2(g) and form their hydroxides.
- (4)Potassium does not react with gaseous N_2 whereas sodium forms its nitride by reacting with N_2.
- (5)The reaction of both sodium and potassium with dilute mineral acids is endothermic.

Answer and review

Answer **(2)** Prepared answer (no official scheme available)

Both metals react vigorously and exothermically with water: $2M + 2H_2O \rightarrow 2MOH + H_2$. In air Na forms mainly Na_2O_2 but K forms the superoxide KO_2. With H_2 they form ionic hydrides (NaH, KH), not hydroxides. Among Group 1 only Li forms a nitride.

RB U6 §4.1 · p. 122

Question 7 · Q1–30 · single answer

Consider the following compounds from A to E.
A: CH_3CH_2CHO B: $CH_3CH_2CH_2CHO$ C: $CH_3CH_2CH_2OH$ D: $CH_3CH_2CH_2CH_2OH$ E: $CH_3CH(OH)CH_2CH_3$
The compound that has the lowest water solubility is

- (1)A
- (2)B
- (3)C
- (4)D
- (5)E

Answer and review

Answer **(2)** Prepared answer (no official scheme available)

Solubility in water depends on hydrogen bonding with water and falls as the hydrocarbon chain grows. Alcohols can both donate and accept hydrogen bonds; aldehydes can only accept them. B is the larger aldehyde (four carbons), so it dissolves least.

RB U9 §3.1 · p. 54 RB U2 §2.6 · p. 79

Question 8 · Q1–30 · single answer

Which of the following is **incorrect**?

- (1)When a small amount of 0.10 mol dm^{-3} HCl(aq) is added to a given volume of a mixture of NH_3(aq)/NH_4Cl(aq), the pH of the system drops approximately from 9 to 1.
- (2)Dropwise addition of 0.10 mol dm^{-3} NaOH(aq) to a given volume of H_2O(l) results in the rapid increase of pH of the system from approximately 7 to 12.
- (3)When a small amount of 0.10 mol dm^{-3} NaOH(aq) is added to a given volume of a mixture of CH_3COOH(aq)/CH_3COONa(aq), the change in pH is insignificant.
- (4)When a small amount of 0.10 mol dm^{-3} NaOH(aq) is added to a given volume of a mixture of CH_3COOH(aq)/CH_3COONa(aq) the reaction, OH^-(aq) + CH_3COOH(aq) → CH_3COO^-(aq) + H_2O(l) occurs.
- (5)Dropwise addition of 0.10 mol dm^{-3} HCl(aq) to a given volume of 0.10 mol dm^{-3} NH_3(aq) solution results in the change of pH from approximately 11 to 2.

Answer and review

Answer **(1)** Prepared answer (no official scheme available)

NH_3/NH_4Cl is a basic buffer (pH about 9). A small amount of acid is removed by NH_3 + H^+ → NH_4^+, so the pH hardly changes; it cannot fall to 1. Water has no buffering, so its pH rises quickly with NaOH, and the CH_3COOH/CH_3COO^- buffer removes added OH^- as shown in (4).

RB U12 §2.3 · p. 167

Question 9 · Q1–30 · single answer

What is the IUPAC name of the given compound?
CH_3–CH(OH)–CH(Br)–CH=CH–COOH

- (1)5-hydroxy-4-bromohex-2-enoic acid
- (2)4-bromo-5-hydroxyhex-4-enoic acid

- (3)4-bromo-5-hydroxyhex-2-enoic acid
- (4)3-bromo-2-hydroxyhex-4-enoic acid
- (5)5-hydroxy-4-bromohex-4-enoic acid

Answer and review

Answer **(3)** Prepared answer (no official scheme available)

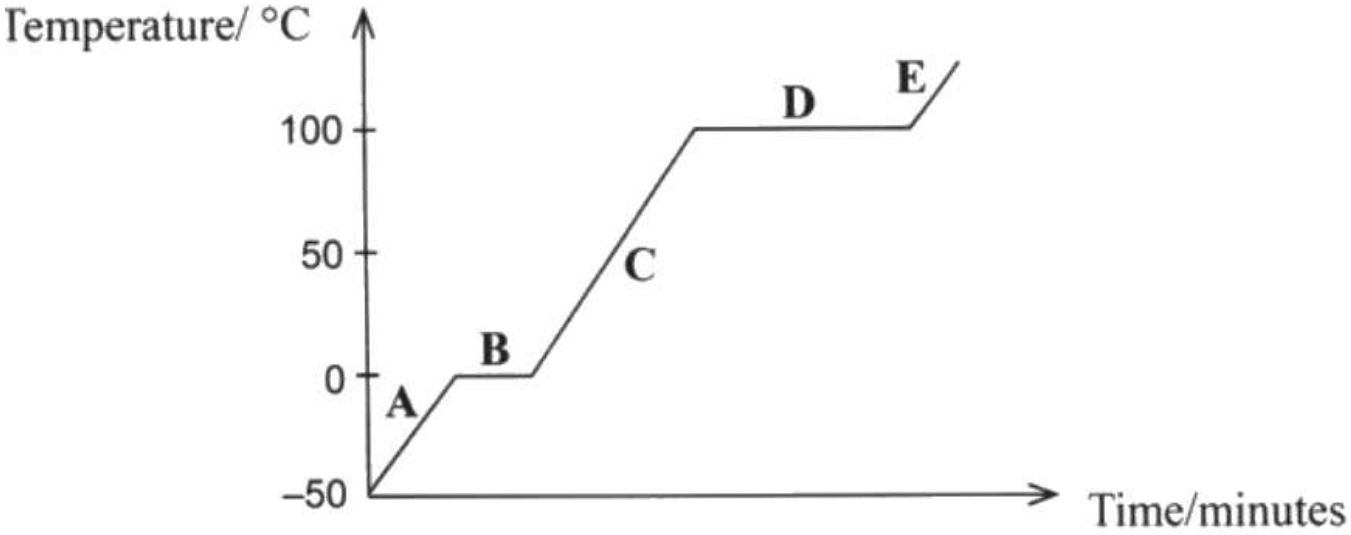
The principal group is –COOH, so C1 is the carboxyl carbon. The double bond is then C2=C3, Br is on C4 and OH on C5 in a six-carbon chain. Prefixes are listed alphabetically (bromo before hydroxy): 4-bromo-5-hydroxyhex-2-enoic acid.

RB U7 §1.3 · p. 7

Question 10 · Q1–30 · single answer

The diagram below shows the temperature variation of a sample of a given mass of water starting from the solid state, upon heating under constant pressure of 1 atm in a closed container.

Which of the following gives the correct representation of the phases or phase equilibria of water present in the regions marked as A, B, C, D and E? Assume that no mass loss occurred during the process.



- (1)A: $H_2O(l)$ · B: $H_2O(s)$ · C: $H_2O(s) \rightleftharpoons H_2O(l)$ · D: $H_2O(g)$ · E: $H_2O(l) \rightleftharpoons H_2O(g)$
- (2)A: $H_2O(s) \rightleftharpoons H_2O(l)$ · B: $H_2O(s)$ · C: $H_2O(s) \rightleftharpoons H_2O(l)$ · D: $H_2O(g)$ · E: $H_2O(l) \rightleftharpoons H_2O(g)$
- (3)A: $H_2O(s)$ · B: $H_2O(s) \rightleftharpoons H_2O(l)$ · C: $H_2O(g)$ · D: $H_2O(l) \rightleftharpoons H_2O(g)$ · E: $H_2O(g)$
- (4)A: $H_2O(l)$ · B: $H_2O(s) \rightleftharpoons H_2O(l)$ · C: $H_2O(s)$ · D: $H_2O(l) \rightleftharpoons H_2O(g)$ · E: $H_2O(g)$
- (5)A: $H_2O(s)$ · B: $H_2O(s) \rightleftharpoons H_2O(l)$ · C: $H_2O(l)$ · D: $H_2O(l) \rightleftharpoons H_2O(g)$ · E: $H_2O(g)$

Answer and review

Answer **(5)** Prepared answer (no official scheme available)

In a sloping region only one phase is being heated; on a flat region two phases coexist at equilibrium while the latent heat is absorbed. So A is ice warming from −50 °C, B is melting at 0 °C (s ⇌ l), C is liquid water warming, D is boiling at 100 °C (l ⇌ g) and E is steam being heated.

RB U12 §2.5 · p. 199 RB U5 §2.4 · p. 53

Question 11 · Q1–30 · single answer

To prepare 250.00 cm^3 of 0.005 mol dm^{-3} aqueous solution of Fe^{2+} ions, a student uses a compound with the formula $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ found in a bottle in the laboratory. The label on the bottle indicates that the purity of the compound is 80%. The mass of the compound required to prepare the solution is, (H = 1, N = 14, O = 16, S = 32, Fe = 56)

- (1)6.125 g
- (2)1.96 g
- (3)0.6125 g
- (4)0.490 g
- (5)0.392 g

Answer and review

Answer **(3)** Prepared answer (no official scheme available)

M = 56 + 2(18) + 2(96) + 6(18) = 392 g mol^{-1}. Moles of Fe^{2+} needed = 0.250 × 0.005 = 1.25 × 10^{-3} mol, so the mass of pure salt = 1.25 × 10^{-3} × 392 = 0.490 g. Only 80% of the sample is the salt, so the mass to weigh = 0.490 ÷ 0.80 = 0.6125 g.

RB U3 §3.7 · p. 113

Question 12 · Q1–30 · single answer

Which of the following statements is **false** regarding oxoanions of chlorine?

- (1)The Lewis dot-dash structures of ClO_2^−, ClO_3^− and ClO_4^− contain one, two and three oxygen-chlorine double bonds respectively.
- (2)The oxidation numbers of chlorine in ClO_2^−, ClO_3^− and ClO_4^− are +3, +5 and +7 respectively.
- (3)ClO_2^− has an angular shape.
- (4)The structure of ClO^- contains an O–Cl double bond.
- (5)The electron pair geometry around Cl in ClO_3^− is tetrahedral.

Answer and review

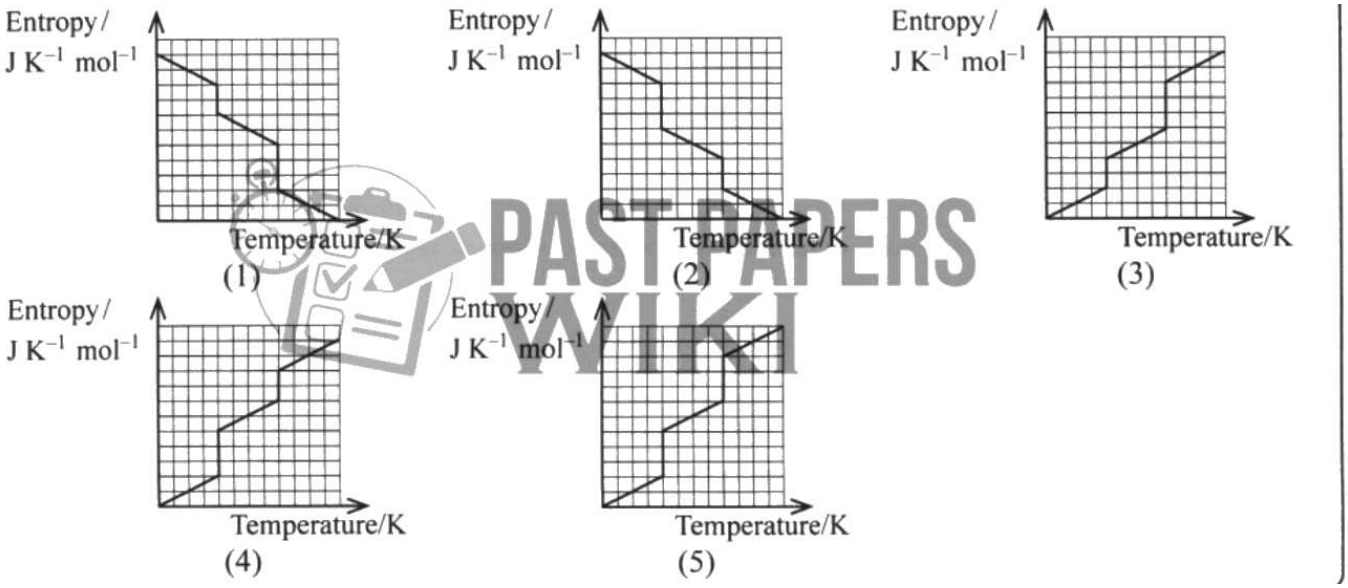
Answer **(4)** Prepared answer (no official scheme available)

ClO^- has 14 valence electrons. The most acceptable structure is Cl–O with one negative formal charge on O; a Cl=O double bond would give larger formal charges (+1 on Cl, −2 on O). In the other ions, double bonds reduce the formal charge on Cl, giving one, two and three Cl=O bonds. ClO_3^− has three bonding pairs and one lone pair on Cl, so its electron pair geometry is tetrahedral.

RB U2 §2.1 · p. 44 RB U6 §4.7 · p. 149

Question 13 · Q1–30 · single answer

Which of the following graphs represents the variation of entropy of a substance when it changes its state as solid → liquid → gas upon heating?



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- (1)Graph (1)
- (2)Graph (2)
- (3)Graph (3)
- (4)Graph (4)
- (5)Graph (5)

Answer and review

Answer **(3)** Prepared answer (no official scheme available)

Entropy rises steadily as each phase is heated and jumps vertically at the melting point and the boiling point. The jump on boiling is much larger than on melting, because a gas is far more disordered than a liquid ($\Delta S_{vap} \gg \Delta S_{fus}$). Graphs (1) and (2) fall with temperature; (4) has the larger jump at melting and (5) has equal jumps. Only (3) shows a small jump followed by a large one.

RB U5 §2.4 · p. 53

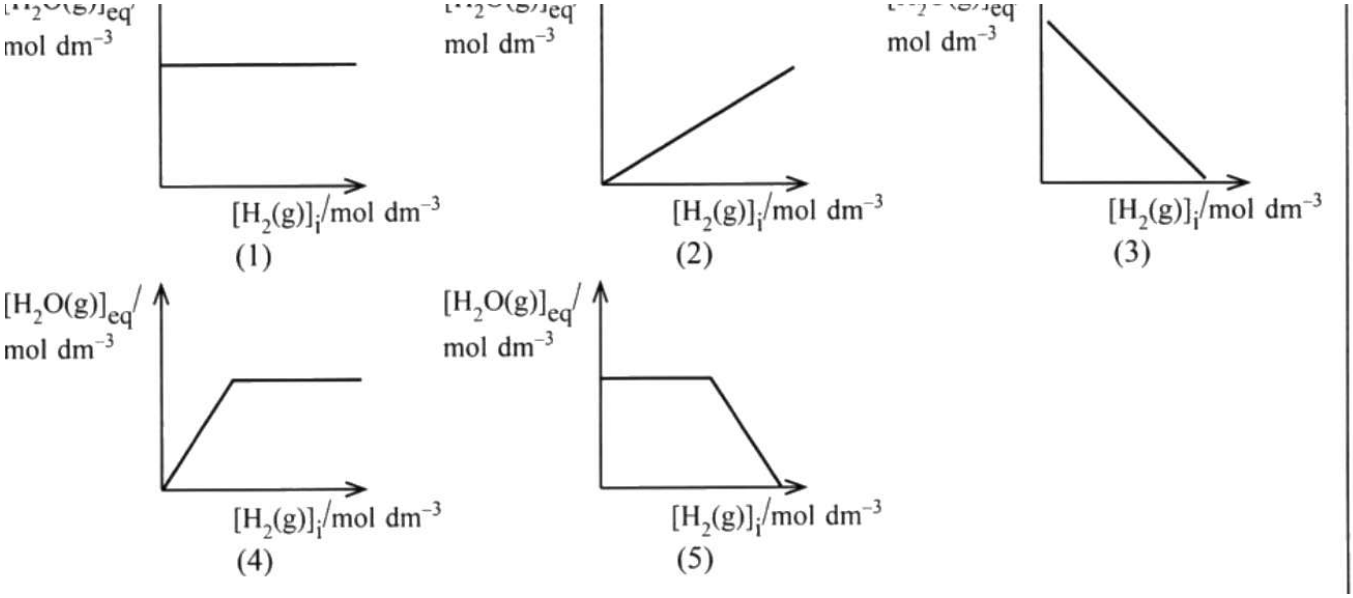
Question 14 · Q1–30 · single answer

Consider the following equilibrium which exists in a closed-rigid container at a given temperature. M is a metal.

$MO(s) + H_2(g) \rightleftharpoons M(s) + H_2O(g)$

A series of experiments were carried out with different initial concentrations of $H_2(g)$ keeping MO(s) in excess. Which of the following graphs represents the variation of equilibrium concentration of $H_2O(g)$ with the initial concentration of $H_2(g)$?

initial concentration of $H_2(g) = [H_2(g)]_i$; equilibrium concentration of $H_2O(g) = [H_2O(g)]_{eq}$



- (1)Graph (1)
- (2)Graph (2)
- (3)Graph (3)
- (4)Graph (4)
- (5)Graph (5)

Answer and review

Answer **(2)** Prepared answer (no official scheme available)

Solids are left out of the equilibrium expression, so $K_c = [H_2O(g)]/[H_2(g)]$. If x mol dm^{-3} of H_2 reacts, $K_c = x/([H_2]_i - x)$, giving $[H_2O]_{eq} = \{K_c/(1 + K_c)\}[H_2]_i$. The equilibrium concentration of H_2O is directly proportional to the initial H_2 concentration: a straight line through the origin.

RB U12 §2.1 · p. 76

Question 15 · Q1–30 · single answer

Consider the reaction scheme given below.
$(CH_3)_2C{=}CH_2$ —(cold conc. H_2SO_4)→ X —(H^+/H_2O, Δ)→ Y
In the reaction scheme given above, the structures of X and Y are respectively,

- (1)$(CH_3)_3C–SO_2OH$ and $(CH_3)_3C–OH$
- (2)$(CH_3)_2CH–SO_2OH$ and $(CH_3)_2CH–CH_2OH$
- (3)$(CH_3)_2CH–CH_2–OSO_2OH$ and $(CH_3)_2CH–CH_2OH$
- (4)$(CH_3)_3C–OSO_2OH$ and $(CH_3)_3C–OH$
- (5)$(CH_3)_2CH–CH_2–SO_2OH$ and $(CH_3)_2CH–CH_2OH$

Answer and review

Answer **(4)** Prepared answer (no official scheme available)

H_2SO_4 adds across the C=C by electrophilic addition. H^+ adds to the CH_2 end to give the more stable tertiary carbocation (Markovnikov), and HSO_4^− bonds to it through oxygen, giving the alkyl hydrogen sulfate $(CH_3)_3C–OSO_2OH$. Hydrolysis replaces $–OSO_2OH$ by –OH, giving 2-methylpropan-2-ol.

RB U8 §2.2 · p. 33

Question 16 · Q1–30 · single answer

Two rigid containers A and B are connected through a valve as shown below. Initially, container A is filled with an ideal gas while container B is empty. Predict how the entropy and Gibbs free energy of the system change when the valve is opened. (Consider that the temperature does **not** change)

- (1)Entropy increase · Gibbs free energy increase
- (2)Entropy decrease · Gibbs free energy decrease
- (3)Entropy increase · Gibbs free energy decrease
- (4)Entropy increase · Gibbs free energy unchanged
- (5)Entropy decrease · Gibbs free energy unchanged

Answer and review

Answer **(3)** Prepared answer (no official scheme available)

The gas spreads into a larger volume, so its entropy increases. For an ideal gas at constant temperature there are no intermolecular forces, so $\Delta H = 0$, and $\Delta G = \Delta H - T\Delta S = -T\Delta S < 0$. The expansion is spontaneous, as expected.

RB U5 §2.4 · p. 53

Question 17 · Q1–30 · single answer

The elementary reaction $2X(g) + Y(g) \rightarrow Z(g)$ takes place in a closed container at a given temperature. By what factor would the rate of the reaction increase if the initial concentration of X(g) is doubled and that of Y(g) is tripled?

- (1)5
- (2)6
- (3)12
- (4)18
- (5)24

Answer and review

Answer **(3)** Prepared answer (no official scheme available)

For an elementary step the orders equal the coefficients: rate = $k[X]^2[Y]$. Doubling [X] multiplies the rate by $2^2 = 4$ and tripling [Y] by 3, so the rate rises $4 \times 3 = 12$ times.

RB U11 §1.10 · p. 57

Question 18 · Q1–30 · single answer

Consider the following reactions.
$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l) : \Delta G°_{rxn} = -1010 \text{ kJ mol}^{-1}$
$2NO_2(g) \rightarrow 2NO(g) + O_2(g) : \Delta G°_{rxn} = 70 \text{ kJ mol}^{-1}$
$4NO_2(g) + O_2(g) + 2H_2O(l) \rightarrow 4HNO_3(aq) : \Delta G°_{rxn} = -170 \text{ kJ mol}^{-1}$
$\Delta G°$ of the reaction, $4NH_3(g) + 8O_2(g) \rightarrow 4HNO_3(aq) + 4H_2O(l)$ in kJ mol^{-1} is

- (1)−1320

- (2)−1250
- (3)−1100
- (4)−1040
- (5)1100

Answer and review

Answer **(1)** Prepared answer (no official scheme available)

G is a state function, so ΔG values combine like Hess's law. Add equation 1 (−1010), twice the reverse of equation 2 ($4NO + 2O_2 \rightarrow 4NO_2$, −140) and equation 3 (−170). The NO, NO_2 and two H_2O cancel, leaving the target reaction: $\Delta G^\circ = -1010 - 140 - 170 = -1320$ kJ mol^{-1}.

RB U5 §2.2 · p. 36

Question 19 · Q1–30 · single answer

Upon the addition of excess dil. HCl which of the solid compounds given below gives a clear solution and evolves a gas which turns a filter paper soaked with acidified $K_2Cr_2O_7$ green?

- (1)$ZnBr_2$
- (2)Ag_2CO_3
- (3)$Na_2S_2O_3$
- (4)$SrSO_3$
- (5)$Cr(OH)_3$

Answer and review

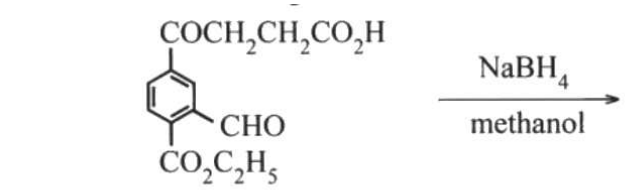
Answer **(4)** Prepared answer (no official scheme available)

The gas must be the reducing gas SO_2, which turns orange $Cr_2O_7^{2-}$ green (Cr^{3+}). $SrSO_3 + 2HCl \rightarrow SrCl_2(aq) + SO_2 + H_2O$ leaves a clear solution. $Na_2S_2O_3$ also gives SO_2, but the solution turns cloudy with yellow sulfur. Ag_2CO_3 gives CO_2 and a white AgCl precipitate.

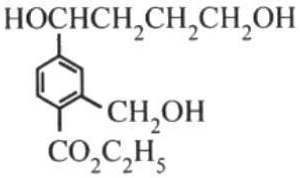
RB U6 §4.6 · p. 141

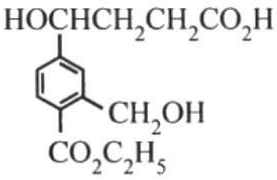
Question 20 · Q1–30 · single answer

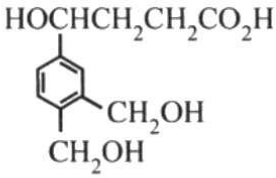
Consider the following reaction. A benzene ring carrying $–COCH_2CH_2CO_2H$, –CHO and $–CO_2C_2H_5$ groups is treated with $NaBH_4$ in methanol. The product formed is,

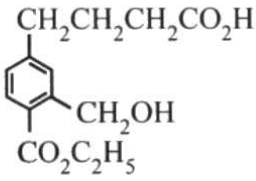


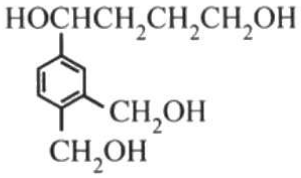
The product formed is,

(1) 

(2) 

(3) 

(4) 

(5) 

- (1)ring with –CH(OH)$CH_2CH_2CH_2OH$, –CH_2OH, –$CO_2C_2H_5$
- (2)ring with –CH(OH)$CH_2CH_2CO_2H$, –CH_2OH, –$CO_2C_2H_5$
- (3)ring with –CH(OH)$CH_2CH_2CO_2H$, –CH_2OH, –CH_2OH
- (4)ring with –$CH_2CH_2CH_2CO_2H$, –CH_2OH, –$CO_2C_2H_5$
- (5)ring with –CH(OH)$CH_2CH_2CH_2OH$, –CH_2OH, –CH_2OH

Answer and review

Answer **(2)** Prepared answer (no official scheme available)

$NaBH_4$ is a mild reducing agent. It reduces aldehydes and ketones to alcohols but leaves carboxylic acids and esters unchanged ($LiAlH_4$ would reduce those too). So –CHO becomes –CH_2OH, the ketone C=O becomes CH(OH), and –CO_2H and –$CO_2C_2H_5$ stay as they are.

RB U9 §3.4 · p. 60

Question 21 · Q1–30 · single answer

Consider the reaction, ½A_2(g) + ½B_2(g) → AB(g).
The ratio of the values of enthalpy of bond dissociation of A_2(g), B_2(g) and AB(g) is 2 : 1 : 2. The enthalpy change for this reaction is −100 kJ mol^{-1}. Bond dissociation enthalpy value of A_2(g) in kJ mol^{-1} is,

- (1)100
- (2)300
- (3)350
- (4)400
- (5)450

Answer and review

Answer **(4)** Prepared answer (no official scheme available)

Let the bond enthalpies be 2x (A_2), x (B_2) and 2x (AB). ΔH = (bonds broken) − (bonds formed) = ½(2x) + ½(x) − 2x = −0.5x. So −0.5x = −100 and x = 200 kJ mol^{-1}; the A_2 bond enthalpy is 2x = 400 kJ mol^{-1}.

RB U5 §2.2 · p. 36

Question 22 · Q1–30 · single answer

An electrochemical cell was constructed using Pt(s) | Fe^{2+}(aq), Fe^{3+}(aq) and Pt(s) | Mn^{2+}(aq), H^{+}(aq), MnO_4^−(aq) half cells at 25 °C. Which of the following is correct about this cell at 25 °C? E°(Fe^{3+}(aq)/Fe^{2+}(aq)) = +0.77 V, E°(MnO_4^−(aq)/Mn^{2+}(aq)) = +1.51 V

- (1)Anode Fe^{3+}(aq) | Fe^{2+}(aq) · Cathode MnO_4^−(aq) | Mn^{2+}(aq) · Pt(s) | Fe^{2+}(aq), Fe^{3+}(aq) || MnO_4^−(aq), H^{+}(aq), Mn^{2+}(aq) | Pt(s) · −0.74 V
- (2)Anode Fe^{3+}(aq) | Fe^{2+}(aq) · Cathode MnO_4^−(aq) | Mn^{2+}(aq) · Pt(s) | Fe^{2+}(aq), Fe^{3+}(aq) || MnO_4^−(aq), H^{+}(aq), Mn^{2+}(aq) | Pt(s) · +0.74 V
- (3)Anode MnO_4^−(aq) | Mn^{2+}(aq) · Cathode Fe^{3+}(aq) | Fe^{2+}(aq) · Pt(s) | Fe^{2+}(aq), Fe^{3+}(aq) || MnO_4^−(aq), H^{+}(aq), Mn^{2+}(aq) | Pt(s) · +0.74 V
- (4)Anode Fe^{3+}(aq) | Fe^{2+}(aq) · Cathode MnO_4^−(aq) | Mn^{2+}(aq) · Pt(s) | Mn^{2+}(aq), H^{+}(aq), MnO_4^−(aq) || Fe^{3+}(aq), Fe^{2+}(aq) | Pt(s) · +0.74 V
- (5)Anode Fe^{3+}(aq) | Fe^{2+}(aq) · Cathode MnO_4^−(aq) | Mn^{2+}(aq) · Pt(s) | Mn^{2+}(aq), H^{+}(aq), MnO_4^−(aq) || Fe^{3+}(aq), Fe^{2+}(aq) | Pt(s) · −0.74 V

Answer and review

Answer **(2)** Prepared answer (no official scheme available)

The couple with the more positive E° (MnO_4^−/Mn^{2+}) is reduced at the cathode, and Fe^{2+} is oxidized at the anode. The anode goes on the left of the cell notation, and $E°_{cell} = E°_{cathode} − E°_{anode} = 1.51 − 0.77 = +0.74$ V.

RB U13 §3.3 · p. 250

Question 23 · Q1–30 · single answer

Consider the following compounds.
A: C_6H_5–$CH(CH_3)_2$ (isopropylbenzene) B: C_6H_5–$COCH_2CH_3$ C: C_6H_5–OCH_3
The increasing order of ease of the Friedel-Crafts acylation of these compounds is

- (1)A < B < C
- (2)A < C < B
- (3)B < A < C
- (4)B < C < A
- (5)C < B < A

Answer and review

Answer **(3)** Prepared answer (no official scheme available)

Friedel–Crafts acylation is an electrophilic substitution, so it is faster when the ring is richer in electrons. –$COCH_2CH_3$ withdraws electrons (deactivating, meta-directing), an alkyl group donates weakly, and –OCH_3 donates strongly through its lone pair. Order: B < A < C.

RB U8 §2.5 · p. 49

Question 24 · Q1–30 · single answer

The steps in the mechanism of a reaction in the presence of a catalyst are shown below.
Step I : $Ag^{+}(aq) + Ce^{4+}(aq) \rightarrow Ag^{2+}(aq) + Ce^{3+}(aq)$
Step II : $Tl^{+}(aq) + Ag^{2+}(aq) \rightarrow Tl^{2+}(aq) + Ag^{+}(aq)$
Step III : $Tl^{2+}(aq) + Ce^{4+}(aq) \rightarrow Tl^{3+}(aq) + Ce^{3+}(aq)$
Which of the following correctly identifies the overall reaction, the catalyst and the intermediate/intermediates?

- (1)$2Ce^{4+}(aq) + Tl^{+}(aq) \rightarrow 2Ce^{3+}(aq) + Tl^{3+}(aq)$ · catalyst $Ag^{+}(aq)$ · intermediates $Ag^{2+}(aq)$, $Tl^{2+}(aq)$
- (2)$2Ce^{4+}(aq) + Tl^{+}(aq) \rightarrow 2Ce^{3+}(aq) + Tl^{3+}(aq)$ · catalyst $Tl^{2+}(aq)$ · intermediate $Ag^{2+}(aq)$
- (3)$Ce^{4+}(aq) + Tl^{+}(aq) \rightarrow Tl^{2+}(aq) + Ce^{3+}(aq)$ · catalyst $Ag^{+}(aq)$ · intermediate $Ag^{2+}(aq)$
- (4)$Ce^{4+}(aq) + Tl^{+}(aq) \rightarrow Tl^{2+}(aq) + Ce^{3+}(aq)$ · catalyst $Ag^{2+}(aq)$ · intermediate $Ag^{+}(aq)$
- (5)$Ce^{4+}(aq) + Tl^{2+}(aq) \rightarrow Tl^{3+}(aq) + Ce^{3+}(aq)$ · catalyst $Ag^{+}(aq)$ · intermediates $Ag^{2+}(aq)$, $Tl^{+}(aq)$

Answer and review

Answer **(1)** Prepared answer (no official scheme available)

Adding the three steps cancels Ag^{+}, Ag^{2+} and Tl^{2+}, leaving $2Ce^{4+} + Tl^{+} \rightarrow 2Ce^{3+} + Tl^{3+}$. Ag^{+} is used in step I and regenerated in step II, so it is the catalyst. Ag^{2+} and Tl^{2+} are formed and then used up, so they are intermediates.

RB U11 §1.10 · p. 57

Question 25 · Q1–30 · single answer

Which of the following statements is **incorrect**?

- (1)When an inert gas is added to a gaseous equilibrium system in a closed-rigid container at a given temperature, total pressure of the system increases while the equilibrium constant remains unchanged.
- (2)When an inert gas is added to a gaseous equilibrium system in a closed-flexible container at a given temperature keeping the total pressure constant, the equilibrium constant remains unchanged.
- (3)When the pressure of the equilibrium system $2HgO(s) \rightleftharpoons 2Hg(l) + O_2(g)$ in a closed-rigid container at a given temperature is increased, the equilibrium point shifts to the right side.
- (4)To increase the yield of $SO_3(g)$ in the equilibrium system $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ at a constant temperature in a closed-flexible container the volume of the container should be decreased by applying an external pressure.
- (5)When the pressure of the equilibrium system $C(s) + 2H_2(g) \rightleftharpoons CH_4(g)$ in a closed-rigid container at constant temperature is increased, rate of the forward reaction increases.

Answer and review

Answer **(3)** Prepared answer (no official scheme available)

For $2HgO(s) \rightleftharpoons 2Hg(l) + O_2(g)$, only O_2 is a gas, so $K_p = P_{O2}$. Raising the pressure moves the equilibrium towards fewer moles of gas, which is to the left, not the right. Only temperature changes K, and inert gas added at constant volume leaves the partial pressures unchanged.

RB U12 §2.1 · p. 76

Question 26 · Q1–30 · single answer

The solubility of $Mg(OH)_2(s)$ in water at 25 °C and 100 °C are 1.0×10^{-4} mol dm^{-3} and 4.0×10^{-3} mol dm^{-3}, respectively. How do the concentration of $OH^-(aq)$ and the pH value of a $Mg(OH)_2$ solution at 100 °C differ from those of a solution at 25 °C?
At 25 °C, $K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6} and at 100 °C $K_w = 5.5 \times 10^{-14}$ mol^2 dm^{-6}.

- (1)$[OH^-(aq)]$ higher · pH no change
- (2)$[OH^-(aq)]$ higher · pH higher
- (3)$[OH^-(aq)]$ no change · pH higher
- (4)$[OH^-(aq)]$ lower · pH lower
- (5)$[OH^-(aq)]$ higher · pH lower

Answer and review

Answer **(2)** Prepared answer (no official scheme available)

$[OH^-]$ = 2s: 2.0×10^{-4} mol dm^{-3} at 25 °C and 8.0×10^{-3} mol dm^{-3} at 100 °C, so it is higher. At 25 °C, $[H^+] = 1.0 \times 10^{-14} \div 2.0 \times 10^{-4} = 5 \times 10^{-11}$ (pH ≈ 10.3). At 100 °C, $[H^+] = 5.5 \times 10^{-14} \div 8.0 \times 10^{-3} \approx 6.9 \times 10^{-12}$ (pH ≈ 11.2). The pH is higher. The rise in K_w does not outweigh the 40-fold rise in $[OH^-]$.

RB U12 §2.4 · p. 175

Question 27 · Q1–30 · single answer

How many isomeric compounds exist with the molecular formula C_8H_8O, which have a benzene ring in its structure and gives a coloured precipitate with 2,4-dinitrophenylhydrazine (2,4-DNP)?

- (1)2
- (2)3
- (3)4
- (4)5
- (5)6

Answer and review

Answer **(4)** Prepared answer (no official scheme available)

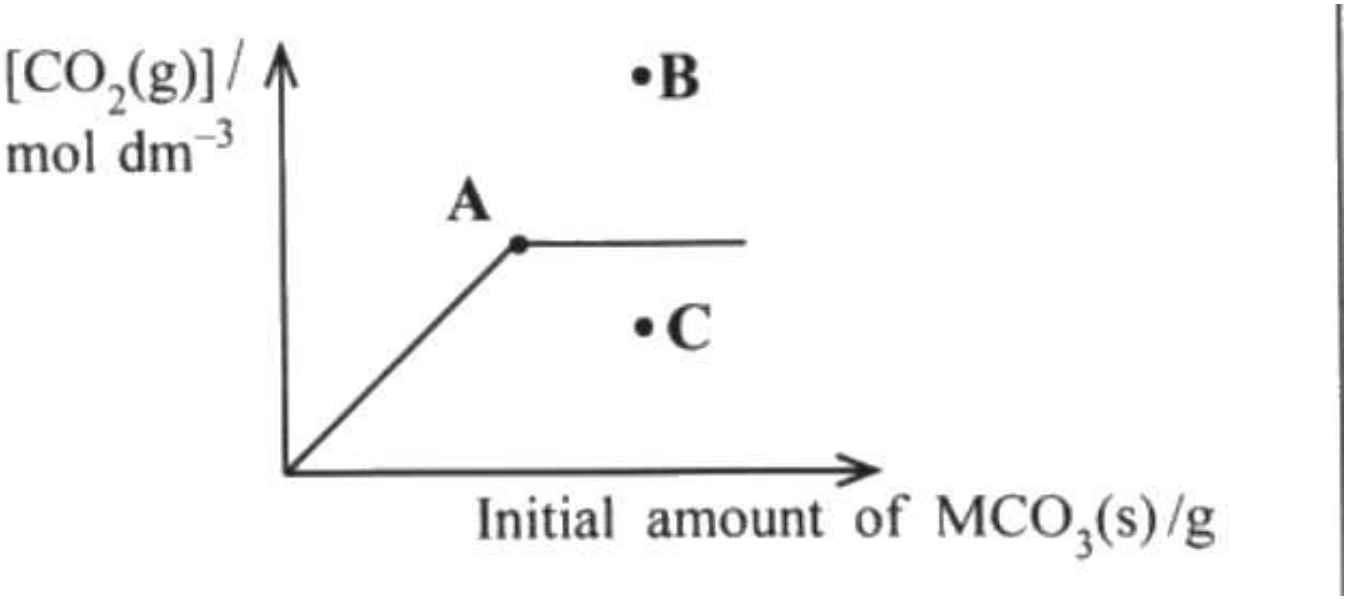
2,4-DNP reacts with aldehydes and ketones, so the isomers must contain C=O. With a benzene ring and C_8H_8O there are five: acetophenone ($C_6H_5COCH_3$), phenylethanal ($C_6H_5CH_2CHO$) and 2-, 3- and 4-methylbenzaldehyde.

RB U7 §1.4 · p. 21 RB U9 §3.4 · p. 60

Question 28 · Q1–30 · single answer

The given graph was obtained from several experiments carried out for the dissociation of the metal carbonate $MCO_3(s)$ to MO(s) and $CO_2(g)$ at a particular temperature in a closed-rigid container. The concentrations of $CO_2(g)$ were measured on changing the initial amount of $MCO_3(s)$.

Which of the following statements is **incorrect** about this system? K is the equilibrium constant and Q is the reaction quotient.



- (1)The equilibrium, $MCO_3(s) \rightleftharpoons MO(s) + CO_2(g)$ is established only after the point A.
- (2)At the point B, Q > K.
- (3)At the point C, Q < K.
- (4)Beyond the point A, pressure of the system does not change.
- (5)At both points B and C, Q = K.

Answer and review

Answer **(5)** Prepared answer (no official scheme available)

For this heterogeneous equilibrium $K_c = [CO_2(g)]$. Up to point A every bit of MCO_3 decomposes, so $[CO_2]$ rises with the amount taken. From A onwards solid MCO_3 remains, equilibrium is reached and $[CO_2]$ stays fixed at K, so the pressure stays constant. B lies above the plateau (Q > K) and C below it (Q < K); neither is at equilibrium.

RB U12 §2.1 · p. 76

Question 29 · Q1–30 · single answer

The reaction of metallic sodium with water is an irreversible reaction. 1.80 g of pure water was cautiously added to 460 g of metallic Na. Maximum amount of H_2 gas produced, in moles, is, (H = 1, O = 16 and Na = 23)

- (1)20
- (2)10
- (3)0.20
- (4)0.10
- (5)0.05

Answer and review

Answer **(5)** Prepared answer (no official scheme available)

$2Na + 2H_2O \rightarrow 2NaOH + H_2$. Water: 1.80 ÷ 18 = 0.10 mol; sodium: 460 ÷ 23 = 20 mol, a large excess. Water is the limiting reagent, so H_2 = 0.10 ÷ 2 = 0.050 mol.

RB U3 §3.8 · p. 115

Question 30 · Q1–30 · single answer

When dilute HCl is added to a solid sample of a mixture containing $CaCO_3$ and $ZnCO_3$ in a 1 : 1 mass ratio, a clear solution was obtained. The Ca^{2+} : Zn^{2+} mole ratio in the final solution is approximately, (C = 12, O = 16, Ca = 40 and Zn = 65)

- (1)1 : 1
- (2)5 : 4
- (3)4 : 5
- (4)2 : 1
- (5)1 : 2

Answer and review

Answer **(2)** Prepared answer (no official scheme available)

Take m g of each. $CaCO_3$ = 100 g mol^{-1} and $ZnCO_3$ = 125 g mol^{-1}, so the mole ratio is (m/100) : (m/125) = 125 : 100 = 5 : 4. Both carbonates dissolve completely, so the ions are in the same ratio.

RB U3 §3.3 · p. 97

Questions 31–40: response code

(1)	(2)	(3)	(4)	(5)
Only (a) and (b) are correct	Only (b) and (c) are correct	Only (c) and (d) are correct	Only (d) and (a) are correct	Any other number or combination of responses is correct

Question 31 · Q31–40 · response code

Which of the following statements is/are correct regarding the standard hydrogen electrode?

- E° value of the electrode is considered as 0.00 V.
- The half-reaction is irreversible.
- The half-reaction is always spontaneous.
- It can act as the anode or cathode depending on the electrochemical cell under consideration.

Answer and review

Answer **(4)** Prepared answer (no official scheme available)

The SHE (Pt, H_2 at 1 atm, $[H^+]$ = 1 mol dm^{-3}) is the reference with E° = 0.00 V by definition. Its half-reaction $2H^+ + 2e^- \rightleftharpoons H_2$ is reversible, so it can be the cathode (against Zn) or the anode (against Cu). Its direction is not fixed. Only (a) and (d) are correct.

RB U13 §3.2 · p. 238

Question 32 · Q31–40 · response code

Which of the following statements is/are correct regarding the reaction of acetone with 2,4-dinitrophenylhydrazine (2,4-DNP)?

- It is a two-step reaction where the second step is a dehydration reaction.

- The product formed in the first step of this reaction can be isolated.
- The structure of the coloured product formed in this reaction is $(CH_3)_2C(OH)–N=N–C_6H_3(NO_2)_2$ (2,4-dinitrophenyl).
- This reaction can be used to distinguish acetone from acetic acid.

Answer and review

Answer **(4)** Prepared answer (no official scheme available)

The hydrazine first adds to C=O (nucleophilic addition) and the unstable addition product immediately loses water (elimination), so it cannot be isolated. The orange product is the hydrazone $(CH_3)_2C=N–NH–C_6H_3(NO_2)_2$, not an azo alcohol. Carboxylic acids do not give this precipitate, so the test distinguishes acetone from acetic acid. Only (a) and (d) are correct.

RB U9 §3.4 · p. 60

Question 33 · Q31–40 · response code

Soap is a sodium or potassium salt of fatty acids. Identify the correct statement/statements regarding hard water and soap.

- The cleaning efficiency of soap is higher in hard water than in pure water.
- Precipitates formed by reacting polyvalent cations with soap are more dense than water.
- A precipitate is formed by the attraction of anions of fatty acids to a polyvalent cation.
- Some of the polyvalent cations in hard water are Ca^{2+}, Mg^{2+} and Fe^{2+}.

Answer and review

Answer **(3)** Prepared answer (no official scheme available)

Hardness is caused by polyvalent cations such as Ca^{2+}, Mg^{2+} and Fe^{2+}. The fatty-acid anions of soap bind to them and form an insoluble scum (for example $(C_{17}H_{35}COO)_2Ca$), which wastes soap and lowers its cleaning efficiency. The scum collects as a floating layer rather than sinking. Only (c) and (d) are correct.

RB U14 §1.4 · p. 14

Question 34 · Q31–40 · response code

Which of the following statements is/are true with regard to the chemistry of nitrogen?

- Nitrogen is slightly soluble in water under atmospheric pressure while the solubility of nitrogen in water increases with pressure.
- Nitrogen shows oxidation numbers from −3 to +5 in compounds.
- Nitrogen has several allotropes.
- Atmospheric nitrogen is converted to NH_3 during lightning.

Answer and review

Answer **(1)** Prepared answer (no official scheme available)

N_2 is non-polar and only slightly soluble, and like any gas it dissolves more at higher pressure. Its oxidation numbers range from −3 (NH_3) to +5 (HNO_3). Nitrogen has no common allotropes. Lightning converts N_2 and O_2 to NO (and then NO_2 and nitrate), not to NH_3. Only (a) and (b) are true.

RB U6 §4.5 · p. 136

Question 35 · Q31–40 · response code

Consider the following half reactions at 25 °C.
$Ag^{+}(aq) + e \rightarrow Ag(s)$: E° = +0.80 V
$Cu^{2+}(aq) + 2e \rightarrow Cu(s)$: E° = +0.34 V
$Zn^{2+}(aq) + 2e \rightarrow Zn(s)$: E° = −0.76 V
Which of the following statements is/are correct?

- When a rod of Zn(s) metal is placed in a $CuSO_4(aq)$ solution, Cu(s) metal is deposited on the Zn(s) rod.
- Among the electrochemical cells that could be assembled from the half-cells represented by the above, $Zn(s) \mid Zn^{2+}(aq) \parallel Ag^{+}(aq) \mid Ag(s)$ has the highest e.m.f. value.
- When a rod of Ag(s) metal is placed in a $CuSO_4(aq)$ solution, Cu(s) metal is deposited on the Ag(s) rod.
- $H_2(g)$ is not liberated when Cu(s) is added to a solution of 0.50 mol dm^{-3} $H_2SO_4(aq)$ acid.

Answer and review

Answer **(5)** Prepared answer (no official scheme available)

Zn (−0.76 V) is a stronger reducing agent than Cu, so it displaces Cu^{2+}. The largest difference in E° is between Ag^{+}/Ag and Zn^{2+}/Zn (0.80 + 0.76 = 1.56 V). Ag cannot reduce Cu^{2+}. Cu (+0.34 V) lies above hydrogen (0.00 V), so it does not release H_2 from dilute acid (0.50 mol dm^{-3} H_2SO_4 gives $[H^{+}]$ = 1 mol dm^{-3}). (a), (b) and (d) are correct, so the code is (5).

RB U13 §3.3 · p. 250

Question 36 · Q31–40 · response code

Which of the following compounds will **not** form a Grignard reagent as the final product, when it is reacted with Mg in dry ether?

- $CH_3COCH_2CH_2Br$
- $CH_3CH(NH_2)CH_2CH_2Cl$
- $CH_3C{\equiv}C–H$
- $BrCH_2CH{=}CH_2$

Answer and review

Answer **(5)** Prepared answer (no official scheme available)

A Grignard reagent survives only if the molecule has no group it reacts with. In (a) any RMgBr formed would attack the ketone C=O; in (b) the acidic N–H protons would destroy it. (c) has no carbon–halogen bond, so Mg does not react. Allyl bromide (d) forms $CH_2{=}CHCH_2MgBr$ normally. (a), (b) and (c) do not give a Grignard reagent, so the code is (5).

RB U8 §2.6 · p. 49

Question 37 · Q31–40 · response code

Dichlorodifluoromethane (R-12) is used as a refrigerant in household refrigerators. Identify the correct statement/statements.

- The volatile compound R-12 once released has a high potential to reach the stratosphere.
- While R-12 is stable in the troposphere, it decomposes to form chlorine radicals, in the stratosphere.
- R-12 is a greenhouse gas that contributes to global warming.

- R-12 depletes the ozone formed from photochemical smog.

Answer and review

Answer **(5)** Prepared answer (no official scheme available)

CF_2Cl_2 is volatile and unreactive, so it survives long enough to drift into the stratosphere. There UV light breaks C–Cl bonds and the Cl• radicals destroy stratospheric ozone. CFCs also absorb infrared radiation and are greenhouse gases. They do not remove the ground-level ozone of photochemical smog. (a), (b) and (c) are correct, so the code is (5).

RB U14 §1.13 · p. 58

Question 38 · Q31–40 · response code

At a given temperature, a rigid-closed container having a volume of 1.0 dm^3 filled with a real gas has a lower pressure than the pressure calculated for the equal amount of an ideal gas. Which of the following statements **does not/do not** give valid reasons for the observed non-ideal behaviour?

- The volume of the real gas molecules cannot be neglected when compared to the volume of the container.
- Velocities of the real gas molecules are lower than that of an ideal gas.
- Because the molecules of the real gas are attracted to each other, they do not exert a force on the container walls which is equal to that exerted by an ideal gas.
- The molecules of the real gas are attracted towards the walls of the container.

Answer and review

Answer **(5)** Prepared answer (no official scheme available)

A pressure lower than ideal is caused by attractions between molecules, which pull molecules back as they approach a wall and reduce the force of their collisions (c). Non-negligible molecular volume would make the pressure higher, not lower (a). At the same temperature the average kinetic energy is the same (b), and the attractions are between molecules, not towards the walls (d). (a), (b) and (d) are not valid reasons, so the code is (5).

RB U4 §1.5 · p. 24

Question 39 · Q31–40 · response code

Which of the following industrial processes utilize/utilizes the counter current principle?

- The production of NaOH by the membrane cell method
- The extraction of Fe by a blast furnace
- The production of H_2SO_4 by the contact process
- The production of NH_3 by the Haber-Bosch process

Answer and review

Answer **(2)** Prepared answer (no official scheme available)

In the blast furnace, ore, coke and limestone move down while hot gases rise. In the contact process, SO_3 rises through absorption towers against a downward flow of concentrated H_2SO_4. Opposing flows give the best contact and transfer. The membrane cell and the Haber process do not depend on this principle. Only (b) and (c) are correct.

RB U14 §1.1 · p. 2

Question 40 · Q31–40 · response code

Which of the following statements is/are true with regard to oxoacids of sulfur?

- Concentrated sulfuric acid can act as a dehydrating agent.
- The reaction of SO_2(g) with water produces sulfuric acid.
- Hot concentrated sulfuric acid can react as an oxidizing agent with certain metals and non-metals.
- Both H_2SO_4 and H_2SO_3 contain two S=O bonds each, in their structures.

Answer and review

Answer **(5)** Prepared answer (no official scheme available)

Concentrated H_2SO_4 removes water (for example from sugar) and, when hot, oxidizes Cu, C and S, being reduced to SO_2. SO_2 dissolves to give sulfurous acid, H_2SO_3, not sulfuric acid. In the most acceptable structures H_2SO_4 has two S=O bonds but H_2SO_3 has only one. Only (a) and (c) are true, which is not a coded pair, so the code is (5).

RB U6 §4.6 · p. 141

Questions 41–50: statement pairs

Response	First statement	Second statement
(1)	True	True, and correctly explains the first statement
(2)	True	True, but does not explain the first statement correctly
(3)	True	False
(4)	False	True
(5)	False	False

Question 41 · Q41–50 · statement pair

Statement 1

Benzene reacts with Cl_2 in the presence of $FeCl_3$, and yields chlorobenzene, C_6H_5Cl.

Statement 2

Cl_2 reacts with $FeCl_3$ to form the electrophile Cl^+, which reacts with the electron rich benzene ring.

Answer and review

Answer **(1)** Prepared answer (no official scheme available)

Halogenation of benzene needs a Lewis-acid catalyst. $FeCl_3$ polarizes Cl_2 ($Cl_2 + FeCl_3 \rightarrow Cl^+ + FeCl_4^-$). The electrophile attacks the π electrons of the ring and the arenium ion loses H^+, giving chlorobenzene. Both statements are true and the second explains the first.

RB U8 §2.4 · p. 44

Question 42 · Q41–50 · statement pair

Statement 1

Unlike s-block elements, p-block elements do not give a characteristic colour to the oxidizing flame in the flame test.

Statement 2

The first ionization energies of all p-block elements of periods 2 and 3 in the Periodic Table are greater than those of s-block elements of the corresponding period.

Answer and review

Answer **(3)** Prepared answer (no official scheme available)

The flame test in the syllabus identifies s-block metals (Li, Na, K, Ca, Sr, Ba) by their characteristic colours; p-block elements are not identified this way. The second statement is false: B (801 kJ mol^{-1}) is lower than Be (900), and Al (578) is lower than Mg (738), because the first p electron is easier to remove.

RB U6 §4.9 · p. 155 RB U1 §1.6 · p. 32

Question 43 · Q41–50 · statement pair

Statement 1

$H_2O(s) \rightleftharpoons H_2O(l)$ is an endothermic process.

Statement 2

The process of melting of ice is favoured by high temperature and high pressure.

Answer and review

Answer **(2)** Prepared answer (no official scheme available)

Melting absorbs heat, so it is endothermic; higher temperature therefore favours it. Ice is less dense than water, so higher pressure also favours the liquid (the solid–liquid line of water slopes backwards). Both statements are true, but the second describes conditions; it does not explain why melting is endothermic.

RB U12 §2.5 · p. 199

Question 44 · Q41–50 · statement pair

Statement 1

Ozone reduces the mechanical strength of rubber.

Statement 2

Ozone reacts with double bonds present in rubber.

Answer and review

Answer **(1)** Prepared answer (no official scheme available)

Natural rubber (cis-polyisoprene) contains a C=C in every repeating unit. Ozone attacks these double bonds and breaks the chains (ozone cracking), weakening the rubber. Both statements are true and the second explains the first.

RB U14 §1.11 · p. 37

Question 45 · Q41–50 · statement pair

Statement 1

Even though the number of valence shell electron pairs of the central atoms in ICl_2^-, N_3^- and $BeCl_2$ differ from each other, they have the same shape.

Statement 2

In molecules and ions, lone pairs of electrons on the central atom are held as far as possible from each other to reduce repulsing each other.

Answer and review

Answer **(1)** Prepared answer (no official scheme available)

All three are linear. $BeCl_2$ has two bonding pairs and N_3^- has two bonding regions (no lone pairs on the central N). ICl_2^- has five pairs on I (two bonding, three lone): the three lone pairs take the equatorial positions, as far apart as possible, leaving the two Cl atoms opposite each other. The second statement gives the reason ICl_2^- is still linear. (Prepared answer: the examiners could also judge the explanation incomplete, giving (2).)

RB U2 §2.3 · p. 52

Question 46 · Q41–50 · statement pair

Statement 1

The entropy change of freezing of liquid water to ice is higher than the entropy change of sublimation of ice.

Statement 2

Solids have less entropy compared to liquids and gases.

Answer and review

Answer **(4)** Prepared answer (no official scheme available)

Freezing lowers entropy (ΔS negative), while sublimation (solid → gas) raises it by a large amount (ΔS large and positive). So ΔS for freezing is lower, and the first statement is false. The second statement is true.

RB U5 §2.4 · p. 53

Question 47 · Q41–50 · statement pair

Statement 1

At a given temperature, the molar solubility of $Ag_2C_2O_4(s)$ in a $HNO_3(aq)$ solution is higher than its molar solubility in distilled water.

Statement 2

In the presence of a dilute acid, $C_2O_4^{2-}(aq)$ ions are converted to $HC_2O_4^-(aq)$ ions and/or to $H_2C_2O_4(aq)$.

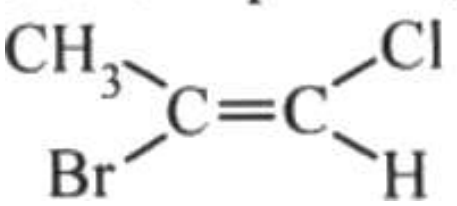
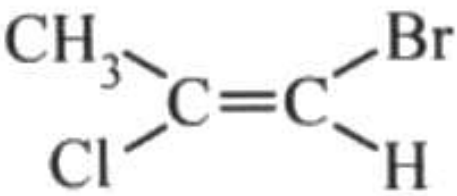
Answer and review

Answer **(1)** Prepared answer (no official scheme available)

Oxalate is the conjugate base of a weak acid. Acid removes $C_2O_4^{2-}$ as $HC_2O_4^-$ and $H_2C_2O_4$, lowering $[C_2O_4^{2-}]$ below the value needed to satisfy K_{sp}, so more $Ag_2C_2O_4$ dissolves. Both true; the second explains the first.

RB U12 §2.4 · p. 175

Question 48 · Q41–50 · statement pair

The compounds,  and  are

Statement 1

The compounds $CH_3(Br)C=C(Cl)H$ and $CH_3(Cl)C=C(Br)H$ (structures shown) are diastereoisomers.

Statement 2

Any two compounds which are **not** mirror images of each other are diastereoisomers.

Answer and review

Answer **(5)** Prepared answer (no official scheme available)

In the first compound Br is on the same carbon as CH_3 and Cl on the other carbon; in the second it is the reverse. The atoms are connected differently, so these are constitutional (positional) isomers, not stereoisomers. Diastereoisomers must be stereoisomers (same connectivity) that are not mirror images, so the second statement is also false.

RB U7 §1.4 · p. 21

Question 49 · Q41–50 · statement pair

Statement 1

Polyethylene is categorized as an addition polymer.

Statement 2

The double bonds in ethylene are responsible for its reactions.

Answer and review

Answer **(1)** Prepared answer (no official scheme available)

Ethylene molecules join by opening their C=C double bonds, with no small molecule lost, which defines an addition polymer. Both true; the reactivity of the C=C bond explains the polymerization.

RB U14 §1.11 · p. 37

Question 50 · Q41–50 · statement pair

Statement 1

Concentrated nitric acid is stored in brown coloured glass bottles in laboratories.

Statement 2

Nitric acid decomposes to nitrogen dioxide in the presence of light.

Answer and review

Answer **(1)** Prepared answer (no official scheme available)

Light decomposes HNO_3: $4HNO_3 \rightarrow 4NO_2 + O_2 + 2H_2O$, turning the acid yellow-brown. Brown glass blocks light and slows this. Both true; the second explains the first.

RB U6 §4.5 · p. 136

Structured essay · answer all four

SEQ · Paper II Part A

Question 1 · Part A · structured essay

(a) [32 marks]

You are provided with the following list of chemical species (elements, ions and compounds). Selecting from the list, write the answers to the questions on the relevant dotted lines.
Li^+, Cs^+, Br^-, I^-, CCl_4, ICl, C, Al, SO_3, SO_2, S

(i) element which as the central atom in a compound, can display sp, sp^2, sp^3 hybridizations
(ii) ion having the highest polarizability
(iii) ion having the highest polarizing power
(iv) element which can form electron deficient compounds
(v) compound having the strongest London forces
(vi) compound which displays the strongest dipole-dipole interactions
(vii) compound displaying bond angles of 120°
(viii) element which can form compounds by exceeding 8 valence electrons

Answer

(i) C (ii) I^- (iii) Li^+ (iv) Al (v) CCl_4 (vi) SO_2 (vii) SO_3 (viii) S

Review.

C is sp in ethyne, sp^2 in ethene and sp^3 in methane. The largest anion (I^-) is the most easily distorted; the smallest cation (Li^+) has the highest charge density. Al forms electron-deficient $AlCl_3$ (6 electrons around Al). CCl_4 has the most electrons and largest surface of the molecules listed. SO_2 (bent, about 1.6 D) has a larger dipole than ICl (about 1.2 D). SO_3 is trigonal planar. S can expand its octet (SF_6, H_2SO_4). (vi) is a prepared answer: ICl is the other polar compound in the list.

(b) [21 marks]

(i) Draw the **most** acceptable Lewis dot-dash structure for the molecule $HCNO_2$. Its skeleton is O–N–C(–O)–H (the second O is bonded to C).
(ii) Draw **two** Lewis dot-dash structures (resonance structures) for $HCNO_2$, excluding the Lewis structure you have drawn above.

Answer

(i) O=N–CH=O, with two lone pairs on each O and one lone pair on N. Total valence electrons = 1 + 4 + 5 + 12 = 22. Every atom has an octet (H two electrons) and every formal charge is zero, so this is the most acceptable structure.

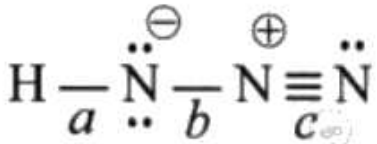
(ii) Structure 1: $O=N^+=CH–O^-$ (N has no lone pair, formal charge +1; the O on C has three lone pairs, formal charge −1; all octets complete).
Structure 2: $O=N–C^+H–O^-$ (C has only six electrons, formal charge +1; O on C has three lone pairs, formal charge −1). Structure 2 is less stable because C has an incomplete octet.

Review.

Resonance structures keep the atoms in place and move only π electrons and lone pairs. The most acceptable structure has the smallest formal charges, with any negative charge on the more electronegative atom.

(c) [32 marks]

(i) In the given HN_3 molecule, identify the bonds (as a, b, c) formed by the overlap of the following atomic/hybrid orbitals. Indicate whether the bond is σ or π type. **Note:** c is a triple bond.



orbitals	bond	σ or π
$s — sp^3$		
$sp — sp$		
$sp — sp^3$		
$p — p$		

Orbitals: s—sp^3 · sp—sp · sp—sp^3 · p—p

Answer

orbitals	bond	σ or π
s—sp^3	a	σ
sp—sp	c	σ
sp—sp^3	b	σ
p—p	c	π

Review.

The N bonded to H has two bonds (to H and to N) and two lone pairs, so it is sp^3. The central N has two σ bonds and no lone pair (linear), so it is sp. The terminal N (one σ bond, one lone pair) is sp. Bond a is H 1s with N sp^3; bond b is sp^3 with sp; the triple bond c is one sp–sp σ bond plus two p–p π bonds.

(ii) Write the number of VSEPR pairs, electron pair geometry, shape and hybridization of the central sulfur atom in each of the following molecules: SF_3N, Cl_2SO.

Answer

molecule	VSEPR pairs	electron pair geometry	shape	hybridization
SF_3N	4	tetrahedral	tetrahedral	sp^3
Cl_2SO	4	tetrahedral	trigonal pyramidal	sp^3

Review.

In SF_3N, S forms three S–F bonds and an S≡N bond and has no lone pair: four electron domains. In Cl_2SO, S forms two S–Cl bonds and an S=O bond and keeps one lone pair: four domains, one of them a lone pair. Multiple bonds count as one VSEPR pair.

(d) [15 marks]

Arrange the following species in increasing order of the property given in parenthesis.
I. Li_2CO_3, Na_2CO_3, $MgCO_3$ (decomposition temperature)
II. Li, Na, B (atomic radius)
III. SO_3^{2-}, SO_4^{2-}, SO_3 (electronegativity of S)

Answer

I. $MgCO_3 < Li_2CO_3 < Na_2CO_3$
II. B < Li < Na
III. $SO_3^{2-} < SO_4^{2-} < SO_3$

Review.

I: a smaller, more highly charged cation polarizes the carbonate ion more and lowers its decomposition temperature (Mg^{2+} most, then Li^+; Na_2CO_3 is very stable). II: radius falls across a period (Li > B) and rises down a group (Na > Li). III: S is more electronegative in a higher oxidation state (+4 in SO_3^{2-}, +6 in the others) and less electronegative when the species carries negative charge ($SO_4^{2-} < SO_3$).

Read: RB U2 §2.3 · p. 52 RB U1 §1.6 · p. 32 RB U2 §2.4 · p. 75 RB U6 §4.2 · p. 126

Question 2 · Part A · structured essay

(a) [54 marks]

(i) W is a p-block element in the Periodic Table. Its atomic number is less than 20. It has two allotropes; one of them (A) is odourless and the other (B), has a pungent smell. In many countries B is used to disinfect water. Identify W, A and B.

Answer

W = oxygen (O), A = O_2, B = O_3 (ozone)

(ii) W and the other elements in the group which W belongs to, form simple covalent hydrides. C is the hydride formed by W. Except for C, the other hydrides in the group are poisonous.
I. Identify C.
II. C has remarkably different properties to those of the other hydrides. List **three** such properties (other than being non-poisonous) and give **the reason** for those differences.
III. On going down the group; does the covalent bond angle of these hydrides increase or decrease? Briefly explain your answer. Does the bond length of these hydrides increase or decrease? Briefly explain your answer.

Answer

I. C = H_2O
II. Properties (any three): it is a liquid at room temperature (the others are gases); it has an unusually high boiling point and melting point; high enthalpy of vaporization; high specific heat capacity; high surface tension; the solid (ice) is less dense than the liquid. Reason: strong hydrogen bonding between H_2O molecules, because O is small and highly electronegative.
III. The bond angle decreases (H_2O 104.5° → H_2S about 92°). Down the group the central atom becomes less electronegative and larger, so the bonding pairs lie further from it and repel each other less, allowing them to close up. The bond length increases, because the atomic radius of the central atom increases down the group.

(iii) D is a compound composed of the same elements as C (ratio of elements is different). It is a viscous liquid. It can act as both an oxidizing agent as well as a reducing agent. It also undergoes disproportionation.
I. Identify D.
II. Write balanced **half reactions** for D acting as an oxidizing agent and D acting as a reducing agent.
III. Write the balanced chemical equation for the disproportionation of D.

Answer

I. D = H_2O_2
II. Oxidizing agent: $H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$
Reducing agent: $H_2O_2(aq) \rightarrow O_2(g) + 2H^+(aq) + 2e^-$
III. $2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$

(b) [24 marks]

(i) X is also a p-block element of the Periodic Table with an atomic number less than 20. It also exists as allotropes. One of the allotropes is a thermal and electrical conductor.
I. Identify X. II. Name **three** allotropes of X.

Answer

I. X = carbon (C) II. Diamond, graphite and fullerene (C_{60}); graphene is also accepted.

(ii) E is a compound of X and W, in the ratio 1:1. It is an odourless, poisonous gas. Identify E.

Answer

E = CO (carbon monoxide)

(iii) F is a compound of X and W, in the ratio 1:2. It contributes to global warming. Its solid form is used as a freezing agent in the food industry.
I. Identify F. II. What is the common name used for the solid form of F?

Answer

I. F = CO_2 II. Dry ice

(c) [14 marks]

M is a s-block element in the Periodic Table. Its first three successive ionization energies in kJ mol^{-1} are respectively; 589, 1145 and 4912. M reacts readily with cold water to give compound G and a gas. The cation of M is a major contributor to hardness of water.
(i) Identify M and G.
(ii) Write the balanced chemical equations for the reactions below. I. The initial reaction of G with F. II. The reaction of G with excess F.

Answer

(i) M = Ca (the big jump after the second ionization energy shows Group 2; Ca^{2+} causes hardness), G = $Ca(OH)_2$
(ii) I. $Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$
II. $CaCO_3(s) + CO_2(g) + H_2O(l) \rightarrow Ca(HCO_3)_2(aq)$ (overall: $Ca(OH)_2 + 2CO_2 \rightarrow Ca(HCO_3)_2$)

(d) [08 marks]

J is a common oxoacid of X. It can be prepared by dissolving F in C under pressure.
(i) Write the chemical formula of J. (ii) Draw the structure of J showing all the bonds.

Answer

(i) J = H_2CO_3 (carbonic acid)
(ii) H–O–C(=O)–O–H: a central C double-bonded to one O and single-bonded to two O–H groups; each O carries two lone pairs.

Review.

The clues are O_2/O_3 allotropes, water's hydrogen bonding, H_2O_2 as both oxidant and reductant, carbon allotropes, and Ca from an IE pattern with a jump after IE_2.

Read: RB U6 §4.6 · p. 141 RB U6 §4.4 · p. 133 RB U6 §4.2 · p. 126

Question 3 · Part A · structured essay

HA(aq) is a weak acid with $K_a = 4.0 \times 10^{-4}$ mol dm^{-3} at 25 °C. In an experiment, 20.00 cm^3 of 0.25 mol dm^{-3} HA(aq) solution was titrated with 0.10 mol dm^{-3} KOH(aq) solution at 25 °C. (log values: log 2 = 0.30, log 3 = 0.48, log 4 = 0.60, log 5 = 0.70, log 6 = 0.78, log 7 = 0.85, log 8 = 0.90, log 9 = 0.95)

(i)

Calculate the initial pH value of the HA(aq) solution at 25 °C.

Answer

HA(aq) ⇌ H^+(aq) + A^-(aq). $K_a = [H^+][A^-]/[HA] = x^2/(0.25 - x)$. Since $x \ll 0.25$, $x^2 = 4.0 \times 10^{-4} \times 0.25 = 1.0 \times 10^{-4}$, so $[H^+] = 1.0 \times 10^{-2}$ mol dm^{-3} and **pH = 2.0**. (Check: α = 0.01/0.25 = 4%, so the approximation is valid.)

(ii)

Calculate the volume of KOH(aq) solution needed to reach the equivalence point.

Answer

$n(HA) = 0.02000\ dm^3 \times 0.25$ mol $dm^{-3} = 5.0 \times 10^{-3}$ mol. $HA + OH^- \rightarrow A^- + H_2O$ (1 : 1), so $V(KOH) = 5.0 \times 10^{-3} \div 0.10 = 0.050\ dm^3$ = **50.00 cm^3**.

(iii)

State whether the mixture at the equivalence point is acidic, basic or neutral. Justify your answer using an appropriate calculation.

Answer

Basic.

−3

−

3

−

−3

−2

−3

−

−

2

−

b

w

a

−14

−4

−11

−3

−

−11

−2

−6

−3

pH ≈ 8.1

(iv)

It was found that the pH value of the mixture after the addition of 80.00 cm^3 of KOH(aq) was between 12 and 13. Explain this observation with an appropriate calculation.

Answer

KOH added = 0.08000 × 0.10 = 8.0×10^{-3} mol; HA neutralized = 5.0×10^{-3} mol; excess OH^- = 3.0×10^{-3} mol in 100.00 cm^3. $[OH^-] = 3.0 \times 10^{-2}$ mol dm^{-3}, pOH = 2 − log 3 = 1.52, **pH = 12.48**, which lies between 12 and 13. The excess strong base controls the pH; hydrolysis of A^- adds a negligible amount of OH^-.

(v)

Calculate the pH value of the mixture at the half-equivalence point.

Answer

At half-equivalence (25.00 cm^3 KOH), [HA] = $[A^-]$, so pH = pK_a + log($[A^-]$/[HA]) = pK_a = −log(4.0×10^{-4}) = 4 − 0.60 = **3.40**.

(vi)

Sketch the titration curve for this titration. Mark the points of pH values and corresponding volumes of KOH(aq) obtained in (i)–(v) above on the titration curve.

Answer

0

10

20

30

40

50

60

70

80

0

2

4

6

8

10

12

14

(i) pH 2.0

(v) 3.4

(iii) 8.1

(iv) 12.5

Volume of KOH (cm³)

pH

The curve starts at pH 2.0, rises slowly through the buffer region (pH 3.4 at 25 cm^3), rises steeply around the equivalence point (pH 8.1 at 50 cm^3) and levels off near pH 12.5 at 80 cm^3.

(vii)

Explain why the pH of the solution is acidic in the range of 10–40 cm^3 volume of KOH added, and basic after the equivalence point.

Answer

Between 10 and 40 cm^3, unreacted HA is still present along with A^- (a buffer); HA ionizes ($HA \rightleftharpoons H^+ + A^-$) and keeps $[H^+]$ above 10^{-7} mol dm^{-3} (pH ≈ pK_a ± 1, about 2.8–4.0). After the equivalence point there is no HA left; the solution contains A^-, which hydrolyses to give OH^-, and excess OH^- from KOH, so it is basic.

Review.

Use $[H^+] = \sqrt{(K_a\ c)}$ for the weak acid alone, $K_b = K_w/K_a$ for the salt at equivalence, the Henderson equation in the buffer region, and the excess strong base after equivalence.

(viii) [Q3 total 100 marks]

pK_a values of acid-base indicators of methyl red and bromothymol blue are 5.1 and 7.1, respectively. Identify, giving reasons which indicator is the most suitable to observe a sharp end point of the above titration.

Answer

Bromothymol blue.

In

Read: RB U12 §2.2 · p. 118 RB U12 §2.3 · p. 167

Question 4 · Part A · structured essay

(a) [55 marks]

The compound A having five (05) carbon atoms contains only C, H, and Cl. Its relative molecular mass is 137. When A reacts with aqueous NaOH, compound B having a relative molecular mass of 100 is formed. (C = 12, H = 1, O = 16, Cl = 35.5)
(i) Write the molecular formula of A. (ii) Write the molecular formula of B.

Answer

(i) A = $C_5H_6Cl_2$ (5 × 12 + 6 × 1 + 2 × 35.5 = 137)
(ii) B = $C_5H_8O_2$ (both Cl replaced by OH: 60 + 8 + 32 = 100)

When A is hydrogenated with H_2/Pd in the presence of $BaSO_4$/quinoline, compound C having a relative molecular mass of 139 is formed. Both compounds A and B exhibit optical isomerism. A and B do not give precipitates with ammoniacal $AgNO_3$. When B is oxidised with pyridinium chlorochromate, compound D ($C_5H_4O_2$) is formed. When treated with aqueous NaOH, D undergoes a self condensation reaction. Compound B is converted to E (C_5H_7OCl) when treated with conc. HCl and $ZnCl_2$.
(iii) Draw the structures of A, B, C, D and E in the relevant boxes.

Answer

A: CH_3–CHCl–C≡C–CH_2Cl (1,4-dichloropent-2-yne)
B: CH_3–CH(OH)–C≡C–CH_2OH (pent-2-yne-1,4-diol)
C: CH_3–CHCl–CH=CH–CH_2Cl, the cis (Z) alkene
D: CH_3–CO–C≡C–CHO
E: CH_3–CHCl–C≡C–CH_2OH

Review.

Reasoning: $C_5H_6Cl_2$ has two degrees of unsaturation. Lindlar hydrogenation adds only 2 H (137 → 139), so A contains one C≡C that becomes a cis C=C. No precipitate with ammoniacal $AgNO_3$ means the alkyne is internal. A and B are chiral, so one Cl/OH is on a CH carbon carrying four different groups. PCC oxidizes both alcohol groups of B ($C_5H_8O_2$ → $C_5H_4O_2$): the CH_2OH becomes CHO and the CH(OH) becomes C=O. D self-condenses in NaOH, so it has α-hydrogens (the CH_3 next to the ketone); the isomer CH_3C≡C–CO–CHO has none and is ruled out. In Lucas reagent the secondary OH is replaced faster than the primary one, giving E.

(b) [24 marks]

For the reactions given below, write the type of reaction [Nucleophilic addition (A_N), Nucleophilic substitution (S_N), Electrophilic addition (A_E), Electrophilic substitution (S_E), Elimination (E), acid-base (AB)] and draw the structure of the major product.
(i) CH_3CH_2C≡C–H + HBr (excess) →
(ii) CH_3CH_2MgBr + H_2O →
(iii) $(CH_3)_2$CH–Br + alcoholic KOH →
(iv) C_6H_5–CO–CH_3 + $CH_3C≡C^-$ Na^+ →

Answer

	Type	Major product
(i)	A_E	$CH_3CH_2CBr_2CH_3$ (2,2-dibromobutane)
(ii)	AB	CH_3CH_3 (with Mg(OH)Br)
(iii)	E	$CH_3CH{=}CH_2$
(iv)	A_N	C_6H_5–C(CH_3)(O^−Na^+)–C≡C–CH_3

Review.

(i) Two Markovnikov additions of HBr put both Br on the same carbon. (ii) The Grignard carbon is strongly basic and takes H^+ from water. (iii) Alcoholic KOH removes HBr. (iv) The acetylide ion is a nucleophile and adds to the carbonyl carbon, giving an alkoxide.

(c) [21 marks]

(i) Draw the structure of the major product F of the following reaction.
$CH_3CH_2CH{=}CHCH_2CH_3 + Br_2 \rightarrow F$
(ii) Write the mechanism of the reaction stated above.

Answer

(i) F = CH_3CH_2CHBr–$CHBrCH_2CH_3$ (3,4-dibromohexane)

(ii) Step 1: as Br_2 approaches the electron-rich C=C, it is polarized ($Br^{\delta+}$–$Br^{\delta-}$). The π electrons attack $Br^{\delta+}$ and the Br–Br bond breaks, giving Br^- and a cyclic three-membered bromonium ion (a curly arrow from the C=C to $Br^{\delta+}$ and a curly arrow from the Br–Br bond to the far Br).
Step 2: Br^- attacks one carbon of the bromonium ion from the side opposite the ring, opening it (a curly arrow from a Br^- lone pair to that carbon and a curly arrow from the C–Br^+ bond to Br), giving 3,4-dibromohexane.

Review.

Electrophilic addition: the RB describes the bromonium-ion intermediate. Show the partial charges, both curly arrows in each step and the charge on the intermediate.

Read: RB U8 §2.2 · p. 33 RB U9 §3.1 · p. 54 RB U9 §3.4 · p. 60 RB U8 §2.6 · p. 49

Answer two from each part

Essay · Paper II Parts B and C

Part B

Question 5 · Part B · essay

(a) [120 marks]

Consider the reaction shown below at 300 K and 1 atm: $Fe_2O_3(s) + 3CO(g) \rightleftharpoons 2Fe(s) + 3CO_2(g)$. The following thermodynamic data at 300 K and 1 atm are given.

	CO(g)	CO_2(g)	Fe(s)	Fe_2O_3(s)
ΔH_f°/kJ mol^{-1}	−111	−394	0	−824
S°/J K^{-1} mol^{-1}	197	213	27	87

(i) Calculate the $\Delta H°_{rxn}$ of the reaction at 300 K.

Answer

$\Delta H° = [2(0) + 3(-394)] - [(-824) + 3(-111)] = -1182 - (-1157) =$ **-25 kJ mol^{-1}**

(ii) Calculate the $\Delta S°_{rxn}$ of the reaction at 300 K.

Answer

$\Delta S° = [2(27) + 3(213)] - [87 + 3(197)] = 693 - 678 =$ **$+15$ J K^{-1} mol^{-1}**

(iii) Show that the reaction is "Theoretically possible at any temperature". State the assumption you made.

Answer

$\Delta G° = \Delta H° - T\Delta S° = -25$ kJ mol^{-1} $-$ T(0.015 kJ K^{-1} mol^{-1}). Both terms are negative for every $T > 0$, so $\Delta G° < 0$ at all temperatures and the reaction is spontaneous at any temperature. Assumption: $\Delta H°$ and $\Delta S°$ do not change with temperature (and no substance changes state).

(iv) Write the expression for the equilibrium constant, K_P of the reaction at 300 K.

Answer

$K_P = (P_{CO2})^3 / (P_{CO})^3$ (the solids Fe_2O_3 and Fe are left out)

(v) Derive the expression for the equilibrium constant, K_C of the reaction, in terms of K_P at 300 K.

Answer

For an ideal gas $P = cRT$. $K_P = ([CO_2]RT)^3 / ([CO]RT)^3 = K_C(RT)^{3-3} = K_C(RT)^0$, so **$K_C = K_P$** ($\Delta n_{gas} = 0$).

(vi) It was found that the K_P value of the reaction is 125 at 300 K, while the value is 27 at 900 K.
I. Calculate the ratios of partial pressures of CO_2(g) and CO(g), ($P_{CO2(g)}/P_{CO(g)}$) at these two temperatures.
II. Give reasons for the difference in the two values obtained in I above.

Answer

I. $P_{CO2}/P_{CO} = K_P^{1/3}$: at 300 K, $125^{1/3} =$ **5**; at 900 K, $27^{1/3} =$ **3**.
II. The forward reaction is exothermic ($\Delta H° = -25$ kJ mol^{-1}). Raising the temperature favours the endothermic (backward) direction, so K_P falls and less CO_2 is present relative to CO.

(vii) Explain the effect on the equilibrium position when the total pressure of the system is increased at a given temperature.

Answer

No effect. There are 3 mol of gas on each side ($\Delta n_{gas} = 0$), so changing the total pressure changes both partial pressures by the same factor and Q stays equal to K_P.

(viii) The reduction of Fe_2O_3(s) to Fe(s) can be carried out in a blast furnace by using CO(g). The maximum temperature achievable in a blast furnace is 2300 K. Even though Al_2O_3(s) can be reduced to Al(s) in a similar reaction using CO(g), explain by means of a suitable calculation why it is **not** carried out in a blast furnace.
Data: $\Delta H_f°$/kJ mol^{-1}: CO(g) -111, CO_2(g) -394, Al(s) 0, Al_2O_3(s) -1676; S°/J K^{-1} mol^{-1}: CO(g) 197, CO_2(g) 213, Al(s) 28, Al_2O_3(s) 51.

Answer

$Al_2O_3(s) + 3CO(g) \rightarrow 2Al(s) + 3CO_2(g)$
$\Delta H° = 3(-394) - [(-1676) + 3(-111)] = -1182 + 2009 = +827$ kJ mol^{-1}
$\Delta S° = [2(28) + 3(213)] - [51 + 3(197)] = 695 - 642 = +53$ J K^{-1} mol^{-1}
At 2300 K: $\Delta G° = 827 - 2300 \times 0.053 = 827 - 122 =$ **+705 kJ mol^{-1}** > 0, so the reaction is not spontaneous. It would need $T > \Delta H°/\Delta S° = 827\,000/53 \approx 15\,600$ K, far above what a blast furnace can reach.

Review.

Use $\Delta X_{rxn} = \Sigma X(\text{products}) - \Sigma X(\text{reactants})$ with the coefficients; convert ΔS to kJ before combining with ΔH. Solids are omitted from K_P, and $K_P = K_C(RT)^{\Delta n}$.

(b) [30 marks]

$Ag_2CrO_4(s)$ is a sparingly soluble salt in water with $K_{sp} = 4.0 \times 10^{-12}$ mol^3 dm^{-9} at 25 °C.
(i) Write the equilibrium reaction that exists in a saturated aqueous solution of $Ag_2CrO_4(s)$ at 25 °C.
(ii) Calculate the concentration of $Ag^+(aq)$ in a saturated aqueous solution of $Ag_2CrO_4(s)$ at 25 °C.

Answer

(i) $Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$
(ii) $K_{sp} = [Ag^+]^2[CrO_4^{2-}] = (2s)^2(s) = 4s^3 = 4.0 \times 10^{-12}$, so $s^3 = 1.0 \times 10^{-12}$ and $s = 1.0 \times 10^{-4}$ mol dm^{-3}.
$[Ag^+] = 2s = 2.0 \times 10^{-4}$ mol dm^{-3}

(iii) When dil. HCl was added dropwise to a saturated Ag_2CrO_4 solution in a beaker, first the reddish-colour of the solution decreased and turned yellow with formation of a precipitate on the bottom of the beaker. When the addition of HCl is further continued, the colour of the solution turned to an intense-orange. Explain these observations using appropriate chemical reactions.

Answer

Cl^- removes Ag^+ as AgCl, which is much less soluble: $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$ (white precipitate). Overall, red-brown Ag_2CrO_4 is converted: $Ag_2CrO_4(s) + 2Cl^-(aq) \rightarrow 2AgCl(s) + CrO_4^{2-}(aq)$, so the solution becomes yellow from CrO_4^{2-}. Further acid converts chromate to dichromate: $2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$, giving the orange colour.

Review.

$K_{sp} = 4s^3$ for an A_2B salt. A precipitate with a smaller solubility forms at the expense of a more soluble one; chromate/dichromate is an acid-controlled equilibrium (RB Unit 6).

Read: RB U5 §2.2 · p. 36 RB U5 §2.4 · p. 53 RB U12 §2.1 · p. 76 RB U12 §2.4 · p. 175 RB U6 §4.10 · p. 160

Question 6 · Part B · essay

(a) [90 marks]

At a given temperature, the rate law of a first-order reaction A → P can be expressed as $2.303 \log(A_0/A_t) = kt$, where A_0 is the concentration of A at time $t = 0$, A_t is the concentration of A at time t, and k is the rate constant. **Note:** partial pressures can also be used instead of concentrations.

(i) In an experiment carried out for a gas-phase first order reaction, the time required to complete 99% of the reaction was t_1, and that for the 90% completion was t_2. Show that $t_1 = 2t_2$.

Answer

99% complete: $A_t = 0.01A_0$, so $kt_1 = 2.303 \log 100 = 2 \times 2.303$. 90% complete: $A_t = 0.10A_0$, so $kt_2 = 2.303 \log 10 = 2.303$. Dividing: $t_1/t_2 = 2$, so $t_1 = 2t_2$.

(ii) Show that the half-life ($t_{½}$) of the above reaction is given by the expression $t_{½} = 0.693/k$. k is the rate constant. ($\log_{10}2 = 0.301$)

Answer

At $t = t_{½}$, $A_t = A_0/2$: $kt_{½} = 2.303 \log 2 = 2.303 \times 0.301 = 0.693$, so $t_{½} = 0.693/k$ (independent of A_0).

(iii) A first-order gas phase elementary decomposition reaction A(g) → B(g) + C(g) occurs in a closed-rigid container at a given temperature. When pure A(g) was placed initially in the empty container, the pressure of the system was 40 mmHg. The pressure of the system was 76 mmHg, when t = 300 s. Calculate the rate constant (k) and half-life ($t_{½}$) of the reaction at this temperature.

Answer

If x mmHg of A reacts: $P_A = 40 - x$, $P_B = P_C = x$, total $= 40 + x = 76$, so $x = 36$ and $P_A = 4$ mmHg at 300 s.
$k = (2.303/300\ s) \log(40/4) = 2.303/300 =$ **$7.7 \times 10^{-3}\ s^{-1}$**
$t_{½} = 0.693/k = 0.693 \times 300/2.303 \approx$ **90 s**

(iv) Calculate the rate of the reaction given in part (iii) above in mmHg s^{-1} when the pressure of the system is 50 mmHg.

Answer

Total $= 40 + x = 50$, so $x = 10$ and $P_A = 30$ mmHg. Rate $= kP_A = 7.68 \times 10^{-3} \times 30 =$ **0.23 mmHg s^{-1}**

Review.

In a rigid container partial pressure is proportional to concentration, so it can be used in the first-order law. Work out P_A from the total pressure using the stoichiometry (1 mol gas → 2 mol gas).

(b) [30 marks]

(i) Explain the following observation. The boiling point of a liquid mixture prepared by mixing two completely miscible liquids A and B in a specified ratio was greater than the boiling points of each of the two liquids A and B.

Answer

The mixture shows a negative deviation from Raoult's law: the A–B attractions are stronger than the A–A and B–B attractions, so molecules escape less easily and the vapour pressure is lower than predicted. At one composition the total vapour pressure reaches a minimum. That mixture needs the highest temperature to make its vapour pressure equal atmospheric pressure, so it boils above both pure liquids (a maximum-boiling azeotrope).

(ii) Sketch the diagram for the variation of partial pressures of A and B against composition of liquid mixtures of A and B. Pure liquid B has a higher boiling point than pure liquid A.

Answer

A

B

total

azeotrope

P°A

P°B

0

1

B

vapour pressure

B boils higher, so its pure vapour pressure $P°_B$ is lower than $P°_A$. Both partial-pressure curves sag below the ideal straight lines (dashed), and the total vapour pressure passes through a minimum.

(c) [30 marks]

(i) Define the partition coefficient (K_D) of a substance which distributes in two immiscible liquid phases.

Answer

At a given temperature, when a substance distributes between two immiscible liquids at equilibrium, the ratio of its concentrations in the two phases is a constant, $K_D = [X]_{phase\ 1}/[X]_{phase\ 2}$, provided the substance has the same molecular form in both phases.

(ii) In an experiment to evaluate the partition coefficient of ammonia between trichloromethane and water, at a given temperature the following procedure was carried out. A given amount of liquid ammonia was added to a given volume of water and then a given volume of trichloromethane was added and shaken vigorously. After reaching the equilibrium, 10.00 cm^3 of aqueous layer required 12.00 cm^3 of 0.25 mol dm^{-3} HCl(aq) for the complete neutralization, while 25.00 cm^3 of trichloromethane layer required 6.00 cm^3 of 0.05 mol dm^{-3} HCl(aq). Calculate K_D of ammonia between trichloromethane and aqueous layers at this temperature.

Answer

$NH_3 + HCl \rightarrow NH_4Cl$ (1 : 1)
Aqueous: n = $0.01200 \times 0.25 = 3.0 \times 10^{-3}$ mol in 10.00 cm^3 → $[NH_3]_{aq} = 0.30$ mol dm^{-3}
Organic: n = $0.00600 \times 0.05 = 3.0 \times 10^{-4}$ mol in 25.00 cm^3 → $[NH_3]_{org} = 0.012$ mol dm^{-3}
$K_D = [NH_3]_{CHCl3}/[NH_3]_{water} = 0.012/0.30 = 0.040$

Read: RB U11 §1.7.4 · p. 40 RB U12 §2.6 · p. 216 RB U12 §2.7 · p. 229

Question 7 · Part B · essay

(a) [75 marks]

Consider the following reduction potentials at 25 °C.
$E°(H^+(aq)/H_2(g)) = 0.00$ V, $E°(H_2O(l)/H_2(g)) = -0.83$ V, $E°(Na^+(aq)/Na(s)) = -2.71$ V, $E°(Cl_2(g)/Cl^-(aq)) = 1.36$ V, $E°(O_2(g)/H_2O(l)) = 1.23$ V

(i) Sketch a labelled diagram of an electrochemical cell that can be used to electrolyse an aqueous NaCl solution using inert electrodes.

Answer

A beaker (or U-tube) of concentrated NaCl(aq) with two inert electrodes (graphite or Pt) dipping in it, connected to a d.c. power supply. Label: anode connected to the positive terminal (Cl_2 bubbles), cathode connected to the negative terminal (H_2 bubbles), the electrolyte NaCl(aq), and the direction of electron flow in the external wire (from the anode to the power supply, and from the power supply to the cathode).

(ii) Write **all the possible** half reactions that can take place at the anode and the cathode.

Answer

Cathode (reduction): $Na^+(aq) + e^- \rightarrow Na(s)$; $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$; $2H^+(aq) + 2e^- \rightarrow H_2(g)$
Anode (oxidation): $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$; $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

(iii) Giving reasons, identify the half reactions actually occurring at the anode and the cathode.

Answer

Cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$. Water ($E° = -0.83$ V) is far easier to reduce than Na^+ (-2.71 V), and $[H^+]$ in neutral solution is only about 10^{-7} mol dm^{-3}.
Anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$. Although $E°(O_2/H_2O)$ is slightly lower, the Cl^- concentration in brine is high and O_2 formation needs a large extra voltage (overpotential), so Cl_2 is released.

(iv) If the gas formed at the anode is collected at 1 atm and 25 °C by passing a constant current of 1.2 A for 2 hours through the cell, calculate the volume of the gas. (1 F = 96 500 C mol^{-1}) **Note:** Assume that the gas does not react with or dissolve in the electrolyte solution. State any other assumptions made in your calculation. (1 atm = 101 kPa)

Answer

$Q = It = 1.2 \text{ A} \times 2 \times 3600 \text{ s} = 8640$ C; $n(e^-) = 8640/96\,500 = 0.0895$ mol; $n(Cl_2) = 0.0895/2 = 0.0448$ mol.
$V = nRT/P = 0.0448 \times 8.314 \times 298/(101 \times 10^3) = 1.10 \times 10^{-3}$ m^3 = **1.10 dm^3**
Assumptions: Cl_2 behaves as an ideal gas; all the charge is used to form Cl_2 (100% current efficiency, no O_2); the temperature stays at 298 K.

(v) Write the half reactions occurring at the anode and the cathode, when molten NaCl(l) is used as the electrolyte in the above cell.

Answer

Anode: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$ · Cathode: $Na^+(l) + e^- \rightarrow Na(l)$

Review.

With no water present, Na^+ is the only species that can be reduced. Use $Q = It$ and $n(e^-) = Q/F$, then the mole ratio from the half-equation.

(b) [47 marks]

X is a d-block element that belongs to the fourth period of the Periodic Table. X forms an amphoteric oxide X_1. The most common ion of X is X^{n+}. In dilute aqueous solution, X^{n+} forms the coloured species X_2. On treatment of the solution containing X_2 separately with: aqueous NH_3, the blue-green gelatinous precipitate X_3 is formed; excess dil. NaOH, followed by H_2O_2, the yellow species X_4 is formed. In acidic medium X_4 gives species X_5. On bubbling $SO_2(g)$ through an acidic solution containing X_5, the ions X^{n+} and SO_4^{2-} are formed.

(i) Identify X, X^{n+}, X_1, X_2, X_3, X_4 and X_5. (Give chemical formulae. Reasons are **not** required.)

Answer

X = Cr; $X^{n+} = Cr^{3+}$; $X_1 = Cr_2O_3$; $X_2 = [Cr(H_2O)_6]^{3+}$; $X_3 = Cr(OH)_3$; $X_4 = CrO_4^{2-}$; $X_5 = Cr_2O_7^{2-}$

(ii) Write balanced ionic equations for I, II and III given below. I. Formation of X_4 from X_2 on treatment with excess dil. NaOH followed by H_2O_2. II. Formation of X_5 from X_4 in acidic medium. III. Reaction of X_5 with $SO_2(g)$ in acidic medium.

Answer

I. $2[Cr(H_2O)_6]^{3+}(aq) + 3H_2O_2(aq) + 10OH^-(aq) \rightarrow 2CrO_4^{2-}(aq) + 20H_2O(l)$
II. $2CrO_4^{2-}(aq) + 2H^+(aq) \rightarrow Cr_2O_7^{2-}(aq) + H_2O(l)$
III. $Cr_2O_7^{2-}(aq) + 3SO_2(g) + 2H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + H_2O(l)$

(iii) Write the IUPAC name of X_2.

Answer

Hexaaquachromium(III) ion

(c) [28 marks]

Y is also a d-block element, which belongs to the fourth period in the Periodic Table. Y has two common oxidation numbers, p and q. q is greater than p. Y^{p+} forms the dirty-green precipitate Y_1 with dil. NaOH. Y^{q+} forms a yellow/yellow-brown species Y_2 in aqueous solution. On reaction of Y^{q+} with $NH_4SCN(aq)$, a red complex Y_3 is formed.

(i) Identify Y, Y_1, Y_2 and Y_3. (Give chemical formulae). Write the oxidation numbers p and q. (Reasons are not required.)

Answer

Y = Fe; $Y_1 = Fe(OH)_2$; $Y_2 = [Fe(H_2O)_6]^{3+}$; $Y_3 = [Fe(SCN)(H_2O)_5]^{2+}$; p = +2, q = +3

(ii) Give the balanced ionic equation for the reaction of Y^{p+} with an acidic solution of MnO_4^− ions.

Answer

MnO_4^−(aq) + $5Fe^{2+}(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$

(iii) Write the IUPAC name of Y_2.

Answer

Hexaaquairon(III) ion

Review.

Key tests: Cr^{3+} gives a grey/blue-green $Cr(OH)_3$, oxidized by H_2O_2 in alkali to yellow CrO_4^{2-}, which becomes orange $Cr_2O_7^{2-}$ in acid. Fe^{2+} gives a dirty-green $Fe(OH)_2$; Fe^{3+} gives a blood-red colour with SCN^-.

Read: RB U13 §3.4 · p. 261 RB U6 §4.10 · p. 160 RB U6 §4.10.6 · p. 169

Part C

Question 8 · Part C · essay

(a) [30 marks]

Identify the reagents K and L, and the products P, Q and R of the following reaction scheme.
CH_3OH —K→ P —L→ CH_3MgBr —($CH_3CH_2CO_2CH_3$)→ Q —(dil. HCl)→ R

Answer

K = PBr_3 (or PCl_5/HBr route giving the bromide; PBr_3 is expected)
P = CH_3Br
L = Mg in dry ether
Q = $CH_3CH_2C(CH_3)_2$–OMgBr (from two equivalents of CH_3MgBr)
R = $CH_3CH_2C(CH_3)_2OH$ (2-methylbutan-2-ol)

Review.

An ester reacts with a Grignard reagent first to give a ketone ($CH_3CH_2COCH_3$), which reacts faster than the ester with a second CH_3MgBr. Acid hydrolysis of the magnesium alkoxide gives the tertiary alcohol.

(b) [30 marks]

Two products are obtained from the compound $CH_3CH_2CH_2Br$ when it reacts with $(CH_3)_2CHO^-$ ion.
(i) Draw the structures of these **two** products.
(ii) Write the mechanisms of the reactions giving these **two** products.
(iii) Give reasons as to why **both** these mechanisms take place.

Answer

(i) $CH_3CH_2CH_2$–O–$CH(CH_3)_2$ (propyl isopropyl ether) and $CH_3CH{=}CH_2$ (propene).

(ii) Substitution (S_{N2}): a lone pair on the O of $(CH_3)_2CHO^-$ attacks the carbon bonded to Br from the back, and the C–Br bond electrons leave with Br^- in the same step, giving the ether.
Elimination (E2): the alkoxide O removes an H from the β-carbon (CH_2 next to CH_2Br); the C–H bond electrons form the C=C and the C–Br bond electrons leave as Br^-, giving propene, $(CH_3)_2CHOH$ and Br^-.

(iii) The alkoxide ion is both a good nucleophile and a strong base. The primary alkyl bromide is not hindered, so nucleophilic attack at carbon (substitution) is possible; the bulky isopropoxide ion also removes a β-hydrogen easily, so elimination competes.

(c) [20 marks]

(i) Draw the resonance structures of aniline.
(ii) Consider the two compounds aniline and ethylamine. Giving reasons, state which of these two compounds is more basic.

Answer

(i) Two Kekulé structures with a neutral $–NH_2$, plus three structures in which the N lone pair forms C=N^+H_2 and the negative charge is placed on the ortho, the other ortho, and the para carbon of the ring.

(ii) **Ethylamine is more basic.** The ethyl group releases electrons, making the N lone pair more available to accept H^+. In aniline the lone pair is delocalised into the benzene ring (as the resonance structures show), so it is less available, and protonation would destroy that delocalisation.

(d)

(i) Show how you would carry out the following conversion using not more than **three** steps: aniline → 2,4,6-tribromobenzonitrile (CN at C1, Br at C2, C4 and C6). [25 marks]

Answer

1. Br_2(aq) at room temperature → 2,4,6-tribromoaniline (white precipitate; $–NH_2$ activates the ortho and para positions)
2. $NaNO_2$ / dil. HCl at 0–5 °C → 2,4,6-tribromobenzenediazonium chloride
3. CuCN → 2,4,6-tribromobenzonitrile (+ N_2)

(ii) Show how you would carry out the following conversion using not more than **five** steps: benzene → 4-nitrobenzaldehyde. [45 marks]

Answer

1. CH_3Cl / anhydrous $AlCl_3$ → methylbenzene (toluene)
2. conc. HNO_3 / conc. H_2SO_4 → 4-nitrotoluene (separate from the 2-isomer; $–CH_3$ directs ortho/para)
3. Cl_2 / light (UV) → 4-nitrobenzyl chloride (free-radical substitution on the side chain)
4. aq. NaOH, heat → 4-nitrobenzyl alcohol
5. PCC → 4-nitrobenzaldehyde

Review.

The order matters: $–NO_2$ is a meta director, so the carbon group must be introduced first. A common alternative after step 2 is $KMnO_4$ (→ 4-nitrobenzoic acid), then $LiAlH_4$ (→ alcohol), then PCC, also five steps. (Prepared answer.)

Read: RB U9 §3.6 · p. 70 RB U8 §2.6 · p. 49 RB U10 §4.2 · p. 77 RB U10 §4.3 · p. 78 RB U8 §2.5 · p. 49

Question 9 · Part C · essay

(a) [75 marks]

A, B, C and D are water soluble inorganic compounds. Only two of these compounds contain d-block elements. A and B are white solids, while C and D are coloured solids. When aqueous solutions of A and B are mixed together the white precipitate E is formed. E is insoluble in hot water and in dil. HCl. When E is separated by filtration and dil. NaOH is added to the filtrate, the white gelatinous precipitate F is formed. F dissolves in excess dil. NaOH and gives G.
Mixing aqueous solutions of B and C gives the white precipitate H. H, is soluble in hot water. H is separated by filtration and the filtrate is divided into two portions. On addition of dil. NH_4OH to one portion of the filtrate a light-blue precipitate, I is formed. On addition of more dil. NH_4OH to the precipitate I, a deep blue solution J is formed.
To the other portion of the filtrate, when a saturated solution of D is added, followed by the slow addition of conc. H_2SO_4 along the wall of the test tube, a brown ring is formed.
On mixing B and D the white precipitate E is formed.
Identify the compounds A, B, C, D, E, F, G, H, I and J. (Give chemical formulae. Explanations are **not** required.)

Answer

A	B	C	D	E
$Al_2(SO_4)_3$	$Pb(NO_3)_2$	$CuCl_2$	$FeSO_4$	$PbSO_4$
F	G	H	I	J
$Al(OH)_3$	$[Al(OH)_4]^-$ ($NaAl(OH)_4$)	$PbCl_2$	$Cu(OH)_2$	$[Cu(NH_3)_4]^{2+}$

Review.

Reasoning: a white precipitate soluble in hot water is $PbCl_2$, so B contains Pb^{2+} and C contains Cl^-. The light-blue precipitate dissolving to a deep blue solution in ammonia shows Cu^{2+} (C = $CuCl_2$). The brown-ring test with $FeSO_4$ shows NO_3^− came from B (B = $Pb(NO_3)_2$, D = $FeSO_4$). $PbSO_4$ is insoluble in hot water and dilute HCl, and the amphoteric white gelatinous hydroxide in the filtrate shows Al^{3+} (A = $Al_2(SO_4)_3$). C and D are the two coloured d-block compounds.

(b) [75 marks]

A sample of 5.00 g of white brass [Cu–Zn–Sn alloy] used to make inexpensive jewellery, was dissolved in 10.00 cm^3 of conc. HNO_3 acid and diluted to 1.00 dm^3 in a volumetric flask with water. The resultant solution X, contains Cu^{2+}, Zn^{2+} and Sn^{2+} as the only metal ions. (Sn = 118.7, Zn = 65.3, Cu = 63.5, O = 16.0, C = 12.0, H = 1.0)
Experiment A: Upon adding dilute NaOH to 50.00 cm^3 of solution X, a precipitate is formed. On the addition of excess NaOH, part of the precipitate dissolves, resulting in a precipitate having a mass of 0.0925 g. **Note:** Consider that Sn^{2+} reacts with dil. NaOH in a manner similar to that of Zn^{2+}.
Experiment B: To 25.00 cm^3 portion of solution X, solid Na_2CO_3 was added to reduce the acidity of the medium. Then excess 5% KI solution was added. Upon adding I^-, Cu^{2+} reduces to CuI(s), producing I_2. A certain amount of the total I_2 formed is reduced back to I^- by Sn^{2+}, which completely oxidizes to Sn^{4+}. The remaining I_2 was titrated with standard 0.05 mol dm^{-3} $Na_2S_2O_3$ solution using a few drops of starch solution as the indicator. The volume of $Na_2S_2O_3$ consumed was 8.00 cm^3. **Note:** Consider that NO_3^− ions do not react under the above conditions.
Experiment C: To a 50.00 cm^3 portion of solution X, excess saturated Na_2CO_3 was added resulting in a precipitate having a mass of 0.4380 g. **Note:** Saturated Na_2CO_3 will precipitate all metal ions except Li^+, Na^+ and K^+.

(i) Write balanced ionic equations for all the reactions relevant to **experiment A**.

Answer

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ (excess acid)
$Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$
$Zn^{2+}(aq) + 2OH^-(aq) \rightarrow Zn(OH)_2(s)$; $Zn(OH)_2(s) + 2OH^-(aq) \rightarrow [Zn(OH)_4]^{2-}(aq)$
$Sn^{2+}(aq) + 2OH^-(aq) \rightarrow Sn(OH)_2(s)$; $Sn(OH)_2(s) + 2OH^-(aq) \rightarrow [Sn(OH)_4]^{2-}(aq)$

(ii) Calculate the percentage of Cu in the solid white brass sample.

Answer

The remaining precipitate is $Cu(OH)_2$ ($M = 97.5\ g\ mol^{-1}$). n(Cu) in 50.00 cm^3 = $0.0925/97.5 = 9.487 \times 10^{-4}$ mol.
In 1.00 dm^3: $9.487 \times 10^{-4} \times 20 = 1.897 \times 10^{-2}$ mol → mass of Cu = $1.897 \times 10^{-2} \times 63.5 = 1.205$ g.
% Cu = 1.205/5.00 × 100 = 24.1%

(iii) Write balanced chemical or ionic equations for all the reactions relevant to **experiments B and C**.

Answer

Experiment B: $2H^+(aq) + CO_3^{2-}(aq) \rightarrow CO_2(g) + H_2O(l)$
$2Cu^{2+}(aq) + 4I^-(aq) \rightarrow 2CuI(s) + I_2(aq)$
$Sn^{2+}(aq) + I_2(aq) \rightarrow Sn^{4+}(aq) + 2I^-(aq)$
$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$
Experiment C: $Cu^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CuCO_3(s)$; $Zn^{2+}(aq) + CO_3^{2-}(aq) \rightarrow ZnCO_3(s)$; $Sn^{2+}(aq) + CO_3^{2-}(aq) \rightarrow SnCO_3(s)$ (and $2H^+ + CO_3^{2-} \rightarrow CO_2 + H_2O$)

(iv) Calculate the mass ratio between Sn and Zn (Sn/Zn) in the white brass sample.

Answer

3

2+

−4

−4

2

−4

2

−3

−4

2

2+

−5

2+

3

3

−5

−3

3

3

−4

3

−5

3

−3

−3

Review.

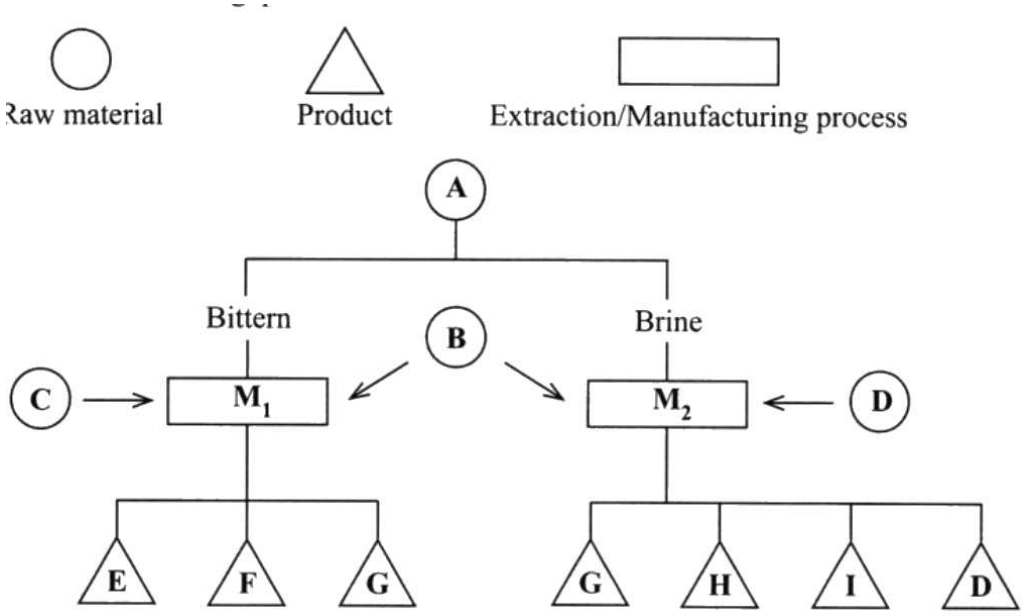
Amphoteric $Zn(OH)_2$ and $Sn(OH)_2$ dissolve in excess NaOH, leaving only $Cu(OH)_2$. In iodometry, I_2 from Cu^{2+} is shared between Sn^{2+} and the thiosulfate titration. (Prepared answer; carbonates are taken as the simple MCO_3 formulas as the note implies.)

Read: RB U6 §4.10 · p. 160 RB U6 §4.3 · p. 131 RB U3 §3.8 · p. 115 RB U12 §2.4 · p. 175

Question 10 · Part C · essay

(a) [60 marks]

The following flow chart shows the industrial extraction/manufacturing process of an element and a compound. The following symbols are used to represent raw materials (circle), products (triangle), and extraction/manufacturing processes (rectangle).



A and B are naturally occurring while C and D are produced by other industrial processes. C can be regenerated by reacting E with water. D is regenerated in M_2. H is used to remove hardness of water. G is a gaseous pollutant, which can be reused in M_2.

(i) Write the raw materials A, B, C and D.

(ii) Name the extraction/manufacturing processes M_1 and M_2.

(iii) Write the products E, F, G, H and I.

(iv) State **two** ways in which the efficiency of the M_2 process can be increased.

(v) State the importance of regenerating C and D.

(vi) Give **two** uses each for D and E (other than what is indicated in the flow chart or given in the question).

Answer

(i) A = sea water; B = limestone ($CaCO_3$) (dolomite or shells are also used); C = HCl; D = NH_3

(ii) M_1 = Dow process (extraction of Mg); M_2 = Solvay (ammonia–soda) process

(iii) E = Cl_2; F = Mg; G = CO_2; H = Na_2CO_3; I = $CaCl_2$

(iv) Any two: cool the ammonification and carbonation towers (both steps are exothermic, and gases dissolve better at low temperature); ammoniate the brine before carbonating it; use the counter-current principle in the towers; recycle the CO_2 from heating $NaHCO_3$ and recover NH_3 from NH_4Cl; use purified, concentrated brine.

(v) It lowers the cost of raw materials (NH_3 and HCl are expensive manufactured chemicals), reduces waste, and prevents the release of toxic NH_3 and Cl_2/HCl into the environment.

(vi) NH_3 (D): manufacture of nitrogen fertilizers (urea, ammonium sulfate), manufacture of nitric acid (Ostwald process), refrigerant. Cl_2 (E): disinfection of drinking water, manufacture of PVC, manufacture of bleaching agents (NaOCl, bleaching powder).

Review.

The RB explains that Cl_2 from the Dow cell is used to make HCl, which is reacted again with $Mg(OH)_2$, and that the CO_2 released from heating $NaHCO_3$ is returned to the carbonation tower in the Solvay process.

(b) [50 marks]

Oxygen is essential for life. Aquatic organisms depend on dissolved oxygen in water. Dissolved oxygen is an important indicator of water quality, commonly measured using the Winkler method. (H = 1, O = 16, S = 32, I = 127)
(i) Explain briefly, why, oxygen has a poor solubility in water.

Answer

O_2 is a non-polar molecule. It cannot form hydrogen bonds with water and attracts water only through weak dipole–induced dipole and London forces, which are much weaker than the hydrogen bonds between water molecules that must be broken to make room for it.

(ii) I. State **two** processes that increase dissolved oxygen in a waterbody. II. State **three** processes that decrease dissolved oxygen in a waterbody.

Answer

I. Photosynthesis by aquatic plants and algae; dissolution from the air (aeration by wind, waves, waterfalls and turbulence); a fall in water temperature.
II. Aerobic decomposition of organic matter (sewage, food-industry waste) by micro-organisms; respiration of aquatic organisms; a rise in temperature (thermal pollution); eutrophication followed by decay of algae; oxidation of chemical pollutants (e.g. Fe^{2+}, sulfides).

(iii) In the Winkler method, determination of dissolved oxygen is done in three steps. First, dissolved oxygen is fixed by oxidizing $Mn(OH)_2$ to MnO_2. Next, excess KI is added in an acidic medium to reduce MnO_2 to Mn^{2+} liberating iodine. Finally, the released iodine is titrated with a standard thiosulfate solution.
I. Write balanced ionic equations to represent the above **three** steps in the Winkler method.
II. If 12.40 cm^3 of 0.015 mol dm^{-3} thiosulfate solution was required for the determination of the amount of dissolved oxygen in a 100.00 cm^3 water sample, calculate the amount of dissolved oxygen in water in mg dm^{-3}.

Answer

I. $2Mn(OH)_2(s) + O_2(aq) \rightarrow 2MnO_2(s) + 2H_2O(l)$
$MnO_2(s) + 2I^-(aq) + 4H^+(aq) \rightarrow Mn^{2+}(aq) + I_2(aq) + 2H_2O(l)$
$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

II. Mole ratio $O_2 : MnO_2 : I_2 : S_2O_3^{2-} = 1 : 2 : 2 : 4$.
$n(S_2O_3^{2-}) = 0.01240 \times 0.015 = 1.86 \times 10^{-4}$ mol $\rightarrow n(O_2) = 4.65 \times 10^{-5}$ mol in 100.00 $cm^3 \rightarrow 4.65 \times 10^{-4}$ mol dm^{-3}.
Dissolved $O_2 = 4.65 \times 10^{-4} \times 32 \times 1000 =$ **14.9 mg dm^{-3}**

(c) [40 marks]

The questions given below are related to the process of manufacturing coconut toddy from sweet toddy.
(i) Write the main compound produced by the fermentation of sweet toddy.
(ii) Write balanced chemical equations to show the chemical changes that take place in sweet toddy during the formation of the main compound you stated in (i) above.
(iii) Name the method used to separate the main compound given by you in (i) above, from coconut toddy.
(iv) State why the method named in (iii) above is used to separate the main compound.

Answer

(i) Ethanol, C_2H_5OH

(ii) Sucrose is hydrolysed by the enzyme invertase (from yeast): $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6$ (glucose) + $C_6H_{12}O_6$ (fructose)
Glucose/fructose is fermented by zymase: $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$

(iii) Fractional distillation

(iv) Ethanol and water are completely miscible liquids with different boiling points (ethanol 78 °C, water 100 °C), so the more volatile ethanol is concentrated in the vapour and can be separated by repeated vaporization and condensation in a fractionating column.

Review.

The RB (Unit 14, products from plant resources) describes yeast fermentation of toddy sugars to ethanol, which is then distilled to make arrack.

Read: RB U14 §1.2 · p. 6 RB U14 §1.5 · p. 18 RB U14 §1.14 · p. 80 RB U14 §1.12 · p. 48

2025 · Chemistry Digital Paper

50 questions · 2 hours

MCQ · Paper I

Question 1 · Q1–30 · single answer

Which of the discoveries given below is Henry Becquerel best known for?

- (1)wave-particle dual nature of matter
- (2)radioactivity
- (3)X-rays
- (4)structure of the nucleus
- (5)neutrons

Answer and review

Answer **(2)** Official marking scheme

Becquerel discovered radioactivity (1896) using uranium salts. Wave–particle duality is de Broglie's idea, X-rays were found by Röntgen, the nucleus by Rutherford and the neutron by Chadwick.

RB U1 §1.1 · p. 2

Question 2 · Q1–30 · single answer

The maximum number of electrons that can exist in an atom with quantum numbers n = 4 and l = 2 in the ground state is

- (1)3
- (2)4
- (3)6
- (4)10
- (5)18

Answer and review

Answer **(4)** Official marking scheme

n = 4, l = 2 is the 4d sub-shell. It has 2l + 1 = 5 orbitals, each holding 2 electrons, so 10 electrons.

RB U1 §1.3 · p. 17

Question 3 · Q1–30 · single answer

The examples to best denote H-bonds, ion-induced dipole interactions, dipole-induced dipole interactions and dipole-dipole interactions are respectively given by

- (1)ortho-nitrophenol, I_2 in KI(aq), HCl/Ar, ClF
- (2)ortho-nitrophenol, HCl/Ar, I_2 in KI(aq), ClF
- (3)para-nitrophenol, ortho-nitrophenol, ClF, I_2 in KI(aq)

- (4)para-nitrophenol, I_2 in KI(aq), ClF, HCl/Ar
- (5)ortho-nitrophenol, ClF, I_2 in KI(aq), HCl/Ar

Answer and review

Answer **(1)** Official marking scheme

o-Nitrophenol has an (intramolecular) hydrogen bond. In KI(aq) the I^- ion induces a dipole in non-polar I_2 (forming I_3^−). Polar HCl induces a dipole in an Ar atom. ClF molecules are permanent dipoles attracting each other.

RB U2 §2.6 · p. 79

Question 4 · Q1–30 · single answer

The correct order of increasing electronegativities of C in the chemical species, CH_2Cl_2, CH_4, COF_2 and CH_2F_2 is

- (1)$CH_4 < CH_2Cl_2 < CH_2F_2 < COF_2$
- (2)$CH_2Cl_2 < CH_4 < CH_2F_2 < COF_2$
- (3)$CH_2Cl_2 < CH_4 < COF_2 < CH_2F_2$
- (4)$COF_2 < CH_2F_2 < CH_2Cl_2 < CH_4$
- (5)$CH_4 < CH_2Cl_2 < COF_2 < CH_2F_2$

Answer and review

Answer **(1)** Official marking scheme

The electronegativity of C rises as it is bonded to more electronegative atoms (a higher oxidation state) and as its s character rises. CH_4 (C is −4) < CH_2Cl_2 (0, Cl less electronegative than F) < CH_2F_2 (0, F) < COF_2 (+4, and sp^2).

RB U2 §2.3 · p. 52

Question 5 · Q1–30 · single answer

At a given temperature, $A_2(g)$ and $B_2(g)$ in a molar ratio of 1:3 were introduced into a closed-rigid container. Then the following reaction takes place.
$A_2(g) + 3B_2(g) \rightleftharpoons 2AB_3(g)$
At equilibrium, total pressure of the system, partial pressure of $AB_3(g)$ and the equilibrium constant are P_T, P_{AB3} and K_p respectively. At this temperature, if $P_{AB3} <<< P_T$, the value of P_{AB3} is

- (1)$3^{3/2}K_p^{1/2}P_T$^2 / 4
- (2)$3^{3/2}K_p^{1/2}P_T$^2 / 16
- (3)$K_p^{1/2}P_T$^2 / 16
- (4)$K_p^{1/2}P_T$^2 / 4
- (5)3^$3K_p^{1/2}P_T$^2 / 16

Answer and review

Answer **(2)** Official marking scheme

Since very little AB_3 forms, $P_{A2} \approx P_T/4$ and $P_{B2} \approx 3P_T/4$. $K_p = P_{AB3}$^2/($P_{A2}P_{B2}$^3) = P_{AB3}^2 × 256/(27P_T^4), so $P_{AB3} = 3^{3/2}K_p^{1/2}P_T$^2/16.

RB U12 §2.1 · p. 76

Question 6 · Q1–30 · single answer

A description of the atoms X and Y is given below. Y is heavier than X.

Atom	X	Y
Number of protons	a	6
Number of neutrons	7	b
Number of electrons	6	c
Mass Number	d	e

- (1)a = 7, b = 6, c = 6, d = 13, e = 14
- (2)a = 6, b = 7, c = 6, d = 13, e = 14
- (3)a = 6, b = 8, c = 6, d = 13, e = 14
- (4)a = 7, b = 7, c = 6, d = 14, e = 13
- (5)a = 6, b = 8, c = 7, d = 13, e = 14

Answer and review

Answer **(3)** Official marking scheme

X has 6 electrons, so as a neutral atom it has 6 protons (a = 6) and mass number 6 + 7 = 13. Y also has 6 protons (carbon) and is heavier, so it is ^{14}C with 8 neutrons and 6 electrons. X and Y are isotopes of carbon.

RB U1 §1.1 · p. 2

Question 7 · Q1–30 · single answer

What is the IUPAC name of the given compound?
CH_3–C≡C–CH(Cl)–CH(CH_3)–CHO

- (1)4-chloro-5-methyl-2-hexynal
- (2)3-chloro-2-formyl-4-hexyne
- (3)4-chloro-5-formyl-2-hexyne
- (4)2-methyl-3-chloro-4-hexynal
- (5)3-chloro-2-methyl-4-hexynal

Answer and review

Answer **(5)** Official marking scheme

–CHO is the principal group, so it is C1. Numbering along the six-carbon chain puts CH_3 on C2, Cl on C3 and the triple bond at C4. Prefixes go in alphabetical order (chloro before methyl): 3-chloro-2-methylhex-4-ynal.

RB U7 §1.3 · p. 7

Question 8 · Q1–30 · single answer

$CaCO_3$ and $Al_2(CO_3)_3$ undergo thermal decomposition as given below.
$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
$Al_2(CO_3)_3(s) \rightarrow Al_2O_3(s) + 3CO_2(g)$
How much CO_2 is formed from $Al_2(CO_3)_3$ when 3.34 g of an equimolar mixture of $CaCO_3$ and $Al_2(CO_3)_3$ is thermally decomposed? Relative molecular mass: CO_2 = 44, $CaCO_3$ = 100, $Al_2(CO_3)_3$ = 234

- (1)0.44 g
- (2)1.32 g
- (3)1.48 g
- (4)1.76 g
- (5)1.88 g

Answer and review

Answer **(2)** Official marking scheme

Let n mol of each: 100n + 234n = 3.34, so n = 0.010 mol. $Al_2(CO_3)_3$ gives 3n = 0.030 mol CO_2 = 0.030 × 44 = 1.32 g.

RB U3 §3.8 · p. 115

Question 9 · Q1–30 · single answer

Which of the following species is **not** formed during the chlorination of methane in the presence of light?

- (1)$\bullet CH_3$
- (2)$\bullet CHCl_2$
- (3)CH_3CH_3
- (4)CH_2Cl_2
- (5)H•

Answer and review

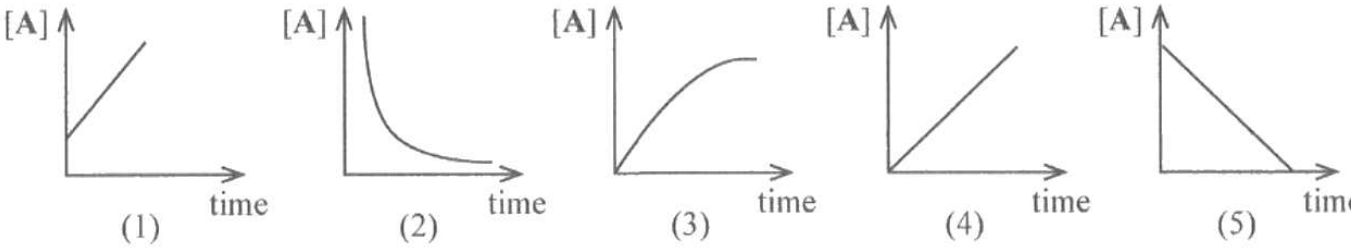
Answer **(5)** Official marking scheme

Light splits Cl_2 into Cl• radicals. Cl• removes H from CH_4 as HCl, giving $\bullet CH_3$ (and later $\bullet CH_2Cl$, $\bullet CHCl_2$). Two $\bullet CH_3$ combine to give ethane in termination. H atoms are never released as free radicals, because the C–H bond is broken by Cl• taking the H.

RB U8 §2.2 · p. 33

Question 10 · Q1–30 · single answer

Consider the unimolecular zero order reaction A → P at temperature T. Which of the following graphs represents the variation of concentration of A with time at temperature T?



- (1)Graph (1)
- (2)Graph (2)
- (3)Graph (3)
- (4)Graph (4)
- (5)Graph (5)

Answer and review

Answer **(5)** Official marking scheme

For a zero-order reaction the rate is constant (rate = k), so [A] = $[A]_0$ − kt: [A] falls in a straight line until A is used up. Graph (2) is the curved first-order decay.

RB U11 §1.7.4 · p. 40

Question 11 · Q1–30 · single answer

Identify the species which has a different shape from that of NCO^- ion.

- (1)NO_2^+
- (2)N_3^−
- (3)XeF_2
- (4)CNO^-
- (5)SF_2

Answer and review

Answer **(5)** Official marking scheme

NCO^- is linear (16 valence electrons, two bonding regions on C). NO_2^+, N_3^− and CNO^- are linear for the same reason, and XeF_2 is linear (three equatorial lone pairs). SF_2 has two bonding pairs and two lone pairs on S, so it is angular.

RB U2 §2.3 · p. 52

Question 12 · Q1–30 · single answer

A volume of 25.00 cm^3 of 0.02 mol dm^{-3} KIO_3 solution was added to a titration flask. The solution was acidified with dil. H_2SO_4 and 15 cm^3 of 0.5 mol dm^{-3} KI solution was added. The liberated I_2 was titrated with a $Na_2S_2O_3$ solution using starch as the indicator. The volume of $Na_2S_2O_3$ solution required for the titration was 20.00 cm^3. The concentration of the $Na_2S_2O_3$ solution in mol dm^{-3} is

- (1)0.05
- (2)0.075
- (3)0.10

- (4)0.125
- (5)0.15

Answer and review

Answer **(5)** Official marking scheme

IO_3^− + $5I^-$ + $6H^+$ → $3I_2$ + $3H_2O$; I_2 + $2S_2O_3^{2-}$ → $2I^-$ + $S_4O_6^{2-}$. n(IO_3^−) = 5.0×10^{-4} mol → I_2 = 1.5×10^{-3} mol → $S_2O_3^{2-}$ = 3.0×10^{-3} mol. c = 3.0×10^{-3}/0.02000 = 0.15 mol dm^{-3}. (KI is in excess: 7.5×10^{-3} mol.)

RB U3 §3.8 · p. 115

Question 13 · Q1–30 · single answer

Enthalpy change, ΔH for the dissolution of NaOH(s) in water at temperature 23 °C is −42 kJ mol^{-1}. An amount of 20 g of NaOH(s) was dissolved in 230 g of water at 23 °C in an insulated container. The specific heat capacity of the resulting solution is 4.2 J g^{-1} K^{-1}. What is the final temperature of the solution? (Neglect the heat exchange taking place with the container). H = 1, O = 16, Na = 23

- (1)20 °C
- (2)21.7 °C
- (3)42 °C
- (4)43 °C
- (5)44.7 °C

Answer and review

Answer **(4)** Official marking scheme

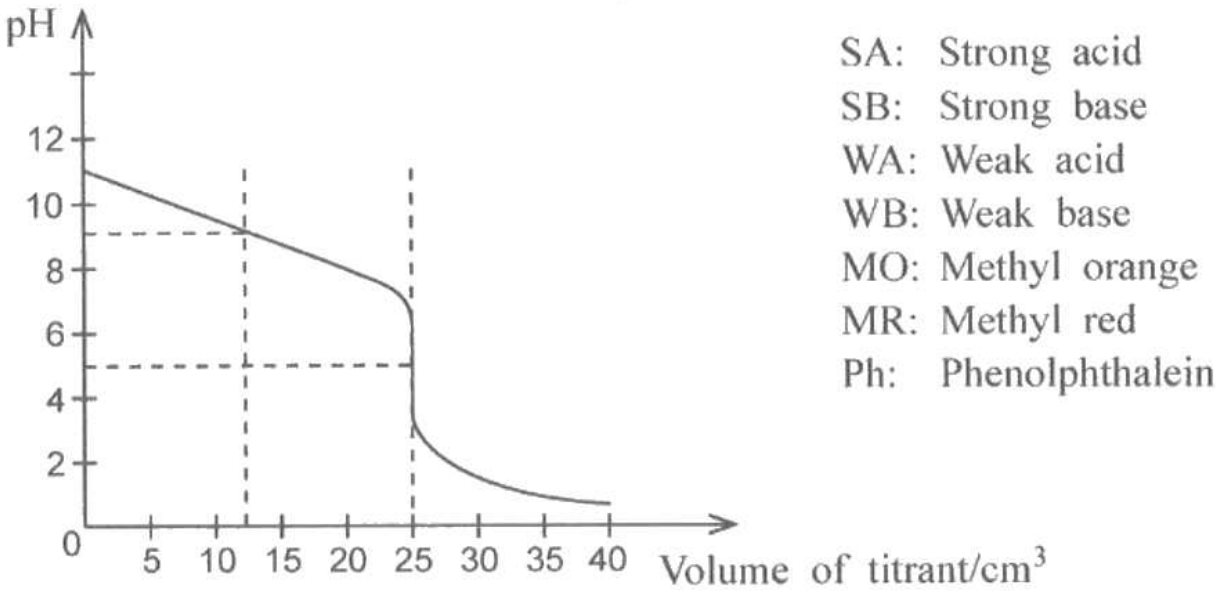
n(NaOH) = 20/40 = 0.50 mol, so heat released = 0.50 × 42 = 21 kJ. This warms 250 g of solution: ΔT = 21 000/(250 × 4.2) = 20 K. Final temperature = 23 + 20 = 43 °C.

RB U5 §2.2 · p. 36

Question 14 · Q1–30 · single answer

The titration curve for a titration of 25.00 cm^3 mono-protic base with mono-basic acid obtained at a given temperature is shown below. (SA: strong acid, SB: strong base, WA: weak acid, WB: weak base, MO: methyl orange, MR: methyl red, Ph: phenolphthalein)

Which of the following descriptions is correct for the above titration curve? (titration · volume of titrant at the end point · pH at the end point · suitable indicator)



- (1)WA + SB · 12.50 cm^3 · 5 · MR
- (2)SA + WB · 25.00 cm^3 · 5 · Ph
- (3)WA + WB · 12.50 cm^3 · 9 · Ph
- (4)SA + SB · 25.00 cm^3 · 7 · MO
- (5)SA + WB · 25.00 cm^3 · 5 · MR

Answer and review

Answer **(5)** Official marking scheme

The pH falls as acid is added, so a base is being titrated. It starts only moderately basic (about 10.5) with a buffer region, so the base is weak; the steep fall ends near pH 2, so the acid is strong. The vertical section is at 25.00 cm^3 with its mid-point at about pH 5, which suits methyl red (pK_{In} 5.1). Phenolphthalein would change in the buffer region.

RB U12 §2.2 · p. 118

Question 15 · Q1–30 · single answer

Which of the following reaction schemes is **not** suitable to prepare 1,2-dibromopropane?

- (1)$CH_3CH(OH)CH_3$ —(conc. H_2SO_4, Δ)→ —(Br_2)→
- (2)$CH_3CH(OH)COOH$ —((1) $LiAlH_4$/dry ether, (2) H^+/H_2O)→ —(excess PBr_3)→
- (3)$CH_3C{\equiv}CH$ —(H_2/Pd-$BaSO_4$, quinoline)→ —(Br_2)→
- (4)$CH_3C{\equiv}CH$ —(excess Br_2)→ —(H_2/Pt)→
- (5)$CH_3CH_2CH_2Br$ —(alcoholic KOH)→ —(Br_2)→

Answer and review

Answer **(4)** Official marking scheme

Excess Br_2 adds twice to the triple bond, giving $CH_3CBr_2CHBr_2$ with no C=C left, so H_2/Pt cannot give 1,2-dibromopropane. The other routes all make propene (by dehydration, Lindlar hydrogenation or elimination) and add Br_2 to it, or make propane-1,2-diol and replace both OH groups with PBr_3.

RB U8 §2.2 · p. 33 RB U9 §3.1 · p. 54

Question 16 · Q1–30 · single answer

The reaction $H_2(g) + I_2(g) \rightarrow 2HI(g)$ proceeds through a fast equilibrium step followed by a slow elementary step. The rate law for the slow elementary step is, rate = $k'[H_2(g)][I(g)]^2$. The rate constant is k'. Which of the following gives the rate law of the overall reaction in terms of $[H_2(g)]$ and $[I_2(g)]$? k is the rate constant of the overall reaction.

- (1)$k[H_2(g)][I_2(g)]$
- (2)$k[H_2(g)][I_2(g)]^2$
- (3)$k[H_2(g)]^2[I_2(g)]$
- (4)$k[H_2(g)][I_2(g)]^3$
- (5)$k[H_2(g)]^3[I_2(g)]$

Answer and review

Answer **(1)** Official marking scheme

The fast equilibrium is $I_2 \rightleftharpoons 2I$, with $K = [I]^2/[I_2]$, so $[I]^2 = K[I_2]$. Substituting: rate = $k'K[H_2][I_2] = k[H_2][I_2]$.

RB U11 §1.10 · p. 57

Question 17 · Q1–30 · single answer

The colours of AgBr(s) and AgI(s) are pale yellow and yellow, respectively. A solution of NaI(aq) was added to a test tube containing AgBr(s). When the contents in the test tube were stirred, its colour turned yellow. The following ideas were proposed to explain this observation.
I. The reaction, $AgBr(s) + I^-(aq) \rightarrow AgI(s) + Br^-(aq)$ occurs.
II. K_{sp} of AgBr(s) > K_{sp} of AgI(s)
III. K_{sp} of AgBr(s) < K_{sp} of AgI(s)
IV. Concentration of $I^-(aq)$ is decreased.
V. Concentration of $Br^-(aq)$ is decreased.
Which of the above are correct with regard to this observation?

- (1)I, III and V
- (2)I, IV and V
- (3)I, II and IV
- (4)I, II and V
- (5)I, III and IV

Answer and review

Answer **(3)** Official marking scheme

AgI is less soluble than AgBr (smaller K_{sp}). The small $[Ag^+]$ above AgBr is enough to exceed K_{sp} of AgI, so AgI precipitates; AgBr keeps dissolving to replace Ag^+. I^- is used up and Br^- is released.

RB U12 §2.4 · p. 175

Question 18 · Q1–30 · single answer

A small sample of water placed in a beaker at room temperature was found to have evaporated completely after 6 hours. Which of the following descriptions of this process is correct with respect to the water sample? (ΔH, ΔS, ΔG)

- (1)>0, >0, >0
- (2)>0, <0, >0
- (3)<0, <0, <0
- (4)>0, >0, <0
- (5)>0, <0, <0

Answer and review

Answer **(4)** Official marking scheme

Evaporation absorbs heat (ΔH > 0) and turns a liquid into a gas (ΔS > 0). It happened spontaneously in an open beaker, so ΔG < 0: the water vapour is continually removed and TΔS outweighs ΔH under these conditions.

RB U5 §2.4 · p. 53

Question 19 · Q1–30 · single answer

Which of the following statements is **incorrect** regarding d-block elements?

- (1)VO is a basic oxide while V_2O_5 is an acidic oxide.
- (2)In Mn_3O_4, manganese is present as a mixture of Mn(II) and Mn(III).
- (3)When NH_4Cl/NH_4OH are added to an aqueous solution containing Fe^{3+} and Co^{2+}, only Fe^{3+} precipitates.
- (4)The white precipitate formed on addition of dil. NaOH to $ZnCl_2$(aq) is insoluble in dil. HCl.
- (5)The first five elements of the 3d transition series achieve their maximum oxidation states by losing all 4s and 3d electrons.

Answer and review

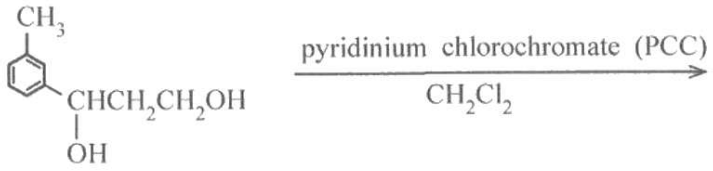
Answer **(4)** Official marking scheme

$Zn(OH)_2$ is amphoteric: it dissolves in acid ($Zn(OH)_2 + 2HCl \rightarrow ZnCl_2 + 2H_2O$) as well as in excess NaOH. The other statements are correct ($Mn_3O_4 = MnO{\cdot}Mn_2O_3$; Co^{2+} stays in solution as an ammine complex; Sc to Mn reach +3 to +7).

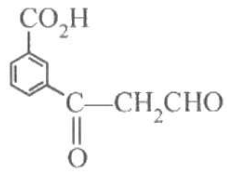
RB U6 §4.10 · p. 160

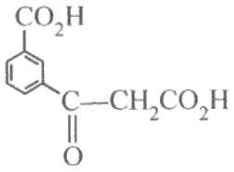
Question 20 · Q1–30 · single answer

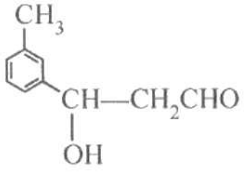
Consider the following reaction: a benzene ring carrying CH_3 and (meta to it) –$CH(OH)CH_2CH_2OH$ is treated with pyridinium chlorochromate (PCC) in CH_2Cl_2. Which is the major product of this reaction?

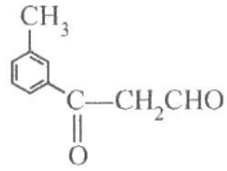


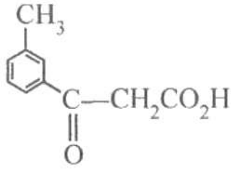
Which is the major product of this reaction?

(1) 

(2) 

(3) 

(4) 

(5) 

- (1)ring with CO_2H and –CO–CH_2CHO
- (2)ring with CO_2H and –CO–CH_2CO_2H
- (3)ring with CH_3 and –CH(OH)–CH_2CHO
- (4)ring with CH_3 and –CO–CH_2CHO
- (5)ring with CH_3 and –CO–CH_2CO_2H

Answer and review

Answer **(4)** Official marking scheme

PCC is a mild oxidizing agent: it oxidizes a primary alcohol only as far as the aldehyde and a secondary alcohol to a ketone. It does not oxidize the CH_3 group on the ring or take the aldehyde on to a carboxylic acid.

RB U9 §3.1 · p. 54

Question 21 · Q1–30 · single answer

Given that Hg(s) → Hg(l), ΔH = 2.4 kJ mol^{-1} and normal freezing point of Hg(l) = −38 °C, what is the entropy change (J K^{-1}) when 47 g of Hg(l) freezes at the normal freezing point? (Hg = 200)

- (1)14.84
- (2)2.40
- (3)−0.49
- (4)−2.40
- (5)−14.84

Answer and review

Answer **(4)** Official marking scheme

n = 47/200 = 0.235 mol. Freezing releases heat: ΔH = −2.4 × 0.235 = −0.564 kJ. At the freezing point (235 K) the process is at equilibrium, so ΔS = ΔH/T = −564 J/235 K = −2.40 J K^{-1}.

RB U5 §2.4 · p. 53

Question 22 · Q1–30 · single answer

Which of the following statements regarding $E°_{cell}$ and the flow of electrons is correct for the galvanic cell of Ni(s) | Ni^{2+}(aq, 1.0 mol dm^{-3}) || Cu^{2+}(aq, 1.0 mol dm^{-3}) | Cu(s), at 25 °C immediately after the electrodes are connected? At 25 °C, $E°(Cu^{2+}/Cu)$ = 0.34 V and $E°(Ni^{2+}/Ni)$ = −0.24 V

- (1)Electrons flow from Ni-electrode to Cu-electrode and $E°_{cell}$ = 0.58 V
- (2)Electrons flow from Ni-electrode to Cu-electrode and $E°_{cell}$ = −0.58 V
- (3)Electrons flow from Ni-electrode to Cu-electrode and $E°_{cell}$ = 0.10 V
- (4)Electrons flow from Cu-electrode to Ni-electrode and $E°_{cell}$ = 0.58 V
- (5)Electrons flow from Cu-electrode to Ni-electrode and $E°_{cell}$ = 0.10 V

Answer and review

Answer **(1)** Official marking scheme

Ni (more negative E°) is oxidized at the anode and releases electrons, which flow through the wire to the Cu cathode. $E°_{cell}$ = 0.34 − (−0.24) = +0.58 V.

RB U13 §3.3 · p. 250

Question 23 · Q1–30 · single answer

Identify the reaction in which the diazonium ion acts as an electrophile. (Each reagent is added to benzenediazonium chloride, $C_6H_5N_2$^+Cl^-.)

- (1)+ H_2O, heat
- (2)+ KI
- (3)+ phenol / NaOH
- (4)+ CuCN
- (5)+ H_3PO_2/H_2O

Answer and review

Answer **(3)** Official marking scheme

In alkaline solution the diazonium ion attacks the electron-rich ring of the phenoxide ion (coupling), giving an orange azo dye with N=N retained. In the other reactions N_2 is lost and the diazonium group is replaced by OH, I, CN or H.

RB U10 §4.3 · p. 78

Question 24 · Q1–30 · single answer

At the temperature at which a pure liquid will boil when it is heated in an open container, the

- (1)average kinetic energy of the liquid is equal to the average kinetic energy of its vapour.
- (2)average kinetic energy of the liquid is equal to the molar-entropy of its vapour.
- (3)entropy of the liquid is equal to the entropy of its vapour.
- (4)entropy of the vapour above the liquid is equal to the entropy of the atmosphere.
- (5)vapour pressure of the liquid is equal to the atmospheric pressure above the liquid surface.

Answer and review

Answer **(5)** Official marking scheme

A liquid boils when its saturated vapour pressure equals the external pressure, so bubbles of vapour can form throughout the liquid.

RB U12 §2.5 · p. 199

Question 25 · Q1–30 · single answer

Consider the following information for an electrochemical cell at 25 °C.
$Br_2(l) + 2e \rightleftharpoons 2Br^-(aq)$: E° = 1.065 V
$BrO_3\text{^}-(aq) + 6H^+(aq) + 5e \rightleftharpoons ½Br_2(l) + 3H_2O(l)$: E° = 1.520 V
Which of the following correctly shows the overall cell reaction, the corresponding $E°_{cell}$ and the number of electrons transferred?

- (1)$3Br_2(l) + 3H_2O(l) \rightleftharpoons 5Br^-(aq) + BrO_3\text{^}-(aq) + 6H^+(aq)$ · −0.460 V · 5
- (2)$6Br_2(l) + 6H_2O(l) \rightleftharpoons 10Br^-(aq) + 2BrO_3\text{^}-(aq) + 12H^+(aq)$ · 0.920 V · 10
- (3)$5Br^-(aq) + BrO_3\text{^}-(aq) + 6H^+(aq) \rightleftharpoons 3Br_2(l) + 3H_2O(l)$ · 0.460 V · 10
- (4)$3Br_2(l) + 3H_2O(l) \rightleftharpoons 5Br^-(aq) + BrO_3\text{^}-(aq) + 6H^+(aq)$ · −0.920 V · 10
- (5)$5Br^-(aq) + BrO_3\text{^}-(aq) + 6H^+(aq) \rightleftharpoons 3Br_2(l) + 3H_2O(l)$ · 0.460 V · 5

Answer and review

Answer **(5)** Official marking scheme

$BrO_3\text{^}-$ (higher E°) is reduced and Br^- is oxidized. Combine $BrO_3\text{^}- + 6H^+ + 5e \rightarrow ½Br_2 + 3H_2O$ with $5Br^- \rightarrow 5/2\ Br_2 + 5e$: $5Br^- + BrO_3\text{^}- + 6H^+ \rightarrow 3Br_2 + 3H_2O$, with 5 electrons. $E°_{cell} = 1.520 − 1.065 \approx +0.46$ V; E° values are not multiplied by coefficients.

RB U13 §3.3 · p. 250

Question 26 · Q1–30 · single answer

The following redox couples are given in the decreasing order of their reduction potentials. $O_2(g)/H_2O(l)$, $Br_2(l)/Br^-(aq)$, $I_2(s)/I^-(aq)$, $H^+(aq)/H_2(g)$, $Cd^{2+}(aq)/Cd(s)$, $Fe^{2+}(aq)/Fe(s)$, $Zn^{2+}(aq)/Zn(s)$, $Al^{3+}(aq)/Al(s)$.
Which of the following reactions will **not** take place spontaneously in an electrochemical cell?

- (1)$Zn(s) + Cd^{2+}(aq) \rightarrow Cd(s) + Zn^{2+}(aq)$
- (2)$2Al(s) + 3Br_2(l) \rightarrow 2Al^{3+}(aq) + 6Br^-(aq)$
- (3)$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
- (4)$H_2(g) + I_2(g) \rightarrow 2H^+(aq) + 2I^-(aq)$
- (5)$2Al^{3+}(aq) + 3Fe(s) \rightarrow 2Al(s) + 3Fe^{2+}(aq)$

Answer and review

Answer **(5)** Official marking scheme

A reaction is spontaneous when the species reduced belongs to the couple higher in the list than the species oxidized ($E°_{cell} > 0$). Al^{3+}/Al is below Fe^{2+}/Fe, so Fe cannot reduce Al^{3+}.

RB U13 §3.3 · p. 250

Question 27 · Q1–30 · single answer

X and Y are two compounds having the molecular formula $C_4H_8O_2$. The observations, when X and Y are reacted with three reagents are given in the following table.

Reagent	X	Y
Na metal	a gas evolved	a gas evolved
2,4-dinitrophenylhydrazine	no precipitate	coloured precipitate
Br_2/H_2O	decolourised	no reaction

- (1)$CH_3CH(COOH)CH_3$ and $CH_3CH(OH)CH_2CHO$
- (2)CH_2=$CHCH(OH)CH_2OH$ and $CH_3COCH_2CH_2OH$
- (3)$CH_3CH(CH_3)COOH$ and $CH_3COCH(OH)CH_3$
- (4)$HOCH_2CH_2CH_2CHO$ and $HOCH_2C(CH_2OH)$=CH_2
- (5)$HOCH_2CH$=$CHCH_2OH$ and $CH_3CH_2CH_2COOH$

Answer and review

Answer **(2)** Official marking scheme

X has –OH (H_2 with Na), no C=O and a C=C (decolourizes bromine water): CH_2=$CHCH(OH)CH_2OH$. Y has –OH and a C=O (2,4-DNP) but no C=C: $CH_3COCH_2CH_2OH$. Aldehydes would also decolourize bromine water, ruling out the aldehyde options for Y.

RB U9 §3.4 · p. 60 RB U8 §2.2 · p. 33

Question 28 · Q1–30 · single answer

Manganese(III) fluoride can be prepared according to the following reaction. $2MnI_2(s) + 13F_2(g) \rightarrow 2MnF_3(s) + 4IF_5(l)$. If the percentage yield is 80%, what is the mass of MnF_3 obtained when 0.10 moles of MnI_2 are reacted with excess F_2? (F = 19, Mn = 55, I = 127). % yield = (obtained mass/theoretical mass) × 100%

- (1)4.48 g
- (2)7.44 g
- (3)8.96 g
- (4)9.20 g
- (5)11.20 g

Answer and review

Answer **(3)** Official marking scheme

MnI_2 : MnF_3 = 1 : 1, so theoretical MnF_3 = 0.10 mol × 112 g mol^{-1} = 11.2 g. At 80% yield: 0.80 × 11.2 = 8.96 g.

RB U3 §3.8 · p. 115

Question 29 · Q1–30 · single answer

Consider the equilibrium reaction below taking place in a closed-rigid container at 300 K. AB(g) + CD_2(s) ⇌ AD(g) + BD(g) + C(s). In an experiment carried out at 300 K it was found that 5% of AB(g) converted to AD(g) and the total pressure of the system at equilibrium was 10 atm. The equilibrium constant K_p of the system at 300 K is

- (1)(19 × 10)/21
- (2)10/(19 × 21)
- (3)0.10/(19 × 21)
- (4)(19 × 19 × 10)/39
- (5)(19 × 19 × 0.10)/39

Answer and review

Answer **(2)** Official marking scheme

Start with n mol AB: at equilibrium AB = 0.95n, AD = BD = 0.05n; gas total = 1.05n. P_{AB} = (0.95/1.05) × 10 = (19/21) × 10 and $P_{AD} = P_{BD}$ = (1/21) × 10. $K_p = P_{AD}P_{BD}/P_{AB} = (10/21)^2 \div (190/21) = 10/(19 \times 21)$ atm. Solids are left out.

RB U12 §2.1 · p. 76

Question 30 · Q1–30 · single answer

The diagram-I below depicts the variation of rates with time of forward and backward reactions of an equilibrium reaction P ⇌ Q at a given temperature. At time t, when an additional amount of P is added to the system the change in rate of the forward reaction is also shown in diagram-I. Which line (A, B, C, D or E) in diagram-II shows the change in the rate of the backward reaction?

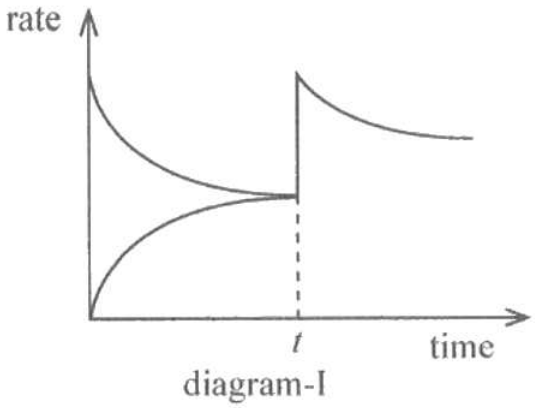


diagram-I

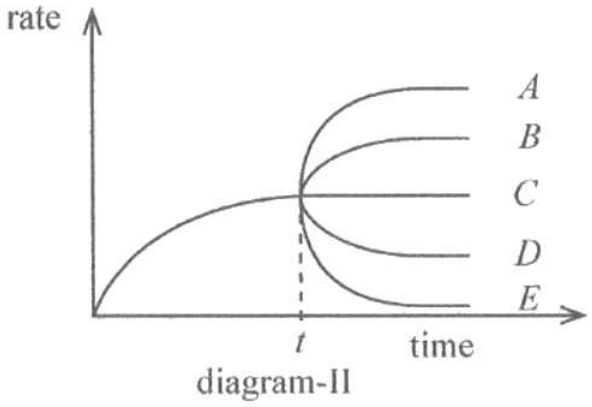


diagram-II

- (1)A
- (2)B
- (3)C
- (4)D
- (5)E

Answer and review

Answer **(2)** Official marking scheme

Adding P raises the forward rate suddenly; it then falls as P is used. Q builds up, so the backward rate rises gradually (no sudden jump) until the two rates become equal again at a new, higher common value. Line B

shows this gradual rise to the new equilibrium rate.

RB U12 §2.1 · p. 76 RB U11 §1.5 · p. 15

Questions 31–40: response code

(1)	(2)	(3)	(4)	(5)
Only (a) and (b) are correct	Only (b) and (c) are correct	Only (c) and (d) are correct	Only (d) and (a) are correct	Any other number or combination of responses is correct

Question 31 · Q31–40 · response code

Consider the mechanism of the nitration of bromobenzene with conc. HNO_3/conc. H_2SO_4. Which of the following structure/structures represent/s the ion/ions formed during this reaction?

- Structure (a)
- Structure (b)
- Structure (c)
- Structure (d)

Answer and review

Answer **(4)** Official marking scheme

Br is an ortho/para director. Attack of NO_2^+ at the ortho or para position gives an arenium (carbocation) ion with the positive charge on the ring carbons ortho/para to the attacked carbon; one resonance form places it on the carbon bearing Br (stabilised by Br's lone pair, giving $C{=}Br^+$). Structures (a) and (d) are valid intermediates; (b) and (c) place the charge or the groups incorrectly.

RB U8 §2.4 · p. 44 RB U8 §2.5 · p. 49

Question 32 · Q31–40 · response code

At a given temperature the following equilibrium exists in a closed-rigid container. $CO(g) + 2O_2(g) \rightleftharpoons 2CO_2(g)$: $\Delta H < 0$ (as printed). Which of the following statements is/are correct for this system?

- Adding more $CO_2(g)$ at the same temperature increases the amount of CO(g) with a change in the value of the equilibrium constant.
- Increasing the temperature of the system increases the amount of CO(g) with a decrease in the value of the equilibrium constant.
- Adding more CO(g) at the same temperature increases the amount of $CO_2(g)$ without a change in the value of the equilibrium constant.
- Adding more $CO_2(g)$ at the same temperature increases the amount of $O_2(g)$ with an increase in the value of the equilibrium constant.

Answer and review

Answer **(2)** Official marking scheme

Only a temperature change alters K. The forward reaction is exothermic, so heating shifts the equilibrium left (more CO) and lowers K. Adding CO shifts it right (more CO_2) at constant K. Statements (a) and (d) wrongly say K changes. Only (b) and (c) are correct.

RB U12 §2.1 · p. 76

Question 33 · Q31–40 · response code

The following statements refer to industrial processes. Which of them is/are correct?

- A catalyst is not required in the manufacture of NH_3 by the Haber-Bosch process.
- Citric acid is used in the purification of soap.
- In the extraction of Mg by the Dow process, CO_2 is added to the atmosphere only by the thermal decomposition of limestone or dolomite.
- HCl is the main by-product in the manufacture of NaOH using the membrane cell method.

Answer and review

Answer **(5)** Official marking scheme

None is correct. The Haber process needs an iron catalyst; soap is separated by salting out with NaCl; in the Dow process CO_2 also comes from burning fuels to keep the cell hot; the membrane cell gives Cl_2 and H_2 as by-products, not HCl. "None correct" is "any other combination", code (5).

RB U14 §1.2 · p. 6 RB U14 §1.3 · p. 8 RB U14 §1.4 · p. 14 RB U14 §1.6 · p. 21

Question 34 · Q31–40 · response code

Which of the following statements is/are correct regarding s-block elements?

- The metallic radii of Group II elements are less than the metallic radii of the corresponding Group I elements.
- The first ionization energies of Group II elements are greater than the first ionization energies of the corresponding Group I elements.
- The densities of Group II elements are lower than the densities of Group I elements.
- Group II elements have weaker metallic bonds than Group I elements.

Answer and review

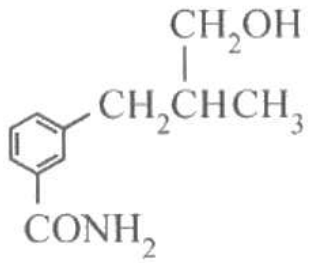
Answer **(1)** Official marking scheme

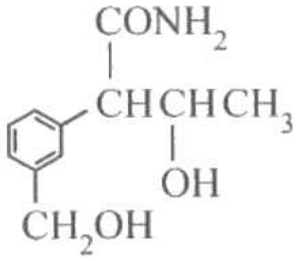
Group II atoms have a higher nuclear charge in the same shell, so they are smaller and hold their outer electrons more tightly (higher IE_1). Two delocalised electrons per atom and smaller atoms give stronger metallic bonding and higher densities, so (c) and (d) are wrong.

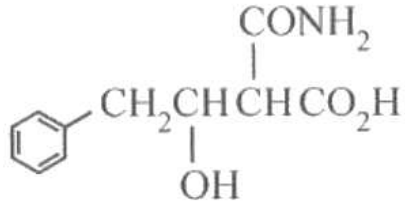
RB U6 §4.2 · p. 126 RB U1 §1.6 · p. 32

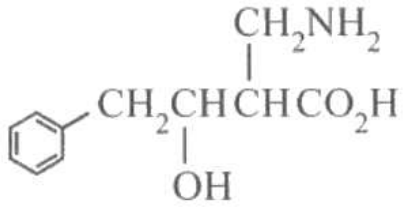
Question 35 · Q31–40 · response code

An organic compound A when heated with aqueous NaOH, liberates ammonia. The compound formed when A is heated with acidified $K_2Cr_2O_7$, gives a coloured precipitate with 2,4-dinitrophenylhydrazine. Which of the following could be A?

(a) 

(b) 

(c) 

(d) 

- benzene ring with $–CONH_2$ and $–CH_2CH(CH_2OH)CH_3$ (meta)
- benzene ring with $–CH(CONH_2)CH(OH)CH_3$ and $–CH_2OH$ (meta)
- $C_6H_5–CH_2CH(OH)CH(CONH_2)CO_2H$
- $C_6H_5–CH_2CH(OH)CH(CH_2NH_2)CO_2H$

Answer and review

Answer **(2)** Official marking scheme

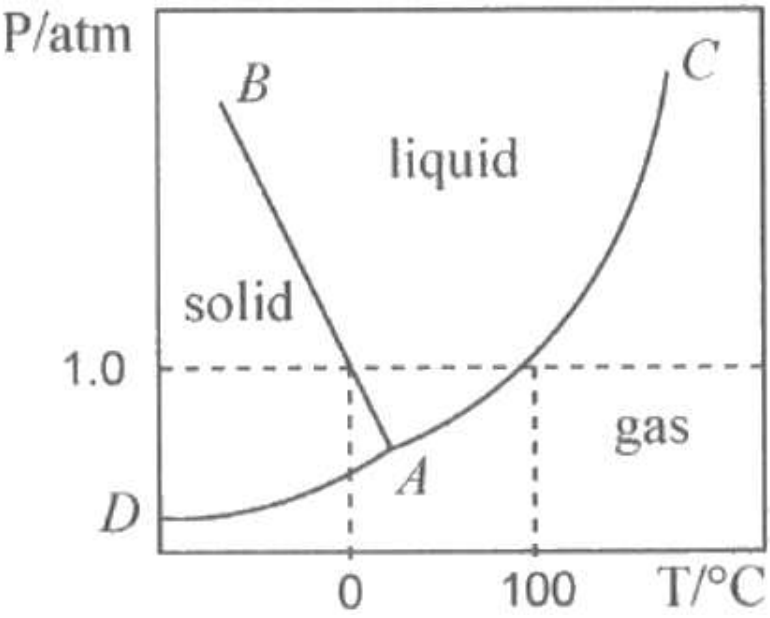
NH_3 with hot NaOH shows an amide ($–CONH_2$), which rules out (d) (an amine). The dichromate product must be a ketone (a primary alcohol is oxidized right through to a carboxylic acid, which gives no 2,4-DNP precipitate), so A needs a secondary alcohol. (b) and (c) have both groups; (a) has only a primary alcohol.

RB U10 §4.1 · p. 75 RB U9 §3.6 · p. 70 RB U9 §3.1 · p. 54

Question 36 · Q31–40 · response code

The phase-diagram of a pure substance X is shown below.

Which of the following statements is/are correct?



- The temperature needed to solidify the liquid decreases as the pressure increases.
- The freezing point of the liquid is higher than its normal freezing point at pressures above 1.0 atm.

- A is the triple point of X.
- At a temperature greater than 100 °C, a pressure above 1.0 atm is needed to liquefy the gas.

Answer and review

Answer **(5)** Official marking scheme

The solid–liquid line AB slopes back to the left (like water), so a higher pressure lowers the freezing point: (a) true, (b) false. A, where the three lines meet, is the triple point. The normal boiling point is 100 °C, so above 100 °C the vapour pressure exceeds 1 atm and a higher pressure is needed to condense the gas. (a), (c) and (d) are correct: code (5).

RB U12 §2.5 · p. 199

Question 37 · Q31–40 · response code

Which of the following statements is/are true about atmospheric ozone?

- The highest ozone concentration is at the ground level.
- Stratospheric ozone protects human life.
- Motor vehicle emissions contribute to the formation of ground level ozone.
- In the ozone layer, ozone is formed and destroyed in the presence of UV radiation.

Answer and review

Answer **(5)** Official marking scheme

Ozone is most concentrated in the stratosphere (15–35 km), where it absorbs harmful UV; there UV both forms it ($O_2 \rightarrow 2O$, $O + O_2 \rightarrow O_3$) and splits it. NO_x and hydrocarbons from vehicles form ground-level ozone in photochemical smog. (b), (c) and (d) are true: code (5).

RB U14 §1.13 · p. 58

Question 38 · Q31–40 · response code

The enthalpy change, ΔH, for the reaction given below at 25 °C is −126 kJ.
$2Na_2O_2(g) + 2H_2O(l) \rightarrow 4NaOH(aq) + O_2(g)$ (as printed)
Which of the following statements about the enthalpy change is/are correct when a given amount of $Na_2O_2(s)$ is added to an excess of water at 25 °C? (H = 1, O = 16, Na = 23)

- 63.0 kJ of energy is released when one mole of $Na_2O_2(s)$ is added.
- 31.5 kJ of energy is absorbed when 39 g of $Na_2O_2(s)$ is added.
- 63.0 kJ of energy is absorbed when one mole of $Na_2O_2(s)$ is added.
- 31.5 kJ of energy is released when 39 g of $Na_2O_2(s)$ is added.

Answer and review

Answer **(All)** Official marking scheme

The official scheme awards the mark for every response, because the equation gives Na_2O_2 as a gas while the question asks about the solid (so ΔH for the solid is not known exactly). Using the printed value, 2 mol releases 126 kJ: 63.0 kJ per mole, and 39 g (0.50 mol) releases 31.5 kJ, which would make (a) and (d) correct.

RB U5 §2.2 · p. 36 RB U3 §3.8 · p. 115

Question 39 · Q31–40 · response code

Which of the following statements is/are correct regarding hydrogen halides?

- Hydrogen halides are acidic in water.
- The bond dissociation energies of hydrogen halides decrease when going down the group.
- The acidic strength of hydrogen halides decreases when going down the group.
- The bond length of hydrogen halides decreases when going down the group.

Answer and review

Answer **(1)** Official marking scheme

All hydrogen halides dissolve to give acidic solutions. Down the group the halogen atom becomes larger, so the H–X bond gets longer and weaker; because the bond breaks more easily, acid strength increases (HF weak, HI strongest). Only (a) and (b) are correct.

RB U6 §4.7 · p. 149

Question 40 · Q31–40 · response code

Which of the following statements is/are true regarding the production of H_2SO_4 by the contact process?

- The reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ is endothermic.
- Fe is the commonly used catalyst for this process.
- SO_2 is converted to SO_3 in four catalytic chambers.
- In this process pressures greater than 1 atm are not utilized.

Answer and review

Answer **(3)** Official marking scheme

The oxidation of SO_2 is exothermic and uses a V_2O_5 catalyst (Fe is the Haber catalyst). The gas passes over several catalyst beds with cooling between them, and the RB gives the conditions as about 450 °C and 1 atm, since the yield is already high. Only (c) and (d) are true.

RB U14 §1.8 · p. 27

Questions 41–50: statement pairs

Response	First statement	Second statement
(1)	True	True, and correctly explains the first statement
(2)	True	True, but does not explain the first statement correctly
(3)	True	False
(4)	False	True
(5)	False	False

Question 41 · Q41–50 · statement pair

Statement 1

Among the elements of the second period of the Periodic Table, the electron gain energy of N and Be have a positive value.

Statement 2

Half filled shells and completely filled shells have a higher stability than other electron configurations.

Answer and review

Answer **(3)** Official marking scheme

Be ($2s^2$, filled sub-shell) and N ($2p^3$, half-filled sub-shell) resist gaining an electron, so their electron gain energies are positive. The second statement refers to shells; the extra stability belongs to filled and half-filled sub-shells, so as written it is false.

RB U1 §1.6 · p. 32

Question 42 · Q41–50 · statement pair

Statement 1

Ketones cannot be prepared from the reaction between esters and Grignard reagents.

Statement 2

Ketones react much faster than esters with Grignard reagents.

Answer and review

Answer **(1)** Official marking scheme

The ester first gives a ketone, but the ketone reacts with Grignard reagent faster than the remaining ester, so the product is a tertiary alcohol and the ketone cannot be isolated. Both true; the second explains the first.

RB U9 §3.6 · p. 70

Question 43 · Q41–50 · statement pair

Statement 1

In an evacuated closed-rigid container water boils at a temperature below 100 °C.

Statement 2

When the external pressure is low it is easy for water molecules to be released from the liquid phase to the vapour phase.

Answer and review

Answer **(4)** Official marking scheme

In a closed container the vapour cannot escape, so the pressure above the water rises to the saturated vapour pressure and liquid–vapour equilibrium is set up; the water evaporates but does not boil. Boiling needs the vapour pressure to equal a fixed external pressure. The second statement is true.

RB U12 §2.5 · p. 199

Question 44 · Q41–50 · statement pair

Statement 1

The bond angles of H_2O, H_2S and H_2Se decrease in the order $H_2O > H_2S > H_2Se$.

Statement 2

The electronegativity of the central atom of H_2O, H_2S and H_2Se decreases in the order O > S > Se.

Answer and review

Answer **(1)** Official marking scheme

As the central atom becomes less electronegative (and larger), the bonding pairs lie further from it and repel each other less, so the bond angle closes (104.5° → 92° → 91°). Both true; the second explains the first.

RB U2 §2.3 · p. 52

Question 45 · Q41–50 · statement pair

Statement 1

Atmospheric water vapour contributes to global warming.

Statement 2

Water vapour is a greenhouse gas.

Answer and review

Answer **(4)** Official marking scheme

The official answer treats the first statement as false: the RB discusses global warming as caused by the extra greenhouse gases released by human activity (CO_2, CH_4, N_2O, CFCs), while the amount of water vapour in the air is set naturally by the water cycle. Water vapour does absorb infrared radiation, so the second statement is true.

RB U14 §1.13 · p. 58

Question 46 · Q41–50 · statement pair

Statement 1

For water, enthalpy of fusion ΔH_{fus} is less than the enthalpy of vaporization ΔH_{vap}.

Statement 2

Water molecules move further apart during fusion compared to vaporization.

Answer and review

Answer **(3)** Official marking scheme

Melting breaks only some hydrogen bonds and the molecules stay close together; vaporization separates them completely, so ΔH_{vap} (about 41 kJ mol^{-1}) ≫ ΔH_{fus} (about 6 kJ mol^{-1}). The second statement reverses this, so it is false.

RB U5 §2.2 · p. 36 RB U12 §2.5 · p. 199

Question 47 · Q41–50 · statement pair

Statement 1

CH_3COCl reacts with excess aqueous NaOH to form $CH_3COO^-Na^+$.

Statement 2

During the reaction of an acid chloride with aqueous NaOH a tetrahedral intermediate is formed.

Answer and review

Answer **(2)** Official marking scheme

OH^- adds to the carbonyl carbon to form a tetrahedral intermediate, which loses Cl^-; the acid formed is then neutralized by excess NaOH to give the sodium salt. Both statements are true, but the second (the mechanism) does not explain why the final product is the salt.

RB U9 §3.6 · p. 70

Question 48 · Q41–50 · statement pair

Statement 1

Solubility of $Cu(OH)_2(s)$ at pH = 5 is higher than that at pH = 10.

Statement 2

In acidic solutions OH^- gets neutralized.

Answer and review

Answer **(1)** Official marking scheme

$Cu(OH)_2(s) \rightleftharpoons Cu^{2+} + 2OH^-$. In acid, H^+ removes OH^- as water, so more $Cu(OH)_2$ dissolves to keep $[Cu^{2+}][OH^-]^2 = K_{sp}$. Both true; the second explains the first.

RB U12 §2.4 · p. 175

Question 49 · Q41–50 · statement pair

Statement 1

In the production of Na_2CO_3 industrially, ammonification precedes carbonation.

Statement 2

When CO_2 is passed into an ammoniated (ammonified) brine solution, $(NH_4)_2CO_3$ is produced in high concentration.

Answer and review

Answer **(3)** Official marking scheme

CO_2 is only slightly soluble in neutral brine, so the brine is ammoniated first; the basic solution then absorbs CO_2 well, giving a high concentration of HCO_3^− (as NH_4HCO_3), from which $NaHCO_3$ crystallizes. The second statement names the wrong product.

RB U14 §1.5 · p. 18

Question 50 · Q41–50 · statement pair

Statement 1

In acidic media, H_2O_2 can act as an oxidizing agent or a reducing agent, depending on the species it reacts with.

Statement 2

Out of the oxidation states oxygen exhibits, 0 is the most stable and abundant.

Answer and review

Answer **(3)** Official marking scheme

O in H_2O_2 is −1, between −2 and 0, so it can be reduced (to H_2O) or oxidized (to O_2): it oxidizes I^- but reduces MnO_4^−. The most stable and common oxidation state of oxygen is −2, not 0.

RB U6 §4.6 · p. 141

Structured essay · answer all four

SEQ · Paper II Part A

Question 1 · Part A · structured essay

(a) [32 marks]

State whether the following statements are true or false. Reasons not required.
(i) The pairing of electrons in a particular subshell does not take place until all the orbitals of the subshell are singly occupied by electrons with parallel spins.
(ii) The atomic orbitals identified by quantum numbers n and l, (I) n = 4, l = 1 (II) n = 4, l = 0 (III) n = 3, l = 2 can be placed in order of increasing energy as (III) < (II) < (I).
(iii) The electron pair geometry of the SOF_4 molecule is square pyramidal.
(iv) The second ionization energy of Li is less than that of Be.
(v) The electron gain energy of fluorine is a negative value.
(vi) Among the atoms Be, C, Si and S, the atomic radii increase in the order C < Be < S < Si.
(vii) The boiling point of CH_3NH_2 is higher than that of CH_3F.
(viii) The ionic radii of Al^{3+}, O^{2-}, F^- and S^{2-} decrease in the order $S^{2-} > F^- > O^{2-} > Al^{3+}$.

Answer

(i) true (ii) false (iii) false (iv) false (v) true (vi) false (vii) true (viii) false
(04 marks × 8 = 32 marks)

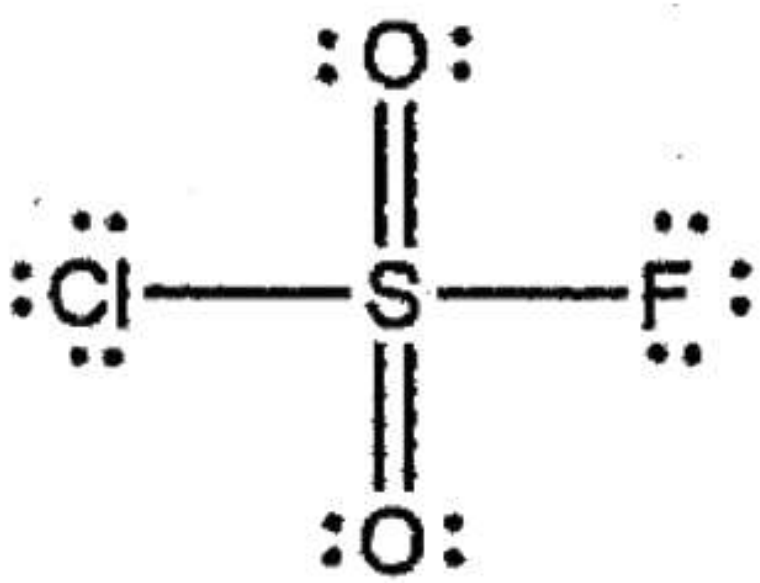
Review.

(ii) 4s (II) < 3d (III) < 4p (I). (iii) SOF_4 has five bonding domains and no lone pair: trigonal bipyramidal. (iv) Li^+ has the $1s^2$ configuration, so IE_2 of Li is far larger than that of Be. (vi) Be (112 pm) is larger than S (104 pm), so the correct order is C < S < Be < Si. (vii) CH_3NH_2 forms hydrogen bonds. (viii) $O^{2-} > F^-$ (isoelectronic, fewer protons).

(b) [52 marks]

(i) Draw the **most** acceptable Lewis dot-dash structure for the molecule $ClSO_2F$.

Answer



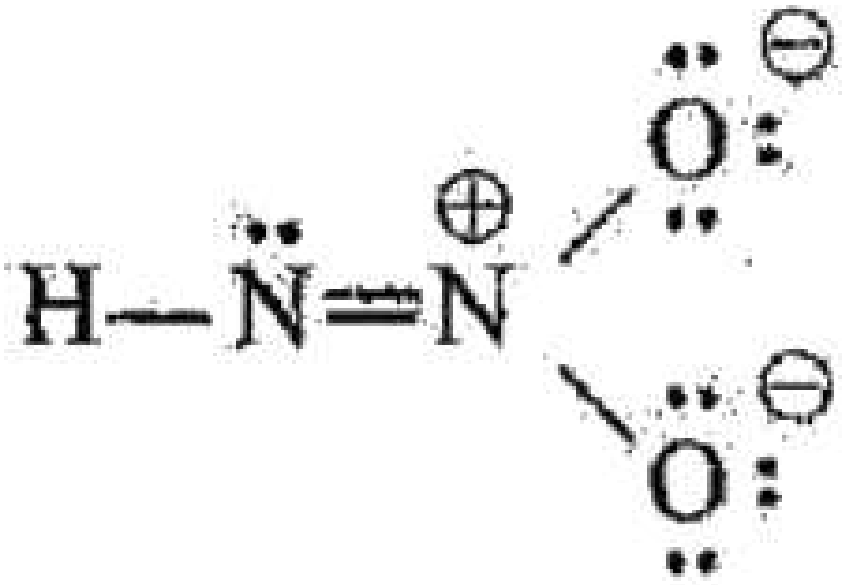
(06 marks)

(ii) Give the oxidation state of S in the structure drawn in (i) above.

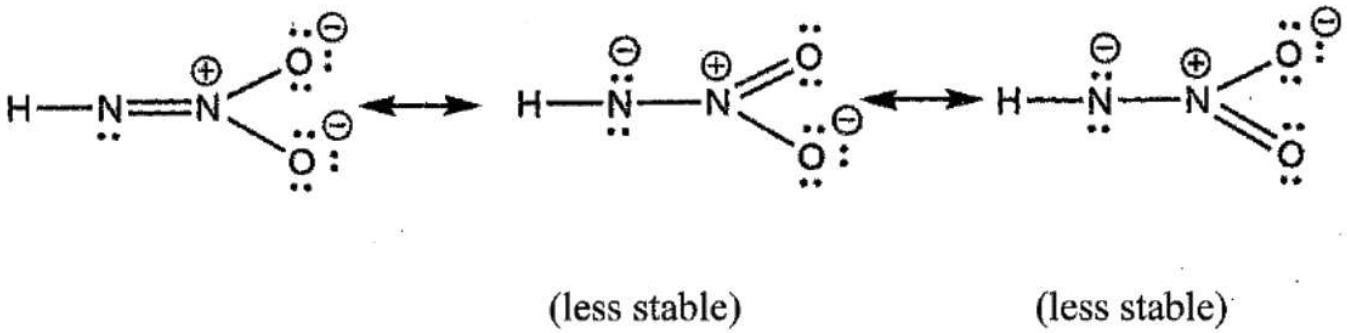
Answer

+6 (or +VI) (02 marks) Award marks for (ii) only if the Lewis structure in (i) is correct.

(iii) A stable Lewis dot-dash structure for the $HN_2O_2^-$ ion is given below. Draw **two** more Lewis dot-dash structures (resonance structures) for this ion. Indicate the stability of each of the structures drawn by you, relative to the structure given, by writing stable, unstable or less stable under the structure.

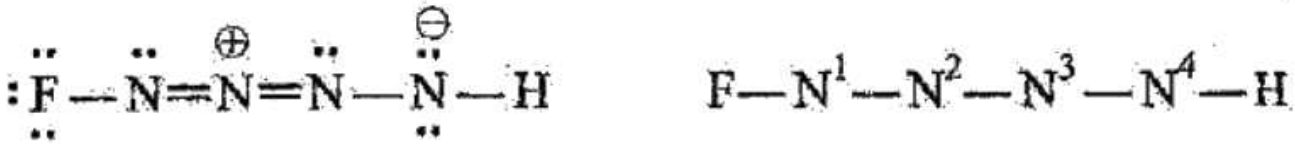


Answer



Both structures drawn: less stable. (02 marks structure + 01 mark stability) × 2 = 06 marks

(iv) Complete the table based on the Lewis dot-dash structure and its labelled skeleton given below (F–N^1–N^2–N^3–N^4–H).



Answer

	N^1	N^2	N^3	N^4
I. VSEPR pairs	3	2	3	4
II. electron pair geometry	trigonal planar	linear	trigonal planar	tetrahedral
III. shape around the atom	angular / V / bent	linear	angular / V / bent	angular / V / bent
IV. hybridization	sp^2	sp	sp^2	sp^3

(01 mark × 16 = 16 marks)

Parts (v) to (viii) are based on the Lewis dot-dash structure given in part (iv).

(v) Identify atomic/hybrid orbitals involved in the formation of σ bonds between the two atoms given below: I. N^1–F II. N^1–N^2 III. N^2–N^3 IV. N^3–N^4 V. N^4–H

Answer

I. N^1 sp^2, F 2p or sp^3 II. N^1 sp^2, N^2 sp III. N^2 sp, N^3 sp^2 IV. N^3 sp^2, N^4 sp^3 V. N^4 sp^3, H 1s (01 mark × 10 = 10 marks)

(vi) Identify the atomic orbitals involved in the formation of π bonds between the two atoms given below: I. N^1–N^2 II. N^2–N^3

Answer

I. N^1 2p, N^2 2p II. N^2 2p, N^3 2p (01 mark × 4 = 04 marks)

(vii) State approximate values of bond angles around the N^1, N^2, N^3 and N^4 atoms.

Answer

N^1 (118° ± 1), N^2 (180° ± 1), N^3 (118° ± 2), N^4 (104° ± 1) (01 mark × 4 = 04 marks)

(viii) Arrange N^1, N^2, N^3 and N^4 atoms in **increasing** order of their electronegativities.

Answer

$N^4 < N^3 < N^1 < N^2$ (04 marks)

Review.

Electronegativity of an atom rises with s character ($sp > sp^2 > sp^3$) and with positive formal charge or bonding to F: N^2 (sp, positive) is highest and N^4 (sp^3, negative) lowest.

(c) [16 marks]

(i) Given below are the six successive ionization energies, IE_1–IE_6 (in kJ/mol) of an element in the third period, starting from the first ionization energy (IE_1): 1012, 1903, 2910, 4956, 6248, 22230. Identify the element and write its electron configuration. I. element II. electron configuration

Answer

I. P (phosphorus) (02 marks)
II. $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$ (02 marks)

Review.

The big jump comes after IE_5, so the atom has five valence electrons: Group 15, period 3.

(ii) A molecule of formula AX_5 has five A–X σ bonds. Here A and X represent symbols of elements and A is the central atom. Complete the table below by naming the possible molecular shape and giving an example (molecular formula required) for each of the shapes. I. If AX_5 is polar II. If AX_5 is nonpolar

Answer

I. Polar: square pyramidal; e.g. BrF_5 / ClF_5 / IF_5 / $BrCl_5$ / ICl_5 (any one; IBr_5 cannot be accepted)
II. Nonpolar: trigonal bipyramidal; e.g. PCl_5 / PF_5
(03 marks × 4 = 12 marks, marked independently)

Read: RB U1 §1.4 · p. 23 RB U1 §1.6 · p. 32 RB U2 §2.1 · p. 44 RB U2 §2.3 · p. 52 RB U2 §2.6 · p. 79

Question 2 · Part A · structured essay

(a) [40 marks]

(i) A is a water soluble white coloured compound. It is composed of three elements in the ratio 4:2:3 (in the increasing order of atomic mass). The atomic number of each element is less than 20. Two of these elements belong to the p-block of the Periodic Table. On heating A, a colourless, non-toxic, neutral, tri-atomic gas with a linear structure is evolved as one of the products. A is used as a fertilizer. Identify A.

Answer

A = NH_4NO_3 (ammonium nitrate)

(ii) B is also a water soluble white coloured compound. It is composed of the same three elements as A. These elements are in the ratio 4:2:2 (in the increasing order of atomic mass). On heating B, a colourless, odourless, homo diatomic gas having a high bond dissociation energy is evolved. This gas is obtained industrially by fractional distillation of liquified air. Identify B.

Answer

B = NH_4NO_2 (ammonium nitrite)

(iii) C is a white coloured ionic compound. It is composed of four elements in the ratio 8:2:4:1 (in the increasing order of atomic mass). The atomic number of each element is less than 20. Three of these elements are found in both A and B. On heating C, a colourless basic gas X having a strong smell, and a strong acid are formed. On addition of $BaCl_2$(aq) to an aqueous solution of C, a white precipitate that is insoluble in dil. HCl is obtained. Identify C.

Answer

C = $(NH_4)_2SO_4$

(iv) D is a white coloured ionic compound. It is composed of four elements in the ratio 8:1:2:3 (in the increasing order of atomic mass). Three of these elements are found in all three compounds A, B and C. Of the products formed on heating D, gas X and another gas that turns lime water milky are obtained as two of the products. Identify D.

Answer

D = $(NH_4)_2CO_3$

(v) E is a strong acid. It is composed of the same elements as A and B. They are in the ratio 3:1:1 (**not** in the increasing order of atomic mass). E is a strong oxidizing agent. E is manufactured using X. Identify E.

Answer

E = HNO_3 (nitric acid)
2(a): 08 × 5 = 40 marks

(b) [32 marks]

Give balanced chemical equations for the reactions that take place on heating A, B, C and D identified in (a) above.

Answer

A: $NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(g)$
B: $NH_4NO_2(s) \rightarrow N_2(g) + 2H_2O(g)$
C: $(NH_4)_2SO_4(s) \rightarrow 2NH_3(g) + H_2SO_4(g)$ (or $SO_3 + H_2O + 2NH_3$)
D: $(NH_4)_2CO_3(s) \rightarrow 2NH_3(g) + CO_2(g) + H_2O(g)$
Physical states are not required. Δ is not required. 2(b): 08 × 4 = 32 marks

(c) [28 marks]

(i) Identify X based on the information given in part (a) above.

Answer

X = NH_3 (04)

(ii) Name the process by which E, identified in part (a)(v) above, is manufactured using X.

Answer

Ostwald process (04)

(iii) State the other raw material/s used in the above process.

Answer

O_2 (air) and H_2O (04)

(iv) I. On reacting X with excess $Cl_2(g)$ a compound Y is formed as one of the products. Write the balanced chemical equation for this reaction.
II. When Y reacts with water, a compound that can be used to disinfect water is formed. Write the balanced chemical equation for the reaction of Y with water.

Answer

I. $3Cl_2(g) + NH_3(g) \rightarrow 3HCl(g) + NCl_3(l)$ (04)
II. $NCl_3(l) + 3H_2O \rightarrow NH_3(g) + 3HOCl(aq)$ (or $NCl_3 + 4H_2O \rightarrow NH_4OH + 3HOCl$) (04)

(v) Give **one** chemical test to identify X, along with its observation.

Answer

Test: X is reacted with conc. HCl. Observation: white fumes are formed. (Without "conc." only 02 marks.)
or Test: X is bubbled through Nessler's reagent (or a filter paper soaked with Nessler's reagent). Observation: brown precipitate / colouration.
(04 + 04) No marks for litmus. 2(c): 28 marks

Review.

The ratios count atoms in order of increasing atomic mass (H : N : O). NH_4NO_3 gives N_2O (linear, triatomic); NH_4NO_2 gives N_2.

Read: RB U6 §4.5 · p. 136 RB U14 §1.7 · p. 25 RB U6 §4.6 · p. 141

Question 3 · Part A · structured essay

Scheme note: PHYSICAL STATES ARE NECESSARY. The symbol of equilibrium ⇌ is also needed for all the reactions.

(a) [70 marks]

HX(aq) is a weak acid with $pK_a = 4$ at 25 °C.
(i) Write the equation for the ionization of HX(aq) in an aqueous solution.

Answer

$HX(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + X^-(aq)$ OR $HX(aq) \rightleftharpoons H^+(aq) + X^-(aq)$ (05)

(ii) Write the expression for the equilibrium constant of (i) above.

Answer

$K_a = [H_3O^+(aq)][X^-(aq)]/[HX(aq)]$ OR $K_a = [H^+(aq)][X^-(aq)]/[HX(aq)]$ (05)

(iii) Calculate the pH of a 0.01 mol dm^{-3} solution of HX(aq) at a temperature of 25 °C.

Answer

	HX(aq)	$H_3O^+(aq)$	$X^-(aq)$
Initial con.	0.01	0	0
Change con.	−x	x	x
Equi. con.	0.01 − x	x	x

(02 + 01)

a

−4

2

(02 + 02 + 02)

2

−6

3

+

−3

−3

(02 + 01)

3

+

(05)

3

+

Alternate answer:

a

a

−4

−3

3

+

−

+

2

a

+

a

+

−4

−3

−3

17 marks

(iv) A volume of 10.00 cm^3 of 0.02 mol dm^{-3} NaOH(aq) solution was added to 25.00 cm^3 of 0.01 mol dm^{-3} HX(aq) solution at a temperature of 25 °C.
I. Write the chemical species present in the solution obtained.

II. What is this type of solution commonly known as?
III. Write the expression for the calculation of pH of this solution.
IV. Calculate the pH of this solution. (log 2 = 0.30, log 3 = 0.48, log 4 = 0.60, log 5 = 0.70, log 6 = 0.78, log 7 = 0.85, log 8 = 0.90, log 9 = 0.95)

Answer

I. HX(aq), H_3O^+(aq), X^-(aq), OH^-(aq), Na^+(aq) (and H_2O(l)) (01 × 05)
II. Buffer solution (03)
III. pH = pK_a + log([X^-(aq)]/[HX(aq)]) or pH = pK_a + log([NaX(aq)]/[HX(aq)]) or pH = pK_a + log([salt]/[acid]) (05)
IV. HX(aq) + NaOH(aq) → NaX(aq) + H_2O(l) (03)
Initial moles: HX 0.01 × 25 × 10^{-3}; OH^- 0.02 × 10 × 10^{-3}. Remaining: HX (0.01 × 25 × 10^{-3} − 0.02 × 10 × 10^{-3}); OH^- 0; X^- 0.02 × 10 × 10^{-3} (01 + 01). Concentrations (mol dm^{-3}): HX 0.05/35, X^- 0.20/35 (01 + 01 + 01)
pH = 4 + log((0.20/35)/(0.05/35)) = 4 + log 4 = 4 + 0.6 = **4.6** (03 + 02). Marks can be awarded with the use of the K_a expression.

V. Calculate the volume of 0.02 mol dm^{-3} NaOH(aq) solution required to be mixed with 100.00 cm^3 of 0.01 mol dm^{-3} HX(aq) to obtain a solution of pH 4.00.

Answer

Volume of NaOH needed: V cm^3. pH = 4 gives 4 = 4 + log([X^-]/[HX]); log([X^-]/[HX]) = 0; [X^-] = [HX] (04)
[HX(aq)] = (0.01 × 100 × 10^{-3} − 0.02 × V × 10^{-3})/((100 + V) × 10^{-3}) (02 + 01); [X^-(aq)] = (0.02 × V × 10^{-3})/((100 + V) × 10^{-3}) (02 + 01)
Equating: 1.0 − 0.02V = 0.02V (02); **V = 25 cm^3** (04 + 01)
Alternative answer: pH = 4 = pK_a (05); this is the half-equivalence point (03); [NaOH] is twice [HX] (03), so the volume of NaOH at equivalence is half the volume of HX (03); at half equivalence the volume of NaOH = ¼ × volume of HX = 25 cm^3 (03). 3(a): 70 marks

(b) [30 marks]

At 25 °C, MgF_2(s) is sparingly soluble in water (K_{sp} = 6.4 × 10^{-9} mol^3 dm^{-9}). Calculate the maximum mass of MgF_2(s) that is completely soluble in 500.00 cm^3 of 0.20 mol dm^{-3} NaF(aq) solution. Assume that there is no change in volume of the solution upon the addition of MgF_2(s). (F = 19, Mg = 24)

Answer

MgF_2(s) ⇌ Mg^{2+}(aq) + 2F^-(aq) (04); K_{sp} = [Mg^{2+}(aq)][F^-(aq)]^2 (04)
Take the solubility of MgF_2 in NaF(aq) as s. Equilibrium: [Mg^{2+}] = s, [F^-] = (2s + 0.20) mol dm^{-3} (04 + 01)
K_{sp} = 6.4 × 10^{-9} = s(0.20 + 2s)^2 ≈ s(0.20)^2 (02); s = 1.6 × 10^{-7} mol dm^{-3} (04 + 01)
Moles in 500 cm^3 = 1.6 × 10^{-7} × 0.5 = 8.0 × 10^{-8} mol (04 + 01)
Mass of MgF_2(s) = 8.0 × 10^{-8} × 62 = **4.96 × 10^{-6} g** (04 + 01) · 3(b): 30 marks

Review.

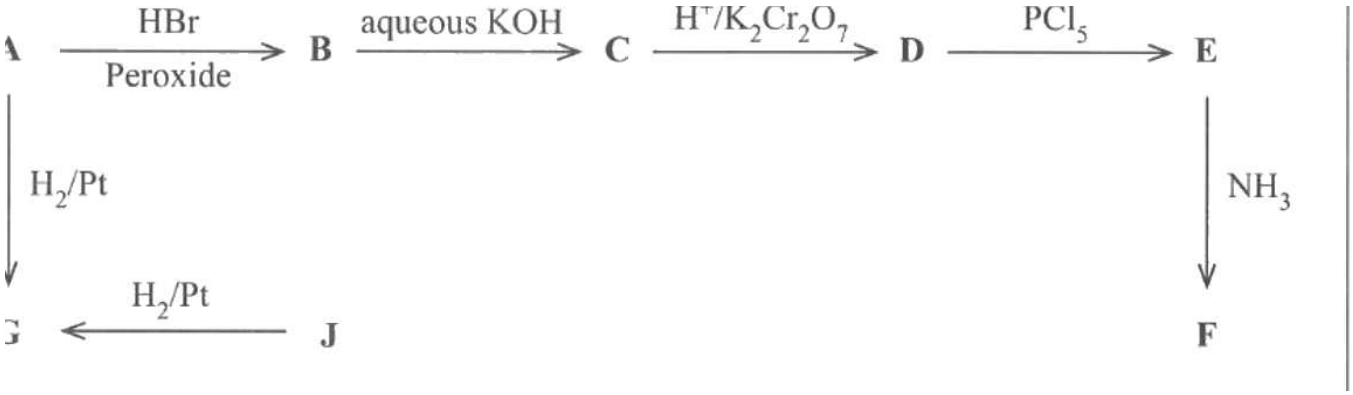
Common-ion effect: the F^- already present lowers the solubility of MgF_2 by about a thousand times compared with pure water.

Read: RB U12 §2.2 · p. 118 RB U12 §2.3 · p. 167 RB U12 §2.4 · p. 175

Question 4 · Part A · structured essay

(a) [60 marks]

Consider the reaction scheme given below, in which: A is a hydrocarbon having the molecular formula C_5H_{10}; D has the molecular formula $C_5H_{10}O_2$. It exhibits optical isomerism. When D is reacted with aqueous Na_2CO_3, CO_2 is liberated; J has the molecular formula C_5H_8. J gives a precipitate with ammoniacal $AgNO_3$.
A —(HBr, peroxide)→ B —(aqueous KOH)→ C —($H^+/K_2Cr_2O_7$)→ D —(PCl_5)→ E —(NH_3)→ F; A —(H_2/Pt)→ G; J —(H_2/Pt)→ G



(i) Draw the structures of A, B, C, D, E, F, G and J in the relevant boxes.

Answer

A: $CH_3CH_2C(CH_3)=CH_2$ · B: $CH_3CH_2CH(CH_3)CH_2Br$ · C: $CH_3CH_2CH(CH_3)CH_2OH$ · D: $CH_3CH_2CH(CH_3)CO_2H$
E: $CH_3CH_2CH(CH_3)COCl$ · F: $CH_3CH_2CH(CH_3)CONH_2$ · G: $CH_3CH_2CH(CH_3)CH_3$ · J: $HC{\equiv}C–CH(CH_3)CH_3$ 06 × 8 = 48 marks

When J is reacted with $HgSO_4$/dil. H_2SO_4, K is formed. K can be converted to G in one (01) step.
(ii) Draw the structure of K and give the reagent/s that can be used to convert K to G.

Answer

K: $CH_3COCH(CH_3)CH_3$ (3-methylbutan-2-one). Reagent: Zn(Hg)/conc. HCl. 06 × 2 = 12 marks When J is wrong, K is also wrong; do not mark independently. 4(a): 60 marks

Review.

HBr with peroxide adds anti-Markovnikov, putting Br on the terminal carbon. Oxidation of the primary alcohol gives the chiral acid D; Clemmensen reduction (Zn(Hg)/HCl) converts C=O to CH_2.

(b) [18 marks]

For the reactions given below, write the type of reaction [nucleophilic addition (A_N), electrophilic addition (A_E), nucleophilic substitution (S_N), electrophilic substitution (S_E), elimination (E)] and the major product.
(i) $CH_3CH=C(CH_3)CH_3 + Br_2$ →
(ii) $CH_3CH_2CH(OH)CH_2CH_3$ —(anhydrous Al_2O_3, heat)→
(iii) $CH_3CH_2CH_2OH + HBr$ →

Answer

(i) A_E · $CH_3CHBr–CBr(CH_3)CH_3$
(ii) E · $CH_3CH=CHCH_2CH_3$
(iii) S_N · $CH_3CH_2CH_2Br$ 03 × 6 = 18 marks

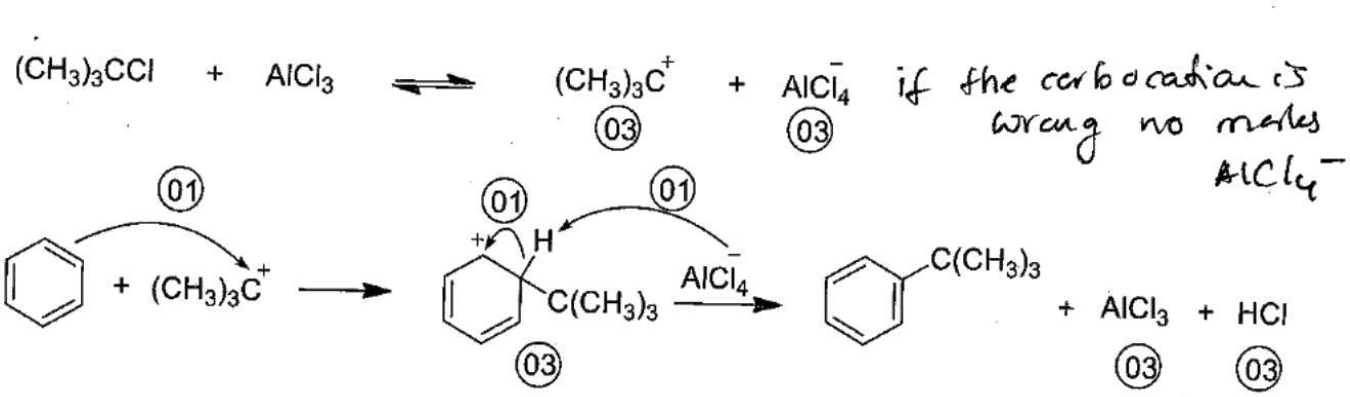
(c) [22 marks]

Draw the structure of the major product L of the reaction given below. Write the mechanism of this reaction.
C_6H_6 + $(CH_3)_3CCl$ —(anhydrous $AlCl_3$)→ L

Answer

L = $C_6H_5C(CH_3)_3$ (tert-butylbenzene) (04)

Mechanism:



$(CH_3)_3CCl + AlCl_3 \rightleftharpoons (CH_3)_3C^+$ (03) + $AlCl_4^-$ (03) (if the carbocation is wrong, no marks for $AlCl_4^-$)
Benzene π electrons attack $(CH_3)_3C^+$ (curly arrow 01) → arenium ion with H and $C(CH_3)_3$ on the same carbon (03); $AlCl_4^-$ removes H^+ (curly arrows 01 + 01) → $C_6H_5C(CH_3)_3$ + $AlCl_3$ (03) + HCl (03). 4(c): 22 marks

Review.

Friedel–Crafts alkylation is an electrophilic substitution. The Lewis acid $AlCl_3$ generates the tertiary carbocation electrophile and is regenerated at the end.

Read: RB U8 §2.2 · p. 33 RB U8 §2.6 · p. 49 RB U9 §3.1 · p. 54 RB U9 §3.5 · p. 66 RB U9 §3.6 · p. 70 RB U8 §2.4 · p. 44

Answer two from each part

Essay · Paper II Parts B and C

Part B

Question 5 · Part B · essay

Scheme note: PHYSICAL STATES ARE NECESSARY.

(a) [60 marks]

At 450 °C, 1.0 mol of $N_2(g)$ and 2.0 mol of $H_2(g)$ were mixed in a 1.0 dm^3 previously evacuated closed-rigid container and allowed to reach the equilibrium given below. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. It was found that 1.0 mol of $NH_3(g)$ was present at the equilibrium.
(i) Calculate the total pressure of the equilibrium system at 450 °C (RT = 6×10^3 J mol^{-1} at 450 °C).

Answer

	$N_2(g)$	$3H_2(g)$	$2NH_3(g)$
Initial con	1.0	2.0	0
Changed con	−x	−3x	2x
Eqm con.	1 − x	2 − 3x	1.0

(04 + 01)

−3

(01 + 01)

2

2

3

−3

(02 + 01)

(03)

3

−1

−3

3

7

(04 + 01) · 18 marks

(ii) Calculate the partial pressures of $N_2(g)$, $H_2(g)$ and $NH_3(g)$ at 450 °C in the equilibrium system.

Answer

Using $P_i = X_{iP}$ (02)
$P_{N2(g)} = (0.5/2) \times 1.20 \times 10^7$ Pa = 3.0×10^6 Pa (03 + 01)
$P_{H2(g)} = (0.5/2) \times 1.20 \times 10^7$ Pa = 3.0×10^6 Pa (03 + 01)
$P_{NH3(g)} = (1.0/2) \times 1.20 \times 10^7$ Pa = 6.0×10^6 Pa (03 + 01) (OR use PV = nRT for the three gases) 14 marks

(iii) Calculate the equilibrium constant K_p of the system at 450 °C.

Answer

$K_p = P^2_{NH3(g)}/(P_{N2(g)}\ P^3_{H2(g)})$ (05) = $(6.0 \times 10^6\ Pa)^2/[(3.0 \times 10^6\ Pa)(3.0 \times 10^6\ Pa)^3]$ = **4.40×10^{-13} Pa^{-2}** (04 + 01)

(iv) Using the value obtained for K_p in (iii) above, calculate the equilibrium constant K_c of the system at 450 °C.

Answer

$K_p = K_c(RT)^{\Delta n}$, $\Delta n = 2 - 4 = -2$, so $K_c = K_p(RT)^2 = 4.44 \times 10^{-13}\ Pa^{-2} \times (6 \times 10^3\ J\ mol^{-1})^2 = 1.6 \times 10^{-5}$ $mol^{-2}\ m^6$ = **16 mol^{-2} dm^6** (check: $K_c = 1.0^2/(0.5 \times 0.5^3) = 16\ mol^{-2}\ dm^6$ from the concentrations).
Prepared answer.

(v) State what changes, if any, take place in the values of partial pressures of $N_2(g)$, $H_2(g)$ and $NH_3(g)$ and the value of K_p, when 1.0 mol of Ar(g) is added to the above system at 450 °C (calculations are **not** required).

Answer

No change in any of them. In a rigid container the volume and temperature are fixed, so adding an inert gas raises the total pressure but leaves the amount and partial pressure of each reacting gas unchanged; Q still equals K_p, and K_p depends only on temperature. Prepared answer.

(b) [60 marks]

Assume that ΔH° and ΔS° of the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ do not change with the temperature.
(i) Predict the effect on the equilibrium concentration of $NH_3(g)$ when the temperature of the system is increased.

Answer

The forward reaction is exothermic, so raising the temperature shifts the equilibrium to the left and the equilibrium concentration of $NH_3(g)$ decreases.

(ii) For the above reaction, $\Delta H° = -90$ kJ mol^{-1} and $\Delta S° = -200$ J K^{-1} mol^{-1}. Show that the prediction you made in (i) above is correct by calculating the ΔG° values of the reaction at 27 °C and 527 °C.

Answer

$\Delta G° = \Delta H° - T\Delta S°$.
At 300 K: $\Delta G° = -90 - 300(-0.200) =$ **-30 kJ mol^{-1}** (negative: products favoured, $K > 1$).
At 800 K: $\Delta G° = -90 - 800(-0.200) =$ **$+70$ kJ mol^{-1}** (positive: reactants favoured, $K < 1$).
ΔG° becomes less negative and then positive as T rises, so less NH_3 is present at the higher temperature.

(iii) Consider the reaction $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ occurring in a closed-rigid container at 450 °C.
I. Predict the effect of increasing the temperature on the value of $[NH_3(g)]^2/([N_2(g)][H_2(g)]^3)$.
II. Comment on the time taken for the reaction above to reach the equilibrium in the presence and absence of a catalyst at 450 °C.
III. Explain your answer in II above.

Answer

I. This ratio is $1/K_c$ for the decomposition, i.e. K_c for NH_3 formation. Decomposition is endothermic, so raising T increases its K and the ratio **decreases**.
II. Equilibrium is reached in a shorter time with a catalyst, but the equilibrium composition is the same.
III. A catalyst provides an alternative pathway with a lower activation energy for both the forward and the backward reactions, increasing both rates by the same factor; it does not change ΔG° or K.

(c) [30 marks]

(i) Define the 'normal boiling point' of a pure liquid.

Answer

The temperature at which the saturated vapour pressure of the liquid equals 1 atm (101 325 Pa).

(ii) Write the equilibrium present at the boiling point of pure $CCl_4(l)$.

Answer

$CCl_4(l) \rightleftharpoons CCl_4(g)$

(iii) Given that, $\Delta H_f°(CCl_4(g)) = -95$ kJ mol^{-1}, $\Delta H_f°(CCl_4(l)) = -128$ kJ mol^{-1}, $S°(CCl_4(g)) = 309$ J K^{-1} mol^{-1}, $S°(CCl_4(l)) = 214$ J K^{-1} mol^{-1}. Calculate the normal boiling point of $CCl_4(l)$.

Answer

$\Delta H°_{vap} = -95 - (-128) = +33$ kJ mol^{-1}; $\Delta S°_{vap} = 309 - 214 = +95$ J K^{-1} mol^{-1}.
At the boiling point $\Delta G = 0$, so $T_b = \Delta H°/\Delta S° = 33\,000/95 =$ **347 K** (about 74 °C).

Review.

Prepared answers for (iv) onwards use $K_p = K_c(RT)^{\Delta n}$, $\Delta G = \Delta H - T\Delta S$, and $\Delta G = 0$ at a phase change.

Read: RB U12 §2.1 · p. 76 RB U4 §1.3 · p. 16 RB U5 §2.4 · p. 53 RB U12 §2.5 · p. 199 RB U11 §1.9 · p. 54

Question 6 · Part B · essay

(a) [75 marks]

Consider the reaction $2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$ at 25 °C. The results of an initial-rate experiment carried out at 25 °C for the reaction above are shown below. $[NO(g)]_0$ and $[Cl_2(g)]_0$ are the initial concentrations of NO(g) and $Cl_2(g)$, respectively.

Experiment	$[NO(g)]_0$/mol dm^{-3}	$[Cl_2(g)]_0$/mol dm^{-3}	$-\Delta[Cl_2(g)]/\Delta t$ /mol dm^{-3} s^{-1}
1	0.25	0.50	0.75
2	0.25	1.00	3.00
3	0.50	2.00	24.00

(i) Write the expressions for the rate of the reaction with respect to each species appearing in the equation of the reaction.

Answer

Rate = $-\frac{1}{2}\,\Delta[NO(g)]/\Delta t = -\Delta[Cl_2(g)]/\Delta t = \frac{1}{2}\,\Delta[NOCl(g)]/\Delta t$

(ii) Write the rate expression/law for the reaction if the order of the reaction with respect to NO(g) and $Cl_2(g)$ are a and b respectively, and the rate constant is k.

Answer

Rate = k[NO(g)]^a[Cl_2(g)]^b

(iii) Calculate the values of a and b and overall order of the reaction.

Answer

Exp 1 → 2: [NO] constant, [Cl_2] ×2, rate ×4, so 2^b = 4 and **b = 2**.
Exp 2 → 3: [NO] ×2, [Cl_2] ×2, rate ×8: 2^a × 2^2 = 8, so **a = 1**. Overall order = a + b = **3**.

(iv) Calculate the rate constant k of the reaction at 25 °C.

Answer

From Exp 1: $0.75 = k(0.25)(0.50)^2$, so $k = 0.75/0.0625 =$ **12 mol^{-2} dm^6 s^{-1}**

(v) Calculate the rate of disappearance of $Cl_2(g)$ at 25 °C when the initial concentrations of NO(g) and $Cl_2(g)$ are 0.50 and 0.10 mol dm^{-3}, respectively.

Answer

Rate = $12 \times 0.50 \times (0.10)^2 =$ **0.060 mol dm^{-3} s^{-1}**

(vi) Calculate the rate of formation of NOCl(g) at 25 °C when the rate of disappearance of Cl_2(g) is 4.5 mol dm^{-3} s^{-1} at 25 °C.

Answer

$\Delta[NOCl]/\Delta t = 2 \times (-\Delta[Cl_2]/\Delta t) = 2 \times 4.5 =$ **9.0 mol dm^{-3} s^{-1}**

(vii) Calculate the rate of formation of NOCl(g) at 25 °C when the initial concentrations of NO(g) and Cl_2(g) are 0.20 and 0.30 mol dm^{-3}, respectively.

Answer

$-\Delta[Cl_2]/\Delta t = 12 \times 0.20 \times (0.30)^2 = 0.216$ mol dm^{-3} s^{-1}; rate of formation of NOCl = $2 \times 0.216 =$ **0.432 mol dm^{-3} s^{-1}**

(b) [35 marks]

The reaction of Cu powder with nitric acid results in the formation of a red-brown gas containing N and O. In an experiment carried out at 33 °C, the produced gas was collected to a 150 cm^3 vessel. The pressure and mass of the gas were 831.4 mm Hg and 0.300 g, respectively. Calculate the molar mass of the produced gas and give its chemical formula. State the assumption/s made. (1 mm Hg = 133.3 Pa, N = 14, O = 16)

Answer

$P = 831.4 \times 133.3 = 1.108 \times 10^5$ Pa; $V = 1.50 \times 10^{-4}$ m^3; T = 306 K.
$n = PV/RT = (1.108 \times 10^5 \times 1.50 \times 10^{-4})/(8.314 \times 306) = 6.53 \times 10^{-3}$ mol.
$M = 0.300/6.53 \times 10^{-3} =$ **46 g mol^{-1}**, so the gas is **NO_2** (14 + 32 = 46).
Assumptions: the gas behaves ideally; the gas is pure NO_2 (no N_2O_4 formed by dimerisation, no water vapour or air).

(c) [15 marks]

Two identical containers A and B, contain equal volumes of pure water and 3.0 mol dm^{-3} glycerol aqueous solution, respectively, at a given temperature. Giving reasons, compare,
(i) the vapour pressures of the contents in A and B.
(ii) the boiling points of the contents in A and B.

Answer

(i) Vapour pressure of A > B. Glycerol is practically non-volatile; in B it lowers the mole fraction of water (and occupies part of the surface), so $P_{water} = x_{water}\, P°_{water}$ is lower.
(ii) Boiling point of B > A. Because B has the lower vapour pressure, it must be heated to a higher temperature before its vapour pressure equals atmospheric pressure.

(d) [25 marks]

At a given temperature, an ideal binary liquid mixture was prepared by mixing liquids C and D in a closed container. At this temperature, vapour pressures of C and D are P_C and P_D respectively, and saturated vapour pressures of C and D are $P°_C$ and $P°_D$ respectively. The mole fractions of C and D in the liquid phase are X_C and X_D respectively.
(i) Derive the expression for the relative lowering of the vapour pressure of C at this temperature.

Answer

Raoult's law: $P_C = X_C\, P°_C$. Relative lowering $= (P°_C - P_C)/P°_C = (P°_C - X_C\, P°_C)/P°_C = 1 - X_C =$ **X_D**.

(ii) A solution was prepared by dissolving 1.0 mol of glycerol in 900 g of water at 25 °C. Calculate I. the relative lowering of the vapour pressure (mm Hg) II. the vapour pressure (mm Hg) of the solution. At 25 °C, saturated vapour pressure of water is 24 mm Hg. (H = 1, O = 16) At 25 °C, saturated vapour pressure of glycerol is negligible.

Answer

n(water) = 900/18 = 50 mol; $X_{glycerol}$ = 1.0/51 = 0.0196.
I. Relative lowering = $X_{glycerol}$ = **0.0196** (a ratio, so it has no units; the actual lowering is 24 × 0.0196 = 0.47 mm Hg).
II. $P_{solution} = X_{water}\ P°_{water}$ = (50/51) × 24 = **23.5 mm Hg**.

Review.

Prepared answers: orders come from initial-rate ratios; stoichiometric factors convert between species rates; molar mass from M = mRT/PV.

Read: RB U11 §1.7.4 · p. 40 RB U11 §1.3 · p. 9 RB U4 §1.2 · p. 5 RB U12 §2.6 · p. 216

Question 7 · Part B · essay

(a) [75 marks]

The following electrochemical cell was constructed to study the electrochemical behaviour of the reaction, $3Cu^{+}(aq) + Au^{3+}(aq) \rightarrow 3Cu^{2+}(aq) + Au(s)$ at 25 °C. The cell consists of an Au(s) electrode in a beaker with 1.0 mol dm^{-3} $Au(NO_3)_3(aq)$ solution and a Pt(s) electrode in another beaker filled with a solution containing 1.0 mol dm^{-3} each of $CuNO_3(aq)$ and $Cu(NO_3)_2(aq)$. The two half-cells were connected via a salt-bridge filled with saturated $KNO_3(aq)$ solution and a voltmeter. $E°(Au^{3+}(aq)/Au(s))$ = 1.50 V and $E°(Cu^{2+}(aq)/Cu^{+}(aq))$ = 0.16 V at 25 °C.

(i) Draw a sketch of the electrochemical cell.

Answer

Two beakers joined by a salt bridge (saturated KNO_3) and an external wire through a voltmeter. Left: Pt electrode in Cu^{+}/Cu^{2+} (1.0 mol dm^{-3} each), labelled anode (−). Right: Au electrode in 1.0 mol dm^{-3} $Au(NO_3)_3$, labelled cathode (+). Arrow for electron flow in the wire from Pt to Au. Cell notation: Pt(s) | $Cu^{+}(aq)$, $Cu^{2+}(aq)$ || $Au^{3+}(aq)$ | Au(s).

(ii) Identify the anode and the cathode of the cell and write the respective half reactions.

Answer

Anode: Pt(s) electrode — $Cu^{+}(aq) \rightarrow Cu^{2+}(aq) + e^{-}$
Cathode: Au(s) electrode — $Au^{3+}(aq) + 3e^{-} \rightarrow Au(s)$

(iii) Identify the positive and negative terminals of this electrochemical cell.

Answer

Positive terminal: Au(s) electrode (cathode). Negative terminal: Pt(s) electrode (anode).

(iv) Calculate $E°_{cell}$ at 25 °C.

Answer

$E°_{cell} = E°_{cathode} - E°_{anode}$ = 1.50 − 0.16 = **+1.34 V**

(v) Does the mass of the Pt(s) electrode increase, decrease or remain the same as the cell operates? Explain your answer.

Answer

It remains the same. Pt is an inert electrode: it only transfers electrons between Cu^{+} and the external circuit and takes no part in the reaction (Cu^{+} is oxidized to Cu^{2+}, which stays in solution).

(vi) State the ionic species present in the Au(s)-half cell before and after the cell operates.

Answer

Before: Au^{3+}(aq), NO_3^−(aq) (with H^+/OH^- from water). After: Au^{3+}(aq) (lower concentration), NO_3^−(aq) and K^+(aq), because K^+ ions move in from the salt bridge to balance the positive charge removed as Au^{3+} is deposited.

(vii) After the cell has operated for 30 minutes at 25 °C, 0.197 g of Au(s) was deposited on the Au(s) electrode. I. Calculate the number of Au moles deposited. (Au = 197 g mol^{-1}) II. Calculate the current (mA) which passed through the cell during the 30 minute period, assuming the current remained constant.

Answer

I. n(Au) = 0.197/197 = **1.0×10^{-3} mol**
II. n(e^-) = $3 \times 1.0 \times 10^{-3} = 3.0 \times 10^{-3}$ mol; Q = $3.0 \times 10^{-3} \times 96\,500 = 289.5$ C; I = Q/t = 289.5/1800 = 0.161 A = **161 mA**

(b) [75 marks]

(i) A, B, C, D and E are coordination compounds. They have an octahedral geometry.
I. Give the structural formulae or draw the structures of these coordination compounds, selecting the appropriate species from the list: Na^+, Cu^+, Cu^{2+}, Br^-, NH_3.
A: An equal number of two types of ligands are coordinated to the metal ion. Its complex ion has a charge of −1.
B: Two types of ligands are coordinated to the metal ion. On addition of $AgNO_3$(aq) to an aqueous solution of B, a pale yellow precipitate soluble in conc. NH_4OH is formed.
C and D: C and D contain the same elements. However, the complex ion of C has a charge of −2, while that of D has a charge of −3.
E: Only one type of ligand is coordinated to the metal ion. E gives two ions in aqueous solution.
Note: A complex ion has one metal ion with multiple ligands coordinated to it.
II. Give the IUPAC name of E.

Answer

I. A: $Na[Cu(NH_3)_3Br_3]$ (Cu^{2+}: +2 − 3 = −1)
B: $[Cu(NH_3)_5Br]Br$ (the Br^- outside the sphere gives pale yellow AgBr)
C: $Na_2[Cu(NH_3)_2Br_4]$ (Cu^{2+}: −2)
D: $Na_3[Cu(NH_3)_2Br_4]$ (Cu^+: −3) ($Na_3[Cu(NH_3)Br_5]$ with Cu^{2+} also fits)
E: $[Cu(NH_3)_6]Br$ (Cu^+; gives $[Cu(NH_3)_6]^+$ and Br^-)
II. E: hexaamminecopper(I) bromide

(ii) X and Y are complex ions of a d-block metal ion M(II). They have a square planar geometry. X: Only ethylenediamine is coordinated to M(II). Y: Ethylenediamine and H_2O are coordinated to M(II). Write the structural formulae of X and Y and draw their structures. (Ethylenediamine NH_2–CH_2–CH_2–NH_2 coordinates through both N atoms; use 'en' in the structural formula.)

Answer

X = $[M(en)_2]^{2+}$: M at the centre of a square, with the four corners occupied by the N atoms of two en ligands, each en forming a five-membered ring (M–N–CH_2–CH_2–N–M).
Y = $[M(en)(H_2O)_2]^{2+}$: one en occupies two adjacent (cis) corners and the two H_2O molecules (bonded through O) occupy the other two corners.

Review.

Prepared answers. Work out the metal's oxidation state from the overall charge; ions outside the square brackets are free in solution and give precipitates (e.g. AgBr).

Read: RB U13 §3.3 · p. 250 RB U13 §3.4 · p. 261 RB U6 §4.10.6 · p. 169

Part C

Question 8 · Part C · essay

(a) [35 marks]

Given below is a reaction scheme for the preparation of compound S using 2-methylpropanamide as the starting compound.
$(CH_3)_2CHCONH_2$ —(Reaction 1)→ P —(Reaction 2)→ Q —(Reaction 3)→ R —(Reaction 4)→ S = $(CH_3)_2CH–CH=N–C_6H_5$
Complete the above reaction scheme by drawing the structures of compounds P, Q and R, and writing the appropriate reagents for reactions 1–4, selecting **only** from the list given below. List of reagents: $LiAlH_4$/dry ether, $NaNO_2$, dil. HCl, Pyridinium chlorochromate (PCC), $C_6H_5NH_2$

Answer

Reaction 1: $LiAlH_4$/dry ether → P = $(CH_3)_2CHCH_2NH_2$
Reaction 2: $NaNO_2$ / dil. HCl → Q = $(CH_3)_2CHCH_2OH$ (with N_2)
Reaction 3: PCC → R = $(CH_3)_2CHCHO$
Reaction 4: $C_6H_5NH_2$ → S (the imine, with loss of H_2O)

Review.

$LiAlH_4$ reduces an amide to a primary amine; a primary aliphatic amine with nitrous acid gives an alcohol and N_2; PCC stops at the aldehyde; amines condense with aldehydes to give imines.

(b) [30 marks]

Consider the reaction of 2-methyl-2-butene with HBr.
(i) Give the structures of the two products that could possibly be formed in this reaction.
(ii) Stating the type of the reaction and considering the mechanism of the reaction, explain which of these two products is the major product.

Answer

(i) $(CH_3)_2CBr–CH_2CH_3$ (2-bromo-2-methylbutane) and $(CH_3)_2CH–CHBrCH_3$ (2-bromo-3-methylbutane).

(ii) Electrophilic addition. In the first (rate-determining) step H^+ adds to one carbon of the C=C, forming a carbocation. Adding H^+ to C3 gives the tertiary carbocation $(CH_3)_2C^+–CH_2CH_3$; adding it to C2 gives the secondary carbocation $(CH_3)_2CH–C\text{^}+HCH_3$. The tertiary carbocation is more stable (three alkyl groups release electrons and spread the positive charge), so it forms faster, and Br^- then attacks it. Major product: **2-bromo-2-methylbutane** (Markovnikov's rule).

(c) [50 marks]

Consider the two compounds, phenol and acetic acid.
(i) State which of these two compounds is more acidic.
(ii) Write the chemical equations for the equilibria existing in aqueous medium for each of the compounds.
(iii) Draw the resonance structures of the organic chemical species written in the answer to (ii) above.
(iv) Considering the resonance structures, explain your answer to (i) above.

Answer

(i) Acetic acid is more acidic.

(ii) $CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$
$C_6H_5OH(aq) + H_2O(l) \rightleftharpoons C_6H_5O^-(aq) + H_3O^+(aq)$

(iii) Acetate ion: two equivalent structures, $CH_3–C(=O)–O^-$ ↔ $CH_3–C(–O^-)=O$. Acetic acid: $CH_3–C(=O)–OH$ ↔ $CH_3–C(–O^-)=O\text{^}+H$ (charge-separated, minor).

Phenoxide ion: negative charge on O, and (with C=O^ formed) on the two ortho carbons and the para carbon, plus the two Kekulé forms. Phenol: the two Kekulé forms plus charge-separated forms with O^+ and negative charge on the ortho and para carbons.

(iv) In the acetate ion the negative charge is shared equally between two highly electronegative O atoms in two equivalent structures, so the ion is strongly stabilised. In the phenoxide ion the charge is delocalised partly onto ring carbons, which are less electronegative, so those structures contribute less and the ion is less stabilised. Phenol itself is also stabilised by charge-separated structures that are lost on ionisation. The more stable the conjugate base, the further the equilibrium lies to the right, so acetic acid is the stronger acid.

(d) [35 marks]

Show how you would carry out the following conversion in not more than five (05) steps: benzene → C_6H_5–$CH(CH_3)$–O–CO–C_6H_4–NO_2 (meta).

Answer

1. CH_3COCl / anhydrous $AlCl_3$ → acetophenone, $C_6H_5COCH_3$ (use part of it in each branch)
2. (branch A) $NaBH_4$ (or $LiAlH_4$, then H^+/H_2O) → 1-phenylethanol, $C_6H_5CH(OH)CH_3$
2. (branch B) conc. HNO_3 / conc. H_2SO_4 → 3-nitroacetophenone (–$COCH_3$ directs meta)
3. $KMnO_4$ / H^+, heat → 3-nitrobenzoic acid
4. PCl_5 → 3-nitrobenzoyl chloride
5. 3-nitrobenzoyl chloride + 1-phenylethanol → the ester (+ HCl)

Review.

Prepared answer. Any order of nitration and side-chain oxidation works, because both –$COCH_3$ and –COOH direct meta. An acid chloride gives the ester more completely than the acid with conc. H_2SO_4.

Read: RB U10 §4.1 · p. 75 RB U9 §3.4 · p. 60 RB U8 §2.2 · p. 33 RB U9 §3.2 · p. 58 RB U9 §3.5 · p. 66 RB U8 §2.4 · p. 44 RB U8 §2.5 · p. 49

Question 9 · Part C · essay

(a) [75 marks]

An aqueous solution Y contains four cations P, Q, R and S. The following experiments were carried out in sequence to identify these cations.

	Experiment	Observation
1	Y was acidified with dil. HCl.	a white precipitate (P_1)
2	P_1 was separated by filtration and H_2S was bubbled through the resulting filtrate.	no precipitate
3	The above filtrate was boiled to completely remove the H_2S. A few drops of conc. HNO_3 were added, the solution was boiled, cooled and NH_4Cl/NH_4OH were added.	a brown precipitate (Q_1)
4	Q_1 was separated by filtration and H_2S was bubbled through the resulting filtrate.	a black precipitate (R_1)

	Experiment	Observation
5	R_1 was separated by filtration, the resulting filtrate was boiled to completely remove the H_2S, cooled and NH_4Cl/NH_4OH were added. This solution was warmed and $(NH_4)_2CO_3$(aq) was added in excess.	a white precipitate (S_1)

Precipitate	Test	Observation
P_1	dil. NH_4OH was added to P_1. The following solutions were added separately to aliquots of P_2. I. KI(aq) II. $Na_2S_2O_3$(aq)/Δ	a colourless solution (P_2); I. a dark yellow precipitate (P_3); II. a black precipitate (P_4)
Q_1	Q_1 was dissolved in dil. HNO_3. To aliquots: I. NH_4SCN(aq) II. $K_4[Fe(CN)_6]$(aq)	I. a deep red solution (Q_2); II. a dark blue precipitate (Q_3)
R_1	R_1 was dissolved in warm dil. HCl, cooled. To aliquots: I. a few drops of dil. NH_4OH II. excess dil. NH_4OH III. a few drops of dil. NH_4OH/dimethylglyoxime (DMG)	I. a green precipitate (R_2); II. a deep blue solution (R_3); III. a deep red precipitate (R_4)
S_1	S_1 was dissolved in dil. HCl. To aliquots: I. dil. H_2SO_4 II. K_2CrO_4(aq). S_1 was subject to the flame test.	I. a white precipitate that was insoluble in dil. HNO_3 (S_2); II. a yellow precipitate (S_3); a pale green flame

1

4

1

3

1

4

1

3

Answer

Cation	Species
P = Ag^+	P_1 AgCl · P_2 $[Ag(NH_3)_2]^+$ · P_3 AgI · P_4 Ag_2S
Q = Fe^{3+} (Fe^{2+} is also consistent, being oxidized by conc. HNO_3)	Q_1 $Fe(OH)_3$ · Q_2 $[Fe(SCN)(H_2O)_5]^{2+}$ · Q_3 $Fe_4[Fe(CN)_6]_3$ (Prussian blue)
R = Ni^{2+}	R_1 NiS · R_2 $Ni(OH)_2$ · R_3 $[Ni(NH_3)_6]^{2+}$ · R_4 $Ni(DMG)_2$
S = Ba^{2+}	S_1 $BaCO_3$ · S_2 $BaSO_4$ · S_3 $BaCrO_4$

Review.

Group separation: HCl precipitates Ag^{+} (as AgCl, soluble in ammonia); H_2S in acid precipitates nothing here; NH_4Cl/NH_4OH precipitates $Fe(OH)_3$; H_2S in basic solution precipitates NiS; $(NH_4)_2CO_3$ precipitates $BaCO_3$. DMG is a specific test for Ni^{2+}; the pale green flame confirms Ba.

(b) [75 marks]

The mineral named siderite, contains mainly $FeCO_3$. Siderite is formed when calcium ions (Ca^{2+}) of $CaCO_3$ in limestone are replaced by ferrous ions (Fe^{2+}) over a long period of time. Therefore, $FeCO_3$ in siderite is mixed with $CaCO_3$. In addition, siderite also contains impurities such as silica in small quantities.
8.5 g of such a siderite sample was thermally decomposed at 900 °C under oxygen free conditions until a constant mass was obtained. The mass of the remaining sample was 5.2 g. During thermal decomposition, $CaCO_3$ is converted to CaO and $FeCO_3$ is converted to FeO.
Another 1.7 g of the above siderite sample was dissolved in excess dilute H_2SO_4 acid, filtered, and the resulting solution was diluted to 100.00 cm^3 with distilled water. When 25.00 cm^3 of the resulting solution was titrated with 0.04 mol dm^{-3} $KMnO_4$, the end-point reading of $KMnO_4$ was 12.50 cm^3.
Assume that the quantities of metals other than Fe and Ca in the siderite sample are negligible. (C = 12, O = 16, Ca = 40, Fe = 56)

(i) Calculate the mass percentage of $CaCO_3$ in the siderite sample.

Answer

$MnO_4\text{^}- + 5Fe^{2+} + 8H^{+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$
$n(MnO_4\text{^}-) = 0.04 \times 0.01250 = 5.0 \times 10^{-4}$ mol → Fe^{2+} in 25.00 cm^3 = 2.5×10^{-3} mol → in 100.00 cm^3 (1.7 g sample) = 1.0×10^{-2} mol.
In 8.5 g: $n(FeCO_3) = 5 \times 1.0 \times 10^{-2} = 0.050$ mol (5.80 g).
Mass lost on heating = 8.5 − 5.2 = 3.3 g of CO_2 = 0.075 mol. $FeCO_3$ gives 0.050 mol CO_2, so $CaCO_3$ gives 0.025 mol.
$m(CaCO_3) = 0.025 \times 100 = 2.50$ g → **% $CaCO_3$ = 2.50/8.5 × 100 = 29.4%**

(ii) Calculate the percentage of impurities, other than $CaCO_3$, in the siderite sample.

Answer

Impurities (other than $FeCO_3$ and $CaCO_3$) = 8.5 − 5.80 − 2.50 = 0.20 g → **2.35%** ($FeCO_3$ is 68.2%).

(iii) When 8.5 g of the siderite sample was thermally decomposed in the presence of oxygen, $FeCO_3$ decomposes giving Fe_2O_3 and Fe_3O_4 in 1:1 molar ratio whereas $CaCO_3$ decomposes to CaO. Calculate the mass of the remaining residue after this thermal decomposition.

Answer

Let x mol each of Fe_2O_3 and Fe_3O_4: Fe atoms 2x + 3x = 0.050, so x = 0.010 mol.
Fe_2O_3 = 0.010 × 160 = 1.60 g; Fe_3O_4 = 0.010 × 232 = 2.32 g; CaO = 0.025 × 56 = 1.40 g; impurities 0.20 g.
Residue = 1.60 + 2.32 + 1.40 + 0.20 = 5.52 g

Review.

Prepared answer. Iron(II) is found by $KMnO_4$ titration (1 : 5); the mass loss on heating is CO_2 from both carbonates; silica stays unchanged.

Read: RB U6 §4.10 · p. 160 RB U6 §4.2 · p. 126 RB U3 §3.8 · p. 115 RB U12 §2.4 · p. 175

Question 10 · Part C · essay

(a) [50 marks]

Consider the industrial manufacture of TiO_2.
(i) Name the process by which TiO_2 is produced from rutile.
(ii) Name the required raw materials (other than rutile) for the above process.
(iii) Name the **two** main steps associated with the above process.
(iv) Give balanced chemical equations for the reactions which take place under each of the above mentioned steps.
(v) Explain how the above process contributes to Global Warming.

Answer

(i) The chloride process
(ii) Coke (carbon), chlorine gas and oxygen (air)
(iii) 1. Chlorination 2. Oxidation
(iv) Chlorination (about 950 °C): $TiO_2(s) + 2C(s) + 2Cl_2(g) \rightarrow TiCl_4(g) + 2CO(g)$ (also written with CO_2: $TiO_2 + C + 2Cl_2 \rightarrow TiCl_4 + CO_2$)
Oxidation: $TiCl_4(g) + O_2(g) \rightarrow TiO_2(s) + 2Cl_2(g)$ (the Cl_2 is recycled)
(v) Coke is oxidized to CO/CO_2 in the chlorination step, and fossil fuels are burned to reach the high temperatures; CO_2 is a greenhouse gas.

(b) [50 marks]

NO, NO_2, SO_2, CH_4, CF_2Cl_2 and CF_2HCl are among the pollutants that contribute to various environmental problems. Except for the two halogenated compounds, the others are released into the environment through both natural processes and human activities.
(i) State **two** natural processes and **two** human activities that release NO to the environment.

Answer

Natural: lightning ($N_2 + O_2 \rightarrow 2NO$); bacterial action in soil (nitrification/denitrification); volcanic activity; forest fires.
Human: high-temperature combustion in vehicle engines; thermal power stations and industrial furnaces; burning biomass.

(ii) Acid rain, global warming, ozone layer depletion and photochemical smog are four major atmospheric problems. Briefly describe each of these phenomena and identify **two** gases each from the above list that make a **significant contribution** to each of the phenomena.

Answer

Acid rain

2

x

2

4

3

2

2

Global warming

4

2

2

2

Ozone layer depletion

2

2

2

Photochemical smog

x

3

2

(iii) Explain why CF_2HCl was introduced as an alternative to CF_2Cl_2 as an attempt to protect the ozone layer.

Answer

CF_2HCl (an HCFC) contains a C–H bond, so it is attacked by OH radicals and decomposes largely in the troposphere. Less of it reaches the stratosphere, and it has fewer Cl atoms per molecule, so its ozone-depleting potential is much lower than that of CF_2Cl_2.

(iv) In an industrial zone where sulfur containing coal is used as a fuel, it is reported that fish are dying in nearby lakes. Giving reasons suggest a suitable method to control this environmental problem.

Answer

SO_2 from burning the coal forms acid rain, lowering the pH of the lakes (and releasing toxic Al^{3+}), which kills fish. Control: remove SO_2 from the flue gases by scrubbing with lime or limestone slurry (flue-gas desulfurization: $CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2$, then oxidation to $CaSO_4$), or remove sulfur from the coal before burning, or switch to low-sulfur fuel. Adding lime to the lakes neutralizes the acidity in the short term.

(c) [50 marks]

(i) I. Give the classification of polymers according to the type of reaction taking place during the polymerization process. II. Draw **two** structures each, for each of the classes of polymers you stated in (I) above.

Answer

I. Addition polymers and condensation polymers.
II. Addition: polyethene $–[CH_2–CH_2]_n–$; PVC $–[CH_2–CHCl]_n–$ (also polystyrene, Teflon $–[CF_2–CF_2]_n–$).
Condensation: nylon-6,6 $–[NH–(CH_2)_6–NH–CO–(CH_2)_4–CO]_n–$; polyester (Terylene) $–[O–CH_2CH_2–O–CO–C_6H_4–CO]_n–$ (also Bakelite).

(ii) I. Draw the structure of the repeating unit of natural rubber. II. Write the name of the process that is used to change the elastic property of natural rubber and name the substance used in the process.

Answer

I. $–[CH_2–C(CH_3)=CH–CH_2]_n–$ (cis-polyisoprene; CH_3 and H on the same side of each C=C)
II. Vulcanization, using sulfur.

(iii) I. Give a balanced chemical equation to show the synthesis of biodiesel using a triglyceride and methanol. II. Write the name given to the type of reaction used in the production of biodiesel. III. Calculate the mass of biodiesel produced from 7.22 g of the triglyceride of $CH_3(CH_2)_{12}COOH$. (H = 1, C = 12, O = 16)

Answer

I. $CH_2(OCOR)–CH(OCOR)–CH_2(OCOR) + 3CH_3OH \rightarrow 3RCOOCH_3 + CH_2(OH)–CH(OH)–CH_2(OH)$ (NaOH/KOH catalyst)
II. Transesterification
III. Acid $C_{14}H_{28}O_2$, M = 228; triglyceride M = 3(228) + 92 − 3(18) = 722 g mol^{-1}; n = 7.22/722 = 0.010 mol. Methyl ester $CH_3(CH_2)_{12}COOCH_3$, M = 242; mass = 3 × 0.010 × 242 = **7.26 g**

Review.

Prepared answer from RB Unit 14 (TiO_2 chloride process, polymers, biodiesel, air pollution).

Read: RB U14 §1.9 · p. 31 RB U14 §1.13 · p. 58 RB U14 §1.11 · p. 37 RB U14 §1.4 · p. 14

2024 · Chemistry Digital Paper

50 questions · 2 hours

MCQ · Paper I

Question 1 · Q1–30 · single answer

Which of the following chemical species is expected to have the **highest** boiling point?

- (1)He
- (2)Ne
- (3)CH_4
- (4)N_2
- (5)CO

Answer and review

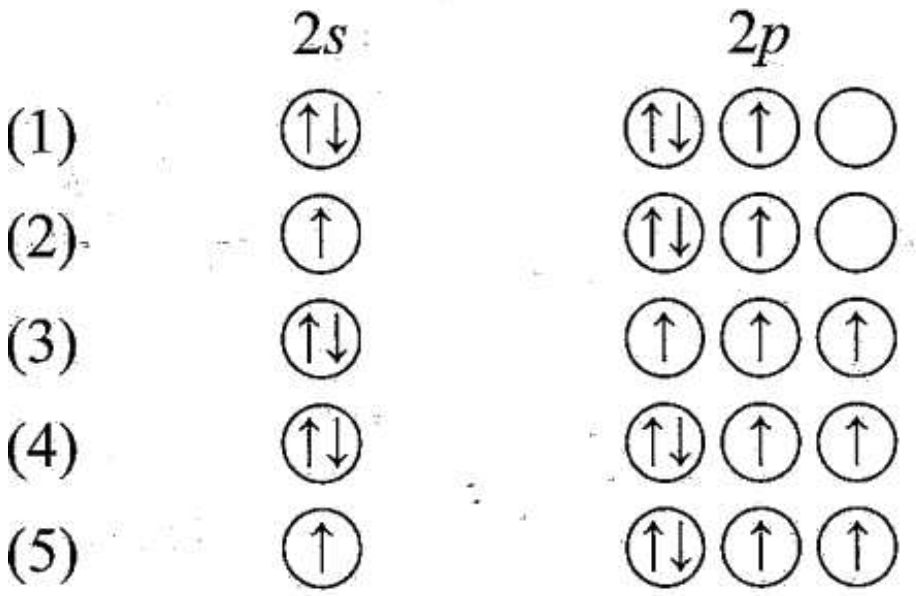
Answer **(5)** Official marking scheme

The official answer is CO: it has the largest molar mass with N_2 (28) and, unlike the other species, a permanent dipole, so it has dipole–dipole forces as well as London forces. (Note: measured data put CH_4 (−162 °C) above CO (−192 °C), because CH_4 is a larger, more polarizable molecule; the scheme's answer follows the reasoning above.)

RB U2 §2.6 · p. 79

Question 2 · Q1–30 · single answer

The orbital diagram in which both Aufbau principle and Hund's rule are violated is



Answer and review

Answer **(2)** Official marking scheme

Aufbau is broken when 2p fills before 2s is complete (2s has only one electron). Hund's rule is broken when electrons pair in one 2p orbital while another 2p orbital is empty. Diagram (2) has both faults.

RB U1 §1.4 · p. 23

Question 3 · Q1–30 · single answer

In an atom, how many orbitals can have the quantum numbers n = 3, $m_l = -1$ and n = 4, $m_l = -1$?

- (1)2
- (2)3
- (3)4
- (4)5
- (5)6

Answer and review

Answer **(4)** Official marking scheme

$m_l = -1$ needs l ≥ 1. For n = 3: l = 1, 2 (2 orbitals). For n = 4: l = 1, 2, 3 (3 orbitals). Total 5.

RB U1 §1.3 · p. 17

Question 4 · Q1–30 · single answer

The de Broglie wavelengths of two particles X and Y are 1 nm and 3 nm respectively. If the mass of X is three times the mass of Y, the ratio of kinetic energies of X and Y (X:Y) would be

- (1)1 : 4
- (2)1 : 3
- (3)3 : 4
- (4)3 : 1
- (5)4 : 1

Answer and review

Answer **(4)** Official marking scheme

$\lambda = h/\sqrt{(2mE_k)}$, so $E_k = h^2/(2m\lambda\text{^}2)$. $E_X/E_Y = (m_Y\ \lambda_Y^2)/(m_X\ \lambda_X^2) = (1 \times 9)/(3 \times 1) = 3$, so 3 : 1.

RB U1 §1.2 · p. 13

Question 5 · Q1–30 · single answer

What is the IUPAC name of the following compound? $CH_3CH(NH_2)CH(OH)CH_2CH_2Cl$

- (1)2-amino-5-chloro-3-pentanol
- (2)4-amino-1-chloro-3-pentanol
- (3)5-chloro-3-hydroxy-2-pentanamine
- (4)1-chloro-3-hydroxy-4-pentanamine
- (5)2-amino-5-chloro-3-hydroxypentane

Answer and review

Answer **(2)** Official marking scheme

–OH has priority over –NH_2, so the name ends in -ol. OH is on C3 from either end; the substituents then get the lowest set {1, 4} by numbering from the Cl end: 4-amino-1-chloropentan-3-ol.

RB U7 §1.3 · p. 7

Question 6 · Q1–30 · single answer

At temperature 25 °C, the pH of a saturated solution of metal hydroxide $M(OH)_2$ is (K_{sp} of $M(OH)_2$ at 25 °C = 4×10^{-12} mol^3 dm^{-9})

- (1)2
- (2)4
- (3)7
- (4)10
- (5)12

Answer and review

Answer **(4)** Official marking scheme

$K_{sp} = 4s^3 = 4 \times 10^{-12}$, so $s = 1 \times 10^{-4}$ mol dm^{-3} and $[OH^-] = 2 \times 10^{-4}$ mol dm^{-3}. pOH = 3.7, pH ≈ 10.3, closest to 10.

RB U12 §2.4 · p. 175

Question 7 · Q1–30 · single answer

The shapes of IO_3^+, $NFCl_2$, F_3ClO_2 and F_4BrO^- are respectively

- (1)trigonal planar, trigonal pyramidal, square pyramidal and trigonal bipyramidal.
- (2)trigonal pyramidal, trigonal planar, square pyramidal and trigonal bipyramidal.
- (3)trigonal pyramidal, T-shape, trigonal bipyramidal and square pyramidal.
- (4)T-shape, trigonal planar, trigonal bipyramidal and square pyramidal.
- (5)trigonal planar, trigonal pyramidal, trigonal bipyramidal and square pyramidal.

Answer and review

Answer **(5)** Official marking scheme

Count electron domains on the central atom. IO_3^+: three I=O, no lone pair → trigonal planar. $NFCl_2$: three bonds + one lone pair → trigonal pyramidal. F_3ClO_2: five bonds, no lone pair → trigonal bipyramidal. F_4BrO^-: five bonds + one lone pair → square pyramidal.

RB U2 §2.3 · p. 52

Question 8 · Q1–30 · single answer

Select the **incorrect** statement.

- (1)Among the chemical species NCl_3, SO_3 and PCl_5 the only polar species is NCl_3.
- (2)Among the elements Mg, Al, Si and P, the lowest first ionization energy is shown by Al.

- (3)Among the elements B, C and O, the lowest negative value for electron gain energy is shown by C.
- (4)Among the chemical species NO_3^−, SO_3, SO_3^{2-} and ClF_3, only NO_3^− and SO_3 have the same shape.
- (5)Among the ions Li^+, Na^+, Be^{2+} and Mg^{2+}, the largest difference in size is between Na^+ and Be^{2+}.

Answer and review

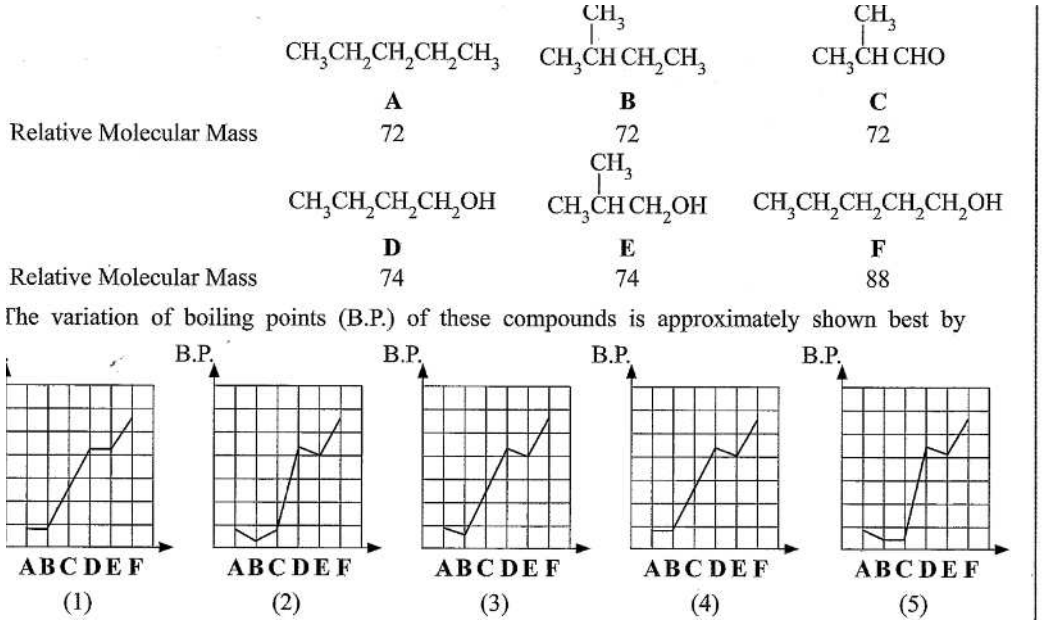
Answer **(3)** Official marking scheme

Electron gain energies: B about −27, C about −122, O about −141 kJ mol^{-1}. The least negative value belongs to B, not C. The other statements are correct (NO_3^− and SO_3 are both trigonal planar; Al has the lowest IE_1 of Mg–P).

RB U1 §1.6 · p. 32 RB U2 §2.3 · p. 52

Question 9 · Q1–30 · single answer

Consider the following compounds, A, B, C, D, E and F (relative molecular mass in brackets): A $CH_3CH_2CH_2CH_2CH_3$ (72); B $(CH_3)_2CHCH_2CH_3$ (72); C $(CH_3)_2CHCHO$ (72); D $CH_3CH_2CH_2CH_2OH$ (74); E $(CH_3)_2CHCH_2OH$ (74); F $CH_3CH_2CH_2CH_2CH_2OH$ (88). The variation of boiling points (B.P.) of these compounds is approximately shown best by



- (1)Graph (1)
- (2)Graph (2)
- (3)Graph (3)
- (4)Graph (4)
- (5)Graph (5)

Answer and review

Answer **(3)** Official marking scheme

Alkanes A and B have only London forces (branched B lower, 28 °C vs 36 °C). The aldehyde C adds dipole–dipole forces (64 °C). The alcohols form hydrogen bonds and boil much higher: branched E (108 °C) below D (118 °C), and the larger F (138 °C) highest.

RB U2 §2.6 · p. 79 RB U9 §3.1 · p. 54

Question 10 · Q1–30 · single answer

At a given temperature, a catalyst increases the rate of a reaction by

- (1)increasing the number of high energy collisions of reactant molecules.
- (2)increasing kinetic energy of reactant molecules.
- (3)increasing number of collisions among reactant molecules.
- (4)increasing the activation energy of the reaction.
- (5)providing a new pathway for the reaction.

Answer and review

Answer **(5)** Official marking scheme

A catalyst provides an alternative pathway with a lower activation energy, so a larger fraction of collisions is successful. It does not change the kinetic energy of the molecules or the collision frequency.

RB U11 §1.9 · p. 54

Question 11 · Q1–30 · single answer

$FeCl_3(s)$ reacts with $NH_3(g)$ and $H_2O(l)$ to produce $Fe(OH)_3$ and NH_4Cl. When 97.5 g of $FeCl_3(s)$, 34 g of $NH_3(g)$ and 27 g of $H_2O(l)$ are made to react, the maximum quantity of $Fe(OH)_3$ that can be obtained is (H = 1, N = 14, O = 16, Cl = 35.5, Fe = 56)

- (1)21.3 g
- (2)23.8 g
- (3)53.5 g
- (4)63.9 g
- (5)71.3 g

Answer and review

Answer **(3)** Official marking scheme

$FeCl_3 + 3NH_3 + 3H_2O \rightarrow Fe(OH)_3 + 3NH_4Cl$. $FeCl_3$ = 0.60 mol, NH_3 = 2.0 mol, H_2O = 1.5 mol. Water is limiting (1.5/3 = 0.50 mol of product), so $Fe(OH)_3$ = 0.50 × 107 = 53.5 g.

RB U3 §3.8 · p. 115

Question 12 · Q1–30 · single answer

Bond energies of H–H, Cl–Cl and H–Cl are 436, 242 and 431 kJ mol^{-1} respectively. Enthalpy change (kJ mol^{-1}) of the reaction $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow HCl(g)$ is

- (1)−184
- (2)−92
- (3)92
- (4)184
- (5)247

Answer and review

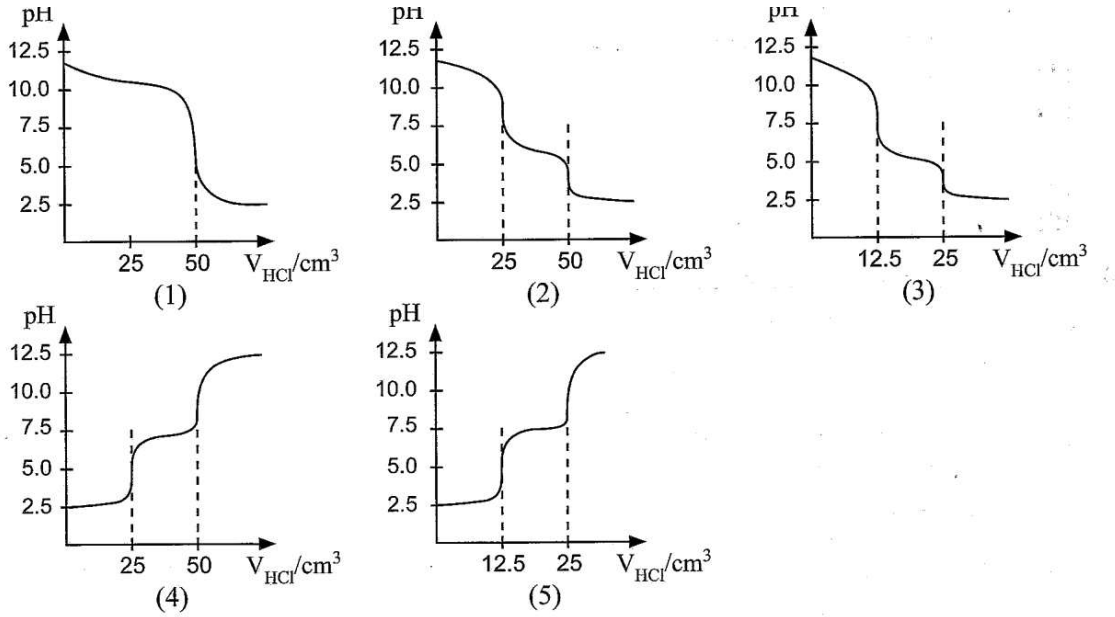
Answer **(2)** Official marking scheme

$\Delta H = \Sigma(\text{bonds broken}) - \Sigma(\text{bonds formed}) = ½(436) + ½(242) - 431 = 339 - 431 = -92$ kJ mol^{-1}.

RB U5 §2.2 · p. 36

Question 13 · Q1–30 · single answer

Which of the following figures correctly represents the titration curve when 0.100 mol dm^{-3} HCl(aq) is added to 25.00 cm^3 of 0.05 mol dm^{-3} CO_3^{2-}(aq) solution?



Answer and review

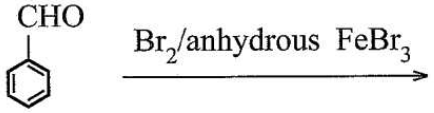
Answer **(3)** Official marking scheme

$n(CO_3^{2-}) = 1.25 \times 10^{-3}$ mol. The pH falls in two steps: $CO_3^{2-} + H^+ \rightarrow HCO_3^-$ (first end point at 12.5 cm^3 of 0.100 mol dm^{-3} HCl), then $HCO_3^- + H^+ \rightarrow H_2CO_3$ (second end point at 25 cm^3). Graph (3) has both end points at the right volumes.

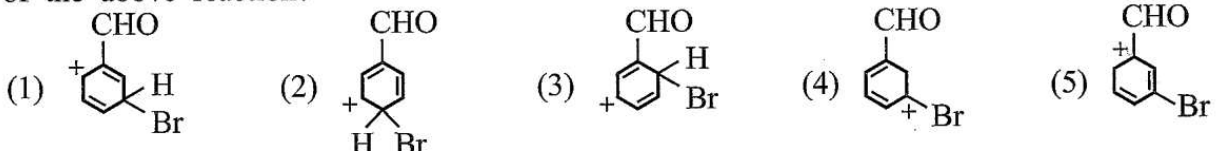
RB U12 §2.2 · p. 118

Question 14 · Q1–30 · single answer

Consider the following reaction: benzaldehyde (C_6H_5CHO) + Br_2/anhydrous $FeBr_3$. Which of the following is a resonance structure of the intermediate which gives the major product of the above reaction?



Which of the following is a resonance structure of the intermediate which gives the major product of the above reaction?



Answer and review

Answer **(1)** Official marking scheme

–CHO withdraws electrons and directs the electrophile to the meta position. In the arenium ion from meta attack, the positive charge is spread over the carbons ortho and para to the attacked carbon, and never sits on the carbon carrying –CHO. Structure (1) is one of these resonance forms.

RB U8 §2.5 · p. 49

Question 15 · Q1–30 · single answer

Consider the reaction of $KMnO_4(aq)$ with $H_2O_2(l)$ in the presence of dilute $H_2SO_4(aq)$. The correct co-efficients of the reactants when the chemical equation of the reaction is balanced with the smallest whole number co-efficients are ($MnO_4\text{^}-(aq)$, $H_2O_2(l)$, $H^+(aq)$)

- (1)2, 3, 10
- (2)2, 4, 6
- (3)2, 5, 6
- (4)2, 5, 8
- (5)2, 5, 16

Answer and review

Answer **(3)** Official marking scheme

$MnO_4\text{^}- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ (×2); $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$ (×5). Sum: $2MnO_4\text{^}- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$.

RB U3 §3.6 · p. 105

Question 16 · Q1–30 · single answer

A first-order gas phase reaction A(g) → B(g) + C(g) occurs in a closed container at a given temperature. The half-life ($t_{½}$) of the reaction is 20 s when the initial pressure is 100 kPa. The half-life of the reaction when the initial pressure is 200 kPa at the same temperature is

- (1)10 s
- (2)20 s
- (3)40 s
- (4)400 s
- (5)800 s

Answer and review

Answer **(2)** Official marking scheme

For a first-order reaction $t_{½} = 0.693/k$, which does not depend on the initial concentration or pressure. At the same temperature k is unchanged, so $t_{½}$ is still 20 s.

RB U11 §1.7.4 · p. 40

Question 17 · Q1–30 · single answer

Consider the reactions shown below.
$H_2(g) + ½O_2(g) \rightarrow H_2O(g)$; $\Delta H = -241.8$ kJ mol^{-1}
$H_2(g) + ½O_2(g) \rightarrow H_2O(l)$; $\Delta H = -285.8$ kJ mol^{-1}
Enthalpy change of vaporization (kJ mol^{-1}) of water is

- (1)−88
- (2)−44
- (3)0
- (4)44
- (5)88

Answer and review

Answer **(4)** Official marking scheme

$H_2O(l) \rightarrow H_2O(g)$: $\Delta H = -241.8 - (-285.8) = +44$ kJ mol^{-1} (Hess's law). Vaporization is endothermic.

RB U5 §2.2 · p. 36

Question 18 · Q1–30 · single answer

When solutions of reactants A and B are mixed in a beaker, a spontaneous reaction takes place with the lowering of the temperature of the mixture. Which of the following is correct for the reaction between A and B? (ΔH, ΔS)

- (1)−, +
- (2)−, −
- (3)−, 0
- (4)+, −
- (5)+, +

Answer and review

Answer **(5)** Official marking scheme

The temperature falls, so the reaction absorbs heat: $\Delta H > 0$. It is still spontaneous ($\Delta G < 0$), which is possible only if $T\Delta S > \Delta H$, so ΔS must be positive.

RB U5 §2.4 · p. 53

Question 19 · Q1–30 · single answer

Select the correct statement with regard to the given reaction. $CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3\hat{}+(aq) + OH^-(aq)$

- (1)$CH_3NH_2(aq)$ behaves as a Lewis-acid in the forward reaction while $CH_3NH_3\hat{}+(aq)$ behaves as a Lewis-base in the reverse reaction.
- (2)$H_2O(l)$ behaves as a Lewis-base in the forward reaction while $OH^-(aq)$ behaves as a Lewis-base in the reverse reaction.
- (3)$CH_3NH_2(aq)$ behaves as a Lewis-base in the forward reaction while $OH^-(aq)$ behaves as a Lewis-acid in the reverse reaction.

- (4)$H_2O(l)$ behaves as a Lewis-acid in the forward reaction while $CH_3NH_3\hat{}+(aq)$ behaves as a Lewis-base in the reverse reaction.
- (5)$CH_3NH_2(aq)$ behaves as a Lewis-base in the forward reaction while $OH^-(aq)$ behaves as a Lewis-base in the reverse reaction.

Answer and review

Answer **(5)** Official marking scheme

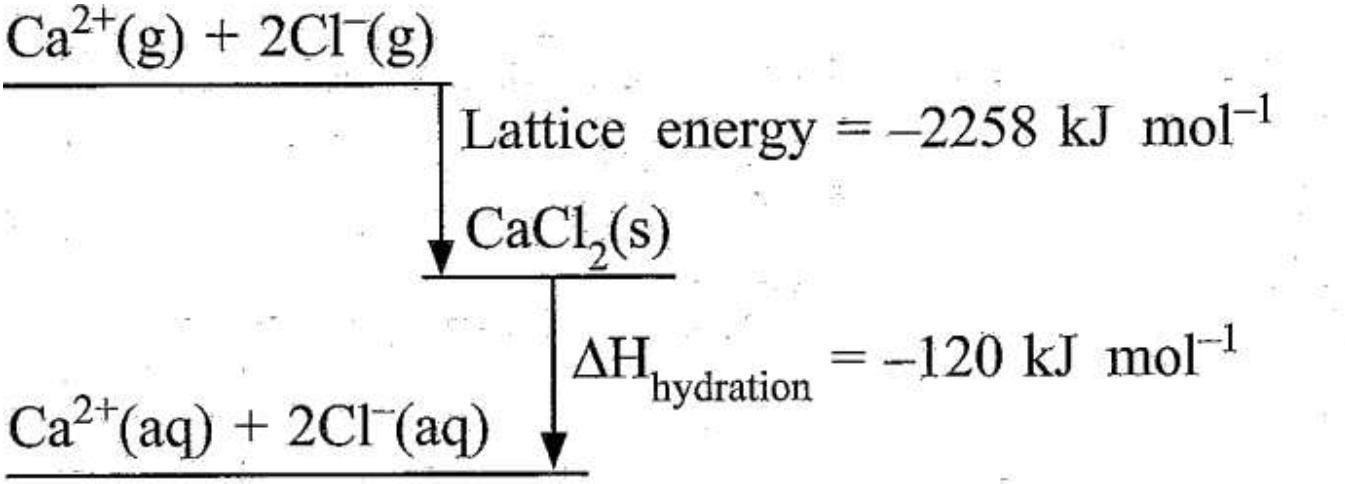
A Lewis base donates a lone pair. In the forward reaction the N lone pair of CH_3NH_2 accepts H^+ from water; in the reverse reaction the lone pair of OH^- takes H^+ from $CH_3NH_3\hat{}+$. Both are Lewis bases.

RB U12 §2.2 · p. 118

Question 20 · Q1–30 · single answer

Consider the enthalpy diagram shown below.

The enthalpy change of hydration of $Ca^{2+}(g)$ is −1650 kJ mol^{-1}. The hydration enthalpy change of $Cl^-(g)$ (kJ mol^{-1}) is



- (1)−728
- (2)−364
- (3)364
- (4)728
- (5)2378

Answer and review

Answer **(2)** Official marking scheme

The diagram shows ΔH(solution) of $CaCl_2$ = −120 kJ mol^{-1} = (lattice dissociation, +2258) + $\Delta H_{hyd}(Ca^{2+})$ + $2\Delta H_{hyd}(Cl^-)$. So −120 = 2258 − 1650 + 2x, giving 2x = −728 and x = −364 kJ mol^{-1}.

RB U5 §2.3 · p. 51

Question 21 · Q1–30 · single answer

Consider the following reaction scheme. $CH_3C{\equiv}CH$ —(H_2/Pd-$BaSO_4$, quinoline)→ A —(HBr, peroxides)→ B. A and B respectively could be:

- (1)$CH_3CH_2CH_3$ and $CH_3CHBrCH_3$

- (2)$CH_3CH=CH_2$ and $CH_3CHBrCH_3$
- (3)$CH_3CH_2CH_3$ and $CH_3CH_2CH_2Br$
- (4)$CH_3CH=CH_2$ and $CH_3CH_2CH_2Br$
- (5)$CH_3CH=CH_2$ and $CH_3CHBrCH_2Br$

Answer and review

Answer **(4)** Official marking scheme

Lindlar's catalyst stops at the alkene (propene). With peroxides, HBr adds anti-Markovnikov (by a free-radical route), putting Br on the terminal carbon: 1-bromopropane.

RB U8 §2.2 · p. 33

Question 22 · Q1–30 · single answer

At a given temperature, the reaction $3ClO^-(aq) \rightarrow ClO_3\hat{}-(aq) + 2Cl^-(aq)$ occurs through the following mechanism.
$ClO^-(aq) + ClO^-(aq) \rightarrow ClO_2\hat{}-(aq) + Cl^-(aq)$ (slow)
$ClO_2\hat{}-(aq) + ClO^-(aq) \rightarrow ClO_3\hat{}-(aq) + Cl^-(aq)$ (fast)
The rate law of this reaction is, (k = rate constant)

- (1)rate = $k[ClO^-(aq)]$
- (2)rate = $k[ClO^-(aq)]^3$
- (3)rate = $k[ClO^-(aq)]^2$
- (4)rate = $k[ClO_2\hat{}-(aq)][ClO^-(aq)]$
- (5)rate = $k[Cl^-(aq)][ClO^-(aq)]$

Answer and review

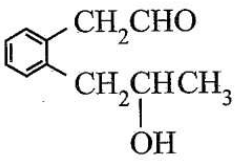
Answer **(3)** Official marking scheme

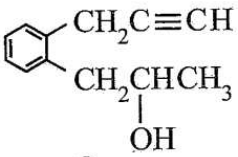
The slow (rate-determining) step is elementary and bimolecular in ClO^-, so rate = $k[ClO^-]^2$. The intermediate $ClO_2\hat{}-$ does not appear in the rate law.

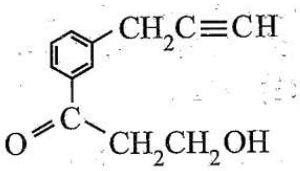
RB U11 §1.10 · p. 57

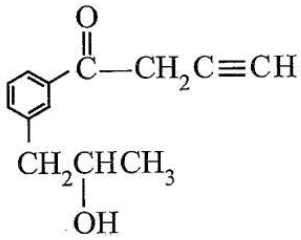
Question 23 · Q1–30 · single answer

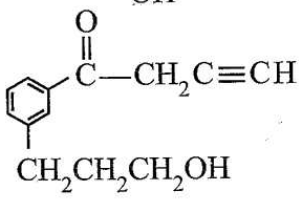
Compound A forms a coloured precipitate with 2,4-dinitrophenylhydrazine (2,4-DNP). Compound A also forms a precipitate with ammoniacal $AgNO_3$. Compound A reacts with acidified $K_2Cr_2O_7$ to give product B and a green colour solution. Compound B does not dissolve in aqueous Na_2CO_3. Compound A could be:

(1) 

(2) 

(3) 

(4) 

(5) 

Answer and review

Answer **(4)** Official marking scheme

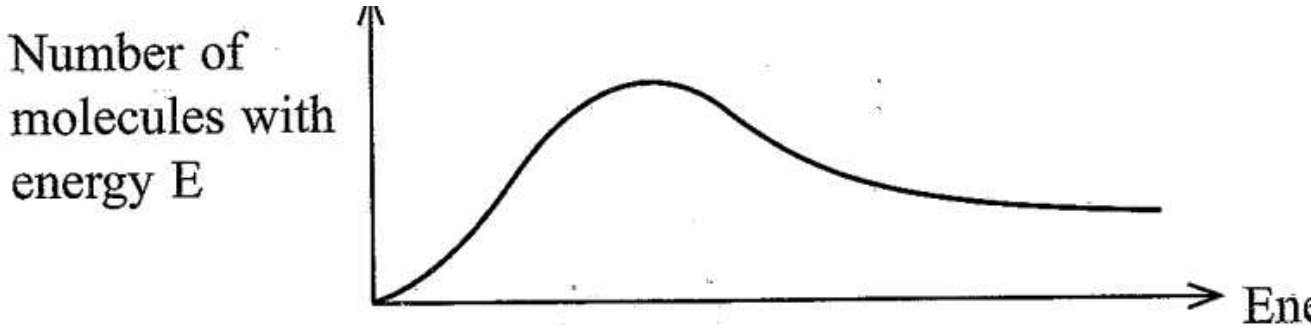
A needs a C=O (2,4-DNP), a terminal C≡C–H (precipitate with ammoniacal $AgNO_3$) and a group oxidized by dichromate. B is not an acid (no reaction with Na_2CO_3), so A must have a secondary alcohol (oxidized to a ketone) and no aldehyde or primary alcohol (which would give a carboxylic acid). Only (4) fits.

RB U9 §3.4 · p. 60 RB U8 §2.2 · p. 33 RB U9 §3.1 · p. 54

Question 24 · Q1–30 · single answer

At a given temperature the distribution of kinetic energies of molecules of a gas within a sealed container is shown in the following graph.

Some of the gas is removed and the container resealed; then the gas is cooled. Which of the following correctly describes the change in the graph? (area under the curve; position of the maximum point)



- (1)decrease; shift to the left
- (2)increase; shift to the left
- (3)no change; shift to the left
- (4)decrease; shift to the right
- (5)no change; no change

Answer and review

Answer **(1)** Official marking scheme

The area under a Maxwell–Boltzmann curve is the number of molecules, so removing gas lowers it. Cooling lowers the average kinetic energy, so the peak moves to lower energy (left) and becomes taller and narrower.

RB U4 §1.4 · p. 19

Question 25 · Q1–30 · single answer

Consider the electrochemical cell operating at temperature 298 K: Zn(s) | Zn^{2+}(aq, 1.0 mol dm^{-3}) || Fe^{2+}(aq, 1.0 mol dm^{-3}), Fe^{3+}(aq, 1.0 mol dm^{-3}) | Pt(s). $E°(Zn^{2+}/Zn) = -0.76$ V, $E°(Fe^{3+}/Fe^{2+}) = +0.77$ V. Which of the following gives the correct overall cell reaction and $E°_{cell}$?

- (1)$Zn(s) + 2Fe^{3+}(aq) \rightarrow 2Fe^{2+}(aq) + Zn^{2+}(aq)$ · 1.53 V
- (2)$Zn(s) + 2Fe^{3+}(aq) \rightarrow 2Fe^{2+}(aq) + Zn^{2+}(aq)$ · −1.53 V
- (3)$Zn(s) + 2Fe^{3+}(aq) \rightarrow 2Fe^{2+}(aq) + Zn^{2+}(aq)$ · 0.01 V
- (4)$Zn^{2+}(aq) + 2Fe^{2+}(aq) \rightarrow 2Fe^{3+}(aq) + Zn(s)$ · −1.53 V
- (5)$Zn^{2+}(aq) + 2Fe^{2+}(aq) \rightarrow 2Fe^{3+}(aq) + Zn(s)$ · −0.01 V

Answer and review

Answer **(1)** Official marking scheme

Zn is oxidized at the left (anode) and Fe^{3+} reduced at the right (cathode). $E°_{cell} = 0.77 - (-0.76) = +1.53$ V.

RB U13 §3.3 · p. 250

Question 26 · Q1–30 · single answer

Consider the reaction below taking place in a closed-rigid container at a given temperature. $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$; $\Delta H = -900$ kJ mol^{-1}. Which of the following statements is true for this reaction?

- (1)High pressure and high temperature give the highest equilibrium amount of NO(g).
- (2)Low pressure and high temperature give the highest equilibrium amount of NO(g).
- (3)High pressure and low temperature give the highest equilibrium amount of NO(g).
- (4)Low pressure and low temperature give the highest equilibrium amount of NO(g).
- (5)Changes in pressure and temperature have no effect on the equilibrium amount of NO(g).

Answer and review

Answer **(4)** Official marking scheme

9 mol of gas form 10 mol, so low pressure favours the products. The forward reaction is exothermic, so low temperature also favours them (Le Chatelier).

RB U12 §2.1 · p. 76

Question 27 · Q1–30 · single answer

The following information is displayed on the label of a bottle which contains concentrated NH_3 solution: NH_3 content – 30.0% (by mass); density – 0.850 g cm^{-3}. When 400.0 cm^3 of this NH_3 solution was reacted completely with H_2SO_4, the amount of ammonium sulfate that can be formed is (H = 1, N = 14, O = 16, S = 32)

- (1)132 g
- (2)396 g
- (3)528 g
- (4)792 g

- (5)1584 g

Answer and review

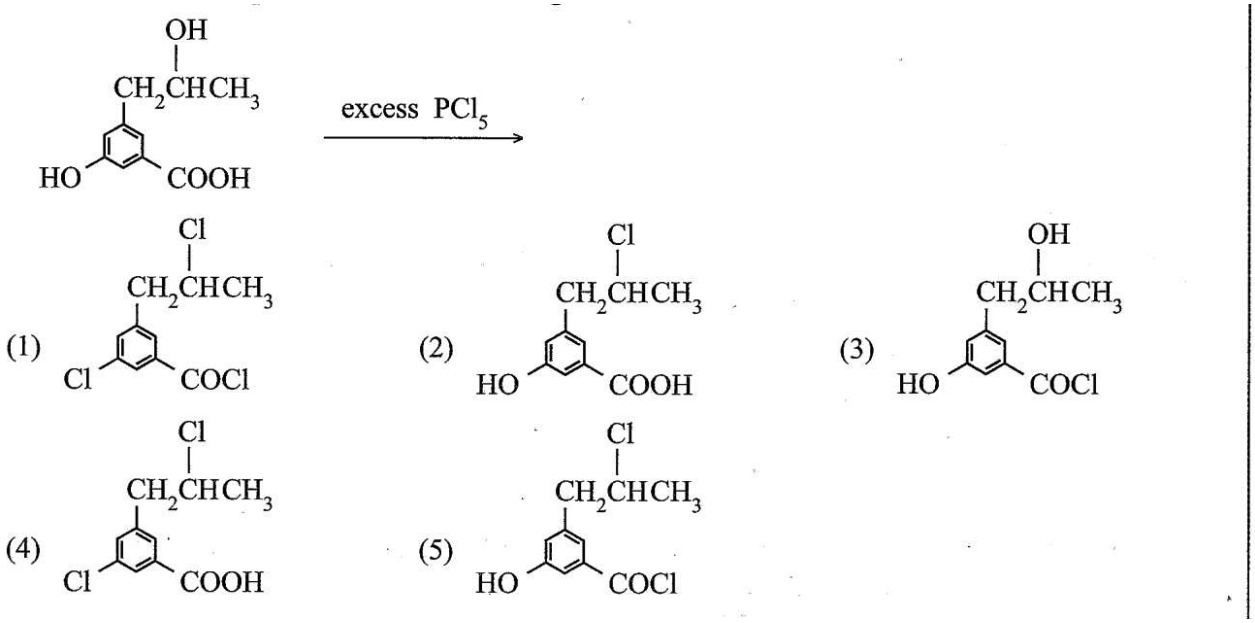
Answer **(2)** Official marking scheme

Mass of solution = 400.0 × 0.850 = 340 g; NH_3 = 0.300 × 340 = 102 g = 6.0 mol. $2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$, so 3.0 mol × 132 = 396 g.

RB U3 §3.5 · p. 102

Question 28 · Q1–30 · single answer

What is the major product of the following reaction? (a benzene ring carrying –OH, –COOH and $-CH_2CH(OH)CH_3$, treated with excess PCl_5)



Answer and review

Answer **(5)** Official marking scheme

PCl_5 replaces the alcohol –OH by Cl and converts –COOH to –COCl. The phenolic –OH is not replaced, because the C–O bond in phenol is strengthened by resonance with the ring.

RB U9 §3.1 · p. 54 RB U9 §3.2 · p. 58 RB U9 §3.5 · p. 66

Question 29 · Q1–30 · single answer

A wood ash sample X contains $CaCO_3$, K_2CO_3, and an inert material. In X the molar ratio of $CaCO_3$:K_2CO_3 is 2:1. A 1.0 g sample of dry powdered X was reacted with excess HCl. The concentration and volume of HCl used was 0.30 mol dm^{-3} and 25.0 cm^3 respectively. After the reaction was completed, the remaining HCl was quantitatively collected and titrated with 0.10 mol dm^{-3} NaOH. The burette reading at the end-point was 15.0 cm^3. The percentage of $CaCO_3$ in the wood ash sample X is

- (1)10%
- (2)16%
- (3)20%
- (4)24%

- (5)40%

Answer and review

Answer **(All)** Official marking scheme

The official scheme accepts all responses. The intended working: HCl added = 7.5×10^{-3} mol; HCl left = 1.5×10^{-3} mol; HCl used = 6.0×10^{-3} mol. With 2x mol $CaCO_3$ and x mol K_2CO_3, HCl used = 2(2x) + 2x = 6x, so x = 1.0×10^{-3}. $CaCO_3$ = 2.0×10^{-3} mol = 0.20 g, i.e. 20%.

RB U3 §3.8 · p. 115

Question 30 · Q1–30 · single answer

Consider the equilibrium reaction given below. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ (K_c = 50 at temperature 600 °C). Equal molar amounts of $H_2(g)$, $I_2(g)$ and HI(g) were inserted into a 2.0 dm^3 previously evacuated closed-rigid container at room temperature and the temperature was increased to 600 °C. Which of the following will occur as the system reaches equilibrium? (Q_c = reaction quotient)

- (1)More $H_2(g)$ and $I_2(g)$ will be produced because $Q_c > K_c$
- (2)Less $H_2(g)$ and $I_2(g)$ will be produced because $Q_c > K_c$
- (3)More $H_2(g)$ and $I_2(g)$ will be produced because $Q_c < K_c$
- (4)Less HI(g) will be produced because $Q_c < K_c$
- (5)More HI(g) will be produced because $Q_c < K_c$

Answer and review

Answer **(5)** Official marking scheme

With equal concentrations, $Q_c = [HI]^2/([H_2][I_2]) = 1$, which is less than K_c = 50. The reaction moves forward, producing more HI until $Q_c = K_c$.

RB U12 §2.1 · p. 76

Questions 31–40: response code

(1)	(2)	(3)	(4)	(5)
Only (a) and (b) are correct	Only (b) and (c) are correct	Only (c) and (d) are correct	Only (d) and (a) are correct	Any other number or combination of responses is correct

Question 31 · Q31–40 · response code

Which of the following statements is/are correct regarding the experiment for determination of the order of the reaction between $Fe^{3+}(aq)$ and $I^-(aq)$ (iodine-clock experiment)?

- The time taken to react a constant amount of $S_2O_3^{2-}(aq)$ is measured.
- The concentration of $S_2O_3^{2-}(aq)$ must be much higher than the concentration of $I^-(aq)$.
- $S_2O_3^{2-}(aq)$ cannot be used in the experiment determining the rate constant of the reaction between $Fe^{3+}(aq)$ and $I^-(aq)$.
- The concentration of $S_2O_3^{2-}(aq)$ must be much smaller than the concentration of $I^-(aq)$.

Answer and review

Answer **(4/5)** Official marking scheme

The official scheme accepts (4) or (5). A small, fixed amount of $S_2O_3^{2-}$ removes the I_2 as it forms (I_2 + $2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$); the time until it is used up and the starch turns blue is measured. Its concentration must be much smaller than $[I^-]$ so the reactant concentrations barely change. (a) and (d) are correct; (c) can be argued either way, hence both codes are accepted.

RB U11 §1.7.4 · p. 40

Question 32 · Q31–40 · response code

Which of the following statements is/are true regarding the reaction of 2-bromo-2-methylpropane with aqueous NaOH?

- It is an electrophilic substitution reaction.
- A carbocation is formed as an intermediate during the reaction.
- The major product formed is $(CH_3)_3COH$.
- $(CH_3)_2C{=}CH_2$ can be formed as a byproduct.

Answer and review

Answer **(5)** Official marking scheme

A tertiary halide reacts by S_{N1}, a nucleophilic substitution through the $(CH_3)_3C^+$ carbocation, giving 2-methylpropan-2-ol. Some of the carbocation loses H^+ to give 2-methylpropene. (b), (c) and (d) are true: code (5).

RB U8 §2.7 · p. 50

Question 33 · Q31–40 · response code

Which of the following reactions is/are correct?

- $CH_3COOH \text{—((1) } CH_3MgBr, \text{ (2) } H^+/H_2O) \rightarrow CH_3COCH_3 + Mg(OH)Br$
- $CH_3CH_2CH(CHO)CH_2OH \text{—}(CH_3MgBr) \rightarrow CH_3CH_2CH(CH(OMgBr)CH_3)CH_2OH$
- $CH_3C{\equiv}CH \text{—}(CH_3MgBr) \rightarrow CH_3C{\equiv}CMgBr + CH_4$
- $CH_3CH_2CH_2OH \text{—}(CH_3MgBr) \rightarrow CH_3CH_2CH_2OMgBr + CH_4$

Answer and review

Answer **(3)** Official marking scheme

A Grignard reagent is a strong base and reacts first with any acidic H (–COOH, –OH, terminal ≡C–H), giving CH_4. So (c) and (d) are correct; in (a) the acid is just deprotonated, and in (b) the –OH would destroy the Grignard reagent before it adds to –CHO.

RB U8 §2.6 · p. 49 RB U9 §3.5 · p. 66

Question 34 · Q31–40 · response code

Which of the following statements is/are true with regard to s and p block elements and their compounds?

- Be reacts with hydrogen gas to produce an ionic metal hydride.
- Mg has the highest electronegativity among s-block elements.

- NH_3, SO_2 and H_2S can act as oxidizing agents as well as reducing agents.
- Na and Ba react with excess oxygen gas when heated to give Na_2O_2 and BaO_2 respectively.

Answer and review

Answer **(3)** Official marking scheme

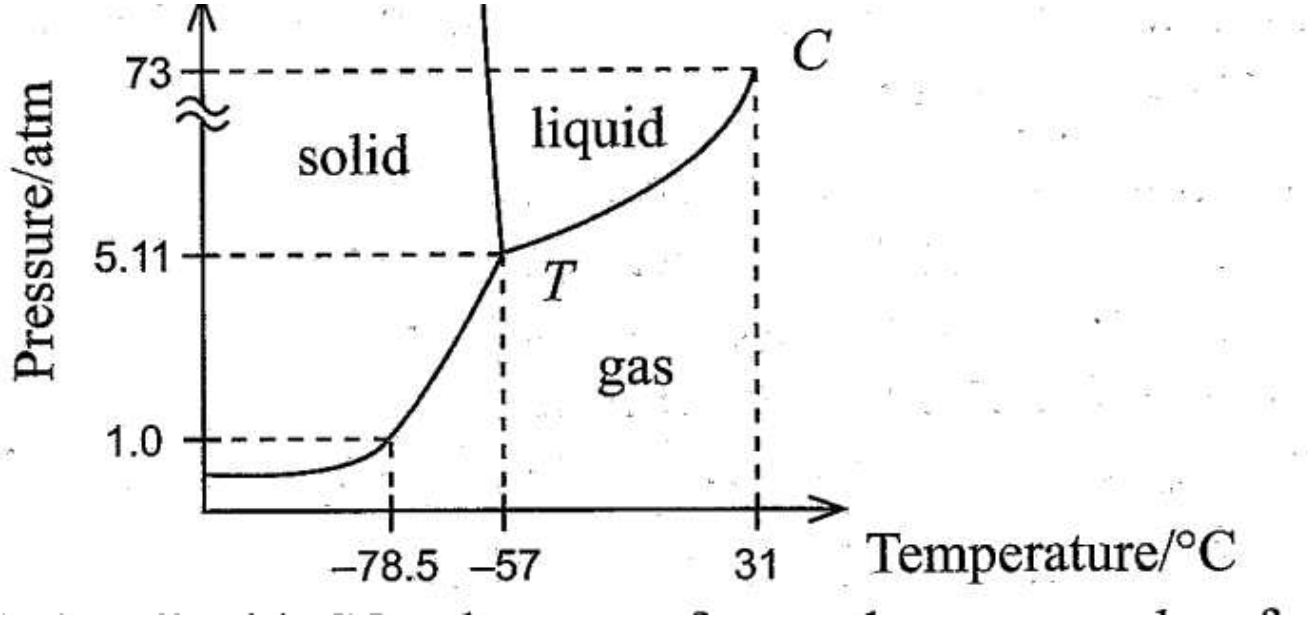
Be does not react directly with H_2, and BeH_2 is covalent; Be (not Mg) is the most electronegative s-block element. NH_3 (with Na), SO_2 (with H_2S) and H_2S (with active metals) can act as oxidizing agents as well as reducing agents. Na and Ba form the peroxides in excess O_2. Only (c) and (d) are true.

RB U6 §4.1 · p. 122 RB U6 §4.2 · p. 126 RB U6 §4.5 · p. 136 RB U6 §4.6 · p. 141

Question 35 · Q31–40 · response code

The phase-diagram of carbon dioxide (CO_2) is shown below.

It is observed that liquid CO_2 does not form when a sample of solid CO_2 (dry-ice) is placed in a beaker at 25 °C and 1 atm pressure. According to the above diagram which of the following statement/s explain/s this observation?



- The temperature at the triple-point is less than the critical temperature.
- The temperature at the critical point is higher than 25 °C.
- The pressure of the triple-point is higher than 1 atm.
- At 1 atm pressure solid CO_2 is in equilibrium only with the gas phase.

Answer and review

Answer **(3)** Official marking scheme

Liquid CO_2 can exist only above the triple-point pressure (5.11 atm). At 1 atm the solid–gas line is crossed directly, so dry ice sublimes at −78.5 °C. (a) and (b) are true facts but do not explain the observation.

RB U12 §2.5 · p. 199

Question 36 · Q31–40 · response code

Which of the following statements is/are true?

- Following a systematic method of waste-disposal contributes to minimize global warming.
- Minimizing deforestation contributes to increase global warming.
- NO gas emitted from transportation contributes to increase global warming.
- Coolant gases used in refrigerators and air-conditioners contribute to increase global warming.

Answer and review

Answer **(4)** Official marking scheme

Proper waste disposal reduces CH_4 from rotting waste, and CFC/HFC coolants are strong greenhouse gases. Reducing deforestation lowers global warming, and NO is not a significant greenhouse gas (N_2O is). Only (a) and (d) are true.

RB U14 §1.13 · p. 58

Question 37 · Q31–40 · response code

Which of the following statements is/are true with regard to the function of the ozone layer in the stratosphere?

- NO_2 is required for the formation of ozone.
- Atomic oxygen produced in the troposphere produces ozone after reaching the stratosphere.
- Ozone level in the stratosphere fluctuates throughout the year.
- Infrared radiation is essential for the formation of ozone.

Answer and review

Answer **(5)** Official marking scheme

Stratospheric ozone forms when UV (not IR) splits O_2 there: $O_2 \rightarrow 2O$, $O + O_2 \rightarrow O_3$; NO_2 is not needed (it forms ground-level ozone in smog). The ozone level varies with season. Only (c) is true, so the code is (5).

RB U14 §1.13 · p. 58

Question 38 · Q31–40 · response code

Consider the following cells. A: Zn(s) | Zn^{2+}(aq, 1.0 mol dm^{-3}) ¦ Cu^{2+}(aq, 1.00 mol dm^{-3}) | Cu(s) (porous partition); B: Zn(s) | Zn^{2+}(aq, 1.0 mol dm^{-3}) || Cu^{2+}(aq, 1.00 mol dm^{-3}) | Cu(s) (salt bridge)

- Ion migration occurs at both A and B.
- Mixing of electrolytes is prevented in both A and B.
- Ion migration occurs only in B.
- Mixing of electrolytes is prevented only in B.

Answer and review

Answer **(1)** Official marking scheme

Both a porous partition (¦) and a salt bridge (||) let ions move to complete the circuit while keeping the two solutions from mixing. (a) and (b) are correct.

RB U13 §3.3 · p. 250

Question 39 · Q31–40 · response code

Which of the following statements is/are correct regarding 3d-block elements and their compounds?

- The correct IUPAC name of $[Cr(NH_3)_6]Br_3$ is hexaamminechromium(III) tribromide.
- Based on the electronic configurations of the 3d-block metals, Zn is expected to have the lowest melting point.
- Cu shows the lowest stable oxidation state among 3d-block elements.
- CrO_3 dissolves in aqueous NaOH and gives $Cr_2O_7^{2-}$ ion.

Answer and review

Answer **(2)** Official marking scheme

The name is hexaamminechromium(III) bromide (no "tri"). Zn ($3d^{10}4s^2$) has no unpaired d electrons for metallic bonding, so it has the lowest melting point. Cu shows the +1 state. Acidic CrO_3 dissolves in NaOH to give CrO_4^{2-} ($Cr_2O_7^{2-}$ forms in acid). Only (b) and (c) are correct.

RB U6 §4.10 · p. 160 RB U6 §4.10.6 · p. 169

Question 40 · Q31–40 · response code

Which of the following statements is/are true regarding some industrial processes?

- The entropy change for the reaction of $N_2(g)$ with $H_2(g)$ to produce $NH_3(g)$ in the Haber-Bosch process is positive ($\Delta S > 0$).
- The reaction of $N_2(g)$ with $H_2(g)$ to produce $NH_3(g)$ in the Haber-Bosch process is an exothermic reaction.
- The industrial process for the production of high purity TiO_2 from rutile by chlorination followed by oxidation, results in the release of CO_2 to the environment.
- The reaction of $SO_2(g)$ with $O_2(g)$ to give $SO_3(g)$ in the contact process for producing sulphuric acid is an endothermic reaction.

Answer and review

Answer **(2)** Official marking scheme

$N_2 + 3H_2 \rightarrow 2NH_3$ lowers the number of gas molecules ($\Delta S < 0$) and is exothermic. In the chloride process coke is oxidized to CO/CO_2. The oxidation of SO_2 is exothermic. Only (b) and (c) are true.

RB U14 §1.6 · p. 21 RB U14 §1.8 · p. 27 RB U14 §1.9 · p. 31

Questions 41–50: statement pairs

Response	First statement	Second statement
(1)	True	True, and correctly explains the first statement
(2)	True	True, but does not explain the first statement correctly
(3)	True	False
(4)	False	True
(5)	False	False

Question 41 · Q41–50 · statement pair

Statement 1

Metallic bonding in Group 1 elements (Li–Cs) is weaker than metallic bonding in Group 2 elements (Be–Ba).

Statement 2

Metallic bonding involves only one valence electron in Group 1 elements whereas two electrons are involved in Group 2 elements.

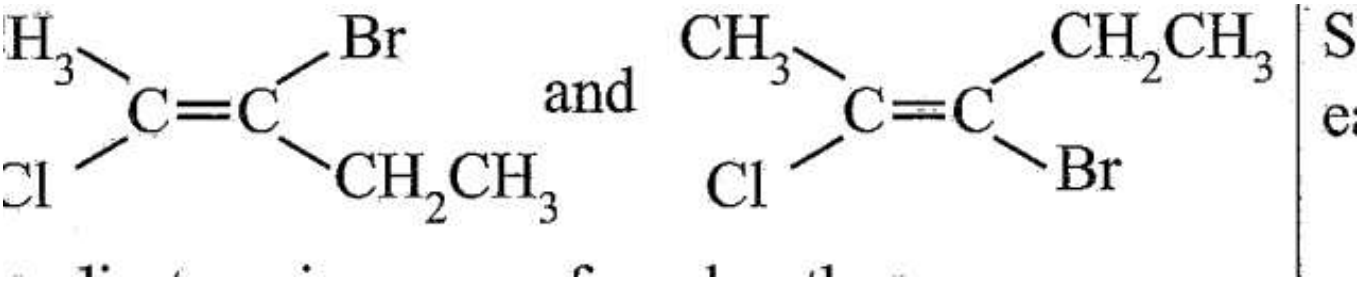
Answer and review

Answer **(1)** Official marking scheme

Group 2 atoms each give two electrons to the delocalised sea and form smaller, doubly charged cations, so their metallic bonding is stronger (higher melting points). Both true; the second explains the first.

RB U6 §4.1 · p. 122 RB U2 §2.5 · p. 78

Question 42 · Q41–50 · statement pair



Statement 1

The two compounds shown ($CH_3(Cl)C=C(Br)CH_2CH_3$ and $CH_3(Cl)C=C(CH_2CH_3)Br$) are diastereoisomers of each other.

Statement 2

Stereoisomers which are not mirror images of each other are diastereoisomers.

Answer and review

Answer **(1)** Official marking scheme

The two structures have the same connectivity and differ only in the arrangement of Br and CH_2CH_3 about the C=C: they are geometric (E/Z) isomers, which are stereoisomers that are not mirror images. Both true; the second explains the first.

RB U7 §1.4 · p. 21

Question 43 · Q41–50 · statement pair

Statement 1

When a few drops of dilute mineral acid are added to a 100 cm^3 solution of $CH_3NH_2(aq)/CH_3NH_3Cl(aq)$, the pH of the solution does not change significantly.

Statement 2

A solution containing $CH_3NH_2(aq)$ and $CH_3NH_3Cl(aq)$ acts as a buffer solution.

Answer and review

Answer **(1)** Official marking scheme

A weak base with its salt is a buffer: added H^+ is removed by $CH_3NH_2 + H^+ \rightarrow CH_3NH_3^+$. Both true; the second explains the first.

RB U12 §2.3 · p. 167

Question 44 · Q41–50 · statement pair

Statement 1

Aqueous solutions of Ni^{2+}, Cu^{2+} and Zn^{2+} when individually treated with excess $NH_4OH(aq)$ do not give permanent precipitates.

Statement 2

All three ions $Ni^{2+}(aq)$, $Cu^{2+}(aq)$ and $Zn^{2+}(aq)$ give ammine complexes when individually treated with excess $NH_4OH(aq)$.

Answer and review

Answer **(1)** Official marking scheme

Each first gives a hydroxide precipitate, which dissolves in excess ammonia as $[Ni(NH_3)_6]^{2+}$, $[Cu(NH_3)_4]^{2+}$ or $[Zn(NH_3)_4]^{2+}$. Both true; the second explains the first.

RB U6 §4.10 · p. 160

Question 45 · Q41–50 · statement pair

Statement 1

Benzene reacts with electrophilic reagents to give substitution products and not addition products.

Statement 2

The carbocation intermediate formed by the reaction between benzene and the electrophile is stabilized by the delocalization of its positive charge.

Answer and review

Answer **(2)** Official marking scheme

Substitution happens because losing H^+ restores the very stable aromatic ring, whereas addition would destroy it. The arenium ion is indeed resonance-stabilized (true), but that is not the reason substitution is preferred over addition.

RB U8 §2.3 · p. 41 RB U8 §2.4 · p. 44

Question 46 · Q41–50 · statement pair

Statement 1

In an electrochemical cell constructed by $Ag^+(aq)/Ag(s)$ and $Cu^{2+}(aq)/Cu(s)$ electrodes, electrons flow from Cu to Ag. $E°(Cu^{2+}/Cu) = 0.34$ V, $E°(Ag^+/Ag) = 0.80$ V

Statement 2

In the electrochemical cell Cu(s) | Cu^{2+}(aq, 1 M) || Ag^+(aq, 1 M) | Ag(s), the $Cu^{2+}(aq)$ | Cu(s) electrode is the cathode.

Answer and review

Answer **(3)** Official marking scheme

Cu (lower E°) is oxidized, so it is the anode and electrons flow from Cu to Ag. The Cu electrode is the anode, not the cathode, so statement 2 is false.

RB U13 §3.3 · p. 250

Question 47 · Q41–50 · statement pair

Statement 1

$N_2(g)$ cannot behave as an oxidizing agent.

Statement 2

When heated $N_2(g)$ reacts with Li to give an ionic product which reacts with water liberating $NH_3(g)$.

Answer and review

Answer **(4)** Official marking scheme

$6Li + N_2 \rightarrow 2Li_3N$: N goes from 0 to −3, so N_2 is acting as an oxidizing agent. $Li_3N + 3H_2O \rightarrow 3LiOH + NH_3$. Statement 1 is false; statement 2 is true.

RB U6 §4.5 · p. 136

Question 48 · Q41–50 · statement pair

Statement 1

Addition of dilute $HNO_3(aq)$ to a saturated solution of PbC_2O_4 increases the solubility of $PbC_2O_4(s)$.

Statement 2

In the equilibrium $PbC_2O_4(s) \rightleftharpoons Pb^{2+}(aq) + C_2O_4{}^{2-}(aq)$, $C_2O_4{}^{2-}(aq)$ can be considered as the conjugate-base of $H_2C_2O_4(aq)$ acid.

Answer and review

Answer **(3)** Official marking scheme

H^+ removes $C_2O_4{}^{2-}$ (as HC_2O_4^−), so more PbC_2O_4 dissolves. But $C_2O_4{}^{2-}$ is the conjugate base of HC_2O_4^−, not of $H_2C_2O_4$ (a conjugate pair differs by one H^+), so statement 2 is false.

RB U12 §2.4 · p. 175 RB U12 §2.2 · p. 118

Question 49 · Q41–50 · statement pair

Statement 1

The amount of CO(g) produced by the reaction of coke and $O_2(g)$ in a blast furnace increases with increasing temperature.

Statement 2

The reaction between coke and $O_2(g)$ which produces CO(g) has a positive entropy change.

Answer and review

Answer **(1)** Official marking scheme

$2C(s) + O_2(g) \rightarrow 2CO(g)$ increases the moles of gas ($\Delta S > 0$), so $-T\Delta S$ becomes more negative and the reaction is favoured more at higher temperature (also via $CO_2 + C \rightarrow 2CO$). Both true; the second explains the first.

RB U14 §1.10 · p. 33 RB U5 §2.4 · p. 53

Question 50 · Q41–50 · statement pair

Statement 1

Thermoset polymers cannot be softened by heating.

Statement 2

Thermoset polymers have a molecular structure arranged as a three dimensional network.

Answer and review

Answer **(1)** Official marking scheme

Cross-links form a rigid three-dimensional network that heating cannot loosen, so thermosets (e.g. Bakelite) char rather than soften. Both true; the second explains the first.

RB U14 §1.11 · p. 37

Structured essay · answer all four

SEQ · Paper II Part A

Question 1 · Part A · structured essay

(a) [32 marks]

State whether the following statements are true or false. Reasons not required.
(i) Particles in both cathode rays and β rays have the same charge to mass ratio (e/m).
(ii) In a copper (Cu) atom there are 6 electrons having magnetic quantum number, $m_l = -1$.
(iii) The F_2ClO^+ ion has a trigonal planar shape.
(iv) Sulphur (S) has the lowest first ionization energy among the elements F, S and Cl.
(v) Rules related to polarizing power of cations and polarizability of anions, predict that the melting point of LiCl is higher than that of KF.
(vi) In nitrous acid (HNO_2) the two N–O bonds are equal in length.
(vii) The number of Lewis dot-dash structures (resonance structures) that can be drawn for the ion CN_2^{2-} is 3.
(viii) The boiling point of hexane is higher than that of 2,2-dimethylbutane.

Answer

(i) true (ii) true (iii) false (iv) true (v) false (vi) false (vii) true (viii) true (04 marks × 8 = 32 marks)

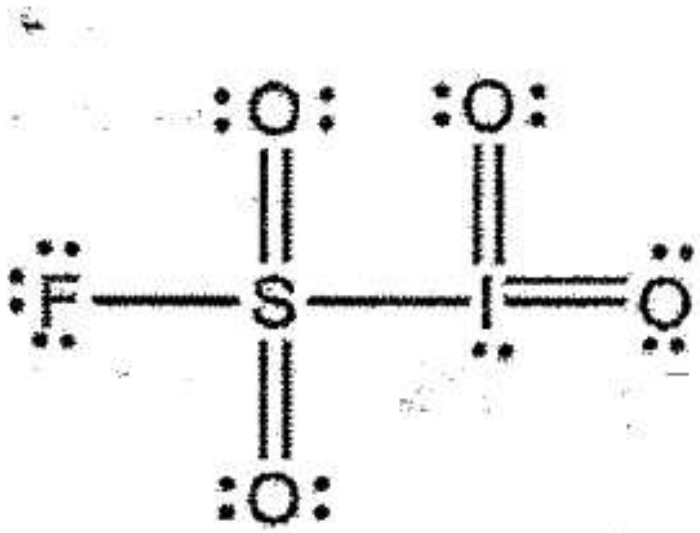
Review.

(i) Both are electrons. (ii) Cu: 2p, 3p and 3d each have one orbital with $m_l = -1$, all filled: 6 electrons. (iii) F_2ClO^+ has a lone pair on Cl: trigonal pyramidal. (v) Li^+ polarizes Cl^- strongly, giving LiCl more covalent character and a lower melting point than KF. (vi) HNO_2 is H–O–N=O, so one N–O is single and one double. (viii) Branching lowers London forces.

(b) [56 marks]

(i) Draw the **most** acceptable Lewis dot-dash structure for the molecule ISO_4F. Its skeleton is given (F–S–I with two O on S and two O on I).

Answer



(06 marks)

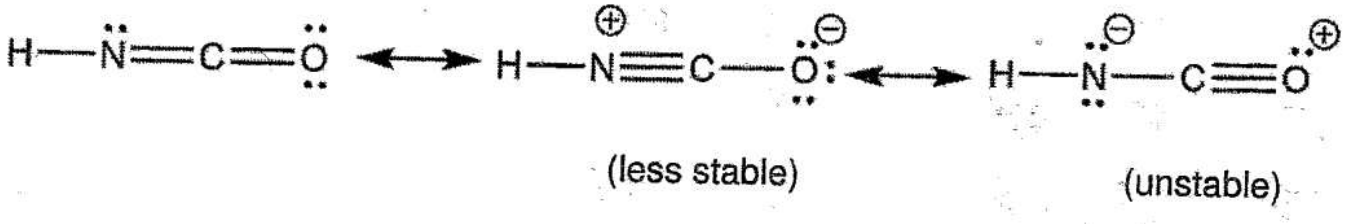
(ii) Give oxidation numbers of the S and I atoms in the structure drawn in (i) above.

Answer

S: +5 (or +V); I: +4 (or +IV) (01) + (01). Award marks for (ii) only if the Lewis structure in (i) is correct.

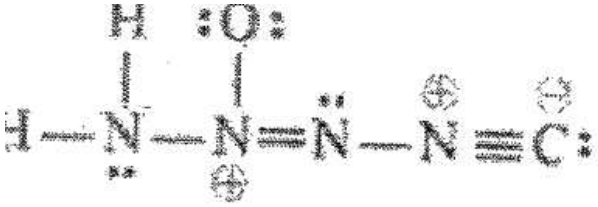
(iii) An acceptable (stable) Lewis dot-dash structure for the HNCO molecule is H–N=C=O. Draw **two** more Lewis dot-dash structures (resonance structures) for this molecule and indicate their stabilities relative to the structure given by writing stable or less stable or unstable under these structures.

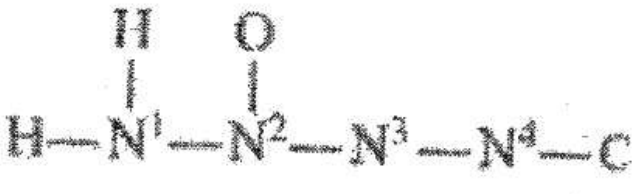
Answer



H–N≡C–O^- with N^+: less stable; H–N^-–C≡O^+: unstable. (02 marks structure + 01 mark stability) × 2 = 06 marks

(iv) Complete the table based on the Lewis dot-dash structure and its labelled skeleton given below (H_2N^1–N^2(O)–N^3–N^4–C).





Answer

	N^1	N^2	N^3	N^4
I. VSEPR pairs	4	3	3	2
II. electron pair geometry	tetrahedral	trigonal planar	trigonal planar	linear
III. shape	pyramidal / trigonal pyramidal	trigonal planar	angular / V / bent	linear
IV. hybridization	sp^3	sp^2	sp^2	sp

(01 mark × 16 = 16 marks)

Parts (v) to (viii) are based on the Lewis structure in part (iv).
(v) Identify atomic/hybrid orbitals involved in the formation of σ bonds between: I. H–N^1 II. N^1–N^2 III. N^2–O IV. N^2–N^3 V. N^3–N^4 VI. N^4–C

Answer

I. H 1s, N^1 sp^3 II. N^1 sp^3, N^2 sp^2 III. N^2 sp^2, O 2p/sp^3 IV. N^2 sp^2, N^3 sp^2 V. N^3 sp^2, N^4 sp VI. N^4 sp, C 2p/sp (01 mark × 12 = 12 marks)

(vi) Identify the atomic orbitals involved in the formation of π bonds between: I. N^2–N^3 II. N^4–C

Answer

I. N^2 2p, N^3 2p II. N^4 2p, C 2p (two π bonds, each 2p–2p) (01 mark × 6 = 06 marks)

(vii) State approximate bond angles around the N^1, N^2, N^3 and N^4 atoms.

Answer

N^1 (107° ± 1), N^2 (120° ± 1), N^3 (117° ± 2), N^4 (180° ± 1) (01 mark × 4 = 04 marks)

(viii) Arrange the atoms N^1, N^2, N^3 and N^4 in **increasing** order of their electronegativities.

Answer

$N^1 < N^3 < N^2 < N^4$ (04 marks) · 1(b): 56 marks

(c) [12 marks]

Arrange the following species in the **increasing** order of the property indicated in parenthesis. (Reasons are not required)
(i) B, O, F, S, Na, Mg (electronegativity)
(ii) K^+, Mg^{2+}, Ca^{2+}, Al^{3+}, Cl^-, S^{2-} (ionic radius)

Answer

(i) Na < Mg < B < S < O < F (06 marks)
(ii) $Al^{3+} < Mg^{2+} < Ca^{2+} < K^+ < Cl^- < S^{2-}$ (06 marks) · 1(c): 12 marks

Read: RB U1 §1.1 · p. 2 RB U1 §1.3 · p. 17 RB U2 §2.1 · p. 44 RB U2 §2.3 · p. 52 RB U1 §1.6 · p. 32 RB U2 §2.4 · p. 75

Question 2 · Part A · structured essay

(a) [50 marks]

(i) I. X is an orange coloured ionic compound. It is composed of three elements in the ratio 7:2:2 (not in the order of writing the chemical formula). Of these, two are metals that belong to the same row of the Periodic Table. One of these two metals belongs to the s-block and the other to the d-block. The d-block metal is widely used for electroplating.
II. Y is a mineral acid. It is composed of three elements in the ratio 1:2:4 (not in the order of writing the chemical formula). One of the elements in Y is also found in X. Y is used in the manufacture of phosphate fertilizer.
III. Z is a tri-atomic gas with a pungent smell. It has a V-shape. It is used in the manufacture of Y.
Identify X, Y and Z.

Answer

X: $K_2Cr_2O_7$ · Y: H_2SO_4 · Z: SO_2 (06 marks × 3 = 18 marks)

(ii) Write the oxidation numbers and the electronic configurations of the two metals in X.

Answer

Metal K: oxidation number +1; $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ (or the atom, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$)
Metal Cr: oxidation number +6; $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ (or the atom, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$) (02 marks × 6 = 12 marks)

(iii) I. Name the process by which Y is manufactured using Z.
II. When the gas formed on reaction of Z with $O_2(g)$ is dissolved in a concentrated solution of Y, the compound P is formed. When compound P reacts with water, Y is obtained again. Write the name and the chemical formula of compound P.

Answer

I. Contact process (02 marks)
II. Oleum / pyrosulfuric acid / fuming sulfuric acid; $H_2S_2O_7$ (04 marks × 2 = 08 marks)

(iv) Write the balanced chemical equation for the reaction taking place when X, Y and Z are reacted together.

Answer

$K_2Cr_2O_7(aq) + H_2SO_4(aq) + 3SO_2(g) \rightarrow K_2SO_4(aq) + Cr_2(SO_4)_3(aq) + H_2O(l)$ (10 marks)
or $Cr_2O_7^{2-}(aq) + 3SO_2(g) + 2H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + H_2O(l)$ (06 marks). Physical states are not required. 2(a): 50 marks

(b) [50 marks]

A student is provided with eight bottles labelled A–H with aqueous solutions of $BaCl_2$, NaI, $Pb(NO_3)_2$, dil. HCl, $Al_2(SO_4)_3$, $AgNO_3$, conc. NH_4OH and dil. NH_4OH (not in order). Observations on mixing two solutions at a time:

	Solutions mixed	Observation
I	A + C	a yellow precipitate soluble in hot water
II	B + C	a yellow precipitate insoluble in H
III	A + E	a white precipitate soluble in hot water
IV	B + E	a white precipitate soluble in D
V	E + F	a white precipitate insoluble in G

	Solutions mixed	Observation
VI	A + F	a white precipitate insoluble in G
VII	D + G	a colourless solution
VIII	H + G	a colourless solution

Answer

A $Pb(NO_3)_2$ · B $AgNO_3$ · C NaI · D dil. NH_4OH · E $BaCl_2$ · F $Al_2(SO_4)_3$ · G dil. HCl · H conc. NH_4OH (04 marks × 8 = 32 marks)

(ii) Give balanced chemical equations for the formation of precipitates, in each of the reactions I to VI. Use the symbol ↓ to indicate precipitates.

Answer

I. $Pb(NO_3)_2 + 2NaI \rightarrow PbI_2\downarrow + 2NaNO_3$
II. $AgNO_3 + NaI \rightarrow AgI\downarrow + NaNO_3$
III. $Pb(NO_3)_2 + BaCl_2 \rightarrow PbCl_2\downarrow + Ba(NO_3)_2$
IV. $2AgNO_3 + BaCl_2 \rightarrow 2AgCl\downarrow + Ba(NO_3)_2$
V. $3BaCl_2 + Al_2(SO_4)_3 \rightarrow 3BaSO_4\downarrow + 2AlCl_3$
VI. $3Pb(NO_3)_2 + Al_2(SO_4)_3 \rightarrow 3PbSO_4\downarrow + 2Al(NO_3)_3$ (03 marks × 6 = 18 marks)
Note: deduct 01 mark if precipitates are not indicated using the symbol ↓. 2(b): 50 marks

Review.

PbI_2 and $PbCl_2$ dissolve in hot water; AgI does not dissolve even in conc. ammonia, while AgCl dissolves in dilute ammonia; $BaSO_4$ and $PbSO_4$ are insoluble in dilute acid.

Read: RB U6 §4.10 · p. 160 RB U6 §4.6 · p. 141 RB U14 §1.8 · p. 27 RB U6 §4.1 · p. 122

Question 3 · Part A · structured essay

Scheme note: PHYSICAL STATES ARE NECESSARY. The symbol of equilibrium ⇌ is also needed for all the reactions.

(a) [60 marks]

At temperature 25 °C, dissociation constants of $H_2CO_3(aq)$ acid are, $K_1 = 4.5 \times 10^{-7}$ mol dm^{-3} and $K_2 = 4.7 \times 10^{-11}$ mol dm^{-3}.
(i) Write the equilibrium reactions for the first and second dissociations of $H_2CO_3(aq)$.

Answer

1st dissociation: $H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3\text{^}-(aq)$ (OR $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3\text{^}-(aq)$) (05)
2nd dissociation: $HCO_3\text{^}-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$ (OR $HCO_3\text{^}-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$) (05)

(ii) Considering the first dissociation, calculate the concentrations of $H_3O^+(aq)$ and $HCO_3\text{^}-(aq)$ in 0.05 mol dm^{-3} $H_2CO_3(aq)$ solution at 25 °C.

Answer

$K_1 = [H_3O^+(aq)][HCO_3\text{^}-(aq)]/[H_2CO_3(aq)]$ (05)
Initial: 0.05, 0, 0; change: −x, x, x; equilibrium: 0.05 − x, x, x mol dm^{-3} (05)
$K_1 = 4.50 \times 10^{-7} = x \cdot x/(0.05 - x) \approx x^2/0.05$ (05); $x^2 = 225 \times 10^{-10}$; $x = 1.5 \times 10^{-4}$ mol dm^{-3} (04 + 01)
$[H_3O^+(aq)] = [HCO_3\text{^}-(aq)] =$ **1.5×10^{-4} mol dm^{-3}** (04 + 01)

(iii) Considering the second dissociation, show that [CO_3^{2-}(aq)] of the solution is approximately equal to K_2. State any assumption/s made.

Answer

K_2 = [H_3O^+(aq)][CO_3^{2-}(aq)]/[HCO_3^−(aq)] (05)
HCO_3^−: 1.5 × 10^{-4} − y; H_3O^+: 1.5 × 10^{-4} + y; CO_3^{2-}: y (05)*
K_2 = 4.70 × 10^{-11} = (1.5 × 10^{-4} + y)·y/(1.5 × 10^{-4} − y) ≈ y (05)*
*If the student writes in words that the amount dissociated from HCO_3^− is very small, so the concentration changes of the two species are negligible, award these 05 + 05 marks.
[CO_3^{2-}(aq)] ≈ K_2 (05). Assumption: the 2nd dissociation is much less compared to the 1st. (05) · 3(a): 60 marks

(b) [40 marks]

You are provided with an aqueous solution containing 0.01 mol dm^{-3} Al^{3+}(aq) ions and 0.01 mol dm^{-3} Ag^+(aq) ions at temperature 25 °C. To 1.0 dm^3 of this solution, a concentrated solution of PO_4^{3-}(aq) ions was added dropwise with continuous stirring. At 25 °C, $K_{sp}(AlPO_4)$ = 1.3 × 10^{-20} mol^2 dm^{-6} and $K_{sp}(Ag_3PO_4)$ = 8.1 × 10^{-12} mol^4 dm^{-12}.
(i) Neglecting any volume change that may occur when the PO_4^{3-}(aq) solution is added, state which metal ion (Al^{3+} or Ag^+) will precipitate first from the mixture. Give reasons for your answer based on a suitable calculation.

Answer

The precipitates formed are $AlPO_4$ and Ag_3PO_4.
For $AlPO_4$: $AlPO_4$(s) ⇌ Al^{3+}(aq) + PO_4^{3-}(aq) (02); K_{sp} = [Al^{3+}(aq)][PO_4^{3-}(aq)] (02); 1.30 × 10^{-20} = 0.01 × [PO_4^{3-}(aq)] (04); [PO_4^{3-}(aq)] = 1.30 × 10^{-18} mol dm^{-3} needed to precipitate $AlPO_4$(s) (03 + 01)
For Ag_3PO_4: Ag_3PO_4(s) ⇌ 3Ag^+(aq) + PO_4^{3-}(aq) (02); K_{sp} = [Ag^+(aq)]^3[PO_4^{3-}(aq)] (02); 8.10 × 10^{-12} = (0.01)^3 × [PO_4^{3-}(aq)] (04); [PO_4^{3-}(aq)] = 8.10 × 10^{-6} mol dm^{-3} needed to precipitate Ag_3PO_4(s) (03 + 01)
[PO_4^{3-}]$_{AlPO4}$ < [PO_4^{3-}]$_{Ag3PO4}$ (04), so **$AlPO_4$(s) precipitates first**. (04)

(ii) Calculate the concentration of the ion which precipitated first when the second ion starts to precipitate.

Answer

[Al^{3+}(aq)] left after precipitation of $AlPO_4$(s) = $K_{sp}(AlPO_4)$/8.10 × 10^{-6} (04) = 1.30 × 10^{-20}/8.10 × 10^{-6} = **1.6 × 10^{-15} mol dm^{-3}** (03 + 01) · 3(b): 40 marks

Review.

The salt that needs the lower concentration of the precipitating ion forms first; compare the required [PO_4^{3-}], not the K_{sp} values directly, because the two salts have different formulas.

Read: RB U12 §2.2 · p. 118 RB U12 §2.4 · p. 175

Question 4 · Part A · structured essay

(a) [68 marks]

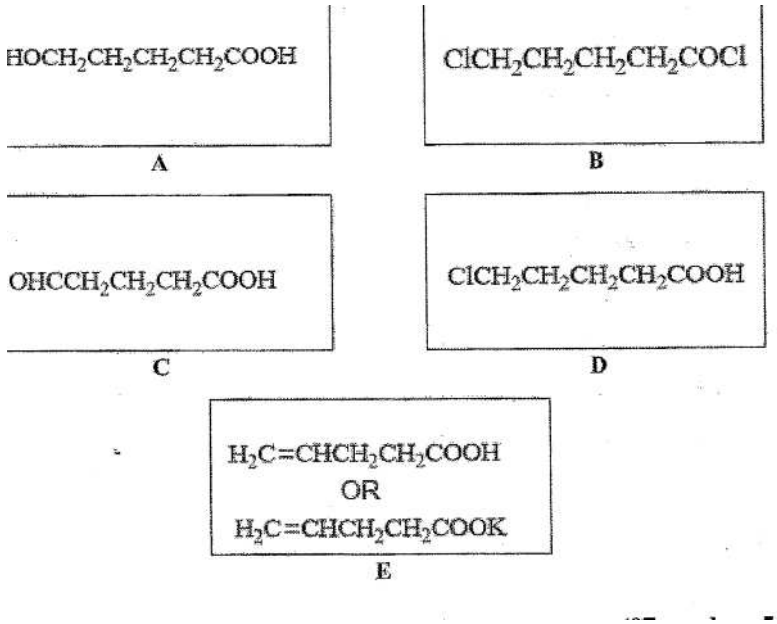
The organic compound A having the molecular formula $C_5H_{10}O_3$ reacts with excess PCl_5 to give compound B, having a relative molecular mass of 155. Compound A liberates CO_2 with aqueous Na_2CO_3. (C = 12.0, H = 1.0, O = 16.0, Cl = 35.5)
(i) Write the functional groups present in compound A.

Answer

OH / hydroxy / hydroxyl, and COOH / carboxylic acid. Note: no marks if 'acid' is not written. (05 marks × 2 = 10 marks)

Compound A does not exhibit optical isomerism. Compound A reacts with pyridinium chlorochromate to give compound C. Compound C gives a silver mirror with ammoniacal $AgNO_3$. Compound B reacts with water to form compound D. Compound D reacts with alcoholic KOH to give the product E which contains a double bond.
(ii) Draw the structures of A, B, C, D and E in the relevant boxes.

Answer



A: $HOCH_2CH_2CH_2CH_2COOH$ · B: $ClCH_2CH_2CH_2CH_2COCl$ · C: $OHCCH_2CH_2CH_2COOH$ · D: $ClCH_2CH_2CH_2CH_2COOH$ · E: $H_2C{=}CHCH_2CH_2COOH$ (or $H_2C{=}CHCH_2CH_2COOK$) (07 marks × 5 = 35 marks)

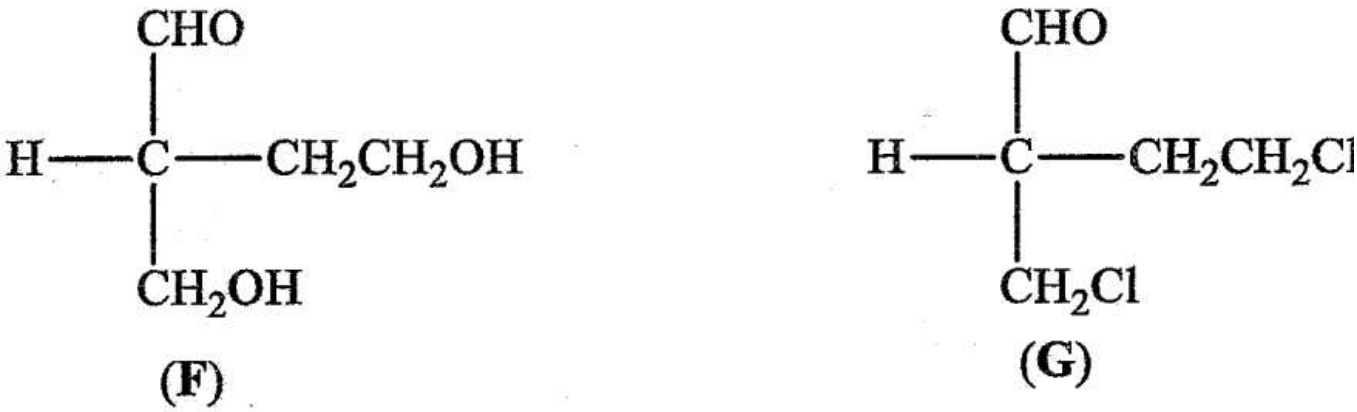
Compound F is a structural isomer of A. Compound F reacts with excess PCl_5 to give compound G having a relative molecular mass of 155. Compound F does not liberate CO_2 with aqueous Na_2CO_3. Compound F exhibits optical isomerism. Compound F does not give a turbidity when treated with conc. HCl/anhydrous $ZnCl_2$. Compound F forms a coloured precipitate with 2,4-dinitrophenylhydrazine (2,4-DNP) and gives a silver mirror with ammoniacal $AgNO_3$.
(iii) Write the functional groups present in F.

Answer

CHO / aldehyde, and OH / hydroxy / hydroxyl. Note: if both are correct, award 09 marks; if only one is correct, award 05 marks only. (05 + 04 = 09 marks)

(iv) Draw the structures of F and G in the relevant boxes.

Answer



F: OHC–CH(CH_2OH)–CH_2CH_2OH · G: OHC–CH(CH_2Cl)–CH_2CH_2Cl (07 marks × 2 = 14 marks) · 4(a): 68 marks

Review.

B has M = 155 = $C_5H_8OCl_2$: both –OH groups of A (alcohol and acid) are replaced by Cl. F has two primary alcohols (no Lucas turbidity) and an aldehyde, with a chiral carbon.

(b) [12 marks]

(i) Draw the structure of the product H formed when acetone is reacted with dilute aqueous NaOH.
(ii) Draw the structure of the product I formed when H is heated with hydrochloric acid.

Answer

H: $(CH_3)_2C(OH)CH_2COCH_3$ (4-hydroxy-4-methylpentan-2-one)
I: $(CH_3)_2C{=}CHCOCH_3$ (4-methylpent-3-en-2-one) (06 marks × 2 = 12 marks)

Review.

Aldol addition of acetone in base, then acid-catalysed dehydration to the conjugated enone.

(c) [20 marks]

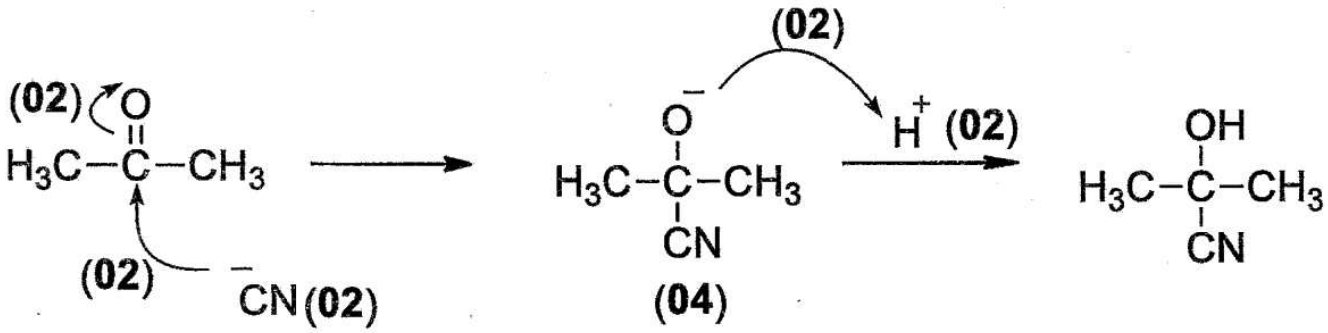
(i) Draw the structure of the product J formed from the reaction between acetone and HCN.

Answer

J: $(CH_3)_2C(OH)CN$ (06 marks)

(ii) Write the mechanism of the above reaction.

Answer



otes:

Step 1: ^−CN attacks the carbonyl carbon (curly arrow 02, ^−CN 02) while the C=O π electrons move onto O (curly arrow 02), giving the alkoxide $(CH_3)_2C(O^-)CN$ (04). Step 2: the alkoxide O takes H^+ (curly arrow 02, H^+ 02), giving $(CH_3)_2C(OH)CN$.
Note: if HCN is used instead of ^−CN, deduct the 02 marks allocated for ^−CN. (14 marks) · 4(c): 20 marks

Review.

Nucleophilic addition to C=O: the nucleophile is the cyanide ion, not the HCN molecule.

Read: RB U9 §3.1 · p. 54 RB U9 §3.4 · p. 60 RB U9 §3.5 · p. 66 RB U9 §3.6 · p. 70 RB U7 §1.4 · p. 21

Answer two from each part

Essay · Paper II Parts B and C

Part B

Question 5 · Part B · essay

Scheme note: PHYSICAL STATES ARE NECESSARY.

(a) [70 marks]

A mixture of NO(g) and O_2(g) in 2:1 molar ratio respectively, was introduced to a rigid closed container of volume 10 dm^3 and allowed to react at temperature T. After a certain time, the system reached the equilibrium as given below, at temperature T: $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$. At equilibrium, the following observations were noted: the pressure of the gaseous mixture was $32 \times 8.314 \times 10^3$ Pa; the total number of moles of the three gases was 0.64; the mass of O_2 was 6.4 g.
(i) Calculate the concentration of each gaseous species in mol dm^{-3} at equilibrium. (O = 16)

Answer

Moles of O_2(g) = 6.4 g/32 g mol^{-1} = 0.20 (02); [O_2(g)] = 0.20 mol/10 dm^3 = 2.0×10^{-2} mol dm^{-3} (02 + 01)
Moles of NO(g) = 0.40 (2:1 ratio maintained, since NO and O_2 react 2:1) (02); [NO(g)] = 0.40/10 = 4.0×10^{-2} mol dm^{-3} (02 + 01)
Moles of NO_2(g) = 0.64 − (0.40 + 0.20) = 0.04 (02); [NO_2(g)] = 0.04/10 = 4.0×10^{-3} mol dm^{-3} (02 + 01)

(ii) Calculate the equilibrium constant, K_c at temperature T.

Answer

$K_c = [NO_2(g)]^2/([O_2(g)][NO(g)]^2)$ (05) = $(4.0 \times 10^{-3})^2/[(2.0 \times 10^{-2})(4.0 \times 10^{-2})^2]$ (05) = **0.50 mol^{-1} dm^3** (05)

(iii) Calculate the value of temperature T (in K) under these conditions. State any assumption/s made.

Answer

Assuming ideal gas behaviour (03): PV = nRT (02); T = PV/nR = ($32 \times 8.314 \times 10^3$ Pa × 10×10^{-3} m^3)/(0.64 mol × 8.314 J K^{-1} mol^{-1}) (05) = **500 K** (04 + 01)

(iv) Calculate the equilibrium constant K_p for the reaction $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$ at the temperature determined in (iii) above.

Answer

This is the reverse of the original reaction (05). $K_c' = 1/K_c$ (05) = 1/0.50 = 2 mol dm^{-3} (04 + 01)
$K_p = K_c(RT)^{\Delta n}$, Δn = 1 (03 + 02); K_p = 2 × (8.314 J K^{-1} mol^{-1} × 500 K) = **8.314×10^3 Pa** (04 + 01) · 5(a): 70 marks

(b) [80 marks]

Consider the information given below at temperature 298 K: $\Delta H_f°(NO(g))$ = 90 kJ mol^{-1} (A); $\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g)$, ΔH° = 33 kJ mol^{-1} (B); $4NO_2(g) + O_2(g) \rightarrow 2N_2O_5(g)$, ΔH° = −102 kJ mol^{-1} (C).
(i) Calculate ΔH° at temperature 298 K for the reaction $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$.

Answer

From (A): $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightarrow NO(g)$, ΔH° = 90 kJ mol^{-1} (D) (05)
(B) − (D): $\frac{1}{2}O_2(g) + NO(g) \rightarrow NO_2(g)$ (E) (05); ΔH° = (33 − 90) = −57 kJ mol^{-1} (05 + 05)
(E) × 2: $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$, **ΔH° = −114 kJ mol^{-1}** (04 + 01)
OR (B) × 2 − (D) × 2: ΔH° = (66 − 180) = −114 kJ mol^{-1}; OR by a Hess cycle through $N_2(g) + 2O_2(g)$: ΔH° = $\Delta H_2 - \Delta H_1$ = (2 × 33 − 2 × 90) = −114 kJ mol^{-1}; or other acceptable method(s).

(ii) Calculate $\Delta H_f°(N_2O_5(g))$ at temperature 298 K.

Answer

Formation reaction: $N_2(g) + 5/2\ O_2(g) \rightarrow N_2O_5(g)$ (05)
(D) × 2: $N_2(g) + O_2(g) \rightarrow 2NO(g)$, $\Delta H° = 180$ kJ mol^{-1} (F) (05 + 05); $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$, $\Delta H° = -114$ kJ mol^{-1} (G); (C) ÷ 2: $2NO_2(g) + ½O_2(g) \rightarrow N_2O_5(g)$, $\Delta H° = -51$ kJ mol^{-1} (H) (05)
(F) + (G) + (H): $\Delta H_f°(N_2O_5(g)) = [180 + (-114) + (-51)] =$ **15 kJ mol^{-1}** (05 + 04 + 01)
OR by a Hess cycle: $2\Delta H_f°(N_2O_5(g)) = (4 \times 33 - 102)$ kJ mol^{-1}, so $\Delta H_f° = 15$ kJ mol^{-1}.

(iii) Using the results obtained in (ii) above, predict the following. I. the sign of $\Delta S_f°(N_2O_5(g))$ II. spontaneity of the reaction for the formation of $N_2O_5(g)$ from $N_2(g)$ and $O_2(g)$

Answer

I. $N_2(g) + 5/2\ O_2(g) \rightarrow N_2O_5(g)$: 3.5 mol of gas → 1 mol, the number of moles decreases (05), so $\Delta S°$ is negative (< 0) (05)
II. $\Delta G° = \Delta H° - T\Delta S°$ (05) = (+ve) − (+ve)(−ve) = +ve (05). The reaction is non-spontaneous at 298 K. (05) · 5(b): 80 marks

Read: RB U12 §2.1 · p. 76 RB U4 §1.2 · p. 5 RB U5 §2.2 · p. 36 RB U5 §2.4 · p. 53

Question 6 · Part B · essay

Scheme note: PHYSICAL STATES ARE NECESSARY.

(a) [40 marks]

According to the kinetic molecular theory of gases, for an ideal gas at temperature T, $PV = ⅓mNC^2$. Here P is the pressure of the gas, V is the volume of the gas, m is the mass of a gas molecule, N is the number of molecules of gas and C^2 is the mean square speed of the gas.
(i) Show that $C^2 = 3RT/M$ for an ideal gas. M is the molar mass of the gas.

Answer

$PV = ⅓mNC^2 = ⅓m(nN_A)C^2$ (n = moles, N_A = Avogadro number) (04) = $⅓nMC^2$ (M = molar mass) (04)
$PV = nRT = ⅓nMC^2$ (04), so $C^2 = 3RT/M$ (04)

(ii) A and B are two ideal gases with molar masses M_A and M_B respectively. Show that the mean square speed of gas B at temperature $T = 300M_B/M_A$ is equal to the mean square speed of gas A at T = 300. (Temperatures are given in kelvin)

Answer

For gas A: $C_A\text{^}2 = 3RT/M_A = 3R \times 300/M_A$ (1). For gas B: $C_B\text{^}2 = 3R \times 300(M_B/M_A)/M_B = 3R \times 300/M_A$ (2) (04 + 04). (1) = (2): $C_A\text{^}2 = C_B\text{^}2$ (04)

(iii) Derive an expression for the ratio between the molar kinetic energies of the two gases A and B at any given temperature T.

Answer

$(KE)_A = 3RT_A/2$ (04); $(KE)_B = 3RT_B/2$ (04); as $T_A = T_B$, $(KE)_A = (KE)_B$, i.e. the ratio is 1 : 1 (04). OR: the kinetic energy of a gas depends only on the absolute temperature, so $(KE)_A = (KE)_B$ (12) · 6(a): 40 marks

(b) [75 marks]

(i) Define the term 'an elementary reaction'.

Answer

A reaction that occurs through a single step (without involving an intermediate). (05)*

(ii) Define the term 'molecularity' of a reaction.

Answer

The total number of reacting molecules (particles) participating in an elementary reaction, or in the rate-determining step of a reaction. (05)

(iii) For an elementary reaction what is the relationship between 'reaction order' and 'molecularity'?

Answer

For an elementary reaction, reaction order = molecularity. (05)* *If the student has attempted Q6(b), award marks for parts (i) and (iii).

(iv) The following table gives the variation of the concentration of the reactant in a reaction with time: time (minutes) 0, 10, 20, 30, 40; reactant concentration (mol dm^{-3}) 1.6, 0.8, 0.4, 0.2, 0.1. I. Determine the order of the reaction. II. State the half-life of the reaction.

Answer

In 10 minutes the concentration decreased to half of the initial concentration (05); this is consistent for all the 10 min intervals (05).
I. The reaction is first order (05). II. Half-life ($t_{½}$) of the reaction is 10 min (05).

(v) Consider two first order reactions ① A → P_1 (rate r_A, rate constant k_A, half-life $(t_{½})_A$) and ② B → P_2 (rate r_B, rate constant k_B, half-life $(t_{½})_B$) at a given temperature. A first order reaction with rate constant k has a half-life $t_{½} = 0.693/k$. If $r_B = 3r_A$ when [B] = 2[A], show that $2(t_{½})_A = 3(t_{½})_B$.

Answer

As the reactions are first order: $r_A = k_A[A]$, so $k_A = r_A/[A]$ (03 + 02); $r_B = k_B[B]$, so $k_B = r_B/[B]$ (03 + 02)
Given [B] = 2[A] and $r_B = 3r_A$: $k_A = r_A/[A]$ (I); $k_B = 3r_A/2[A]$ (II) (05)
(I) ÷ (II): $k_A/k_B = 2/3$ (05 + 05)
$(t_{½})_A/(t_{½})_B = (0.693/k_A)/(0.693/k_B) = k_B/k_A = 3/2$ (05 + 05), so **$2(t_{½})_A = 3(t_{½})_B$** (05) · 6(b): 75 marks

(c) [35 marks]

At temperature 25 °C, 50.0 cm^3 of 0.30 g dm^{-3} iodine aqueous solution was shaken well with 10.0 cm^3 of CCl_4. When the system reached equilibrium the concentration of iodine in the water layer was found to be 0.02 g dm^{-3}.
(i) Calculate the concentration of iodine in the CCl_4 layer at equilibrium.

Answer

Initial I_2 mass in water layer = 0.30 g dm^{-3} × 50 × 10^{-3} dm^3 = 0.015 g (03)
Equilibrium I_2 mass in water layer = 0.02 g dm^{-3} × 50 × 10^{-3} dm^3 = 0.001 g (03); $[I_2]_{H2O}$ = 0.02 g dm^{-3}
Equilibrium I_2 mass in CCl_4 layer = (0.015 − 0.001) g = 0.014 g (03)
$[I_2]_{CCl4}$ = 0.014 g/(10 × 10^{-3} dm^3) = **1.4 g dm^{-3}** (03 + 03 + 01)

(ii) At temperature 25 °C, calculate the partition co-efficient of I_2 between CCl_4 and water.

Answer

$K_D = [I_2]_{CCl4}/[I_2]_{H2O}$ = 1.4 g dm^{-3}/0.02 g dm^{-3} = **70** (03 + 03)

(iii) If the above experiment was done at 25 °C with 20.0 cm^3 of CCl_4 instead of 10.0 cm^3, calculate the concentration of iodine in the water layer at equilibrium.

Answer

Take the I_2 mass in the water layer as x: $K_D = 70 = [(0.015 - x)/20]/[x/50]$ (05); x = 0.0005 g (04)
$[I_2]_{H2O} = 0.0005\ g/(50 \times 10^{-3}\ dm^3) =$ **$0.01\ g\ dm^{-3}$** (03 + 01)
Alternate: take the I_2 mass in CCl_4 as x: $70 = (x/20)/[(0.015 - x)/50]$ (05); x = 0.0145 g (02); I_2 in water = 0.0005 g (02); $[I_2]_{H2O} = 0.01\ g\ dm^{-3}$ (03 + 01). 6(c): 35 marks

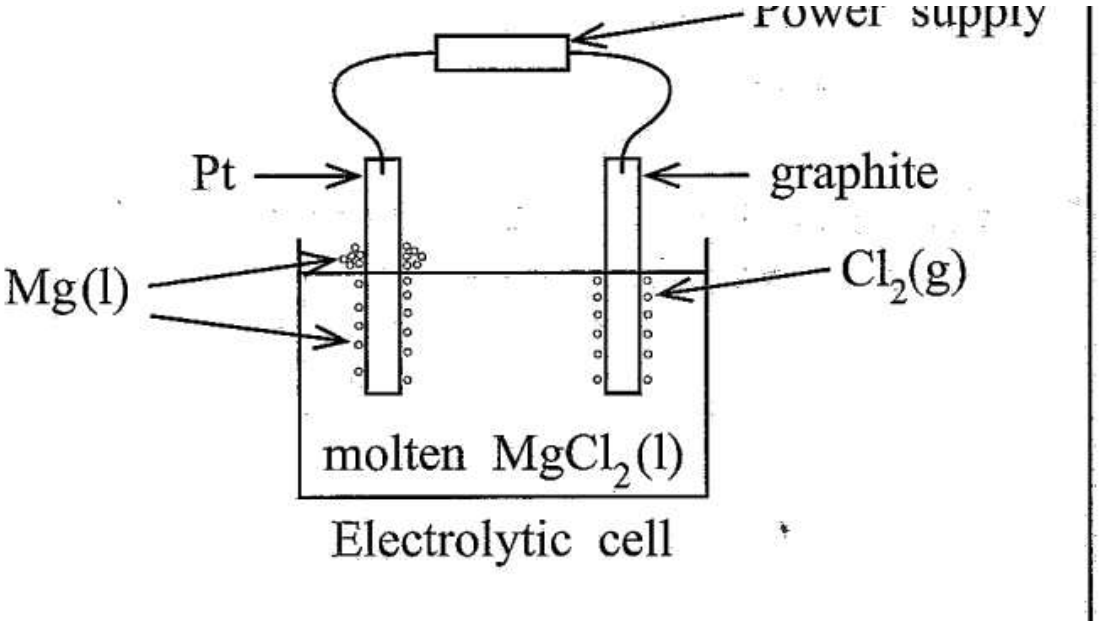
Read: RB U4 §1.4 · p. 19 RB U11 §1.10 · p. 57 RB U11 §1.7.4 · p. 40 RB U12 §2.7 · p. 229

Question 7 · Part B · essay

Scheme note: PHYSICAL STATES ARE NECESSARY.

(a) [75 marks]

Mg metal can be extracted by the electrolysis of molten $MgCl_2(l)$ using inert electrodes (examples: Pt, graphite). A simple setup for this is shown in the diagram. $E°(Mg^{2+}(l)/Mg(s)) = -2.37$ V; $E°(H_2O(l)/H_2(g)) = -0.63$ V.



(i) Identify the anode and the cathode. Write the half reaction taking place at each electrode.

Answer

Anode: C(graphite, s)|$Cl_2(g)$|$MgCl_2(l)$: $2Cl^-(l) \rightarrow Cl_2(g) + 2e$ (05 + 05)
Cathode: Pt(s)|Mg(s)|$MgCl_2(l)$: $Mg^{2+}(l) + 2e \rightarrow Mg(s)$ or Mg(l) (05 + 05)
OR $MgCl_2(l) \rightarrow Mg(s)/(l) + Cl_2(g)$ (05)

(ii) Write the overall cell reaction.

Answer

$Mg^{2+}(l) + 2Cl^-(l) \rightarrow Mg(s)/(l) + Cl_2(g)$, OR $MgCl_2(l) \rightarrow Mg(s)/(l) + Cl_2(g)$ (05)

(iii) State the direction of electron flow through the external circuit as the cell operates.

Answer

From the C(graphite, s)|$Cl_2(g)$ anode to the Pt(s)|Mg(s) cathode. (05)

(iv) Explain the following: I. Molten $MgCl_2(l)$ is used instead of $MgCl_2(s)$ in this extraction process. II. A solution of $MgCl_2(aq)$ cannot be used in this extraction process.

Answer

I. Solid (crystalline) $MgCl_2(s)$ has no movable ions. The molten state has mobile ions $Mg^{2+}(l)$ and $Cl^{-}(l)$. (05)
II. Water molecules would be reduced to $H_2(g)$ instead of $Mg^{2+}(l)$ (E° of water, −0.63 V, is much less negative than −2.37 V). (05)

(v) If a 5.37 A current is passed through this cell for one hour and the $Cl_2(g)$ formed is collected at temperature 300 K and pressure 1 atm (~1.0×10^5 Pa), calculate the volume of $Cl_2(g)$ produced in dm^3. (1 F = 96 500 C)

Answer

Q = It (05) = 5.37 A × (60 × 60) s = 19 300 C (04 + 01)
Moles of electrons = 19 300/96 500 = 0.2 mol (05); 2 mol of electrons ≡ 1 mol of $Cl_2(g)$; moles of $Cl_2(g)$ = 0.10 mol (05)
Assuming ideal gas behaviour: PV = nRT (05); V = nRT/P = (0.10 mol × 8.314 J K^{-1} mol^{-1} × 300 K)/(1×10^5 Pa) (05) = 249.4×10^{-5} m^3 or **2.49 dm^3** (04 + 01) · 7(a): 75 marks

(b) [75 marks]

(i) P, Q, R, S and T are coordination compounds of Co(III). They have an octahedral geometry. Give the structural formulae or draw the structures of these coordination compounds, selecting the appropriate species from the list: Co^{3+}, K^+, NH_3, SO_4^{2-}, NO_2^−, Cl^-. Note: NO_2^− behaves as a monodentate ligand.
P – Only neutral ligands are coordinated to the metal ion. On reaction of an aqueous solution of P with dil. HCl, reddish-brown fumes are evolved. P gives four ions in aqueous solution.
Q – Two types of ligands are coordinated: neutral ligands and mono-atomic anionic ligands. A white precipitate insoluble in dilute acid is formed on addition of $BaCl_2(aq)$ to an aqueous solution of Q. Q gives two ions in aqueous solution.
R – Two types of ligands are coordinated: neutral ligands and multi-atomic anionic ligands. R shows geometric isomerism. On reaction of an aqueous solution of R with $AgNO_3(aq)$, a white precipitate is formed, soluble in dil. NH_4OH. R gives two ions in aqueous solution.
S – It is a non-ionic compound. An equal number of neutral ligands and multi-atomic anionic ligands are coordinated to the metal ion.
T – Only mono-atomic anionic ligands are coordinated to the metal ion. T gives four ions in aqueous solution.

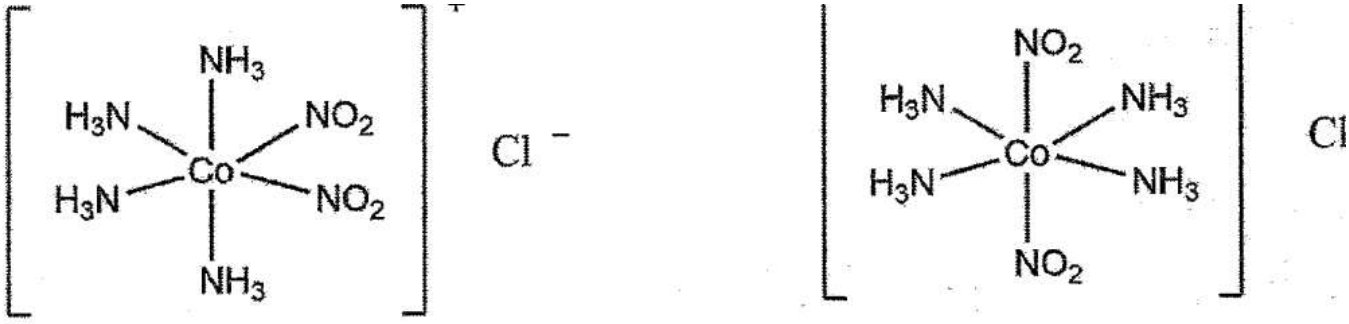
Answer

P: $[Co(NH_3)_6](NO_2)_3$ (10)
Q: $[Co(NH_3)_5Cl]SO_4$ (10)
R: $[Co(NH_3)_4(NO_2)_2]Cl$ (10)*
S: $[Co(NH_3)_3(NO_2)_3]$ (10)
T: $K_3[CoCl_6]$ (10) · 7(b)(i): 50 marks

(ii) I. Write the IUPAC name of T. II. Draw the structures of the geometric isomers of R.

Answer

I. Potassium hexachloridocobaltate(III) (10)



II. cis- and trans-$[Co(NH_3)_4(NO_2)_2]Cl$: in the cis isomer the two NO_2 ligands are adjacent; in the trans isomer they are opposite. (05 marks if both correct; 03 if only one)*
*Concession in the scheme: because geometric isomerism of complexes may be unfamiliar, R = $[Co(NH_3)_5(SO_4)]Cl$ was also credited (06 for (i) R and 03 for (ii) II).

(iii) X is a coordination compound of Co(III) with an octahedral geometry. The ligands H_2O and CO_3^{2-} are coordinated to the metal ion. On treatment of an aqueous solution of X with $AgNO_3(aq)$ a pale yellow precipitate, soluble in conc. NH_4OH is formed. X gives two ions in aqueous solution. Give the structural formula or draw the structure of X. Note: CO_3^{2-} coordinates to the metal ion through two oxygen atoms.

Answer

$[Co(H_2O)_4(CO_3)]Br$ (10) · 7(b): 75 marks

Review.

Count ions in solution (the complex ion plus the counter-ions) and use the precipitation tests to decide which anions are outside the coordination sphere. Pale yellow AgBr dissolves only in concentrated ammonia.

Read: RB U13 §3.4 · p. 261 RB U6 §4.10.6 · p. 169 RB U14 §1.2 · p. 6

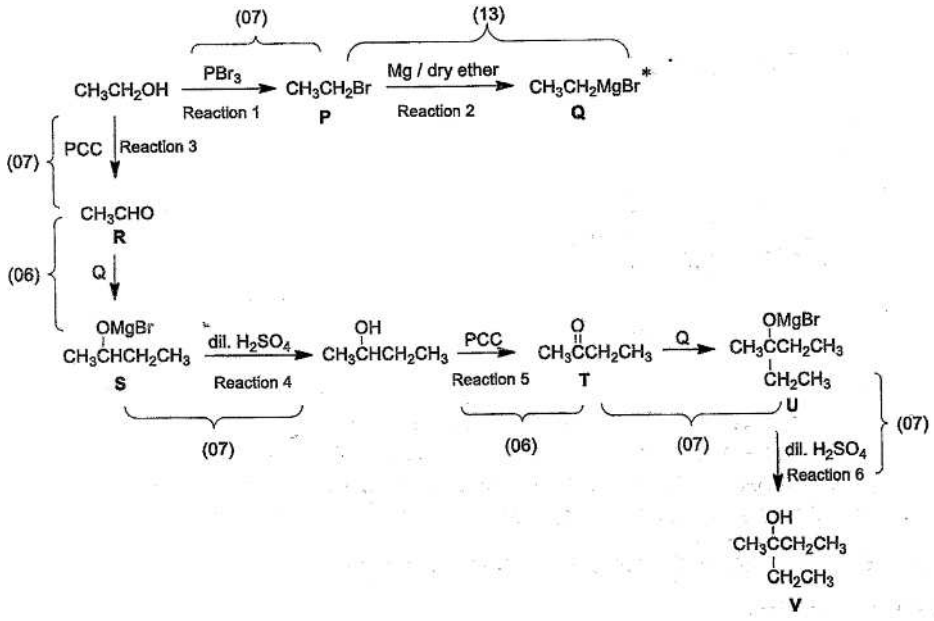
Part C

Question 8 · Part C · essay

(a) [60 marks]

Given below is a reaction scheme for the preparation of compound V using ethanol as the only organic starting material: CH_3CH_2OH —(Reaction 1)→ P —(Reaction 2)→ Q; CH_3CH_2OH —(Reaction 3)→ R —(Q)→ S —(Reaction 4)→ $CH_3CH(OH)CH_2CH_3$ —(Reaction 5)→ T —(Q)→ U —(Reaction 6)→ V = $CH_3C(OH)(CH_2CH_3)CH_2CH_3$. Complete the scheme by drawing the structures of P, Q, R, S, T and U and writing the reagents for reactions 1–6, selected only from: dilute H_2SO_4, Mg/dry ether, PBr_3, pyridinium chlorochromate (PCC).

Answer



Reaction 1: PBr_3 → P = CH_3CH_2Br (07)
Reaction 2: Mg/dry ether → Q = CH_3CH_2MgBr (13)*
Reaction 3: PCC → R = CH_3CHO (07)
R + Q → S = $CH_3CH(OMgBr)CH_2CH_3$ (06)
Reaction 4: dil. H_2SO_4 → $CH_3CH(OH)CH_2CH_3$ (07)
Reaction 5: PCC → T = $CH_3COCH_2CH_3$ (06)
T + Q → U = $CH_3C(OMgBr)(CH_2CH_3)CH_2CH_3$ (07)
Reaction 6: dil. H_2SO_4 → V (07)
*If the structure of Q is not given or wrong but given correctly as a reagent in an appropriate place, award 06 marks once. If Q is wrong or not given, mark the rest of the answer as in the scheme. 8(a): 60 marks

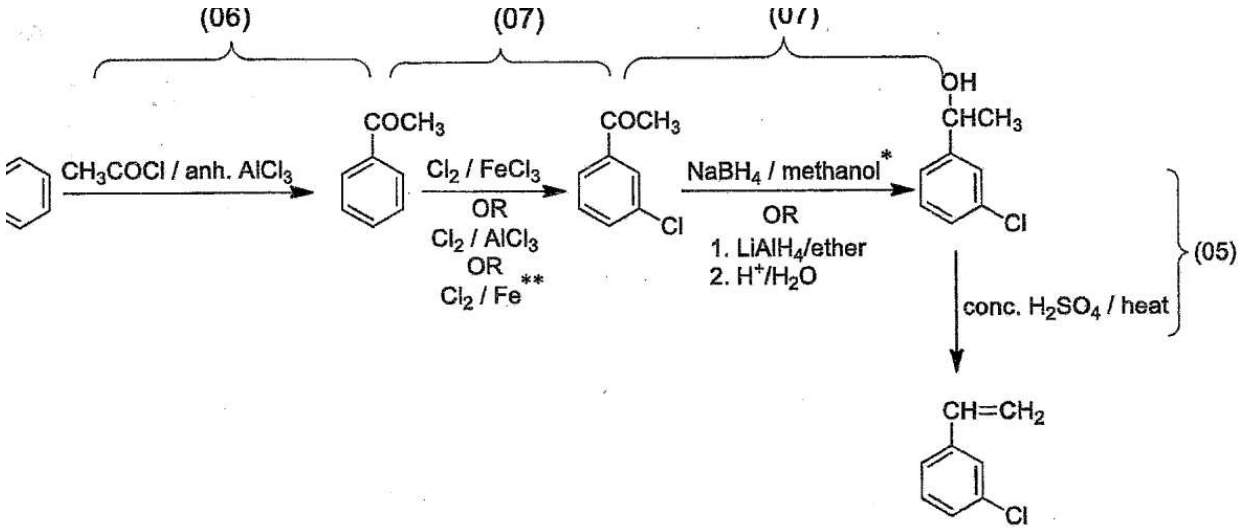
Review.

Grignard reagents add to an aldehyde to give a secondary alcohol and to a ketone to give a tertiary alcohol; PCC oxidizes the secondary alcohol back to a ketone, which is the trick that lets one ethyl Grignard be used twice.

(b) [40 marks]

(i) Show how you would carry out the following conversion in not more than four (04) steps: benzene → 3-chlorostyrene ($CH=CH_2$ and Cl meta on the ring).

Answer



Methanol is necessary for the reaction. If methanol is not written deduct 01 mark.

1. CH_3COCl / anh. $AlCl_3$ → acetophenone (06)
2. $Cl_2/FeCl_3$ (or $Cl_2/AlCl_3$, or Cl_2/Fe**) → 3-chloroacetophenone (–$COCH_3$ directs meta) (07)
3. $NaBH_4$/methanol* (or 1. $LiAlH_4$/ether, 2. H^+/H_2O) → 1-(3-chlorophenyl)ethanol (07)
4. conc. H_2SO_4 / heat → 3-chlorostyrene (05) · 25 marks

*Methanol is necessary for the reaction; if methanol is not written deduct 01 mark. **Cl_2/Fe is obsolete and not in the syllabus, but is accepted.

Alternative accepted: benzene —(CO/HCl/anh. $AlCl_3$)→ benzaldehyde —($Cl_2/FeCl_3$)→ 3-chlorobenzaldehyde —(1. CH_3MgBr, 2. H^+/H_2O)→ alcohol —(conc. H_2SO_4/heat)→ product.

(ii) Propose a method to prepare C_6H_5–N=N–C_6H_4–OH (4-hydroxyazobenzene) from aniline in not more than two (02) steps.

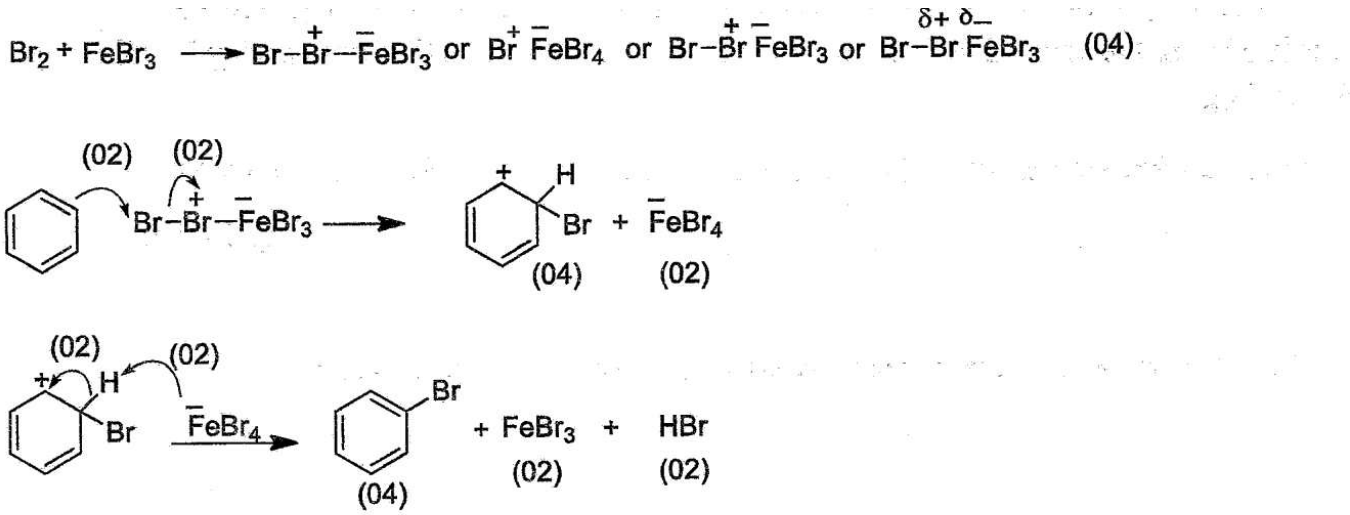
Answer

1. $NaNO_2$ / dil. HCl, 0–5 °C → benzenediazonium chloride (07)
2. phenol / NaOH → C_6H_5–N=N–C_6H_4–OH (08) · 15 marks · 8(b): 40 marks

(c) [50 marks]

(i) Write the product and the mechanism of the reaction that takes place between benzene and bromine in the presence of anhydrous $FeBr_3$.

Answer



Br_2 + $FeBr_3$ → Br^+–Br–$FeBr_3$^− (or Br^+ $FeBr_4$^−, or $Br^{\delta+}$–$Br^{\delta-}$$FeBr_3$) (04)
Benzene π electrons attack the positive Br (curly arrows 02 + 02) → arenium ion (04) + $FeBr_4$^− (02); $FeBr_4$^− removes H^+ (curly arrows 02 + 02) → bromobenzene (04) + $FeBr_3$ (02) + HBr (02) · 26 marks

(ii) Draw the resonance structures of benzene and aniline.

Answer

Benzene: the two Kekulé structures. Aniline: the two Kekulé structures with –N̈H_2, and three structures with C=N^+H_2 and a negative charge (lone pair) at the two ortho positions and the para position. Note: if the lone pair is not written, deduct 02 marks once. (02 marks × 7 = 14 marks)

(iii) Considering the above resonance structures, explain why the benzene nucleus in aniline is more reactive towards electrophilic substitution reactions than benzene itself.

Answer

The benzene ring in aniline is electron rich compared to benzene (03) due to the delocalization of the lone pair of electrons on the nitrogen atom into the benzene ring (03). Therefore the ring in aniline is more reactive towards electrophiles than benzene. (06 marks)

(iv) Draw the structure of the product formed when aniline reacts with bromine.

Answer

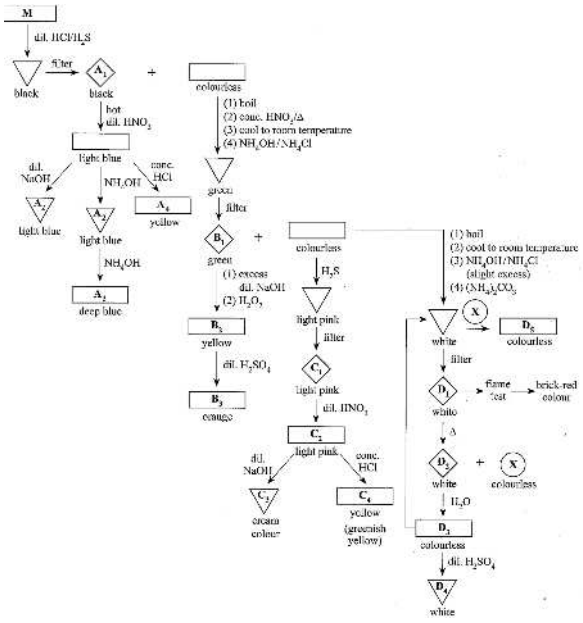
2,4,6-tribromoaniline (Br at both ortho positions and the para position). (04 marks) · 8(c): 50 marks

Read: RB U9 §3.1 · p. 54 RB U9 §3.4 · p. 60 RB U8 §2.6 · p. 49 RB U8 §2.4 · p. 44 RB U10 §4.3 · p. 78

Question 9 · Part C · essay

(a) [75 marks]

The following question is based on the qualitative analysis of cations. An aqueous solution M contains one cation of each of the metals A, B, C and D. M is analysed according to the scheme given below. (▽ precipitate with solution, ◇ solid, ▭ solution, ○ gas)



A_1–A_4, B_1–B_3, C_1–C_4 and D_1–D_5 are compounds/species of the four cations of metals A, B, C and D. X is a gas. Identify A_1, A_2, A_3, A_4, B_1, B_2, B_3, C_1, C_2, C_3, C_4, D_1, D_2, D_3, D_4, D_5 and X. (Write only chemical formulae.)

Answer

A_1 CuS (06)	A_2 $Cu(OH)_2$ (04)	A_3 $[Cu(NH_3)_4]^{2+}$ (04)	A_4 $[CuCl_4]^{2-}$ (04)
B_1 $Cr(OH)_3$ (06)	B_2 Na_2CrO_4 (04)	B_3 $Na_2Cr_2O_7$ (04)	
C_1 MnS (06)	C_2 $[Mn(H_2O)_6]^{2+}$ (04; $Mn^{2+}(aq)$ only 02)	C_3 $Mn(OH)_2$ (04)	C_4 $[MnCl_4]^{2-}$ (04)
D_1 $CaCO_3$ (06)	D_2 CaO (04)	D_3 $Ca(OH)_2$ (04)	D_4 $CaSO_4$ (04)
D_5 $Ca(HCO_3)_2$ (04)	X CO_2 (03)		

(06 × 4 + 04 × 12 + 03 × 1) · 9(a): 75 marks

Review.

So the metals are A = Cu, B = Cr, C = Mn and D = Ca. Light pink MnS and the brick-red flame of Ca are the key clues; $Cr(OH)_3$ is oxidized by H_2O_2 in alkali to yellow chromate, which becomes orange dichromate in acid.

(b) [75 marks]

The main compound present in iron pyrite is FeS_2. A 1.50 g sample of iron pyrite was oxidized under laboratory conditions and all the sulphur in FeS_2 was converted to SO_4^{2-}. The resultant SO_4^{2-} was precipitated as $BaSO_4$. The dry weight of $BaSO_4$ obtained was 4.66 g.
(i) Calculate the weight percentage of FeS_2 present in iron pyrite.

Answer

$BaSO_4$ molar mass = 137 + 32 + 64 = 233 g mol^{-1} (03); FeS_2 molar mass = 56 + 64 = 120 g mol^{-1} (03)
Moles of $BaSO_4$ = 4.66/233 = 0.02 mol (03); 1 mole of FeS_2 gives 2 moles $BaSO_4$ (03); moles of FeS_2 = 0.02/2 = 0.01 mol (03)
Weight of FeS_2 = 0.01 × 120 = 1.20 g (03); weight percentage = 1.20/1.50 × 100 (03) = **80%** (04) · 9b(i): 25 marks

FeS_2 in 20.0 g of iron pyrite was subjected to oxidation by soil microbes under natural conditions for 120 hours: $4FeS_2(s) + 15O_2(g) + 14H_2O(l) \rightarrow 4Fe(OH)_3(s) + 8H_2SO_4(aq)$. H_2SO_4 produced after 120 hours was quantitatively separated and precipitated as $BaSO_4$. The dry weight of $BaSO_4$ obtained was 31.13 g.
(ii) Calculate the percentage conversion of FeS_2 in iron pyrite to SO_4^{2-} after 120 hours by soil microbes. (Percentage conversion = experimentally obtained mass using soil microbes/theoretical mass × 100)

Answer

4 mol FeS_2 → 8 mol H_2SO_4 → 8 mol $BaSO_4$. FeS_2 in 20.0 g of pyrite = 20.0 × 80/100 = 16.0 g (03 + 03)
Theoretical mass of $BaSO_4$: 4 × 120 g FeS_2 gives 8 × 233 g $BaSO_4$ (03); 16 g gives (8 × 233/4 × 120) × 16 (03) = 62.13 g (03); experimental mass = 31.13 g
% conversion = 31.13/62.13 × 100 (03) = **50.1%** (04)
Alternates accepted: via moles of FeS_2 reacted (½ × 31.13/233 × 120 = 8.016 g; 8.016/16 × 100 = 50.1%), or via the mass of H_2SO_4 (13.09 g of a theoretical 26.13 g = 50.1%). 9b(ii): 25 marks

(iii) Calculate the amount of iron pyrite required to produce 8 kg of H_2SO_4 by soil microbes when the conversion percentage of FeS_2 in iron pyrite to SO_4^{2-} is 100%. (O = 16, S = 32, Fe = 56, Ba = 137)

Answer

H_2SO_4 = 8 kg = 8000 g (03); molar mass H_2SO_4 = 98 (03); moles = 8000/98 (03)
Moles of FeS_2 required = (8000/98) × ½ (03) = 40.8 mol (03) = 40.8 × 120 g = 4896 g (03)
Iron pyrite required = 4896/80 × 100 g (03) = 6120 g = **6.12 kg** (04) · 9b(iii): 25 marks · 9(b): 75 marks

Read: RB U6 §4.10 · p. 160 RB U6 §4.2 · p. 126 RB U12 §2.4 · p. 175 RB U3 §3.8 · p. 115

Question 10 · Part C · essay

(a) [50 marks]

The following questions are based on the Solvay process.
(i) What is the main product of the Solvay process?
(ii) What is the main by-product of the Solvay process?
(iii) What are the raw materials (starting materials) used in the Solvay process?
(iv) Which one of these raw materials in (iii) above is not consumed in the process but is recycled repeatedly?

Answer

(i) Na_2CO_3 / sodium carbonate (04)
(ii) $CaCl_2$ / calcium chloride (04)
(iii) NH_3 gas (04); CO_2 gas (04); brine (purified concentrated NaCl solution free from Ca^{2+}, Mg^{2+} and SO_4^{2-}, made from sea water) (04) · 12 marks
(iv) NH_3 gas (04)

(v) Identify the first step of the Solvay process in which raw materials are mixed inside a tower which consists of perforated clay trays. Explain why this is carried out at a low temperature.

Answer

Ammonification (mixing NH_3 gas and brine using the counter current principle) (02). Ammonification is an exothermic process (03); if the temperature increases, the efficiency of dissolving NH_3 gas in brine decreases, hence a low temperature is maintained (03).
OR: dissolution of ammonia is exothermic ($\Delta H < 0$) (01) and the entropy change is negative ($\Delta S < 0$) (01); $\Delta G = \Delta H - T\Delta S$ (01); with ΔS negative, $-T\Delta S$ is +ve (01); as temperature increases ΔG becomes less negative (01), reducing the efficiency of dissolving, so a low temperature is more suitable (03).

(vi) Give **three** uses of the main product of the Solvay process.

Answer

Any three: to remove hardness of water; in the glass industry; in the paper industry; in the soap and detergent industry to improve cleaning action; as a powerful cleaning agent (washing soda). (03 marks × 3 = 09 marks)

(vii) Give **three** reasons contributing to the economic profitability of the Solvay process.

Answer

NaCl and $CaCO_3$ can be obtained easily at low cost; NH_3 is not used up and is recycled repeatedly; a portion of the CO_2 can be reused. (03 marks × 3 = 09 marks) · 10(a): 50 marks

(b) [50 marks]

Briefly explain each of the following statements. In your answer indicate how the chemical species responsible for the given environmental effect in each statement is/are formed.
(i) Agriculture contributes to global warming.

Answer

N_2O (02) and CH_4 (02) contribute to global warming; both are greenhouse gases (02); an increase in their concentration contributes to global warming (02).
Formation of N_2O: action of denitrifying bacteria (02) on nitrogen-containing fertilizers (02) produces N_2O.
Formation of CH_4: paddy cultivation in marsh and water-logged areas (02) favours anaerobic decomposition of organic matter to CH_4 (01); organic matter disposed of indiscriminately (02) undergoes anaerobic decomposition to CH_4 (01); digestion of organic/cellulose matter in the guts of ruminant animals (cows, goats, sheep) under anaerobic conditions (02) produces CH_4. 10b(i): 20 marks

(ii) Iron extraction contributes to global warming.

Answer

CO_2 contributes to global warming; CO_2 is a greenhouse gas; an increase in its concentration contributes to global warming (02 × 3). Formation of CO_2: fossil fuels and coke used in iron extraction are converted to CO_2 during combustion (and $CaCO_3 \rightarrow CaO + CO_2$ in the furnace) (04) · 10b(ii): 10 marks

(iii) Transportation contributes to photochemical smog.

Answer

Species that contribute: NO and volatile hydrocarbons ($CH_3(CH_2)_{nCH3}$, n = 1–4) (02 × 2). NO and volatile hydrocarbons undergo reactions in the presence of sunlight to produce volatile short-chain aldehydes and other toxic chemicals (PAN, PBN); the aldehydes are further polymerized to produce suspended particles; these form large particles by deposition of dust, water vapour etc.; the large particles scatter sunlight, reducing visibility and appearing as a mist in the lower atmosphere. (02 × 8 = 16) · 10b(iii): 20 marks · 10(b): 50 marks

(c) [50 marks]

(i) The following questions are based on vinegar production. I. State what is the process used in the production of natural vinegar. II. Write the name of the active chemical ingredient present in natural vinegar. III. Name the titrant and the indicator used in the quantitative determination of the active chemical ingredient in natural vinegar. IV. State the difference in composition between natural vinegar and artificial vinegar.

Answer

I. Microbial activity / microbial fermentation (04)
II. Acetic acid (04)
III. Titrant: NaOH (04); indicator: phenolphthalein (04)
IV. Natural vinegar contains salts, simple sugars, esters and alcohols in minute quantities (01 × 4); synthetic vinegar contains only acetic acid (02).

(ii) The following questions are based on the extraction of essential oils from plants. I. Name three methods that can be used to extract essential oils. II. State which of the above methods is based on the application of Dalton's law of partial pressures. III. Name the major compound present in each of: citronella oil, cinnamon root oil, cinnamon leaf oil.

Answer

I. Steam distillation; solvent extraction; pressing (04 × 3 = 12)
II. Steam distillation (04)
III. Citronella – geraniol; cinnamon root – camphor; cinnamon leaf – eugenol (04 × 3 = 12) · 10(c): 50 marks

Read: RB U14 §1.5 · p. 18 RB U14 §1.13 · p. 58 RB U14 §1.12 · p. 48 RB U14 §1.10 · p. 33

2023 · Chemistry Digital Paper

0 questions · 2 hours

MCQ · Paper I

1	2	3	4	5	6	7	8	9	10
3	2	1	5	4	4	3/5	4	2	5
11	12	13	14	15	16	17	18	19	20
5	3	3	2	2	4	2	1	5	2
21	22	23	24	25	26	27	28	29	30
3	3	2	1	5	5	1	5	2	3
31	32	33	34	35	36	37	38	39	40
5	5	2	1	5	3	5	4	4	5
41	42	43	44	45	46	47	48	49	50
2	4	1	1	2	1	4	3	2/3	3

Structured essay · answer all four

SEQ · Paper II Part A

Paper II Part A (structured essay questions 1–4) of the 2023(2024) English-medium paper is not in the collection.

Answer two from each part

Essay · Paper II Parts B and C

Part B

Question 5 · Part B · essay

Given at the head of Part B: universal gas constant R = 8.314 J K^{-1} mol^{-1}; Avogadro constant N_A = 6.022 × 10^{23} mol^{-1}.

(a) [80 marks]

CaO(s) reacts with water as shown below.
$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$ $\Delta H° = -64$ kJ mol^{-1}
The following questions are based on the reaction given above.
(i) When 200 g of $H_2O(l)$ was reacted with a certain mass of CaO(s), the temperature of water changed from 25 °C to 75 °C. Calculate the amount of heat (in kJ) absorbed by water. Specific heat capacity of water is 4.2 J g^{-1} $°C^{-1}$. (**Note:** Disregard the change in the mass of water due to the formation of $Ca(OH)_2$.)

Answer

$q = ms\theta$
$q = (200\ g)(4.2\ J\ g^{-1}\ °C^{-1})(75 - 25)\ °C$ (04 + 01)
= **42 kJ** (42 or 42 kJ or 42 000 J) (05)
Examiners' note: if the unit is given as kJ mol^{-1}, the (05) for the answer is not awarded. 5(a)(i): 10 marks

(ii) What is the minimum mass of CaO(s) needed to make the temperature change that occurred in (i) above? (O = 16, Ca = 40)

Answer

Amount of CaO needed to raise the temperature from 25 °C to 75 °C = (42 kJ/64 kJ mol^{-1}) (= 0.656 mol) × 56 g mol^{-1} (04 + 01)
= **36.75 g** (04 + 01) · 5(a)(ii): 10 marks

(iii) Standard entropy values of CaO(s), $H_2O(l)$ and $Ca(OH)_2(s)$ are 40, 70 and 80 J K^{-1} mol^{-1} respectively. Calculate the entropy change of the reaction.

Answer

$\Delta S° = \Sigma S°(products) - \Sigma S°(reactants)$ (04) (Note: the standard-state symbol (°) must be shown.)
$= (80 - (40 + 70))\ J\ K^{-1}\ mol^{-1}$ (04 + 01)
= **$-30\ J\ K^{-1}\ mol^{-1}$** (04 + 01) · 5(a)(iii): 14 marks

(iv) Predict the spontaneity of the reaction at 300 K. State any assumptions made.

Answer

$\Delta G° = \Delta H° - T\Delta S°$ (04) (Note: the standard-state symbol (°) must be shown.)
$= (-64 - 300(-30 \times 10^{-3}))\ kJ\ mol^{-1}$ (04 + 01)
= **$-55\ kJ\ mol^{-1}$** (04 + 01)
The reaction is spontaneous at 300 K. (02) (Note: the 02 marks may be given for a prediction that is correct according to the candidate's final answer.)
Assumption: ΔH° and ΔS° are independent of temperature. (01 + 01) · 5(a)(iv): 18 marks

(v) Predict the spontaneity of the reaction at 400 K if steam ($H_2O(g)$) is used instead of liquid water.
$H_2O(g) \rightarrow H_2O(l)$ $\Delta H° = -44\ kJ\ mol^{-1}$
$S°_{H2O(g)} = 190\ J\ K^{-1}\ mol^{-1}$

Answer

Change in ΔH° when steam is used instead of liquid water: $CaO(s) + H_2O(g) \rightarrow Ca(OH)_2(s)$
$\Delta H° = -108\ kJ\ mol^{-1}$ (04 + 01) [$= -64 + (-44)$]
$\Delta S° = (80 - (40 + 190))\ J\ mol^{-1}\ K^{-1}$ (04 + 01) = $-150\ J\ mol^{-1}\ K^{-1}$ (04 + 01)
$\Delta G° = -108\ kJ\ mol^{-1} - 400\ K(-150 \times 10^{-3})\ kJ\ mol^{-1}\ K^{-1}$ (04 + 01) = **$-48\ kJ\ mol^{-1}$** (04 + 01)
The reaction is still spontaneous. (03) · 5(a)(v): 28 marks
Note: the 03 marks may be given for a prediction that is correct according to the candidate's final answer.
5(a): 80 marks

Review.

The principle is calorimetry ($q = ms\Delta\theta$), then the mole ratio from ΔH°, then $\Delta S° = \Sigma S°(products) - \Sigma S°(reactants)$ and $\Delta G° = \Delta H° - T\Delta S°$. Watch the units: ΔS° in J K^{-1} mol^{-1} must be changed to kJ before it is combined with ΔH°. The "minimum" mass assumes that all the heat released goes into the water. In (v), Hess's law gives ΔH° for steam: $-64 + (-44) = -108\ kJ\ mol^{-1}$. ΔS° becomes much more negative ($-150\ J\ K^{-1}\ mol^{-1}$) because a gas is used up. At 400 K, $-T\Delta S° = +60\ kJ\ mol^{-1}$, which is still smaller than the $-108\ kJ\ mol^{-1}$ of ΔH°, so the reaction stays spontaneous. Common mistakes: using 75 °C instead of the change of 50 °C, giving the heat in kJ mol^{-1}, and not changing J to kJ.

(b) [40 marks]

(i) At temperature 570 °C, the equilibrium given below exists in a closed rigid container.
$Ca(OH)_2(s) \rightleftharpoons CaO(s) + H_2O(g)$
The pressure of the container was found to be 7.0×10^5 Pa. Calculate K_p and K_c for the reaction at the temperature 570 °C (at 570 °C, RT = 7000 J mol^{-1}).

Answer

$K_p = P_{H2O}$ = **7.0×10^5 Pa** (03 + 01)
$K_c = K_p(RT)^{-\Delta n}$ or $K_p = K_c(RT)^{\Delta n}$ (03)
$K_c = 7.0 \times 10^5$ Pa/7.0×10^3 J mol^{-1} (03 + 01) = **100 mol m^{-3} or 1.0×10^{-1} mol dm^{-3}** (03 + 01) · 5(b)(i): 15 marks

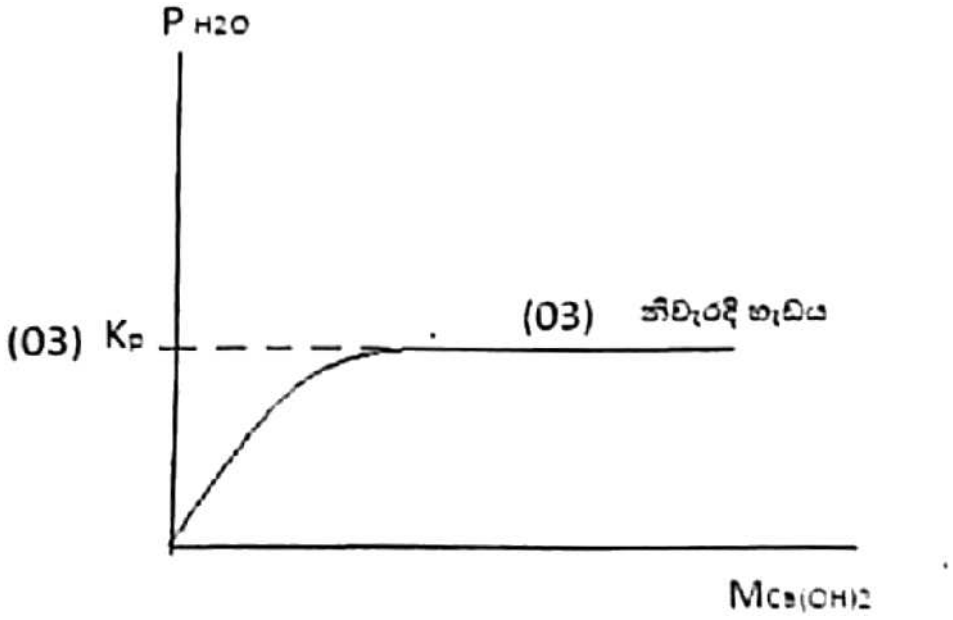
(ii) Giving reasons briefly explain the effect on the equilibrium in (b)(i) above when the following changes are done.
I. When $Ca(OH)_2(s)$ is added.
II. When some amount of $H_2O(g)$ is removed.

Answer

I. There is no effect when $Ca(OH)_2(s)$ is added (02), because the concentration of a solid is constant. (03)
II. The reaction proceeds in the forward direction (02). According to Le Chatelier's principle, the reaction shifts forward to form more water (vapour). (03)
OR: the reaction moves forward, producing more $H_2O(g)$, until P_{H2O} rises back to K_p (03).
OR: the reaction moves forward until the reaction quotient Q_p (Q_c) rises back to K_p (K_c) (03). 5(b)(ii): 10 marks

(iii) To determine the relationship between the pressure of the water vapour produced (P_{H2O}) and the mass of $Ca(OH)_2(s)$ introduced into the container ($M_{Ca(OH)2}$), the pressure was measured introducing small quantities of $Ca(OH)_2(s)$ into an evacuated rigid container at 570 °C. Draw the expected graph for the variation of P_{H2O} with $M_{Ca(OH)2}$ and briefly describe it.

Answer



H2O

Ca(OH)2

p

Graph: P_{H2O} (y-axis) against $M_{Ca(OH)2}$ (x-axis). P_{H2O} rises from zero and then stays constant at K_p. K_p marked on the y-axis (03); correct shape (03). Note: the axes must be labelled correctly for the marks to be awarded.
When $Ca(OH)_2$ is added to the container, the pressure of $H_2O(g)$ increases (03), because at first $Ca(OH)_2(s)$ is converted into $CaO(s)$ and $H_2O(g)$. (03)
Once equilibrium is reached, P_{H2O} stays constant and solid $Ca(OH)_2$ remains in the container. (03) · 5(b)(iii): 15 marks · 5(b): 40 marks

Review.

In this heterogeneous equilibrium the solids do not appear in the equilibrium expression, so $K_p = P_{H2O}$, and with $\Delta n = +1$, $K_c = K_p/RT$. Pa divided by J mol^{-1} gives mol m^{-3}, so divide by 1000 to get mol dm^{-3}. Adding more solid cannot shift the equilibrium. Removing $H_2O(g)$ lowers Q_p below K_p, so more $Ca(OH)_2$ decomposes. In (iii), while all the added $Ca(OH)_2$ decomposes, P_{H2O} (= nRT/V) is proportional to the mass added. Strictly, the graph is a straight line that becomes horizontal at K_p as soon as some $Ca(OH)_2(s)$ remains. The scheme's smoothly curving sketch has the same two features (a rise, then a plateau at K_p) and is the shape accepted.

(c) [30 marks]

(i) Write the reversible reaction for the dissolution of $Ca(OH)_2(s)$ in water at temperature 25 °C.

Answer

$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^{-}(aq)$ (x, 2x) (04)
Note: physical states are necessary. 5(c)(i): 04 marks

(ii) At temperature 25 °C the solubility product (K_{sp}) of $Ca(OH)_2(s)$ is 4.0×10^{-6} mol^3 dm^{-9}. Calculate the molar solubility of $Ca(OH)_2(s)$ at this temperature.

Answer

$K_{sp} = [Ca^{2+}(aq)][OH^{-}(aq)]^2$ (04) (Note: physical states are necessary.)
$K_{sp} = x(2x)^2$; 4.0×10^{-6} mol^3 $dm^{-9} = 4x^3$ (04 + 01)
x = molar solubility of $Ca(OH)_2(s)$; x = **1.0×10^{-2} mol dm^{-3}** (04 + 01) · 5(c)(ii): 14 marks

(iii) State giving reasons whether the solubility of $Ca(OH)_2(s)$ will be higher, lower or the same in aqueous solutions of NaOH, NaCl and $Ca(NO_3)_2$ (concentrations of solutions 0.1 mol dm^{-3}) when compared with the solubility of $Ca(OH)_2(s)$ in water.

Answer

In NaOH: solubility is lower (02), because of the common ion effect (OH^-) (02)
In NaCl: no change in solubility (02), because there is no common ion (02)
In $Ca(NO_3)_2$: solubility is lower (02), because of the common ion effect (Ca^{2+}) (02) · 5(c)(iii): 12 marks · 5(c): 30 marks

Review.

Here $K_{sp} = 4s^3$ for a 1:2 salt. A common mistake is to write $K_{sp} = s^2$ or to forget to square 2s. A common ion (OH^- from NaOH, Ca^{2+} from $Ca(NO_3)_2$) pushes the dissolution equilibrium to the left, so the solubility falls. Na^+ and Cl^- are not involved in the equilibrium, so at the level of this syllabus the solubility is unchanged in NaCl. (In fact, the ionic strength of NaCl would raise the solubility slightly, but this is not expected.)

Read: RB U5 §2.4 · p. 53 RB U5 §2.2 · p. 36 RB U12 §2.1 · p. 76 RB U12 §2.4 · p. 175

Question 6 · Part B · essay

(a) [80 marks]

At 25 °C the methanoate ion, $HCOO^-(aq)$ reacts with water to form methanoic acid, HCOOH(aq) and $OH^-(aq)$ as shown below.
$HCOO^-(aq) + H_2O(l) \rightleftharpoons HCOOH(aq) + OH^-(aq)$
(i) Given that $[OH^-(aq)] = 1.0 \times 10^{-6}$ mol dm^{-3} in a solution prepared by dissolving 0.10 mol of HCO_2Na in 1.0 dm^3 of water, calculate the following at 25 °C.
I. The value of K_b of methanoate ion.
II. The value of K_a of methanoic acid. ($K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6} at 25 °C)

Answer

I. $HCOO^-(aq) + H_2O(l) \rightleftharpoons HCOOH(aq) + OH^-(aq)$; at equilibrium: $C(1 - \alpha)$, $C\alpha$, $C\alpha$
$K_b = [HCOOH(aq)][OH^-(aq)]/[HCOO^-(aq)]$ (05) (Note: physical states are necessary.)
Assumption $1 - \alpha \approx 1$: $K_b = (1.0 \times 10^{-6}$ mol $dm^{-3} \times 1.0 \times 10^{-6}$ mol $dm^{-3})/1.0 \times 10^{-1}$ mol dm^{-3} (04 + 01)
OR: $C\alpha = 1.0 \times 10^{-6}$ mol dm^{-3}; $\alpha = 1.0 \times 10^{-6}$ mol $dm^{-3}/0.1$ mol $dm^{-3} = 1.0 \times 10^{-5}$; $K_b = (1.0 \times 10^{-6}$ mol $dm^{-3} \times 1.0 \times 10^{-6}$ mol $dm^{-3})/[0.10$ mol $dm^{-3}(1 - 1.0 \times 10^{-5})]$ (04 + 01) (the scheme prints 1.0×10^{-6} in this denominator, a misprint for 0.10)
$K_b = 9.9 \times 10^{-12}$ mol $dm^{-3} \cong$ **1.0×10^{-11} mol dm^{-3}** (04 + 01) · 15 marks
II. $K_aK_b = K_w$ (05); $K_a = 1 \times 10^{-14}$ mol^2 $dm^{-6}/1 \times 10^{-11}$ mol dm^{-3} (04 + 01); $K_a =$ **1.0×10^{-3} mol dm^{-3}** (04 + 01) · 15 marks · 6(a)(i): 30 marks

(ii) Calculate the pH of a methanoic acid solution of concentration 0.10 mol dm^{-3}.

Answer

$HCOOH(aq) + H_2O(l) \rightleftharpoons HCOO^-(aq) + H_3O^+(aq)$, or $HCOOH(aq) \rightleftharpoons HCOO^-(aq) + H^+(aq)$ (equation with physical states) (05)
At equilibrium: $C(1 - \alpha)$, $C\alpha$, $C\alpha$; $K_a = (C\alpha)^2/C(1 - \alpha)$
$1 - \alpha \approx 1$ (05); $[H_3O^+] = (K_aC)^{1/2} = (1.0 \times 10^{-3}$ mol $dm^{-3} \times 0.10$ mol $dm^{-3})^{1/2}$; $[H_3O^+] = 1.0 \times 10^{-2}$ mol dm^{-3} (04 + 01)
Note: if this calculation is done by calculating the value of α, award (09 + 01) for the correct steps.
$pH = -\log[H_3O^+(aq)]$ or $pH = -\log[H^+(aq)]$ (05) $= -\log(1.0 \times 10^{-2}) =$ **2.0** (04 + 01) · 6(a)(ii): 25 marks

(iii) When 3.40 g of HCO_2Na was dissolved in 50.00 cm^3 of 0.10 mol dm^{-3} HCOOH(aq) solution, it was observed that there was no change in volume. (H = 1, C = 12, O = 16, Na = 23)
I. Determine the pH of this solution.
II. Explain how this solution acts as a buffer solution.

Answer

I. Molar mass of HCOONa = (12 + 32 + 1 + 23) g mol^{-1} = 68 g mol^{-1} (01)
Amount of HCOONa = 3.4 g/68 g mol^{-1} = 0.05 mol (01)
Concentration of HCOONa = $(5.0 \times 10^{-2}$ mol $\times$ 1000 cm^3 $dm^{-3})/50.0$ $cm^3 = 1.0$ mol dm^{-3} (01 + 01)
$pH = pK_a + \log([salt]/[acid])$ (05) $= -\log(1.0 \times 10^{-3}) + \log(1.0/0.1)$ (05) = **4.0** (04 + 01)
Note: if the calculation is done using the K_a expression, award (10) for the correct steps.
II. When an acid is added: $HCOO^-(aq) + H_3O^+(aq) \rightleftharpoons HCOOH(aq) + H_2O(l)$, or $HCOO^-(aq) + H^+(aq) \rightleftharpoons HCOOH(aq)$ (03) (Note: physical states not necessary; accepted without them.) OR: when an acid is added, the formate ions accept protons and reduce the H^+ concentration.
When a base is added: $HCOOH(aq) + OH^-(aq) \rightleftharpoons HCOO^-(aq) + H_2O(l)$ (03) (Note: physical states not necessary; accepted without them.) OR: when a base is added, formic acid dissociates and reduces the OH^- concentration. 6(a)(iii): 25 marks · 6(a): 80 marks

Review.

The conjugate pair links the two constants: $K_aK_b = K_w$. K_b comes straight from $[OH^-]^2/C$, because hydrolysis of $HCOO^-$ is very small ($\alpha = 10^{-5}$). In (ii) the approximation $1 - \alpha \approx 1$ is borderline ($\alpha = 0.1$). The exact quadratic gives $[H^+] = 9.5 \times 10^{-3}$ mol dm^{-3} and pH 2.02, which still rounds to the scheme's 2.0. In (iii) the 0.05 mol of salt in 50 cm^3 gives 1.0 mol dm^{-3} $HCOO^-$. The Henderson–Hasselbalch equation then gives pH = 3 + log 10 = 4.0. (The scheme's printed 9.9×10^{-12} in (i) should be 1.0×10^{-11}; dividing 1.0×10^{-12} by $0.10(1 - 10^{-5})$ gives 1.00001×10^{-11}.) Explain the buffer action with the two equations: $HCOO^-$ removes added H^+, and HCOOH removes added OH^-. Common mistakes: using the mass of salt as a concentration, and forgetting the 50 cm^3 volume.

(b) [70 marks]

(i) This question is in respect of a solution that could be made by mixing two completely miscible liquids **A** and **B**. Copy the following table on to your answer script and fill in the blanks. Different types of solutions (ideal, non-ideal/positive deviation, non-ideal/negative deviation) that could be made are given in the table. While the mole fractions of **A** and **B** in the solution are X_A and X_B, and the vapour pressures of **A** and **B** at a given temperature are P_A and P_B respectively.
The saturated vapour pressures of **A** and **B** at this temperature are $P°_A$ and $P°_B$ respectively. Intermolecular forces between **A** and **A**, **B** and **B** and **A** and **B** are f_{A-A}, f_{B-B} and f_{A-B} respectively.

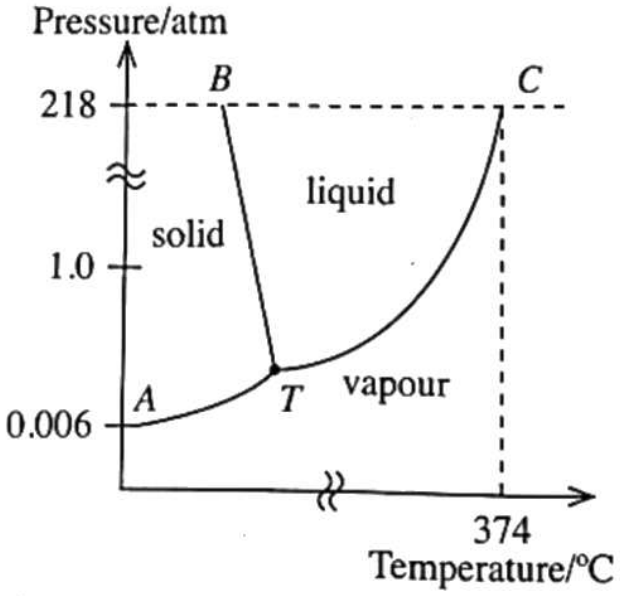
Property	Ideal solution	Non-ideal solution	
Positive deviation from Raoults law	Negative deviation from Raoults law		
ΔH of mixing			
relationship among f_{A-A}, f_{B-B} and f_{A-B}			
relationship among $P°_A$, P_A and X_A			

Answer

Property	Ideal solution	Positive deviation from Raoult's law	Negative deviation from Raoult's law
ΔH of mixing	0 (zero)	ΔH > 0 (ΔH +ve)	ΔH < 0 (ΔH −ve)
Relationship among f_{A-B}, f_{A-A} and f_{B-B}	$f_{A-B} = f_{A-A} = f_{B-B}$	$f_{A-B} < f_{A-A}$, f_{B-B}, or $f_{A-A} > f_{A-B} < f_{B-B}$	$f_{A-B} > f_{A-A}$, f_{B-B}, or $f_{A-A} < f_{A-B} > f_{B-B}$
Relationship among $P°_A$, P_A and X_A	$P_A = P°_AX_A$	$P_A > P°_AX_A$	$P_A < P°_AX_A$

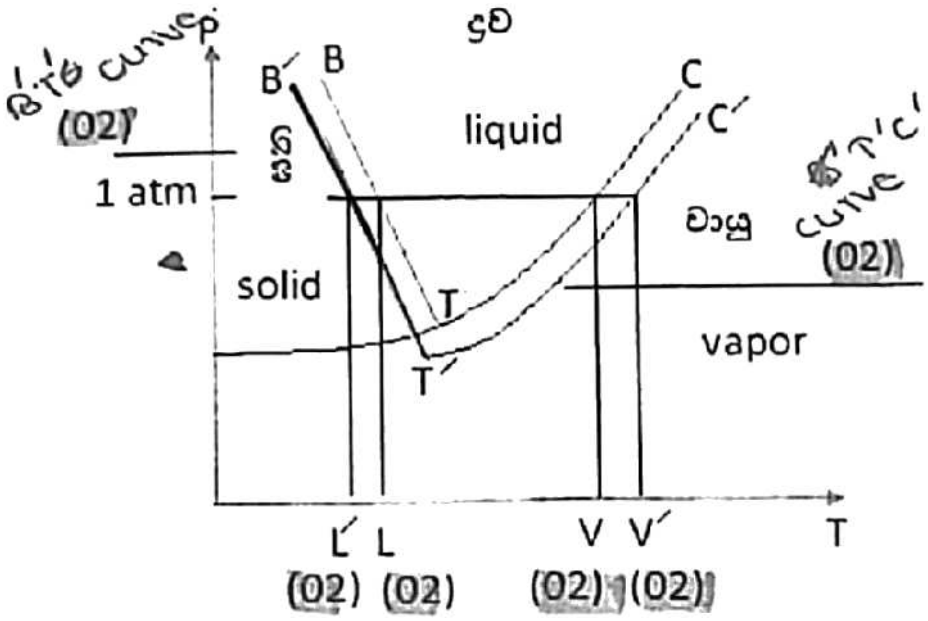
(05 × 9) · 6(b)(i): 45 marks

(ii) The phase diagram of pure water is given below. Copy the diagram on to your answer script and answer the following questions.



I. Mark the normal boiling point (V) and melting point (L) of pure water.
II. What are represented by lines BT, TC and point T?
III. Assume that a small amount of salt (NaCl) is added to the pure water sample. After the addition of salt, positions of the lines BT and TC in the phase diagram were changed. Their new positions are B′T′ and T′C′ respectively. Draw their new positions on the phase diagram you have copied and label them as B′T′ and T′C′. Mark the new boiling point (V′) and the new melting point (L′) on the phase diagram.

Answer



Scheme diagram for I and III. Sinhala labels: □□ = solid, □□□□ = liquid, □□□□ = vapour. The handwritten labels mark the B′T′ curve and the T′C′ curve.

I and III (diagram): a horizontal line at 1 atm cuts BT at L (melting point) and TC at V (boiling point). After NaCl is added, B′T′ lies to the left of BT (lower temperatures) and T′C′ lies below/right of TC (lower vapour pressure), meeting at a new triple point T′. On the 1 atm line, L′ is to the left of L (lower melting point) and V′ is to the right of V (higher boiling point).
B′T′ curve (02); T′C′ curve (02); L′ (02); L (02); V (02); V′ (02) · 12 marks

II. Line BT = variation of the melting point with pressure, or solid–liquid equilibrium (04)
Line TC = variation of the boiling point with pressure, or liquid–vapour equilibrium (04)
Point T = triple point (05) · 13 marks · 6(b)(ii): 25 marks · 6(b): 70 marks

Review.

(i) tests Raoult's law ($P_A = P°_A X_A$) and why real solutions deviate from it. Weaker A–B attractions let molecules escape more easily, so the vapour pressure is higher than ideal (positive deviation) and mixing is endothermic. Stronger A–B attractions give a negative deviation and exothermic mixing. (ii) tests reading a phase diagram. Each line is a two-phase equilibrium, and the normal melting and boiling points lie where the 1 atm line crosses BT and TC. A non-volatile solute lowers the vapour pressure of the liquid, so the liquid–vapour curve moves down (to higher temperature at 1 atm: boiling-point elevation). The solid–liquid curve moves to lower temperature (freezing-point depression). A common mistake is to move both points in the same direction.

Read: RB U12 §2.2 · p. 118 RB U12 §2.3 · p. 167 RB U12 §2.6 · p. 216 RB U12 §2.5 · p. 199

Question 7 · Part B · essay

(a) [75 marks]

A Daniel cell consists of Zn and Cu rods immersed in $ZnSO_4$(aq, 1.0 mol dm^{-3}) and $CuSO_4$(aq, 1.0 mol dm^{-3}) respectively. The solutions are separated by a porous membrane. The overall cell reaction when the cell is operating is given below.
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
(i) Identify the anode and the cathode.

Answer

Anode = Zn (the Zn rod), or $Zn(s)|Zn^{2+}(aq)$ (05)
Cathode = Cu (the Cu rod), or $Cu(s)|Cu^{2+}(aq)$ (05) · 7(a)(i): 10 marks

(ii) Write the anodic half reaction of the cell.

Answer

Anode reaction: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e$ (05)
Note: physical states are necessary. 7(a)(ii): 05 marks

(iii) Write the cathodic half reaction of the cell.

Answer

Cathode reaction: $Cu^{2+}(aq) + 2e \rightarrow Cu(s)$ (05)
Note: physical states are necessary. 7(a)(iii): 05 marks

(iv) Give the cell notation of the cell above.

Answer

$Zn(s)|ZnSO_4$(aq, 1.0 mol dm^{-3}) ⋮ $CuSO_4$(aq, 1.0 mol dm^{-3})$|Cu(s)$
OR $Zn(s)|Zn^{2+}$(aq, 1.0 mol dm^{-3}) ⋮ Cu^{2+}(aq, 1.0 mol dm^{-3})$|Cu(s)$ (10) · 7(a)(iv): 10 marks

(v) Calculate the electromotive force ($E°_{cell}$) of the Daniel cell given above at 25 °C.
$E°_{Cu2+(aq)/Cu(s)} = 0.34$ V $E°_{Zn2+(aq)/Zn(s)} = -0.76$ V

Answer

$E°_{cell} = E°_{cathode} - E°_{anode}$ (02)
= 0.34 V − (−0.76 V) (03 + 01)
= **1.10 V** (03 + 01) · 7(a)(v): 10 marks

(vi) Calculate the time in seconds required to deposit 3.175 g of Cu(s) when a current of 5.0 A flows through the cell. (Cu = 63.5, 1 F = 96500 C mol^{-1})

Answer

Amount of charge Q = It (03)
This charge must deposit 3.175 g of Cu.
Amount of Cu deposited = 3.175 g/63.5 g mol^{-1} = 0.05 mol (03 + 01) (the 0.05 mol may be written or used)
Therefore t = (0.05 mol × 96500 C mol^{-1} × 2)/5.0 C s^{-1} (03 + 01)
t = **1930 s** (03 + 01) · 7(a)(vi): 15 marks

(vii) How does the conductivity of the solution in the cell compartment containing the Zn-rod change when a current is drawn from the cell? Explain giving reasons.

Answer

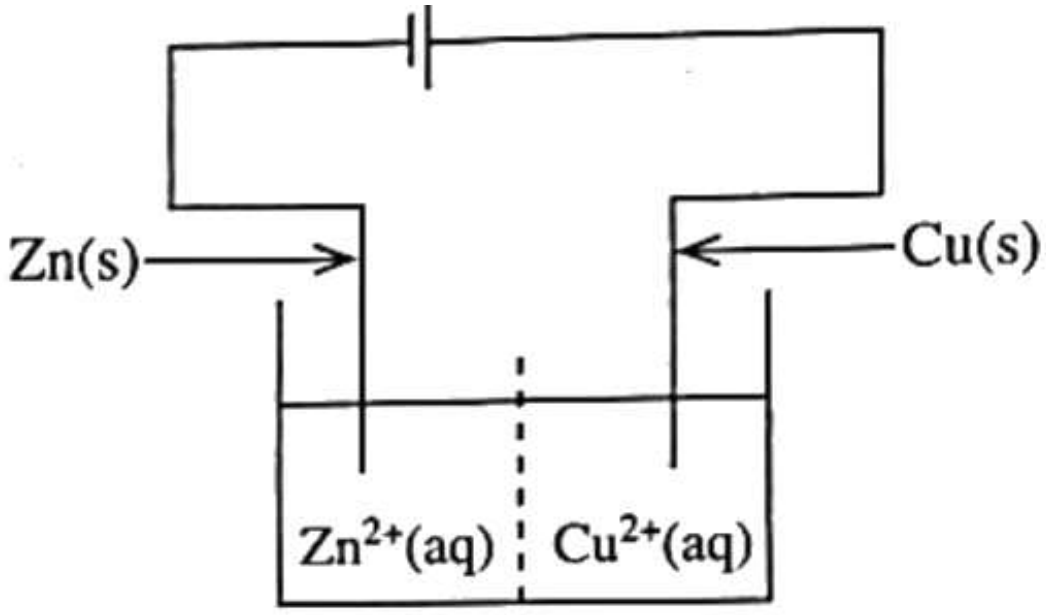
The conductivity increases (04).
This is because Zn^{2+} ions are released (02) and SO_4^{2-} ions migrate into this compartment (02).
Examiners' notes: "the ion concentration increases" alone earns no marks; "due to oxidation of Zn" alone earns no marks. 7(a)(vii): 08 marks

(viii) It was observed that when a current is drawn from the cell, the intensity of the colour of the solution in the cell compartment containing the Cu-rod changes. Explain this observation.

Answer

The intensity of the blue colour decreases (04), because Cu^{2+} ions are deposited as Cu. (04) · 7(a)(viii): 08 marks

(ix) As shown in the diagram, an external voltage higher than the calculated electromotive force in (v) above, was applied to the Daniel cell using another electrochemical cell. Write the overall cell reaction of the Daniel cell under this condition.



Answer

$Cu(s) + Zn^{2+}(aq) \rightarrow Zn(s) + Cu^{2+}(aq)$ (04)
OR $2H_2O(l) + Cu(s) \rightarrow H_2(g) + 2OH^-(aq) + Cu^{2+}(aq)$
OR $2H_2O(l) + Cu(s) + Zn^{2+}(aq) \rightarrow Zn(OH)_2(s) + H_2(g) + Cu^{2+}(aq)$
Note: physical states are necessary for the marks in part (ix). 7(a)(ix): 04 marks · 7(a): 75 marks

Review.

In a galvanic cell oxidation takes place at the anode (Zn, the more negative E°) and reduction at the cathode (Cu). $E°_{cell} = E°_{cathode} - E°_{anode} = 1.10$ V. In the cell notation the porous membrane is shown by a dotted line (⋮), not the double line used for a salt bridge. Faraday's law: $Cu^{2+} + 2e \rightarrow Cu$, so 0.05 mol Cu needs 0.10 mol of electrons = 9650 C, and t = 9650 C/5.0 A = 1930 s. Forgetting the factor 2 is the usual error. As the cell works, Zn^{2+} builds up in the anode compartment and SO_4^{2-} migrates in through the membrane to keep the solution neutral, so the conductivity rises. Meanwhile blue Cu^{2+} is removed at the cathode. An opposing external voltage larger than the emf forces the reverse (non-spontaneous) reaction, so the cell now acts as an electrolytic cell. Zn^{2+} (or water) is reduced at the Zn electrode, and Cu is oxidized.

(b) [75 marks]

A

B

C

D

not in order

14

2

4

3

15

5

2

4

2

4

15

3

3

2

two

A

3

A

A

B

3

B

B

C

3

C

C

D

3

D

(i) What are the common oxidation states of iron (Fe)?

Answer

+2, +3 (03 + 03) · 7(b)(i): 06 marks

(ii) Identify the yellow precipitate. (Give chemical formula.) Name a chemical reagent that can dissolve this precipitate.

Answer

AgBr (03)
Conc. NH_3 / conc. NH_4OH (02) · 7(b)(ii): 05 marks

(iii) Identify the ligands coordinated to the metal ion in each compound **A**, **B**, **C** and **D**.

Answer

A: NH_3, H_2O (01 + 01)
B: NH_3, H_2O (01 + 01)
C: NH_3, Br^- (01 + 01)
D: H_2O, Br^- (01 + 01)
Note: do not award marks for "Br" (written without the negative charge). 7(b)(iii): 08 marks

(iv) In each of the compounds **A**, **B**, **C** and **D**,
I. write the oxidation state of iron.
II. write the electronic configuration of iron.

Answer

I. A: +2 or +II (02); B: +3 or +III (02); C: +2 or +II (02); D: +3 or +III (02)
Examiners' note: the + sign is compulsory; Fe^{2+} or Fe^{3+} is accepted.
II. A: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ (02); B: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ (02); C: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ (02); D: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ (02) · 7(b)(iv): 16 marks

(v) Give the structures of **A**, **B**, **C** and **D**.

Answer

A: $[Fe(NH_3)_3(H_2O)_3]Br_2$ or $[Fe(H_2O)_3(NH_3)_3]Br_2$ (10)
B: $[Fe(NH_3)_2(H_2O)_4]Br_3$ or $[Fe(H_2O)_4(NH_3)_2]Br_3$ (10)
C: $[Fe(NH_3)_5Br]Br$ or $[FeBr(NH_3)_5]Br$ (10)
D: $K[FeBr_4(H_2O)_2]$ or $K[Fe(H_2O)_2Br_4]$ (10)
Note: award the marks if, instead of structural formulae, structures with the correct cations and anions are drawn. 7(b)(v): 40 marks · 7(b): 75 marks

Review.

Match each formula to a compound by its ion count and by the moles of AgBr. Only Br^- outside the coordination sphere is precipitated by Ag^+ (as pale yellow AgBr, which dissolves in concentrated ammonia as $[Ag(NH_3)_2]^+$). B (4 ions, 3 AgBr) must be $[Fe(NH_3)_2(H_2O)_4]Br_3 = FeH_{14}N_2O_4Br_3$, so Fe is +3. A (3 ions, 2 AgBr) is $FeH_{15}N_3O_3Br_2 = [Fe(NH_3)_3(H_2O)_3]Br_2$ with Fe +2. C (2 ions, 1 AgBr) is $FeH_{15}N_5Br_2 = [Fe(NH_3)_5Br]Br$ with Fe +2. D gives no AgBr, so all four Br^- are ligands and K^+ is the counter-ion: $K[FeBr_4(H_2O)_2]$ with Fe +3. Each complex has six ligands, which fits an octahedral geometry. Fe^{2+} is $3d^6$ and Fe^{3+} is $3d^5$, because the 4s electrons are lost first. A common mistake is to write the configuration with 4s electrons.

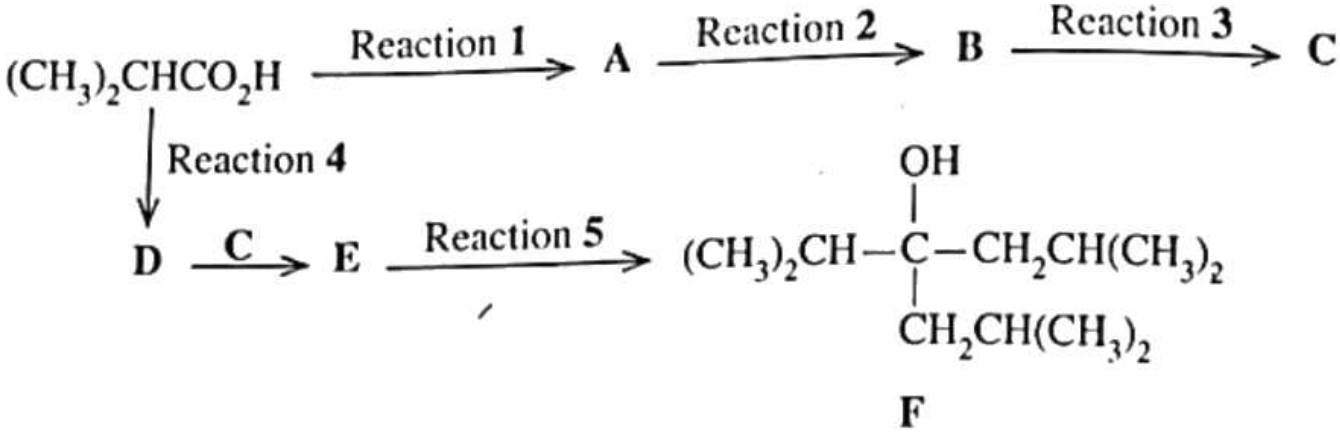
Read: RB U13 §3.3 · p. 250 RB U13 §3.4 · p. 261 RB U6 §4.10.6 · p. 169 RB U6 §4.10 · p. 160

Part C

Question 8 · Part C · essay

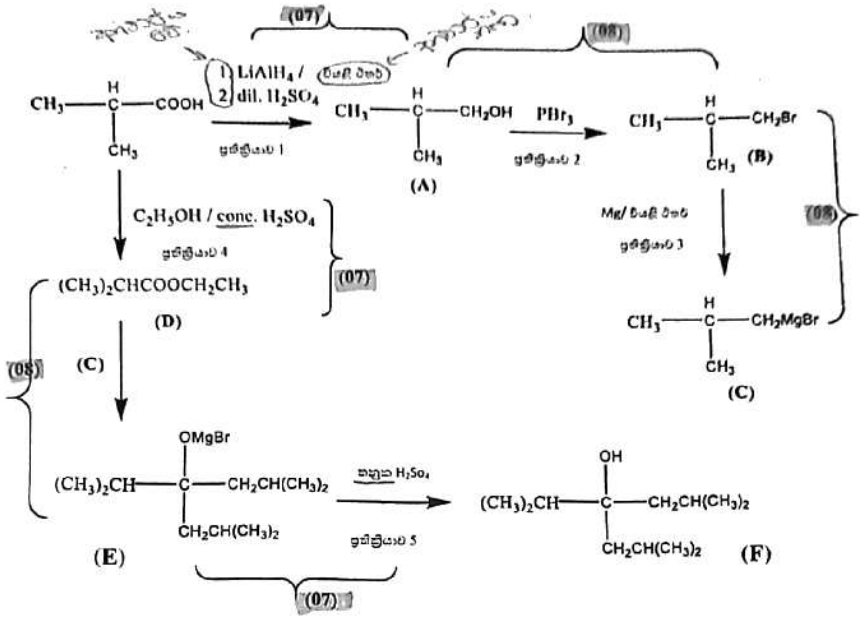
(a) [45 marks]

$(CH_3)_2CHCO_2H$ has been converted to compound **F** by using the reaction scheme given below.



Complete the above reaction scheme by giving the structures of compounds **A**, **B**, **C**, **D** and **E** and the reagents required for the reactions 1 - 5. Only the chemical substances given below should be used (either singly or as combinations) as reagents.
Chemical substances: C_2H_5OH, dry ether, $LiAlH_4$, Mg, PBr_3, conc. H_2SO_4, dil. H_2SO_4

Answer



2

4

2

4

Reaction 1: 1) $LiAlH_4$/dry ether, 2) dil. H_2SO_4 → **A** = $(CH_3)_2CHCH_2OH$ (07) (the numbering 1), 2) is compulsory; "dry ether" is not compulsory)
Reaction 2: PBr_3 → **B** = $(CH_3)_2CHCH_2Br$ (08)
Reaction 3: Mg/dry ether → **C** = $(CH_3)_2CHCH_2MgBr$ (08)
Reaction 4: C_2H_5OH/conc. H_2SO_4 → **D** = $(CH_3)_2CHCOOCH_2CH_3$ (07)
D + **C** → **E** = $(CH_3)_2CH–C(OMgBr)(CH_2CH(CH_3)_2)_2$ (08)
Reaction 5: dil. H_2SO_4 → **F** = $(CH_3)_2CH–C(OH)(CH_2CH(CH_3)_2)_2$ (07)
Note: –OMgBr in the structure of **E** may be shown with +/− charges or partial charges.
Alternative answer for reaction 4: $(CH_3)_2CHCOOH$ —PBr_3→ **D** = $(CH_3)_2CHCOBr$ (07). Note: acyl bromides are not much used, and the reaction between acyl halides and Grignard reagents is not in the syllabus. 8(a): 45 marks

Review.

Work backwards from F. F is a tertiary alcohol carrying two identical $CH_2CH(CH_3)_2$ groups and the $(CH_3)_2CH$ group of the starting acid, so it must come from an ester of $(CH_3)_2CHCOOH$ reacting with **two** moles of the Grignard reagent $(CH_3)_2CHCH_2MgBr$. The first mole gives a ketone, which reacts again at once. The Grignard reagent is built from the same acid: $LiAlH_4$ reduces –COOH to $–CH_2OH$, PBr_3 converts the alcohol to the bromide, and Mg in dry ether gives RMgBr. Esterification with ethanol/conc. H_2SO_4 gives D, and dilute acid hydrolyses the magnesium alkoxide E to F. Common mistakes: reducing the acid with $NaBH_4$ (not in the list and too weak), forgetting the separate acid work-up step after $LiAlH_4$, and using dil. H_2SO_4 for esterification.

(b) [30 marks]

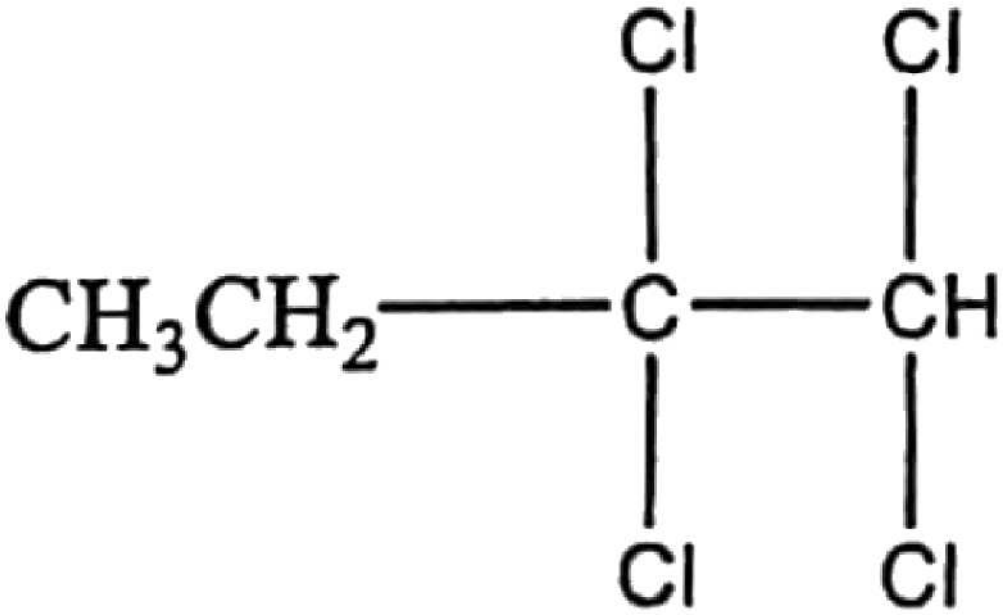
(i) Using C_2H_2 as the only starting compound, show how you would prepare compound **G** using not more than **four (04)** steps.
G: $CH_3CH_2–C≡CH$

Answer

$HC{\equiv}CH \xrightarrow{-H_2/Pd\text{–}BaSO_4/quinoline} H_2C{=}CH_2$ (06)
$H_2C{=}CH_2 \xrightarrow{-HBr} CH_3CH_2Br$ (07)
$HC{\equiv}CH \xrightarrow{-NaNH_2 \text{ or } Na\ (Na/NH_3(l))} HC{\equiv}C^-Na^+$ (06)
$HC{\equiv}C^-Na^+ + CH_3CH_2Br \rightarrow CH_3CH_2\text{–}C{\equiv}CH$ (**G**) (07) · 8(b)(i): 26 marks
Notes: if the catalyst is not written as $H_2/Pd\text{–}BaSO_4$/quinoline and only its name ("Lindlar catalyst") is written, do not award marks. HBr is the most suitable; HCl and HI are also accepted. The alkene may be written with C=C, or as C_2H_4 or CH_2CH_2. $NaNH_2$ (liq. NH_3) or Na (liq. NH_3). C^-Na^+ or CNa is acceptable (C–Na is not accepted). Award marks for the steps that prepare the alkene and the sodium salt of the alkyne. If the synthesis has more than 04 steps, do not award marks for the extra steps even if they are correct. (Examiners' handwritten notes: with 5 steps, marks are given for the first 4 steps; with more than 5 steps, no marks.)

(ii) Give the structure of the compound **H** which is formed when compound **G** is reacted with excess Cl_2.

Answer



3

2

2

2

H

3

2

2

2

(04) · 8(b)(ii): 04 marks · 8(b): 30 marks

Review.

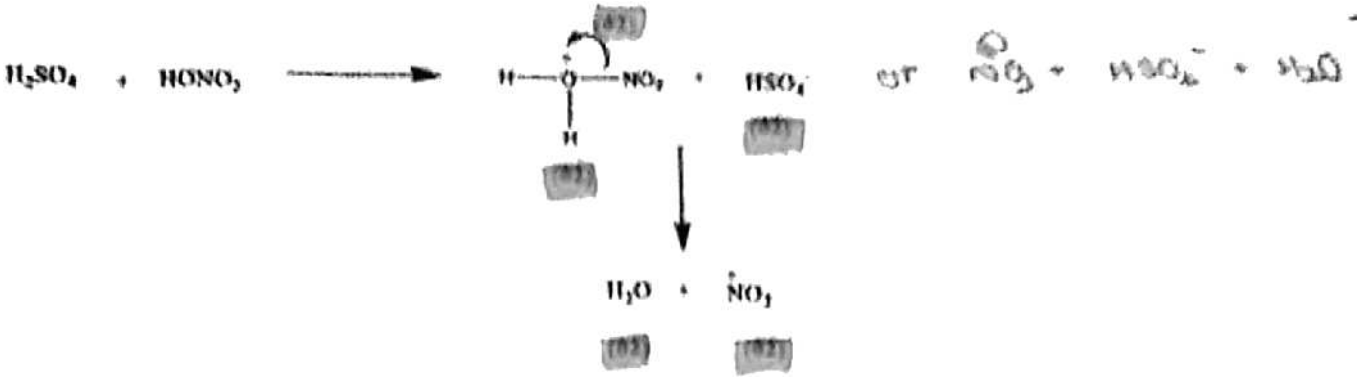
The chain is lengthened by an acetylide ion: the terminal alkyne is acidic, $NaNH_2$ (or Na) gives $HC{\equiv}C^-Na^+$, and this attacks a primary alkyl halide (nucleophilic substitution) to add two carbons. The ethyl bromide is made from the same C_2H_2. Partial hydrogenation stops at ethene only with the poisoned catalyst

Pd/$BaSO_4$/quinoline, and HBr then adds to ethene. The scheme insists on the reagent formula, not the name "Lindlar catalyst". In (ii) the triple bond adds two moles of Cl_2, one across each π bond, so each alkyne carbon gains two Cl atoms. A common mistake is to stop at the dichloroalkene.

(c) [25 marks]

Write the product and the mechanism of the reaction of benzene with conc. HNO_3/conc. H_2SO_4.

Answer



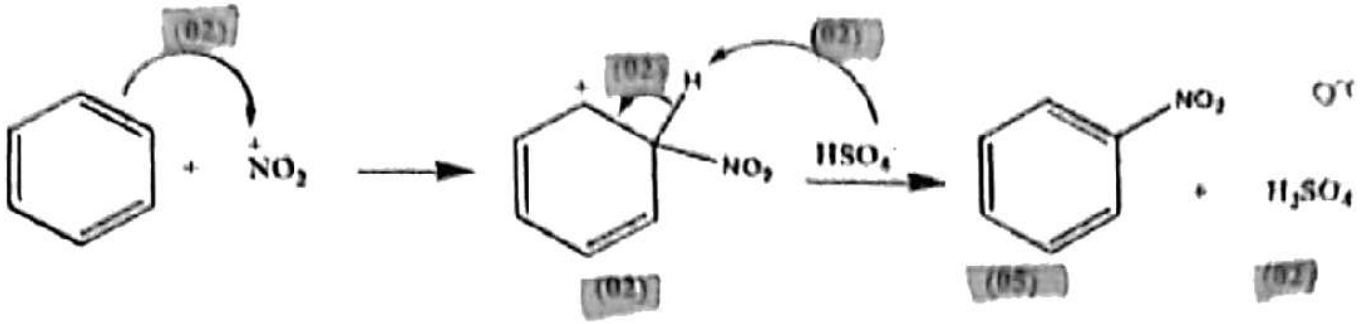
+

2

4

−

2



+

2

+

4

−

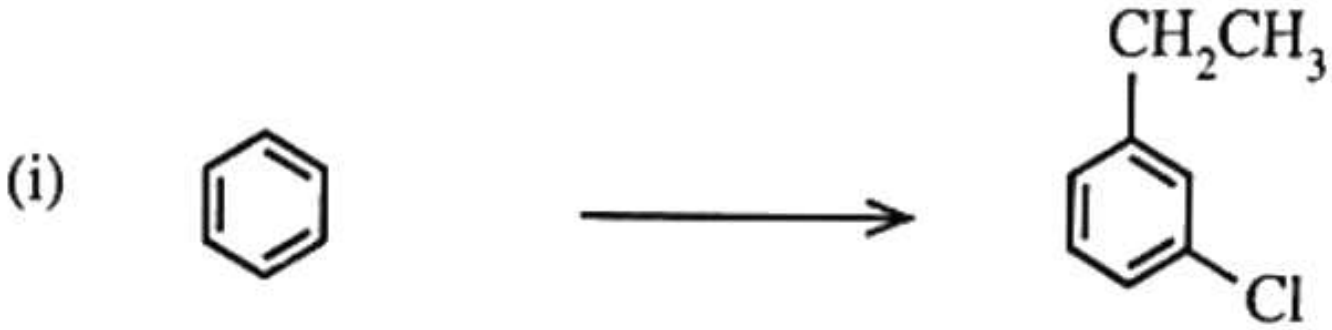
$H_2SO_4 + HONO_2 \rightarrow H\text{–}O^+(H)\text{–}NO_2$ (02) + HSO_4^- (02); curly arrow showing loss of water (02) → H_2O (02) + $^+NO_2$ (02) (or written directly as $H_2SO_4 + HNO_3 \rightarrow {}^+NO_2 + HSO_4^- + H_2O$)
Benzene π electrons attack $^+NO_2$ (curly arrow) (02) → arenium ion (carbocation with H and NO_2 on the same carbon) (02); curly arrow from the C–H bond (02); HSO_4^- removes H^+ (curly arrow) (02) → nitrobenzene (05) + H_2SO_4 (02)
Notes: mark the reaction that forms $^+NO_2$ independently. Mark the reaction of $^+NO_2$ with benzene independently, but to award the marks for the arenium ion, its formation from benzene and $^+NO_2$ must be shown. If only the reaction between benzene and $^+NO_2$ is written, award 02 marks for $^+NO_2$. 8(c): 25 marks

Review.

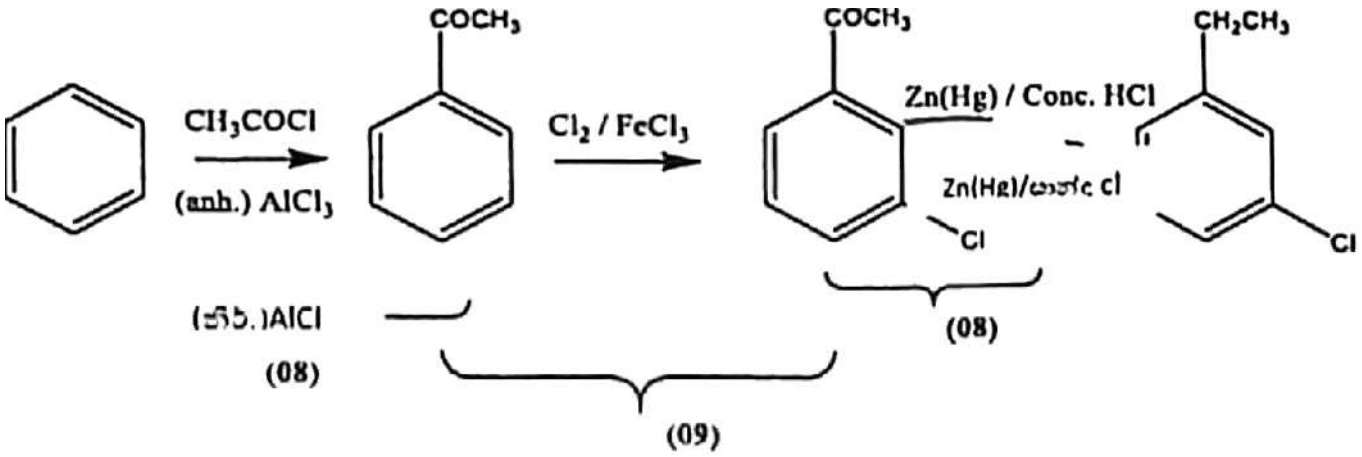
This is electrophilic substitution. Concentrated H_2SO_4 protonates HNO_3, and the protonated acid loses water to give the nitronium ion, $^+NO_2$, the electrophile. The π electrons of benzene attack $^+NO_2$ to form a resonance-stabilized arenium ion (σ-complex). HSO_4^- then removes the H^+ from the sp^3 carbon, which restores aromaticity and regenerates H_2SO_4 (it acts as a catalyst). Curly arrows must start from electrons (a π bond, a C–H bond or a lone pair) and point to the atom that receives them. Showing addition instead of substitution, or drawing the arrow from $^+NO_2$ to the ring, loses marks.

(d) [50 marks]

Show how you would carry out each of the following conversions in not more than **three (03)** steps.
(i) benzene → 1-chloro-3-ethylbenzene



Answer



3

1. $CH_3COCl/(anh.)\ AlCl_3$ → acetophenone ($C_6H_5COCH_3$) (08)
2. $Cl_2/FeCl_3$ → 3-chloroacetophenone (09)
3. Zn(Hg)/conc. HCl → 1-chloro-3-ethylbenzene (08) · 8(d)(i): 25 marks
Note: $Cl_2/FeCl_3$, or Cl_2 with a Lewis acid such as $Fe/FeBr_3/AlCl_3/AlBr_3$.

(ii) $CH_3CH(OH)CH_3$ → $CH_3CH_2CH_2OH$

Answer

1. conc. H_2SO_4/heat (170–180 °C) → $CH_3–CH=CH_2$ (08)
2. HBr/peroxide → $CH_3CH_2CH_2Br$ (09)
3. aq. NaOH (dil. NaOH, aq. KOH or dil. KOH) → $CH_3CH_2CH_2OH$ (08) · 8(d)(ii): 25 marks
Notes: Al_2O_3/heating is accepted (reaction 1). HBr/H_2O_2 is accepted (reaction 2). Aqueous/dilute NaOH or aqueous/dilute KOH is accepted; "NaOH" or "KOH" alone is not accepted (reaction 3). If the synthesis routes in (d)(i) and (ii) have more than 03 steps, do not award marks. 8(d): 50 marks

Review.

(i) depends on the order of steps. The ethyl and Cl groups are meta to each other, but both are ortho/para directors, so a meta-directing group must be in place before chlorination. Friedel–Crafts acylation puts on –$COCH_3$ (meta-directing and deactivating), Cl_2/$FeCl_3$ then substitutes meta, and Clemmensen reduction (Zn(Hg)/conc. HCl) turns C=O into CH_2. Ethylating first would give 2- and 4-chloroethylbenzene. (ii) moves the OH from C-2 to C-1. Dehydration gives propene. HBr in the presence of peroxide adds anti-Markovnikov to give 1-bromopropane, and aqueous NaOH substitutes OH for Br. Without the peroxide, HBr would give 2-bromopropane. With alcoholic KOH, elimination would take place instead of substitution.

Read: RB U9 §3.5 · p. 66 RB U8 §2.7 · p. 50 RB U8 §2.3 · p. 41 RB U8 §2.4 · p. 44

Question 9 · Part C · essay

(a) [75 marks]

(i) Aqueous solutions of compounds $MgSO_4$, NaOH, $BaCl_2$, Na_2SO_4 and $Zn(NO_3)_2$ are contained in five 100 cm^3 beakers labelled **A**, **B**, **C**, **D** and **E** (**not in order**). Identify **A**, **B**, **C**, **D** and **E** based on the observations given below. (Reasons **not** required.)
Note: Small portions of the solutions are mixed in test tubes.
On mixing **D** and **E** a white precipitate is formed. When excess **E** is added to the precipitate, the precipitate dissolves giving a colourless solution. A white precipitate is formed when **E** is added to **C**. Precipitates are not formed when **E** is added to **A** and when **E** is added to **B**. On mixing **A** and **B** a white precipitate is formed. When **C** is added to **A**, a white precipitate is formed. However, a precipitate is not formed when **C** is added to **B**.

Answer

A: $BaCl_2$
B: Na_2SO_4
C: $MgSO_4$
D: $Zn(NO_3)_2$
E: NaOH (05 × 5 = 25) · 9(a)(i): 25 marks

(ii) An aqueous solution **M** contains **three** cations. The following tests (1-5) were carried out to identify these cations.

Test No.	Test	Observation
1	Dilute HCl was added to solution **M**.	A white precipitate (P_1)
2	P_1 was separated by filtration and H_2S was bubbled through the solution.	No precipitate
3	The solution was boiled until all the H_2S was removed and then cooled. NH_4Cl/NH_4OH was added.	No precipitate
4	H_2S was bubbled through this solution.	A pale pink precipitate (P_2)
5	P_2 was separated by filtration and the solution was boiled until all the H_2S was removed. $(NH_4)_2CO_3$ solution was added.	A white precipitate (P_3)

1

2

3

Precipitate	Test	Observation
P_1	Dilute ammonia solution was added to P_1.	P_1 dissolved.
P_2	P_2 was dissolved in dil. HNO_3 and excess dilute NaOH was added to the solution.	A white precipitate which turns brown on standing
P_3	P_3 was dissolved in conc. HCl and the solution was subjected to the flame test.	A green colour flame

three

M

not

1

2

3

Answer

I. Ag^+, Mn^{2+}, Ba^{2+}
II. P_1: AgCl; P_2: MnS; P_3: $BaCO_3$ (04 × 6 = 24) · 9(a)(ii): 24 marks

(iii) **X**, **Y** and **Z** are ionic solids. Sodium is the cation in all three compounds. The following tests were carried out to identify the anions in **X**, **Y** and **Z**.

Test No.	Test	Observation
1	(i) A portion of **X** was dissolved in water in a test tube.	A colourless solution
(ii) $Pb(CH_3COO)_2$ solution was added to the colourless solution.	A yellow precipitate	
(iii) The resulting mixture (yellow precipitate and solution) was heated.	The precipitate dissolved giving a colourless solution.	
(iv) This colourless solution was cooled.	A yellow precipitate (as golden yellow plates)	
2	(i) A portion of **Y** was dissolved in water in a test tube.	A colourless solution
(ii) A $BaCl_2$ solution was added to the colourless solution.	A white precipitate	
(iii) Dilute HCl was added to the resulting mixture (white precipitate and solution).	A clear colourless solution with the evolution of a gas	

Test No.	Test	Observation
(iv) The gas evolved was tested by holding a filter paper moistened with acidified $K_2Cr_2O_7$ over the mouth of the test tube.	Orange filter paper turned green.	
3	(i) A portion of **Z** was dissolved in water in a test tube.	A colourless solution
(ii) $AgNO_3$ solution was added to the colourless solution.	A black precipitate	
(iii) Dilute HCl was added to a portion of **Z** in a test tube.	A colourless gas evolved.	
(iv) The gas evolved was tested by holding a filter paper moistened with $Pb(CH_3COO)_2$ solution over the mouth of the test tube.	Filter paper turned black	

X

Y

Z

not

Answer

I. X: I^- (04); Y: SO_3^{2-} (04); Z: S^{2-} (04)
II.
1. $Pb(CH_3COO)_2 + 2NaI \rightarrow PbI_2 + 2CH_3COONa$, or $Pb^{2+} + 2I^- \rightarrow PbI_2$
2. $BaCl_2 + Na_2SO_3 \rightarrow BaSO_3 + 2NaCl$, or $Ba^{2+} + SO_3^{2-} \rightarrow BaSO_3$
3. $BaSO_3 + 2HCl \rightarrow BaCl_2 + SO_2 + H_2O$, or $BaSO_3 + 2H^+ \rightarrow Ba^{2+} + SO_2 + H_2O$
4. $3SO_2 + Cr_2O_7^{2-} + 2H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$
5. $2AgNO_3 + Na_2S \rightarrow Ag_2S + 2NaNO_3$, or $2Ag^+ + S^{2-} \rightarrow Ag_2S$
6. $Ag_2S + 2HCl \rightarrow 2AgCl + H_2S$ (handwritten alternative in the scheme: $Na_2S + 2HCl \rightarrow 2NaCl + H_2S$)
7. $Pb(CH_3COO)_2 + H_2S \rightarrow PbS + 2CH_3COOH$ (02 × 7 = 14) · 9(a)(iii): 26 marks · 9(a): 75 marks

Review.

(i) is solved from the mixing pattern. The only reagent that gives a precipitate that dissolves in excess of itself is NaOH (E) with Zn^{2+} (D, amphoteric $Zn(OH)_2$). NaOH precipitates $Mg(OH)_2$ from C but nothing from $BaCl_2$ or Na_2SO_4. The $BaSO_4$ precipitates then show that A = $BaCl_2$ (it precipitates both sulfates) and B = Na_2SO_4. (ii) follows the cation group scheme. Group I gives a white chloride soluble in dilute ammonia (AgCl, as $[Ag(NH_3)_2]^+$). There is no Group II or III ion. In Group IV, pale pink (flesh-coloured) MnS appears; $Mn(OH)_2$ is white and darkens as it is oxidized in air. Group V gives a carbonate whose flame is green: Ba^{2+}. (iii) are anion tests. Yellow PbI_2 dissolves in hot water and recrystallizes as golden plates. $BaSO_3$ dissolves in dilute HCl, releasing SO_2, which turns acidified dichromate green. S^{2-} gives black Ag_2S, and with acid gives H_2S, which blackens lead acetate paper. Note on equation 6: test 3(iii) adds HCl to a fresh portion of Z, so the equation that matches it is the scheme's handwritten $Na_2S + 2HCl \rightarrow 2NaCl + H_2S$. Ag_2S is too insoluble to be attacked by dilute HCl.

(b) [75 marks]

A solid sample **X** contains the compounds **P**, **Q** and an inert substance. Here **P** = Fe_2O_3 and **Q** = Fe_3O_4. **Q** is a **single** compound and contains iron in Fe^{2+} and Fe^{3+} oxidation states. It reacts with I^- in an acidic medium as follows.

$Fe_3O_4 + 2I^- + 8H^+ \rightarrow 3Fe^{2+} + 4H_2O + I_2$

The following experimental procedure was used to determine the mass percentages of **P** and **Q** in **X**.

When 3.2 g of sample **X** was treated with excess KI solution in the presence of dilute H_2SO_4, all the Fe^{3+} in it was converted to Fe^{2+} with the liberation of iodine. The resulting solution was diluted to 100.00 cm^3 (labelled as S). To convert the iodine to iodide in a 25.00 cm^3 volume of this diluted solution (S), 15.00 cm^3 of 0.50 mol dm^{-3} $Na_2S_2O_3$ was required.

After complete removal of iodine from another 50.00 cm^3 volume of the diluted solution (S), in dil. H_2SO_4 medium, 14.00 cm^3 of 0.25 mol dm^{-3} $KMnO_4$ was required to oxidize all the Fe^{2+} contained in it.

(i) Write balanced chemical equations for the reactions taking place in the above procedure.

Answer

$Fe_3O_4 + 2I^- + 8H^+ \rightarrow 3Fe^{2+} + 4H_2O + I_2$ (given)
$Fe_2O_3 + 2I^- + 6H^+ \rightarrow 2Fe^{2+} + 3H_2O + I_2$ (05), or $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$
$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$ (05)
$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$ (05) · 9(b)(i): 15 marks

(ii) Calculate the mass percentages of **P** and **Q** in **X**. (O = 16, Fe = 56)

Answer

In sample X, let moles of $Fe_3O_4 = n_1$ and moles of $Fe_2O_3 = n_2$ (02 + 02)
Moles of $S_2O_3^{2-}$ = (0.5/1000) × 15 (02)
Hence moles of I_2 in 25.00 cm^3 = (0.5/1000) × 15.0 × ½ (02)
Hence moles of I_2 in 100.0 cm^3 of solution = (0.5/1000) × 15.0 × ½ × 100/25 (02) = 0.015 (02)
According to the equations: n_1 mol of Fe_3O_4 gives n_1 mol of I_2 (02); n_2 mol of Fe_2O_3 gives n_2 mol of I_2 (02)
Hence $n_1 + n_2 = 0.015$ ……(1) (04)
Moles of MnO_4^- = (0.25/1000) × 14 (02); moles of Fe^{2+} reacted = 5 × (0.25/1000) × 14 (02)
Moles of Fe^{2+} in the diluted solution S = 5 × (0.25/1000) × 14.0 × 100/50 (02) = 5 × (0.25/1000) × 14.0 × 2 = 0.035 (02)
1 mol of Fe_3O_4 gives 3 mol of Fe^{2+} (01); n_1 mol of Fe_3O_4 gives $3n_1$ mol of Fe^{2+} (01)
1 mol of Fe_2O_3 gives 2 mol of Fe^{2+} (01); n_2 mol of Fe_2O_3 gives $2n_2$ mol of Fe^{2+} (01)
Hence $3n_1 + 2n_2 = 0.035$ ……(2) (04)
Equation (1) × 2: $2n_1 + 2n_2 = 0.03$ ……(3)
(2) − (3): $n_1 = 0.005$ mol (03); hence $n_2 = 0.015 - 0.005 = 0.01$ mol (03)
Molar mass of Fe_3O_4 = 232 g mol^{-1} (02); mass of Fe_3O_4 in sample X = 0.005 × 232 = 1.16 g (02)
Molar mass of Fe_2O_3 = 160 g mol^{-1} (02); mass of Fe_2O_3 in sample X = 0.01 × 160 = 1.6 g (02)
% Fe_3O_4 (Q) = (1.16/3.2) × 100 = 36.25 (05)
% Fe_2O_3 (P) = (1.6/3.2) × 100 = 50.00 (05) · 9(b)(ii): 60 marks
Alternative method 01 (same marks): $Fe_3O_4 \equiv Fe_2O_3 \cdot FeO$, so 1 mol $Fe_3O_4 \equiv$ 2 mol Fe^{3+} + 1 mol Fe^{2+}, and 1 mol $Fe_2O_3 \equiv$ 2 mol Fe^{3+}. Moles of $S_2O_3^{2-} = 7.5 \times 10^{-3}$; I_2 in 25.00 $cm^3 = 3.75 \times 10^{-3}$; I_2 in 100.0 $cm^3 = 15 \times 10^{-3} = 0.015$. Moles of Fe^{3+} that reacted with $I^- = 2 \times 0.015 = 0.03$ (02); moles of Fe^{2+} formed from $Fe^{3+} = 0.03$ (02); hence $2n_1 + 2n_2 = 0.03$ ……(1) (04). Then, as above, $3n_1 + 2n_2 = 0.035$ ……(2); (2) − (1): $n_1 = 0.005$ mol, $n_2 = 0.01$ mol, giving 36.25% and 50.00%.
Alternative method 02 (same marks): let the masses be m_1 g (Fe_3O_4) and m_2 g (Fe_2O_3); moles = $m_1/232$ and $m_2/160$. Then $m_1/232 + m_2/160 = 0.015$ ……(1) and $3m_1/232 + 2m_2/160 = 0.035$ ……(2); (2) − 2 × (1): $m_1/232 = 0.005$ mol, so $m_1 = 1.16$ g; $m_2/160 = 0.01$ mol, so $m_2 = 1.6$ g; 36.25% and 50.00%. 9(b): 75 marks

Review.

This is a two-titration redox problem. The iodometric titration counts only the Fe^{3+}: each Fe_3O_4 ($2Fe^{3+}$ + Fe^{2+}) and each Fe_2O_3 ($2Fe^{3+}$) liberates one I_2, which uses 2 $S_2O_3^{2-}$. The permanganate titration counts all the iron, because after reduction by I^- every Fe atom is Fe^{2+} (5 Fe^{2+} per MnO_4^-). Scale each aliquot back to the 100 cm^3 of S (×4 and ×2), then solve $n_1 + n_2 = 0.015$ and $3n_1 + 2n_2 = 0.035$. The percentages add up to only 86.25%; the remaining 13.75% is the inert substance. Common mistakes: forgetting the aliquot factors, using a 1:1 ratio for thiosulfate with I_2, and assuming the $KMnO_4$ measures only the Fe^{2+} originally present in Fe_3O_4.

Read: RB U12 §2.4 · p. 175 RB U6 §4.10 · p. 160 RB U3 §3.8 · p. 115 RB U6 §4.6 · p. 141

Question 10 · Part C · essay

(a) [50 marks]

The following questions are based on the extraction of magnesium by the Dow process.
(i) State the raw materials used.

Answer

Bittern (from sea water) (04)
Limestone or dolomite ($CaCO_3$ or $CaCO_3 \cdot MgCO_3$) (04)
Conc. HCl (04) · 10(a)(i): 12 marks

(ii) Give balanced chemical equations/half reactions in the sequence they occur in the Dow process. Appropriate conditions must be stated as required.

Answer

Step 1

3

2

3

3

2

(02)

Step 2

2

2

2

(02)

2

2+

−

(02)

2+

−

2

(02)

Step 3

2

2

2

2

(02)

2

Step 4

2

2

2

2

2

(01)

2

2

2

2

2

(01)

Step 5

2

(01)

−

2

(03)

(01)

2+

(03)

Correct order

(10)

10(a)(ii): 30 marks

(iii) Give **two** industrial uses of magnesium.

Answer

Any two: 1. to produce alloys; 2. to produce light, strong alloys in the aircraft and vehicle manufacturing industries; 3. to prepare Grignard reagents; 4. to manufacture light equipment such as power tools, camera bodies and laptops; 5. in the fireworks industry; 6. in the pharmaceutical industry (milk of magnesia); 7. to remove sulfur from molten iron; 8. for cathodic protection. (02 × 2) · 10(a)(iii): 04 marks

(iv) Give **two** ways in which the Dow process has a **negative** impact on the environment.

Answer

1. CO_2 released by the thermal decomposition of limestone or dolomite contributes to global warming. (02)
2. CO_2 released by burning petroleum fuels to obtain the high temperature needed for the electrolytic cell contributes to global warming. (02) · 10(a)(iv): 04 marks · 10(a): 50 marks

Review.

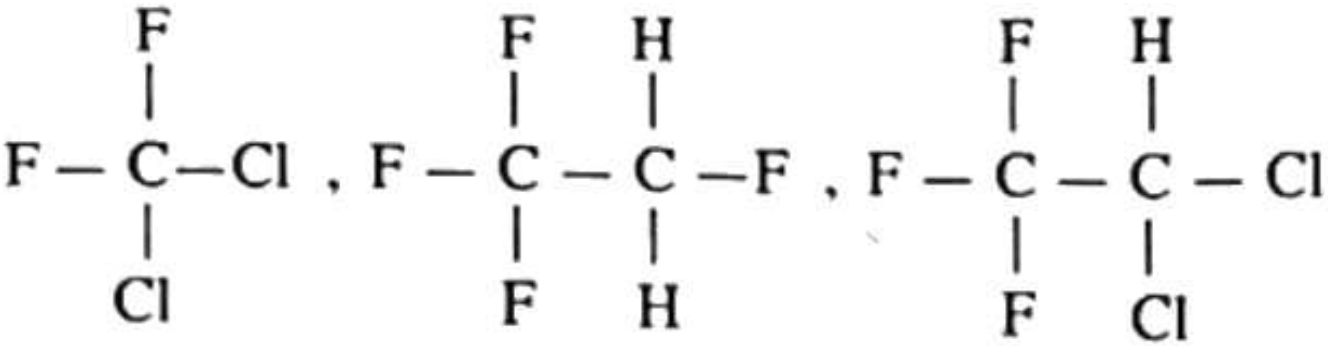
The Dow process (Resource Book Unit 14) uses Mg^{2+} from bittern, the liquor left after salt crystallizes from sea water. $Mg(OH)_2$ is precipitated with OH^- from slaked lime, because its K_{sp} is much lower than that of $Ca(OH)_2$. It is then converted to $MgCl_2$ with HCl and partly dehydrated, and molten $MgCl_2$ is electrolysed at 700–800 °C. Mg(l) forms at the steel cathode and Cl_2(g) at the graphite anode; the Cl_2 is recycled to make HCl. The order of the steps is marked separately, so learn them in sequence. The scheme's dolomite equation omits a coefficient: the balanced form (as in the Resource Book) is $CaCO_3 \cdot MgCO_3(s) \rightarrow CaO(s) + MgO(s) + 2CO_2(g)$. Common mistakes: writing aqueous $MgCl_2$ in the electrolysis, and leaving out physical states or the electrode labels in step 5.

(b) [50 marks]

Given below are some pollutants that exist in the atmosphere.

Pollutant List

CH_4, CO_2, NO, NO_2, N_2O, SO_2, SO_3, $CH_3CH_2CH_2CH_2CH_3$,



2

2

3

2

3

2

The following questions are based on the pollutant list given above.

(i) Identify the pollutant that directly contributes towards increasing the level of ozone in the atmosphere.

Answer

NO_2 (02)

(ii) Explain using balanced chemical equations how the pollutant you identified in (i) above increases the ozone level in the atmosphere.

Answer

$NO_2(g)$ —hν→ $NO(g) + \cdot O(g)$ (03)
$O_2(g) + \cdot O(g) \rightarrow O_3(g)$ (03)

(iii) Identify **two** pollutants that contribute to the reduction of ozone level in the upper atmosphere.

Answer

Any two of: CF_3–$CHCl_2$, CF_2Cl_2, NO (02 + 02)

(iv) Briefly explain using balanced chemical equations how one of the pollutants you identified in (iii) above contributes to the reduction of ozone level in the upper atmosphere.

Answer

CF_2Cl_2 —hν→ $\cdot CF_2Cl + Cl\cdot$ (03)
$Cl\cdot + O_3 \rightarrow O_2 + \cdot OCl$ .....(1) (03)
$O_3 \rightarrow O_2 + \cdot O$ .....(2) (03)
$\cdot OCl + \cdot O \rightarrow O_2 + Cl\cdot$ .....(3) (03)
(1) + (2) + (3): $2O_3 \rightarrow 3O_2$ (03)
OR $\cdot NO + O_3 \rightarrow NO_2 + O_2$ (15) (examiners' handwritten breakdown: $NO + O_3 \rightarrow NO_2 + O_2$ (04); $NO_2 \rightarrow NO + O$ (04); $O + O_3 \rightarrow 2O_2$ (04); overall $2O_3 \rightarrow 3O_2$ (03))
OR $\cdot NO + O_2 \rightarrow NO_2 + \cdot O$ (08); $O_3 + O_2 \rightarrow 2O_2$ (07) (as printed in the scheme)
(The radical dot (·) is not required – "only for this time".)

(v) Identify **two** pollutants that cause photochemical smog.

Answer

Any two of: NO, NO_2 and $CH_3CH_2CH_2CH_2CH_3$ (02 + 02)

(vi) Identify **four** pollutants that can absorb infrared radiation in the atmosphere and remain stable in the atmosphere for a long period of time.

Answer

Any four of: CH_4, CO_2, N_2O, CF_3–CF_2H (the CF_3CH_2F of the list), CF_3–$CHCl_2$, CF_2Cl_2 (02 × 4)

(vii) What is the commonly used name that describes the behaviour of the pollutants you identified in (vi) above?

Answer

Greenhouse gases / greenhouse effect (03)

(viii) Identify **two** pollutants that contribute to make a significant change in some water quality parameters when dissolved in water. State the water quality parameter(s) that will be affected by the pollutants you identified.

Answer

Any two of: NO_2, SO_2, SO_3, CO_2 (02 + 02)
pH and conductivity (02 + 02) · 10(b): 50 marks

Review.

NO_2 is the only listed species that makes O_3 directly: sunlight splits it into NO and an O atom, which combines with O_2. This is how ground-level ozone forms in photochemical smog, together with NO and

volatile hydrocarbons such as pentane. In the stratosphere, Cl atoms from CFCs/HCFCs (CF_2Cl_2, CF_3CHCl_2) and NO destroy ozone catalytically: the Cl or NO is regenerated, so one atom removes many O_3 molecules (net $2O_3 \rightarrow 3O_2$). CF_3CH_2F contains no chlorine, so it does not deplete ozone, but like CH_4, CO_2, N_2O and the CFCs it is a long-lived greenhouse gas. Acidic oxides (NO_2, SO_2, SO_3, CO_2) dissolve to form acids, lowering pH and raising conductivity. Two slips in the scheme: in (vi) the hydrofluorocarbon of the list is CF_3CH_2F (printed $CF_3–CF_2H$), and the last alternative equation for (iv) should be $O_3 + \cdot O \rightarrow 2O_2$ ($O_3 + O_2 \rightarrow 2O_2$ does not balance).

(c) [50 marks]

Consider the polymerization reactions between one monomer from group A and one monomer from group B given below.
Group A monomers: Cl–CO–$(CH_2)_n$–CO–Cl, HO–CO–$(CH_2)_n$–CO–OH
Group B monomers: HO–$(CH_2)_n$–OH, H_2N–$(CH_2)_n$–NH_2
where n is an integer.
(i) Write the pair/pairs of monomers that would release an acidic molecule during the polymerization reaction.

Answer

Cl–CO–$(CH_2)_n$–CO–Cl and HO–$(CH_2)_n$–OH (10)
Cl–CO–$(CH_2)_n$–CO–Cl and H_2N–$(CH_2)_n$–NH_2 (10)

(ii) Write the pair/pairs of monomers that would release a neutral molecule during the polymerization reaction.

Answer

HO–CO–$(CH_2)_n$–CO–OH and HO–$(CH_2)_n$–OH (10)
HO–CO–$(CH_2)_n$–CO–OH and H_2N–$(CH_2)_n$–NH_2 (10) · (i) + (ii): 40 marks

(iii) The molar mass of the repeating unit –[–CO–$(CH_2)_n$–CO–NH–$(CH_2)_n$–NH–]– is 226 g mol^{-1}. Calculate the number of –CH_2– units in a repeating unit.

Answer

Molar mass of the repeating unit: 28 × 2 + 15 × 2 + 14 × 2 × n = 226 (05)
56 + 30 + 28n = 226; 28n = 140; n = 5 (02)
Hence the number of –CH_2– units in the repeating unit = 5 × 2 = **10** (03) · 10 marks · 10(c): 50 marks

Review.

This is condensation polymerization. A diacid chloride eliminates HCl (an acidic molecule) when it reacts with a diol (giving a polyester) or a diamine (giving a polyamide). A dicarboxylic acid eliminates H_2O (a neutral molecule) with either partner. In (iii) the repeating unit contains two C=O groups (28 each), two N–H groups (15 each) and 2n CH_2 groups (14 each), so 86 + 28n = 226 and n = 5. The question asks for the total number of CH_2 units, 2n = 10, not n. Answering 5 is the common mistake.

Read: RB U14 §1.2 · p. 6 RB U14 §1.13 · p. 58 RB U14 §1.14 · p. 80 RB U14 §1.11 · p. 37

2022 · Chemistry Digital Paper

50 questions · 2 hours

MCQ · Paper I

Question 1 · Q1–30 · single answer

Which of the following electronic transitions belongs to the visible region of the line spectrum of atomic hydrogen? (n = Principal quantum number)

- (1)n = 5 → n = 3
- (2)n = 4 → n = 2
- (3)n = 1 → n = 2
- (4)n = 3 → n = 1
- (5)n = 2 → n = 1

Answer and review

Answer **(2)** Prepared answer (no official scheme available)

The visible lines of the hydrogen emission spectrum form the Balmer series, in which the electron falls from a higher level to n = 2. So n = 4 → n = 2 (the blue-green line at 486 nm) is visible. Transitions ending at n = 1 (Lyman series) are in the ultraviolet, and those ending at n = 3 (Paschen series) are in the infrared. n = 1 → n = 2 is an upward (absorption) transition in the UV.

RB U1 §1.3 · p. 17

Question 2 · Q1–30 · single answer

Select the **incorrect** statement.

- (1)Pauli exclusion principle excludes the possibility of the presence of a third electron in an orbital.
- (2)In a potassium atom, the number of electrons having quantum numbers n (principal quantum number) = 3 and m_l (magnetic quantum number) = 0 is 4.
- (3)The effective nuclear charge felt by a valence electron in nitrogen (N), is greater than the effective nuclear charge felt by a valence electron in carbon (C).
- (4)Among the ions Na^+, Mg^{2+}, K^+ and Ca^{2+}, the two ions closest to each other in size are K^+ and Mg^{2+}.
- (5)Electron gain energy of carbon is negative.

Answer and review

Answer **(4)** Prepared answer (no official scheme available)

Ionic radii (pm): Na^+ 102, Mg^{2+} 72, K^+ 138, Ca^{2+} 100. The two closest in size are Na^+ and Ca^{2+} (diagonally related), while K^+ and Mg^{2+} differ the most, so (4) is incorrect. The others are correct: K is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$, so the n = 3, m_l = 0 electrons are the two 3s electrons and the two in the m_l = 0 3p orbital (4 in total). Effective nuclear charge rises across period 2, so it is greater for N than for C. Carbon releases energy on gaining an electron (about -122 kJ mol^{-1}).

RB U1 §1.6 · p. 32 RB U1 §1.4 · p. 23

Question 3 · Q1–30 · single answer

The **increasing** order of the second ionization energy ($X^+(g) \rightarrow X^{2+}(g) + e$) of Be, B and O is,

- (1)Be < B < O
- (2)Be < O < B
- (3)B < O < Be
- (4)B < Be < O
- (5)O < Be < B

Answer and review

Answer **(1)** Prepared answer (no official scheme available)

The second electron is removed from the X^+ ion. Be^+ ($1s^2\ 2s^1$) loses a single 2s electron with nuclear charge +4. B^+ ($1s^2\ 2s^2$) loses a 2s electron with nuclear charge +5, which is harder. O^+ ($1s^2\ 2s^2\ 2p^3$) loses an electron from a stable half-filled 2p subshell with nuclear charge +8, which is hardest. So IE_2: Be (1757) < B (2427) < O (3388 kJ mol^{-1}). The trap is to use the first-ionization pattern (B < Be), which does not apply to the X^+ ions.

RB U1 §1.6 · p. 32

Question 4 · Q1–30 · single answer

The shapes of F_3ClO, $FClO_2$ and $FClO_3$ are respectively,

- (1)tetrahedral, trigonal planar and see-saw.
- (2)square planar, trigonal planar and tetrahedral.
- (3)see-saw, trigonal pyramidal and square planar.
- (4)tetrahedral, trigonal pyramidal and see-saw.
- (5)see-saw, trigonal pyramidal and tetrahedral.

Answer and review

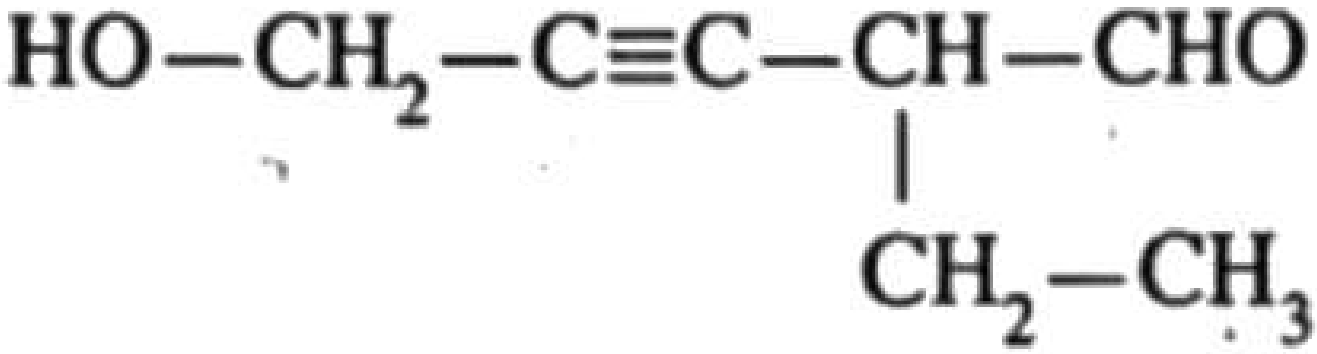
Answer **(5)** Prepared answer (no official scheme available)

Cl has 7 valence electrons. Each Cl–F bond uses one of them and each Cl=O bond uses two. F_3ClO: 3 + 2 = 5 used, one lone pair left, giving 4 bonding domains + 1 lone pair (trigonal bipyramidal electron-pair geometry), so it is see-saw. $FClO_2$: 1 + 4 = 5 used, one lone pair, giving 3 bonding domains + 1 lone pair, so it is trigonal pyramidal. $FClO_3$: all 7 used, no lone pair, giving 4 bonding domains, so it is tetrahedral.

RB U2 §2.3 · p. 52

Question 5 · Q1–30 · single answer

What is the IUPAC name of the following compound?



2

2

3

- (1)5-hydroxy-2-ethylpent-3-ynal
- (2)3-formylhex-4-yn-6-ol
- (3)2-ethyl-5-hydroxypent-3-ynal
- (4)4-formyl-1-hydroxy-2-hexyne
- (5)4-formylhex-2-yn-1-ol

Answer and review

Answer **(3)** Prepared answer (no official scheme available)

–CHO has priority over –OH, so the compound is named as an aldehyde (suffix -al) with –OH as the prefix hydroxy; names with "formyl" are wrong. The parent chain contains the CHO carbon (C-1) and the C≡C: C-1 is CHO, C-2 carries the ethyl group, C-3≡C-4, and C-5 carries the OH, giving pent-3-ynal. Prefixes go in alphabetical order (ethyl before hydroxy), so the name is 2-ethyl-5-hydroxypent-3-ynal. Option (1) has the right locants but the wrong order of prefixes.

RB U7 §1.3 · p. 7

Question 6 · Q1–30 · single answer

A saturated aqueous solution of a sparingly soluble salt AB_2 was prepared at 25 °C. Solubility product of AB_2 at 25 °C is 3.20×10^{-8} mol^3 dm^{-9}. The concentration of ion B^- (mol dm^{-3}) in the saturated solution is,

- (1)$(1.6)^{½} \times 10^{-4}$
- (2)$(3.2)^{½} \times 10^{-4}$
- (3)$(3.2)^{1/3} \times 10^{-3}$
- (4)2.0×10^{-3}
- (5)4.0×10^{-3}

Answer and review

Answer **(5)** Prepared answer (no official scheme available)

$AB_2(s) \rightleftharpoons A^{2+}(aq) + 2B^-(aq)$. If the solubility is s, $K_{sp} = s(2s)^2 = 4s^3 = 3.20 \times 10^{-8}$. So $s^3 = 8.0 \times 10^{-9}$ and $s = 2.0 \times 10^{-3}$ mol dm^{-3}. Then $[B^-] = 2s = 4.0 \times 10^{-3}$ mol dm^{-3}. Option (4) is s (= $[A^{2+}]$), not $[B^-]$.

RB U12 §2.4 · p. 175

Question 7 · Q1–30 · single answer

Select the correct statement.

- (1)The polarizability of F^-, Cl^- and S^{2-} ions increases in the order $F^- < S^{2-} < Cl^-$.
- (2)The polarizing power of Li^+, Na^+ and Mg^{2+} decreases in the order $Mg^{2+} > Na^+ > Li^+$.
- (3)The electronegativity of O, F, Cl and S decreases in the order F > O > S > Cl.
- (4)The boiling points of Xe, CH_4, CH_3NH_2 and CH_3OH increase in the order $CH_4 < Xe < CH_3NH_2 < CH_3OH$.
- (5)The interatomic bond distances of N_2, O_2, F_2 and HF increase in the order $N_2 < O_2 < F_2 < HF$.

Answer and review

Answer **(4)** Prepared answer (no official scheme available)

Boiling points: CH_4 (−162 °C, small molecule, weak London forces) < Xe (−108 °C, large, easily polarized atom) < CH_3NH_2 (−6 °C, N–H···N hydrogen bonds) < CH_3OH (65 °C, stronger O–H···O hydrogen bonds), so (4) is correct. The other orders are wrong. S^{2-} (larger, with a higher charge) is more polarizable than Cl^-. Li^+ is smaller than Na^+, so its polarizing power is higher ($Mg^{2+} > Li^+ > Na^+$). Cl (3.2) is more electronegative than S (2.6). HF (92 pm) has the shortest bond, not the longest (N_2 110, O_2 121, F_2 142 pm).

RB U2 §2.4 · p. 75 RB U2 §2.6 · p. 79 RB U1 §1.6 · p. 32

Question 8 · Q1–30 · single answer

Compounds **P** and **Q** are diastereoisomers of each other. Which of the following could be the molecular formula of compounds **P** and **Q**?

- (1)C_5H_{10}
- (2)C_3H_6
- (3)C_4H_6
- (4)$C_4H_{10}O$
- (5)C_4H_{10}

Answer and review

Answer **(1)** Prepared answer (no official scheme available)

Diastereoisomers are stereoisomers that are not mirror images of each other, for example cis/trans (geometric) isomers. C_5H_{10} includes pent-2-ene, $CH_3CH{=}CHCH_2CH_3$, which exists as cis and trans isomers, so P and Q could have this formula. None of the other formulae allows a C=C with two different groups on each carbon, or two stereocentres. C_3H_6 (propene, cyclopropane), C_4H_6 (butynes, butadienes, cyclobutene) and C_4H_{10} (butane, 2-methylpropane) have no stereoisomers. $C_4H_{10}O$ has at most one stereocentre (butan-2-ol), which gives a pair of enantiomers, not diastereoisomers.

RB U7 §1.4 · p. 21

Question 9 · Q1–30 · single answer

The **increasing** order of electronegativity of the carbon (C) atom in CH_4, CH_3Cl, H_2CO, HCN and NCO^- is

- (1)$CH_4 < H_2CO < CH_3Cl < HCN < NCO^-$
- (2)$CH_3Cl < CH_4 < H_2CO < HCN < NCO^-$
- (3)$CH_4 < CH_3Cl < H_2CO < HCN < NCO^-$

- (4)CH_4 < CH_3Cl < NCO^- < H_2CO < HCN
- (5)NCO^- < HCN < H_2CO < CH_4 < CH_3Cl

Answer and review

Answer **(3)** Prepared answer (no official scheme available)

The Resource Book compares the electronegativity of the same atom first by hybridization (more s character means more electronegative), then by charge on the atom, then by oxidation number. The sp^3 carbons come lowest: CH_4 (oxidation number −4) < CH_3Cl (−2). Next is the sp^2 carbon of H_2CO. The sp carbons are highest: HCN (+2) < NCO^- (+4; the carbon itself carries no formal charge). Hence CH_4 < CH_3Cl < H_2CO < HCN < NCO^-.

RB U2 §2.3 · p. 52

Question 10 · Q1–30 · single answer

The organic compound **X** does not give a coloured precipitate when treated with 2,4-DNP. When compound **X** is treated with acidic $K_2Cr_2O_7$, product **Y** is formed. The product **Y** gives a coloured precipitate with 2,4-DNP. **Y** liberates CO_2 when treated with aqueous Na_2CO_3 solution. Compound **X** could be,

- (1)$CH_3CH_2CH(OH)CH_2CH_2CHO$
- (2)$CH_3CH_2C(OH)(CH_3)CH_2CH_2CH_2OH$
- (3)$CH_3CH_2CH(OH)CH_2CH_2CH_2OH$
- (4)$CH_3CH_2CH(OH)CH_2CH_2CH(OH)CH_3$
- (5)$CH_3CH(OH)CH_2CH_2CO_2CH_3$

Answer and review

Answer **(3)** Prepared answer (no official scheme available)

X must have no C=O group (no 2,4-DNP precipitate). On oxidation it must give both a ketone (2,4-DNP positive) and a –COOH group (CO_2 with Na_2CO_3), so X needs a secondary –OH and a primary $–CH_2OH$. In (3), acidified dichromate gives Y = $CH_3CH_2COCH_2CH_2COOH$. The others fail. (1) already contains –CHO, so X itself would give the 2,4-DNP precipitate. In (2) the tertiary –OH is not oxidized, so Y has no C=O. (4) gives a diketone with no –COOH. (5) gives a keto-ester with no free –COOH.

RB U9 §3.1 · p. 54 RB U9 §3.4 · p. 60 RB U9 §3.5 · p. 66

Question 11 · Q1–30 · single answer

Consider the following equilibrium that exists in a closed rigid container at 500 K.

$A(g) + B(g) \rightleftharpoons 2C(g) : \Delta H < 0$

Which of the following describes/explains the effect on the equilibrium constant K_P when the temperature is increased to 750 K?

- (1)K_P does not change because the pressure does not change.
- (2)K_P will increase because the activation energy of the forward reaction is decreased.
- (3)K_P does not change because the number of reactant molecules and the number of product molecules are equal to each other.
- (4)K_P will decrease because the backward reaction is endothermic which favours the forward reaction.
- (5)K_P will decrease because the forward reaction is exothermic which favours the backward reaction.

Answer and review

Answer **(5)** Prepared answer (no official scheme available)

An equilibrium constant changes only with temperature. The forward reaction is exothermic, so raising the temperature favours the endothermic backward reaction and K_P decreases. Equal numbers of gas molecules on both sides mean pressure does not shift the equilibrium, but that does not keep K_P constant when T changes. Temperature does not change the activation energy. Option (4) gives the right result for the wrong reason: heating favours the endothermic backward reaction, not the forward one.

RB U12 §2.1 · p. 76

Question 12 · Q1–30 · single answer

The details of an initial rate measuring experiment carried out for the reaction X(aq) + Y(aq) → Z(aq) at a given temperature are given in the table below.

Experiment	$[X(aq)]_0$/mol dm^{-3}	$[Y(aq)]_0$/mol dm^{-3}	Initial rate/mol dm^{-3} s^{-1}
①	0.40	0.10	R
②	0.20	0.20	?

The initial rate of formation of Z(aq) in experiment ① is R. The reaction is first order with respect to X(aq) and second order with respect to Y(aq). The initial rate of formation of Z(aq) in experiment ② is,

- (1)R/4
- (2)R/2
- (3)R
- (4)2R
- (5)4R

Answer and review

Answer **(4)** Prepared answer (no official scheme available)

Rate = $k[X][Y]^2$. Experiment ①: $R = k(0.40)(0.10)^2 = 4.0 \times 10^{-3}k$. Experiment ②: rate = $k(0.20)(0.20)^2 = 8.0 \times 10^{-3}k = 2R$. Halving [X] halves the rate, while doubling [Y] multiplies it by $2^2 = 4$, giving 2R overall.

RB U11 §1.6 · p. 16

Question 13 · Q1–30 · single answer

A 0.4314 g sample of pure iron(II) oxalate (FeC_2O_4) was dissolved in excess dilute H_2SO_4. The entire solution was titrated with 0.060 mol dm^{-3} $KMnO_4$ solution. The burette reading at the end point is (relative molecular mass of FeC_2O_4 = 143.8)

- (1)20.00 cm^3
- (2)25.00 cm^3
- (3)30.00 cm^3
- (4)40.00 cm^3
- (5)50.00 cm^3

Answer and review

Answer **(3)** Prepared answer (no official scheme available)

n(FeC_2O_4) = 0.4314/143.8 = 3.000 × 10^{-3} mol. MnO_4^- oxidizes both ions: $Fe^{2+} \rightarrow Fe^{3+}$ (1 e) and $C_2O_4^{2-} \rightarrow 2CO_2$ (2 e), so each FeC_2O_4 gives 3 electrons, 9.000 × 10^{-3} mol in total. $MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$, so n($MnO_4^-$) = 9.000 × 10^{-3}/5 = 1.800 × 10^{-3} mol (overall $5FeC_2O_4 : 3MnO_4^-$). V = 1.800 × 10^{-3}/0.060 = 0.0300 dm^3 = 30.00 cm^3. Counting only the oxalate gives 20.00 cm^3, option (1).

RB U3 §3.8 · p. 115 RB U3 §3.6 · p. 105

Question 14 · Q1–30 · single answer

At a given temperature a certain number of moles of $H_2S(g)$ was inserted into an evacuated 1.0 dm^3 closed rigid container and the system was allowed to reach the equilibrium shown below.

$2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$

At equilibrium, it was found that a fraction x of $H_2S(g)$ has dissociated. At equilibrium the total pressure in the container was P. Which of the following gives the equilibrium constant K_P of the system?

- (1)$x^2P / [(2 + x)(1 - x)^2]$
- (2)$(2 + x)(1 - x)^2P / x^3$
- (3)$x^3P / [(2 + x)(1 - x)^2]$
- (4)$(1 - x)P / [x^2(1 - x)^2]$
- (5)$(2 + x)(1 - x)^2 / (x^3P)$

Answer and review

Answer **(3)** Prepared answer (no official scheme available)

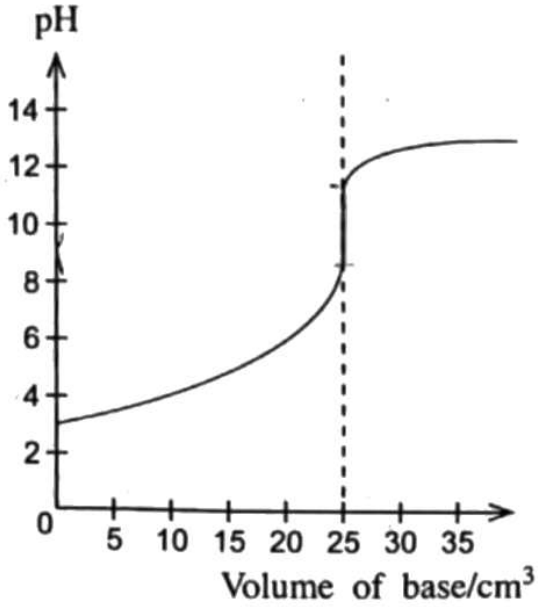
Start with n mol H_2S. At equilibrium: H_2S n(1 − x), H_2 nx, S_2 nx/2; total n(1 + x/2) = n(2 + x)/2. Mole fractions: H_2S 2(1 − x)/(2 + x), H_2 2x/(2 + x), S_2 x/(2 + x). $K_P = p_{H2}^2 \times p_{S2} / p_{H2S}^2 = [4x^2/(2 + x)^2 \times x/(2 + x)]P^3 \div [4(1 - x)^2/(2 + x)^2]P^2 = x^3P/[(2 + x)(1 - x)^2]$. Leaving out the S_2 term gives the x^2 form (1), and inverting the expression gives (2).

RB U12 §2.1 · p. 76

Question 15 · Q1–30 · single answer

The pH curve obtained for a titration of 25.00 cm^3 of 0.10 mol dm^{-3} unknown acid with 0.10 mol dm^{-3} unknown base at a given temperature is shown on the right.

Which of the following is most appropriate regarding the acid and base used in this titration?



- (1)Mono-basic strong acid with a mono-protic strong base
- (2)Mono-basic strong acid with a mono-protic weak base
- (3)Di-basic strong acid with a mono-protic strong base
- (4)Mono-basic weak acid with a mono-protic weak base
- (5)Mono-basic weak acid with a mono-protic strong base

Answer and review

Answer **(5)** Prepared answer (no official scheme available)

The curve starts near pH 3, too high for a 0.10 mol dm^{-3} strong acid (pH 1), so the acid is weak. It levels off near pH 13, as expected for excess 0.10 mol dm^{-3} strong base. There is one sharp rise at 25.00 cm^3, the same volume as the acid at the same concentration, so the reaction is 1 : 1: a monobasic acid and a monoprotic base. The equivalence point is above pH 7, as for the salt of a weak acid and a strong base. A dibasic acid would need 50.00 cm^3 of base, and a weak base would not give a steep rise to pH 12–13.

RB U12 §2.2 · p. 118

Question 16 · Q1–30 · single answer

Which of the following statements is **false** with regard to the elements in the s and p blocks?

- (1)Although xenon (Xe) is an inert gas, it forms compounds with oxidation numbers +2, +4 and +6.
- (2)Among the hydrogen halides, HF has the highest bond dissociation energy.
- (3)The solubility of the hydroxides of Group two (II) elements in water decreases on descending the group, while the solubility of their sulfates increases.
- (4)Among the Group one (I) metals (Li to Cs) cesium has the lowest melting point.
- (5)The oxidation number of nitrogen in NH_2OH is -1.

Answer and review

Answer **(3)** Prepared answer (no official scheme available)

The Group 2 trends run the other way: the hydroxides become more soluble down the group ($Mg(OH)_2$ is sparingly soluble, $Ba(OH)_2$ is soluble), while the sulfates become less soluble ($MgSO_4$ is soluble, $BaSO_4$ is

insoluble). The other statements are true. XeF_2, XeF_4 and XeF_6 contain Xe in the +2, +4 and +6 states. H–F is the strongest H–X bond. Metallic bonding weakens down Group 1, so Cs melts lowest (about 28 °C). In NH_2OH, N + 3(+1) + (−2) = 0, so N = −1.

RB U6 §4.2 · p. 126 RB U6 §4.8 · p. 152 RB U6 §4.7 · p. 149 RB U6 §4.1 · p. 122

Question 17 · Q1–30 · single answer

At 25 °C, to V_1 cm^3 of x mol dm^{-3} $CH_3COOH(aq)$ solution in a beaker, V_2 cm^3 ($V_2 > V_1$) of y mol dm^{-3} (y > x) NaOH(aq) solution was added. The pH of the final mixture is,

(K_w is the dissociation constant of water at 25 °C)

- (1)$pK_w - \log\{(V_2y - V_1x)/(V_1 + V_2)\}$
- (2)$pK_w + \log\{(V_2y - V_1x)/(V_1 + V_2)\}$
- (3)pK_w
- (4)$-pK_w - \log\{(V_2y - V_1x)/(V_1 + V_2)\}$
- (5)$-pK_w + \log\{(V_2y - V_1x)/(V_1 + V_2)\}$

Answer and review

Answer **(2)** Prepared answer (no official scheme available)

Since $V_2y > V_1x$, NaOH is in excess. All the CH_3COOH is neutralized, and the excess OH^-, $(V_2y - V_1x)/1000$ mol, is in $(V_1 + V_2)/1000$ dm^3. So $[OH^-] = (V_2y - V_1x)/(V_1 + V_2)$ mol dm^{-3}. The excess strong base suppresses the hydrolysis of CH_3COO^-, so it alone fixes the pH: pOH = −log[OH^-] and pH = pK_w − pOH = $pK_w + \log\{(V_2y - V_1x)/(V_1 + V_2)\}$. Option (1) has the wrong sign on the log term.

RB U12 §2.2 · p. 118

Question 18 · Q1–30 · single answer

Which of the following statements is **incorrect** with regard to the reaction given below under standard conditions?

$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) : \Delta H° = -483.7$ kJ mol^{-1}

- (1)For one mole of reaction 483.7 kJ heat energy is evolved.
- (2)For two moles of $H_2(g)$ consumed, 483.7 kJ heat energy is evolved.
- (3)For two moles of $H_2O(g)$ produced, 483.7 kJ heat energy is evolved.
- (4)For the reaction $4H_2(g) + 2O_2(g) \rightarrow 4H_2O(g)$, 967.4 kJ heat energy is evolved.
- (5)For one mole of $O_2(g)$ consumed, 241.85 kJ heat energy is evolved.

Answer and review

Answer **(5)** Prepared answer (no official scheme available)

$\Delta H° = -483.7$ kJ mol^{-1} refers to one mole of reaction as written: 2 mol H_2 and 1 mol O_2 consumed and 2 mol $H_2O(g)$ formed. Consuming one mole of O_2 is one mole of reaction, so 483.7 kJ is evolved, not 241.85 kJ. The value 241.85 kJ is the heat per mole of H_2 consumed or H_2O formed. Doubling the equation doubles ΔH (967.4 kJ), so (1)–(4) are all correct.

RB U5 §2.2 · p. 36

Question 19 · Q1–30 · single answer

Which of the following statements is **incorrect** with regard to a galvanic cell?

- (1)Cell reaction is spontaneous.
- (2)Cell produces electrical energy.
- (3)Cathode is negatively charged.
- (4)Reduction half-reaction occurs at the cathode.
- (5)Oxidation half-reaction occurs at the anode.

Answer and review

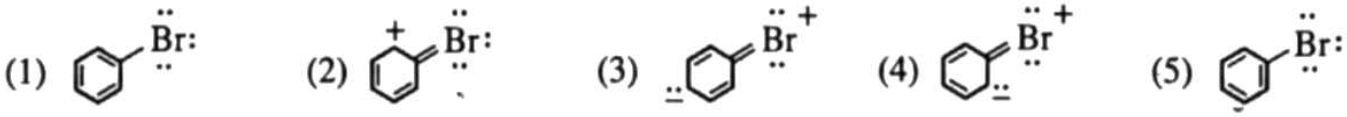
Answer **(3)** Prepared answer (no official scheme available)

In a galvanic cell a spontaneous redox reaction produces electrical energy. Oxidation at the anode releases electrons, which flow through the external circuit to the cathode, where reduction takes place. So the anode is the negative electrode and the cathode is the positive electrode. (The cathode is negative only in an electrolytic cell, where the external supply sets the polarity.)

RB U13 §3.3 · p. 250

Question 20 · Q1–30 · single answer

Which of the following is **not** a resonance structure of bromobenzene?



Answer and review

Answer **(2)** Prepared answer (no official scheme available)

Br can donate one of its lone pairs into the ring, giving C=Br^+ (Br keeps two lone pairs and has a formal charge of +1) with the negative charge on an ortho or para carbon, as in (3) and (4). (1) and (5) are the two Kekulé structures. Structure (2) has a positive ring carbon and a C=Br double bond while Br still has three lone pairs, i.e. 10 electrons around Br. That would require pushing an electron pair onto Br, which already has a full octet, so (2) is not a valid resonance structure.

RB U8 §2.7 · p. 50 RB U2 §2.3 · p. 52

Question 21 · Q1–30 · single answer

Under which of the following conditions of temperature and pressure, would a real gas tend to behave as an ideal gas?

- (1)Temperature: Very high · Pressure: Very high
- (2)Temperature: Very high · Pressure: Very low
- (3)Temperature: Very low · Pressure: Very high
- (4)Temperature: Very low · Pressure: Very low
- (5)Temperature: all temperatures · Pressure: Very low

Answer and review

Answer **(2)** Prepared answer (no official scheme available)

A real gas behaves ideally when two conditions hold. First, the volume of the molecules must be negligible compared with the volume of the gas, which needs low pressure. Second, intermolecular attractions must be negligible compared with the kinetic energy of the molecules, which needs high temperature. At very low temperatures attractions matter (the gas tends to condense) even at low pressure, so (4) and (5) are wrong.

RB U4 §1.5 · p. 24

Question 22 · Q1–30 · single answer

Two identical closed rigid containers at standard temperature and pressure contain 1.0 mol of $H_2(g)$ and 2.0 mol of $O_2(g)$. Which of the following is true of the above two systems?

- (1)Both $H_2(g)$ and $O_2(g)$ have the same average kinetic energy.
- (2)Both $H_2(g)$ and $O_2(g)$ have the same average speed.
- (3)Both $H_2(g)$ and $O_2(g)$ have the same mass.
- (4)Both $H_2(g)$ and $O_2(g)$ have the same density.
- (5)Both $H_2(g)$ and $O_2(g)$ have the same effusion rate.

Answer and review

Answer **(1)** Prepared answer (no official scheme available)

By kinetic molecular theory, the average kinetic energy of gas molecules depends only on the absolute temperature (3kT/2 per molecule). Both gases are at the same temperature, so they have the same average kinetic energy. Since $\frac{1}{2}mc^2$ is the same, the lighter H_2 molecules move faster ($c_{rms} \propto 1/\sqrt{M}$, so H_2 is 4 times faster than O_2), and their speeds and effusion rates differ. The masses (2.0 g and 64 g), and so the densities in equal volumes, also differ.

RB U4 §1.4 · p. 19

Question 23 · Q1–30 · single answer

At 25 °C the molar entropy change of dissolution $\Delta S°_{dissol}$ of the solid X(s) is 70 J K^{-1} mol^{-1}, and the molar entropy of X(s) is 100 J K^{-1} mol^{-1}. Which of the following gives the molar entropy (J K^{-1} mol^{-1}) of X(aq)?

- (1)−170
- (2)−30
- (3)0
- (4)+30
- (5)+170

Answer and review

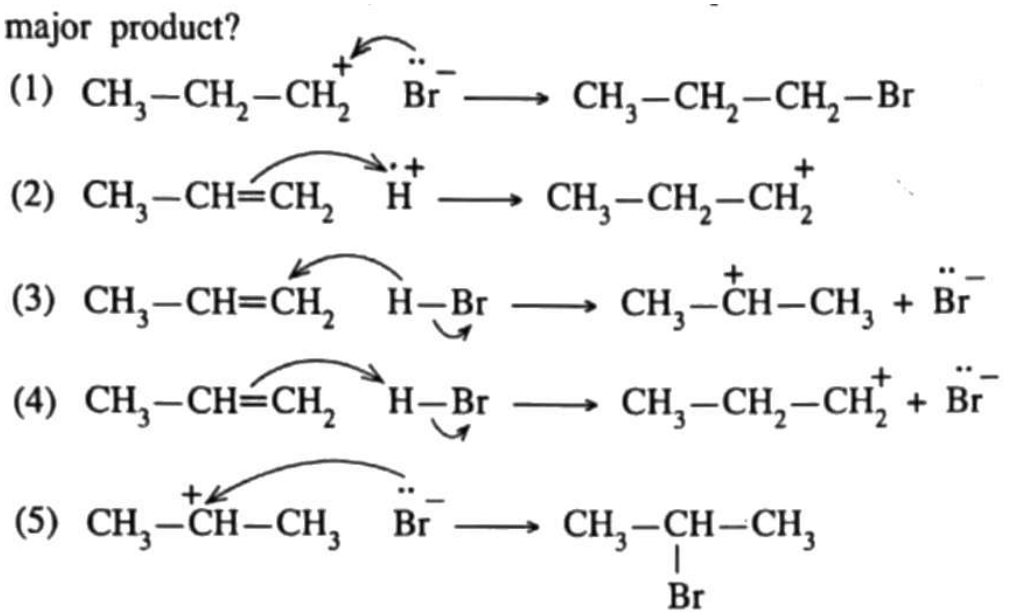
Answer **(5)** Prepared answer (no official scheme available)

For X(s) → X(aq), $\Delta S°_{dissol} = S°[X(aq)] - S°[X(s)]$. So $S°[X(aq)] = 70 + 100 = +170$ J K^{-1} mol^{-1}. The distractors come from subtracting the two values (±30) or from a sign error (−170).

RB U5 §2.4 · p. 53

Question 24 · Q1–30 · single answer

Consider the major product of the electrophilic addition reaction between CH_3–CH=CH_2 and HBr. Which of the following shows a correct step in the mechanism of the reaction which gives the major product?



Answer and review

Answer **(5)** Prepared answer (no official scheme available)

The major product is 2-bromopropane (Markovnikov's rule). In step 1, the C=C π electrons attack the H of H–Br (curly arrow from the π bond to H) as the H–Br bond breaks heterolytically. This gives the more stable secondary carbocation CH_3–C^+H–CH_3 and Br^-. In step 2, a lone pair of Br^- attacks the carbocation, which is exactly what (5) shows. (1), (2) and (4) go through the less stable primary carbocation, which leads to the minor product, 1-bromopropane. In (3) the curly arrow is drawn from H–Br to the alkene, the wrong direction, since an arrow must start at an electron source.

RB U8 §2.2 · p. 33

Question 25 · Q1–30 · single answer

Consider a gaseous equilibrium reaction at constant temperature taking place in a closed system. When doubling the pressure and volume of the system the equilibrium constant of the system,

- (1)becomes one-fourth (¼).
- (2)becomes halved (½).
- (3)remains the same.
- (4)becomes doubled.
- (5)becomes four times.

Answer and review

Answer **(3)** Prepared answer (no official scheme available)

An equilibrium constant (K_c or K_p) depends only on temperature. At constant temperature, changing the pressure or volume may shift the position of equilibrium (when the number of gas moles changes), but the composition then re-adjusts so that the reaction quotient again equals the same K.

RB U12 §2.1 · p. 76

Question 26 · Q1–30 · single answer

Magnesium nitride and lithium nitride react with water according to the following equations.

$Mg_3N_2(s) + 6H_2O(l) \rightarrow 3Mg(OH)_2(aq) + 2NH_3(g)$
$Li_3N(s) + 3H_2O(l) \rightarrow 3LiOH(aq) + NH_3(g)$

A mixture containing three moles of magnesium metal and an unknown amount of lithium metal was reacted completely with excess N_2 gas. When the product mixture resulting from this reaction was completely reacted with excess water, 44.2 g of NH_3 gas was produced. The mass of lithium in the metal mixture is,

(H = 1, Li = 7, N = 14, Mg = 24)

- (1)1.8 g
- (2)4.2 g
- (3)12.6 g
- (4)14.2 g
- (5)20.2 g

Answer and review

Answer **(3)** Prepared answer (no official scheme available)

$3Mg + N_2 \rightarrow Mg_3N_2$ and $6Li + N_2 \rightarrow 2Li_3N$. $n(NH_3) = 44.2/17 = 2.60$ mol. 3 mol Mg gives 1 mol Mg_3N_2, which gives 2.00 mol NH_3. The remaining 0.60 mol NH_3 comes from 0.60 mol Li_3N, which contains 1.80 mol Li = $1.80 \times 7 = 12.6$ g. Option (1) takes the number of moles of Li as grams.

RB U3 §3.8 · p. 115 RB U6 §4.2 · p. 126

Question 27 · Q1–30 · single answer

Ammonia can be synthesized at high temperatures as shown by the following unbalanced chemical equation.

$NO(g) + H_2(g) \rightarrow NH_3(g) + H_2O(g)$

The maximum amount of NH_3 in grams that can be synthesized from 45.0 g of NO and 12.0 g of H_2 is

(Relative molecular mass: H_2 = 2, NO = 30, NH_3 = 17)

- (1)2.4
- (2)4.8
- (3)12.8
- (4)25.5
- (5)40.8

Answer and review

Answer **(4)** Prepared answer (no official scheme available)

Balanced: $2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O$ (O and H balance with 2NO). $n(NO) = 45.0/30 = 1.50$ mol and $n(H_2) = 12.0/2 = 6.00$ mol. 1.50 mol NO needs only $1.50 \times 5/2 = 3.75$ mol H_2, so NO is the limiting reactant and gives 1.50 mol $NH_3 = 1.50 \times 17 = 25.5$ g. Taking H_2 as limiting ($6.00 \times 2/5 = 2.40$ mol $NH_3 = 40.8$ g) gives trap answer (5).

RB U3 §3.8 · p. 115 RB U3 §3.6 · p. 105

Question 28 · Q1–30 · single answer

At a temperature of 25 °C, the $E°_{cell}$ of the reaction $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$ occurring in an electrochemical cell is +0.55 V while the half-reactions of this process are,

$O_2(g) + 4H^+(aq) + 4e \rightarrow 2H_2O(l)$ ---------- (1), $E°_1 = 1.23$ V
$O_2(g) + 2H^+(aq) + 2e \rightarrow H_2O_2(aq)$ ---------- (2), $E°_2 = ?$

The standard reduction potential $E°_2$ of reaction (2) is

- (1)−1.78 V
- (2)−0.68 V
- (3)0.00 V
- (4)+0.68 V
- (5)+1.78 V

Answer and review

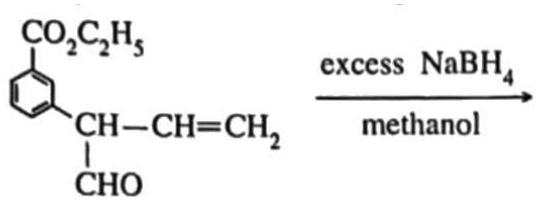
Answer **(4)** Prepared answer (no official scheme available)

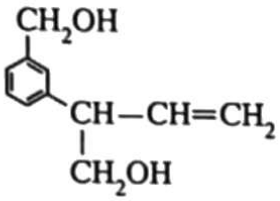
The overall reaction is (1) − 2 × (2). At the cathode O_2 is reduced to H_2O (reaction (1), 4e), and at the anode $2H_2O_2 \rightarrow 2O_2 + 4H^+ + 4e$ (reaction (2) reversed and doubled). The electrons cancel, so $E°_{cell} = E°_{cathode} - E°_{anode} = E°_1 - E°_2$. Then $0.55 = 1.23 - E°_2$, so $E°_2 = +0.68$ V. Electrode potentials are not multiplied when a half-equation is doubled. ±1.78 V comes from adding the two potentials instead of subtracting.

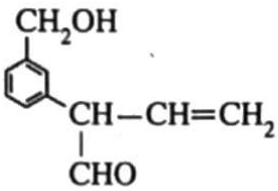
RB U13 §3.3 · p. 250 RB U13 §3.2 · p. 238

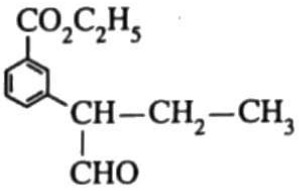
Question 29 · Q1–30 · single answer

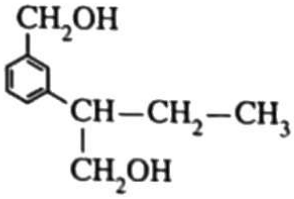
What could be the major product of the following reaction?

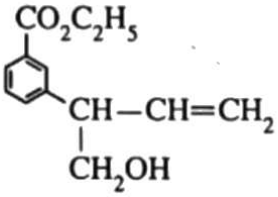


(1) 

(2) 

(3) 

(4) 

(5) 

Answer and review

Answer **(5)** Prepared answer (no official scheme available)

$NaBH_4$ is a mild hydride reducing agent. It reduces aldehydes and ketones to alcohols, but it does not reduce esters or carboxylic acids, and it does not reduce an isolated C=C. So only –CHO → $–CH_2OH$, and the $–CO_2C_2H_5$ and $CH=CH_2$ groups are unchanged, giving (5). Reducing the ester to $–CH_2OH$ (options 1, 2 and 4)

needs $LiAlH_4$, and reducing the C=C (options 3 and 4) needs H_2 with a catalyst.

RB U9 §3.4 · p. 60 RB U9 §3.6 · p. 70

Question 30 · Q1–30 · single answer

Consider the reaction $3O_2(g) \rightleftharpoons 2O_3(g)$, ($K_C = 2.0 \times 10^{-56}$ mol^{-1} dm^3) at temperature 25 °C. $O_2(g)$ 0.30 mol and $O_3(g)$ 0.005 mol were inserted into an evacuated closed rigid 1.0 dm^3 container at 25 °C and the system was allowed to reach the equilibrium above. Which of the following best describes the system approaching equilibrium at 25 °C?

(Q_C is the reaction quotient)

- (1)The amount of $O_3(g)$ increases to reach the equilibrium because $Q_C < K_C$
- (2)The amount of $O_3(g)$ decreases to reach the equilibrium because $Q_C < K_C$
- (3)The amount of $O_3(g)$ decreases to reach the equilibrium because $Q_C > K_C$
- (4)The amount of $O_3(g)$ increases to reach the equilibrium because $Q_C > K_C$
- (5)The amount of $O_3(g)$ does not change because $Q_C = K_C$

Answer and review

Answer **(3)** Prepared answer (no official scheme available)

$Q_C = [O_3]^2/[O_2]^3 = (0.005)^2/(0.30)^3 = 2.5 \times 10^{-5}/0.027 = 9.3 \times 10^{-4}$ mol^{-1} dm^3. This is far greater than $K_C = 2.0 \times 10^{-56}$. With $Q_C > K_C$ the net reaction goes backward ($2O_3 \rightarrow 3O_2$) until Q_C falls to K_C, so the amount of O_3 decreases (practically all of it decomposes).

RB U12 §2.1 · p. 76

Questions 31–40: response code

(1)	(2)	(3)	(4)	(5)
Only (a) and (b) are correct	Only (b) and (c) are correct	Only (c) and (d) are correct	Only (d) and (a) are correct	Any other number or combination of responses is correct

Question 31 · Q31–40 · response code

For a given chemical reaction, which of the following is/are affected by the temperature?

- Collision frequency of reactant molecules
- Kinetic energy of colliding molecules
- Standard enthalpy change of the reaction at 25 °C
- Activation energy of the reaction

Answer and review

Answer **(1)** Prepared answer (no official scheme available)

Raising the temperature increases the average kinetic energy of the molecules, so they move faster and collide more often, and a larger fraction of collisions exceeds E_a. So (a) and (b) are affected. The standard enthalpy change at 25 °C is a fixed value for that stated temperature. The activation energy is a property of the reaction pathway: temperature changes the fraction of molecules with energy ≥ E_a, not E_a itself (only a catalyst, by providing a new pathway, lowers it). Only (a) and (b) are correct: code (1).

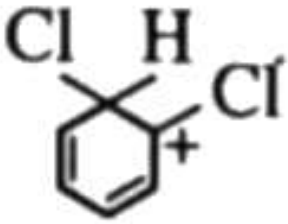
RB U11 §1.5 · p. 15 RB U11 §1.8 · p. 53 RB U5 §2.2 · p. 36

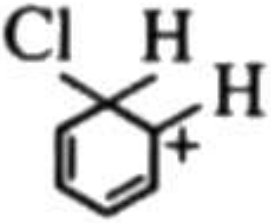
Question 32 · Q31–40 · response code

Consider the mechanism of the following reaction.

C_6H_6 (benzene) —(Cl_2/$FeCl_3$)→ C_6H_5Cl (chlorobenzene)

Which of the following ions is/are formed while this reaction is taking place?

(c) 

(d) 

Structures (c) and (d)

- $FeCl_4^-$
- $FeCl_4^+$
- The cation shown as (c) in the figure below
- The cation shown as (d) in the figure below

Answer and review

Answer **(4)** Prepared answer (no official scheme available)

The Lewis acid $FeCl_3$ polarizes Cl_2: $Cl_2 + FeCl_3 \rightarrow Cl^+ + FeCl_4^-$, so (a) forms but $FeCl_4^+$ (b) does not. Cl^+ attacks benzene to give the arenium (σ-complex) ion (d), with Cl and H on the sp^3 carbon and the positive charge delocalized over the ring. $FeCl_4^-$ then removes H^+, giving chlorobenzene and regenerating $FeCl_3$ (+ HCl). Ion (c) already has a second Cl on the ring, so it would form only if chlorobenzene were chlorinated further, not in this reaction. Hence (a) and (d): code (4).

RB U8 §2.4 · p. 44

Question 33 · Q31–40 · response code

At 25 °C, a 1.0 dm^3 aqueous solution of lead iodide (PbI_2) in equilibrium with an excess of solid lead iodide contains a mol of Pb^{2+}(aq) ions. Which of the following is/are correct for this system?

- The amount of Pb^{2+}(aq) will be 2a mol when the volume is doubled.
- The concentration of Pb^{2+}(aq) will be 2a mol dm^{-3} when the volume is doubled.
- The amount of Pb^{2+}(aq) will decrease when a small amount of solid NaI(s) is added.
- The amount of Pb^{2+}(aq) will be a/2 mol when the volume is doubled.

Answer and review

Answer **(5)** Prepared answer (no official scheme available)

While excess solid remains, the solution stays saturated: $[Pb^{2+}]$ = a mol dm^{-3}, fixed by K_{sp} at 25 °C. If the volume is doubled, more PbI_2 dissolves, so the concentration stays a mol dm^{-3} and the amount becomes 2a mol: (a) is correct, (b) and (d) are wrong. Adding NaI raises $[I^-]$, and by the common-ion effect PbI_2 precipitates, so the amount of Pb^{2+}(aq) decreases: (c) is correct. The correct pair (a) and (c) is not one of

codes (1)–(4), so the response is (5).

RB U12 §2.4 · p. 175

Question 34 · Q31–40 · response code

Which of the following statements is/are correct with regard to the compounds/ions formed by d block elements that belong to the fourth period?

- Cr_2O_3 is expected to react with strong acids and strong bases.
- When NaOH(aq) is added to solutions containing Fe^{2+}(aq), Fe^{3+}(aq), Mn^{2+}(aq) and Ni^{2+}(aq) precipitates which are insoluble in excess NaOH(aq) are formed.
- Both $KMnO_4$ and $K_2Cr_2O_7$ are strong oxidizing agents capable of converting H_2O_2 to O_2 gas under acidic conditions.
- The IUPAC name of $[CuCl_4]^{2-}$ is tetrachlorocuprate(II) ion.

Answer and review

Answer **(5)** Prepared answer (no official scheme available)

(a) is correct: Cr_2O_3 (Cr +3, an intermediate oxidation state) is amphoteric. (b) is correct: $Fe(OH)_2$ (dirty green), $Fe(OH)_3$ (reddish-brown), $Mn(OH)_2$ (white/cream) and $Ni(OH)_2$ (green) are not amphoteric, so they do not dissolve in excess NaOH (unlike $Zn(OH)_2$). (c) is correct: in acid H_2O_2 is oxidized to O_2, as in $2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$ and $Cr_2O_7^{2-} + 3H_2O_2 + 8H^+ \rightarrow 2Cr^{3+} + 3O_2 + 7H_2O$. (d) is not correct under current IUPAC rules, which the Resource Book follows: the Cl^- ligand is named "chlorido", so the name is tetrachloridocuprate(II) ion. Three statements are correct, so the response is (5). Even if (d) were accepted, all four would be correct and the response would still be (5).

RB U6 §4.10 · p. 160 RB U6 §4.10.6 · p. 169 RB U6 §4.6 · p. 141

Question 35 · Q31–40 · response code

Which of the following statements is/are correct?

- The boiling point of propanoic acid is higher than that of 1-butanol.
- The boiling point of pentane is higher than that of 2-methylbutane.
- The boiling point of butanal is higher than that of 1-butanol.
- The boiling point of hexane is higher than that of 1-pentanol.

Answer and review

Answer **(1)** Prepared answer (no official scheme available)

(a) True: propanoic acid (M = 74, b.p. 141 °C) forms stronger and more extensive hydrogen bonds (dimers) than 1-butanol (M = 74, 118 °C). (b) True: unbranched pentane (36 °C) has a larger contact area and stronger London forces than branched 2-methylbutane (28 °C). (c) False: butanal (75 °C) has only dipole–dipole and London forces, so it boils below hydrogen-bonded 1-butanol (118 °C). (d) False: hexane (69 °C) cannot form hydrogen bonds, so it boils below 1-pentanol (138 °C). Code (1).

RB U2 §2.6 · p. 79 RB U9 §3.1 · p. 54 RB U9 §3.5 · p. 66 RB U8 §2.1 · p. 26

Question 36 · Q31–40 · response code

Which of the following statements is/are correct with regard to nitric acid (HNO_3) and its salts?

- Both dilute and concentrated HNO_3 act as oxidizing agents.
- Thermal decomposition of NH_4NO_3 gives N_2O and water.
- N–O bonds of HNO_3 are all equal in length.
- Carbon does not react with concentrated HNO_3 even when heated.

Answer and review

Answer **(1)** Prepared answer (no official scheme available)

(a) True: e.g. $3Cu + 8HNO_3(dil.) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$ and $Cu + 4HNO_3(conc.) \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$. (b) True: on heating, $NH_4NO_3 \rightarrow N_2O + 2H_2O$. (c) False: the N–OH bond is a single bond, longer than the other two N–O bonds, which share a delocalized π bond. (d) False: hot concentrated HNO_3 oxidizes carbon: $C + 4HNO_3 \rightarrow CO_2 + 4NO_2 + 2H_2O$. Code (1).

RB U6 §4.5 · p. 136

Question 37 · Q31–40 · response code

Which of the following statements is/are correct regarding the ozone layer?

- It is a region in the upper atmosphere (stratosphere) where only ozone is present.
- It is a region in the atmosphere where atomic oxygen is abundant.
- It is a region that prevents ultra-violet radiation that is emitted from the sun from reaching the earth surface.
- It is a region where ozone breakdown only occurs via a chlorine free radical mechanism.

Answer and review

Answer **(5)** Prepared answer (no official scheme available)

(c) is correct: the UV absorbed in forming and breaking ozone ($3O_2 \rightleftharpoons 2O_3$) stops most of the harmful UV from the Sun reaching the Earth's surface. (a) is false: the ozone layer (about 20–35 km up, in the stratosphere) holds about 95% of the atmosphere's ozone but is not made of ozone only. (b) is false: O atoms formed by photolysis of O_2 are very reactive and are used up at once ($O + O_2 \rightarrow O_3$), so they are never abundant. (d) is false: ozone is also broken down by UV itself ($O_3 \rightarrow O_2 + O$; $O_3 + O \rightarrow 2O_2$), by NO from aircraft and by bromine compounds. Only one statement is correct, so the response is (5).

RB U14 §1.13 · p. 58

Question 38 · Q31–40 · response code

A 100.00 cm^3 volume of 0.135 mol dm^{-3} aqueous solution of methylamine (CH_3NH_2) was shaken thoroughly with 75.00 cm^3 of water immiscible organic solvent in a closed bottle at 25 °C, and allowed to reach equilibrium. When 50.00 cm^3 of the aqueous layer was titrated with 0.200 mol dm^{-3} HCl solution, the end-point was 15.00 cm^3. No reaction occurs between methylamine and organic solvent. Which of the following is/are correct?

- Partition coefficient K_D of CH_3NH_2 between organic and aqueous layers is 1.67.
- Partition coefficient K_D of CH_3NH_2 between organic and aqueous layers is 4.67.
- CH_3NH_2 is more soluble in the aqueous layer.
- CH_3NH_2 is more soluble in the organic layer.

Answer and review

Answer **(4)** Prepared answer (no official scheme available)

Total CH_3NH_2 = 0.100 × 0.135 = 0.0135 mol. In 50.00 cm^3 of the aqueous layer, n = n(HCl) = 0.0150 × 0.200 = 3.00 × 10^{-3} mol, so [aq] = 0.0600 mol dm^{-3} and the whole 100.00 cm^3 holds 6.00 × 10^{-3} mol. The organic layer holds 0.0135 − 0.0060 = 7.50 × 10^{-3} mol in 75.00 cm^3, i.e. 0.100 mol dm^{-3}. K_D = [org]/[aq] = 0.100/0.0600 = 1.67. Since K_D > 1, methylamine is more soluble in the organic layer. So (a) and (d) are correct: code (4).

RB U12 §2.7 · p. 229

Question 39 · Q31–40 · response code

Which of the following statements is/are correct with regard to dissolved oxygen level of water in water bodies.

- Composition of dissolved oxygen in water is the same as that of atmospheric oxygen.
- Dissolved oxygen level in water decreases due to eutrophication.
- H_2S could be produced in water when the dissolved oxygen level in water is high.
- Aquatic plants contribute to the dissolved oxygen level in water via photosynthesis.

Answer and review

Answer **(5)** Prepared answer (no official scheme available)

(b) True: algal blooms block sunlight, so photosynthesis lower down stops, and aerobic bacteria use up O_2 decomposing the dead organisms. (d) True: dissolved oxygen comes both from atmospheric O_2 dissolving and from O_2 released by photosynthesis of aquatic plants and algae. (a) False: dissolved oxygen is not simply atmospheric oxygen in the same proportion. Gases dissolve according to their own solubilities (dissolved air is richer in O_2 than the 21% in air), and part of the DO comes from photosynthesis. (c) False: H_2S forms under anaerobic conditions, when DO is very low. The correct pair (b) and (d) is not one of codes (1)–(4), so the response is (5).

RB U14 §1.14 · p. 80

Question 40 · Q31–40 · response code

Which of the following statements is/are correct regarding the given industrial processes?

- Coke, a raw material used in the extraction of iron by the Blast Furnance, functions only as a reducing agent.
- A raw material used in the extraction of magnesium (Dow Process) can be regenerated utilizing a by-product formed during the electrolysis step.
- In the manufacture of high purity TiO_2 using rutile, inorganic impurities are removed in the chlorination step.
- The manufacture of nitric acid using Ostwald method uses Fe as the catalyst.

Answer and review

Answer **(2)** Prepared answer (no official scheme available)

(a) False: coke is also the fuel, since its combustion ($C + O_2 \rightarrow CO_2$) keeps the base of the furnace at about 1700 °C; it also forms CO and reduces FeO. (b) True: Cl_2 from the anode is converted to HCl, which is used again to turn $Mg(OH)_2$ into $MgCl_2$. (c) True: at about 950 °C, $TiO_2 + C + 2Cl_2 \rightarrow TiCl_4 + CO_2$. Volatile $TiCl_4$

(b.p. 134 °C) leaves the inorganic impurities behind, as the Resource Book states for this step; the purified $TiCl_4$ is then oxidized back to pure TiO_2. (d) False: NH_3 is oxidized over a Pt/Rh catalyst; Fe is the catalyst in the Haber–Bosch process. So (b) and (c): code (2).

RB U14 §1.10 · p. 33 RB U14 §1.2 · p. 6 RB U14 §1.9 · p. 31 RB U14 §1.7 · p. 25

Questions 41–50: statement pairs

Response	First statement	Second statement
(1)	True	True, and correctly explains the first statement
(2)	True	True, but does not explain the first statement correctly
(3)	True	False
(4)	False	True
(5)	False	False

Question 41 · Q41–50 · statement pair

Statement 1

The decreasing order of the acid strengths of oxoacids of chlorine is $HClO_4 > HClO_3 > HClO_2 > HOCl$

Statement 2

When the oxidation number of the chlorine atom in the oxoacids of chlorine increases, the acidity of the oxoacid increases.

Answer and review

Answer **(1)** Prepared answer (no official scheme available)

Oxidation numbers of Cl: HOCl +1, $HClO_2$ +3, $HClO_3$ +5, $HClO_4$ +7. As the oxidation number (and the number of O atoms on Cl) rises, electron density is drawn away from the O–H bond and the negative charge of the anion is spread over more O atoms, so acid strength increases: $HClO_4 > HClO_3 > HClO_2 > HOCl$. Both statements are true, and the Resource Book uses this oxidation-number trend to explain the order.

RB U6 §4.7 · p. 149

Question 42 · Q41–50 · statement pair

Statement 1

When H_2S gas reacts with an acidic solution of $K_2Cr_2O_7$, elemental sulphur is formed.

Statement 2

H_2S gas can act as a reducing agent in acidic medium.

Answer and review

Answer **(1)** Prepared answer (no official scheme available)

$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3S + 7H_2O$. H_2S reduces Cr(+6) to Cr^{3+} (orange to green) and is itself oxidized from S(−2) to S(0), seen as a yellow precipitate. Both statements are true, and H_2S acting as a reducing agent is why sulphur is formed.

RB U6 §4.6 · p. 141 RB U3 §3.6 · p. 105

Question 43 · Q41–50 · statement pair

Statement 1

An electrochemical cell based on the reaction $Cl_2(g) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(s)$ can be used to generate electricity.

Statement 2

$Cl_2(g)$ is a stronger reducing agent than $I_2(s)$.

Answer and review

Answer **(3)** Prepared answer (no official scheme available)

$E°(Cl_2/Cl^-) = +1.36$ V is higher than $E°(I_2/I^-) = +0.54$ V, so the reaction is spontaneous ($E°_{cell} = +0.82$ V) and a galvanic cell based on it produces electricity: statement 1 is true. This is because Cl_2 is a stronger oxidizing agent than I_2; here Cl_2 is reduced and I^- is the reducing agent. Statement 2 is false.

RB U13 §3.3 · p. 250 RB U6 §4.7 · p. 149

Question 44 · Q41–50 · statement pair

Statement 1

Grignard reagents react with water to give alcohols.

Statement 2

The carbon atom of the carbon-magnesium bond in a Grignard reagent has a partial negative charge.

Answer and review

Answer **(4)** Prepared answer (no official scheme available)

$RMgX + H_2O \rightarrow RH + Mg(OH)X$. The strongly basic carbon takes a proton from water, giving an alkane, not an alcohol, so statement 1 is false. Mg is much less electronegative than C, so the carbon of the C–Mg bond carries a partial negative charge; this is why Grignard reagents are strong bases and nucleophiles. Statement 2 is true. (Alcohols are made from Grignard reagents and aldehydes or ketones, followed by hydrolysis.)

RB U8 §2.6 · p. 49 RB U8 §2.7 · p. 50

Question 45 · Q41–50 · statement pair

Statement 1

While diazonium salts formed from aniline are stable at low temperatures (0–5 °C), diazonium salts formed from primary aliphatic amines are unstable at these temperatures.

Statement 2

The lone pair of electrons on the nitrogen atom of aniline is delocalized on the benzene ring.

Answer and review

Answer **(2)** Prepared answer (no official scheme available)

Aliphatic diazonium salts lose N_2 at once (giving alcohols), while benzenediazonium salts can be kept in solution at 0–5 °C, so statement 1 is true. Statement 2 is also true, but it explains why aniline is a weaker base than aliphatic amines. In the diazonium ion that nitrogen has already used its lone pair to form $–N{\equiv}N^+$. The arenediazonium ion is more stable because the $–N{\equiv}N^+$ group is conjugated with the benzene ring, which delocalizes its positive charge, and because the aryl cation that would form on losing N_2 is very unstable. So

statement 2 does not explain statement 1.

RB U10 §4.1 · p. 75 RB U10 §4.3 · p. 78 RB U10 §4.2 · p. 77

Question 46 · Q41–50 · statement pair

Statement 1

The enthalpy change would be zero when an ideal binary liquid mixture is formed by two completely miscible liquids at a given temperature.

Statement 2

At a given temperature, all intermolecular forces that exist in an ideal binary liquid mixture are equal.

Answer and review

Answer **(1)** Prepared answer (no official scheme available)

In an ideal mixture the A–A, B–B and A–B attractions are equal ($f_{A–A} = f_{B–B} = f_{A–B}$). The energy absorbed in breaking A–A and B–B interactions therefore equals the energy released in forming A–B interactions, so $\Delta H_{mix} = 0$. Both statements are true, and the second explains the first.

RB U12 §2.6 · p. 216

Question 47 · Q41–50 · statement pair

Statement 1

When a pH value of 6.5 is reported in rain water, it is considered as acid rain.

Statement 2

Lowering of pH to below 7 in rain water occurs only due to the dissolution of the acidic gases SO_3 and NO_2.

Answer and review

Answer **(5)** Prepared answer (no official scheme available)

Rain water is naturally slightly acidic, because dissolved CO_2 forms carbonic acid and gives a pH of about 5.6. Acid rain is rain whose pH is below 5.6 because of strong acids formed from NO_x and SO_x. A pH of 6.5 is therefore not acid rain, so statement 1 is false. CO_2 alone lowers the pH below 7, so the fall is not due only to SO_3 and NO_2, and statement 2 is false.

RB U14 §1.13 · p. 58

Question 48 · Q41–50 · statement pair

Statement 1

At a given temperature, the half-life $t_{1/2}$ of a first order reaction is given by the equation $t_{1/2} = 0.693/k$ where k is the first order rate constant.

Statement 2

In a first order reaction with $t_{1/2} = 50$ s, 87.5% of the reaction is completed after 150 s.

Answer and review

Answer **(2)** Prepared answer (no official scheme available)

For a first-order reaction $\ln([A]_0/[A]) = kt$. At $t_{1/2}$, $[A] = [A]_0/2$, so $t_{1/2} = \ln 2/k = 0.693/k$, independent of concentration: statement 1 is true. 150 s is 3 half-lives, which leaves $(½)^3 = 12.5\%$ of the reactant, so 87.5% has reacted: statement 2 is true. Statement 2 is an application of the constant half-life, not the reason for the equation in statement 1.

RB U11 §1.7 · p. 26 RB U11 §1.7.2 · p. 28

Question 49 · Q41–50 · statement pair

Statement 1

In the manufacture of NH_3 gas by the Haber-Bosch process temperatures higher than 600 °C are used.

Statement 2

The activation energy of NH_3 gas producing equilibrium reaction in the Haber-Bosch process decreases with increasing temperature.

Answer and review

Answer **(5)** Prepared answer (no official scheme available)

$N_2 + 3H_2 \rightleftharpoons 2NH_3$ is exothermic, so high temperatures lower the equilibrium yield. A compromise of 450–500 °C, 250–300 atm and an iron catalyst is used, not temperatures above 600 °C, so statement 1 is false. The activation energy does not change with temperature: heating only raises the fraction of molecules with energy ≥ E_a, and the iron catalyst provides a pathway with a lower E_a. Statement 2 is false.

RB U14 §1.6 · p. 21 RB U11 §1.8 · p. 53

Question 50 · Q41–50 · statement pair

Statement 1

Bakelite is classified as an addition polymer.

Statement 2

Bakelite has a three dimensional network structure.

Answer and review

Answer **(4)** Prepared answer (no official scheme available)

Bakelite is formed from phenol and formaldehyde (methanal) by condensation polymerization, in which water is eliminated. It is a condensation polymer, not an addition polymer, so statement 1 is false. Phenol can react at three ring positions, so the chains are cross-linked into a three-dimensional network, which makes Bakelite a thermoset. Statement 2 is true.

RB U14 §1.11 · p. 37

Structured essay · answer all four

SEQ · Paper II Part A

Question 1 · Part A · structured essay

(a) [24 marks]

State whether the following statements are **true** or **false** on the dotted lines. Reasons are **not** required.
(i) The Lyman series observed in the emission spectrum of atomic hydrogen lies in the ultra-violet region of the electromagnetic spectrum.
(ii) There are only 10 electrons in a calcium atom with the azimuthal quantum number l = 0.
(iii) The number of Lewis dot-dash structures (resonance structures) that can be drawn for the N_2O molecule is 3.
(iv) Among the second row elements of the Periodic Table, fluorine has the largest negative value of electron gain energy.
(v) The boiling point of argon (Ar) is higher than that of chlorine (Cl_2).
(vi) Ne has the highest first ionization energy, among the noble gases He, Ne and Ar.

Answer

(i) true (ii) false (iii) true (iv) true (v) false (vi) false

Review.

(i) The Lyman series contains the transitions that end on n = 1; these have the largest energies, so they lie in the ultra-violet. (ii) Ca is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$: only the 1s, 2s, 3s and 4s electrons have l = 0, which is 8 electrons, not 10. (iii) The Resource Book shows three octet structures for N_2O: $N{\equiv}N^+{-}O^-$, $^-N{=}N^+{=}O$ and $^{2-}N{-}N^+{\equiv}O^+$ (the last is the least stable). (iv) Within period 2, F has the most negative electron gain energy (about -328 kJ mol^{-1}); do not confuse this with Cl, which is more negative but is in period 3. (v) Cl_2 (34 electrons, b.p. 239 K) has stronger London forces than Ar (18 electrons, b.p. 87 K). (vi) First ionization energy falls down Group 18, so He (2372 kJ mol^{-1}) is highest, then Ne (2081), then Ar (1521).

(b) [56 marks]

(i) The skeleton of a molecule containing only the elements N, F and S is given below. Draw the **most** acceptable Lewis dot-dash structure for this molecule.
Skeleton: F–N–S–F, with a third F atom also bonded to S (F_2S–N–F).

Answer

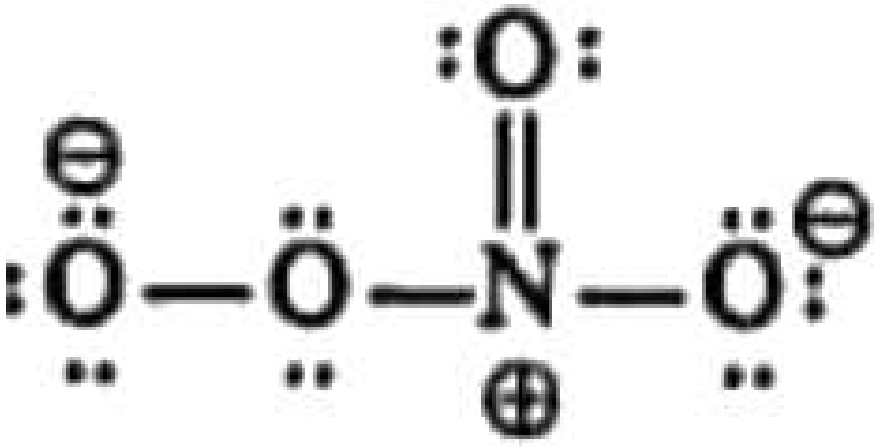
F–N=S(F)–F (the molecule NSF_3): N is single-bonded to F and double-bonded to S; S is single-bonded to two F atoms. Lone pairs: three on each F, one on N, one on S. Total valence electrons = 5 + 6 + 3 × 7 = 32 (5 bonds = 10 electrons + 11 lone pairs = 22 electrons).
Formal charges: N = 5 − 2 − 3 = 0; S = 6 − 2 − 4 = 0; each F = 7 − 6 − 1 = 0. S (a period 3 atom) holds 10 electrons, which is allowed. The all-single-bond structure $F{-}N^-{-}S^+F_2$ (two lone pairs on N) obeys the octet rule but carries formal charges, so it is less acceptable.

(ii) Give, (I) shapes around the N and S atoms and (II) oxidation numbers of the atoms in the structure drawn in (i) above.
(I) N ....., S ..... (shape)
(II) N ....., S ..... (oxidation number)

Answer

(I) N: angular / V-shaped (bent) — 3 VSEPR pairs (2 bonding + 1 lone pair). S: trigonal pyramidal — 4 VSEPR pairs (3 bonding + 1 lone pair).
(II) N: −1 (−I); S: +4 (+IV). (Each F is −1: −1 + 4 + 3(−1) = 0.)

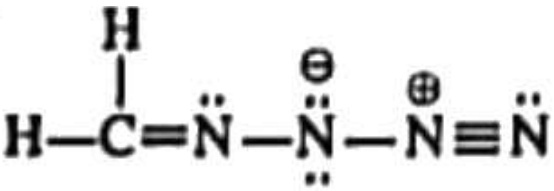
(iii) A Lewis dot-dash structure for the NO_4^- ion is given below. Draw **three** more Lewis dot-dash structures (resonance structures) for the NO_4^- ion.

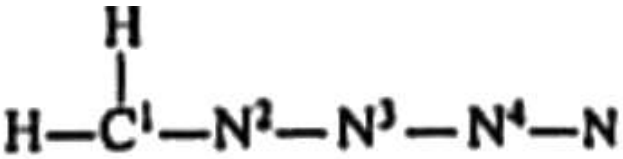


Answer

Label the skeleton O_a–O_b–N(O_c)(O_d), where O_a is the terminal O of the O–O unit and O_c is the O doubly bonded to N in the given structure. Each structure has 30 valence electrons and every atom has an octet.
Structure 1: $^{-}O_a$–O_b–N^{+}(–O_c^{-})=O_d — the N=O double bond moves to the other terminal O on N. O_a: 3 lone pairs (−1); O_b: 2 lone pairs (0); N: no lone pair (+1); O_c: 3 lone pairs (−1); O_d: 2 lone pairs (0).
Structure 2: O_a=O_b^{+}–N(–O_c^{-})–O_d^{-} — double bond between the two O atoms of the O–O unit. O_a: 2 lone pairs (0); O_b: 1 lone pair (+1); N: 1 lone pair (0); O_c and O_d: 3 lone pairs each (−1 each).
Structure 3: $^{-}O_a$–O_b^{+}=N^{+}(–O_c^{-})–O_d^{-} — double bond between O_b and N. O_a: 3 lone pairs (−1); O_b: 1 lone pair (+1); N: no lone pair (+1); O_c and O_d: 3 lone pairs each (−1 each).
(Net charge −1 in every structure. Structure 1 is equivalent to the given structure; structures 2 and 3 carry more formal charges, and 3 has like charges on adjacent atoms, so they are less stable.)

(iv) Complete the given table based on the Lewis dot-dash structure and its labelled skeleton given below. Rows: I. the number of VSEPR pairs around the atom; II. electron pair geometry around the atom; III. shape around the atom; IV. hybridization of the atom. Columns: C^1, N^2, N^3, N^4.





Answer

	C^1	N^2	N^3	N^4
I. VSEPR pairs	3	3	4	2
II. electron pair geometry	trigonal planar	trigonal planar	tetrahedral	linear
III. shape	trigonal planar	angular / V-shaped	angular / V-shaped	linear
IV. hybridization	sp^2	sp^2	sp^3	sp

Parts (v) to (viii) are based on the Lewis dot-dash structure given in part (iv) above. Labelling of atoms is as in part (iv).

(v) Identify the atomic/hybrid orbitals involved in the formation of σ bonds between the two atoms given below.
I. H—C^1 II. C^1—N^2 III. N^2—N^3 IV. N^3—N^4 V. N^4—N

Answer

I. H 1s, C^1 sp^2
II. C^1 sp^2, N^2 sp^2
III. N^2 sp^2, N^3 sp^3
IV. N^3 sp^3, N^4 sp
V. N^4 sp, N sp (or 2p)

(vi) Identify the atomic orbitals involved in the formation of π bonds between the atoms given below.
I. C^1—N^2 II. N^4—N (two π bonds)

Answer

I. C^1 2p, N^2 2p
II. N^4 2p, N 2p and N^4 2p, N 2p (the two π bonds are formed by two mutually perpendicular pairs of 2p orbitals)

(vii) State the approximate bond angles around C^1, N^2, N^3 and N^4 atoms.

Answer

C^1: 120° · N^2: about 117° (slightly less than 120°) · N^3: about 104.5° (less than 109.5°) · N^4: 180°

(viii) Arrange the atoms N^2, N^3 and N^4 in the **increasing** order of their electronegativity.

Answer

$N^3 < N^2 < N^4$

Review.

The structure is $H_2C{=}N{-}N^-{-}N^+{\equiv}N$. Count VSEPR pairs as σ bonds plus lone pairs (a double or triple bond counts once): C^1 has 3 σ bonds; N^2 has 2 σ bonds and 1 lone pair; N^3 has 2 σ bonds and 2 lone pairs; N^4 has 2 σ bonds and none. Lone pairs squeeze the bond angles below the ideal values (120° → about 117°, 109.5° → about 104.5°). Electronegativity rises with s character ($sp^3 < sp^2 < sp$) and with positive charge ($N^- < N < N^+$), so the negatively charged sp^3 N^3 is lowest and the positively charged sp N^4 is highest. In (i), minimise formal charges; S may exceed the octet. In (iii), only π bonds and lone pairs move: with 30 electrons exactly one π bond is possible, and it can sit on any of the four bonds, so there are exactly four structures. Oxidation numbers come from giving all bonding electrons to the more electronegative atom (F > N > S).

(c) [20 marks]

Arrange the following species in the **increasing** order of the property indicated in parentheses. Reasons are **not** required.
(i) CaF_2, $CaCl_2$, $CaBr_2$, CaI_2 (ionic character)
(ii) ClF_5, ClF_2^+, ClF_2^- (bond angle)
(iii) Na^+, S^{2-}, Cl^-, K^+ (ionic radius)
(iv) CO, CO_3^{2-}, HCO_2^-, H_2CO, CH_3OH (C—O bond length)
(v) Li, N, F, Mg, P (first ionization energy)

Answer

(i) $CaI_2 < CaBr_2 < CaCl_2 < CaF_2$
(ii) $ClF_5 < ClF_2^+ < ClF_2^-$
(iii) $Na^+ < K^+ < Cl^- < S^{2-}$
(iv) $CO < H_2CO < HCO_2^- < CO_3^{2-} < CH_3OH$
(v) Li < Mg < P < N < F

Review.

(i) The larger the anion, the more easily Ca^{2+} polarizes it, so covalent character rises (ionic character falls) from F^- to I^-. (ii) ClF_5: 6 VSEPR pairs, square pyramidal, F–Cl–F about 90°; ClF_2^+: 4 pairs (2 lone pairs), angular, below 109.5°; ClF_2^-: 5 pairs (3 lone pairs in the equatorial plane), linear, 180°. (iii) Na^+ (period 3, 10 electrons) is smallest; K^+, Cl^- and S^{2-} are isoelectronic (18 electrons), so the radius increases as nuclear charge falls (K^+ Z = 19 < Cl^- Z = 17 < S^{2-} Z = 16). (iv) C–O bond order: CO 3, H_2CO 2, HCO_2^- 1.5 (two resonance forms), CO_3^{2-} 1.33 (three resonance forms), CH_3OH 1; a higher bond order means a shorter bond. (v) Ionization energies (kJ mol^{-1}): Li 520, Mg 738, P 1012, N 1402, F 1681 — IE rises across a period and falls down a group.

Read: RB U2 §2.3 · p. 52 RB U2 §2.1 · p. 44 RB U1 §1.6 · p. 32 RB U2 §2.4 · p. 75

Question 2 · Part A · structured essay

(a) [80 marks]

The questions (i), (ii) and (iii) are based on the following reactions.
A is an ionic compound composed of three elements in the ratio 1:4:1 (Not in order of the chemical formula). One of these is a d-block element that belongs to the fourth period of the Periodic Table. When A is subjected to the flame test, a lilac (purple) flame is observed. On dissolving A in water, a purple coloured solution is obtained.
B is also an ionic compound composed of the same three elements as in A. B dissolves in water to give a green coloured solution.
C is a viscous colourless liquid composed of two elements. It disproportionates to give another colourless liquid **D** as one of the products. C can act as an oxidizing agent as well as a reducing agent. When C is added to a solution of B, the brown precipitate **E** is obtained.
F is a compound composed of three elements. One of these elements is a 3d element found in hematite. When $BaCl_2$(aq) is added to an aqueous solution of F, the white precipitate **G** that is insoluble in dil. H_2SO_4 is formed.
H is composed of three elements. When an aqueous solution of H in a test tube is treated with a saturated solution of F, followed by addition of a small volume of conc. H_2SO_4 slowly, along the wall of the test tube, a brown colouration is seen on the surface where the liquids meet. The species responsible for the brown colouration is **I**. Brown fumes are not evolved when dil. H_2SO_4 is added to H. When H is subjected to the flame test, a yellow flame is observed.
J is the sodium salt of a weak dibasic acid. On treatment of a solution of J with $CaCl_2$(aq), the white precipitate **K** is formed. K reacts with dil. H_2SO_4 to give the weak dibasic acid **L** as one of the products. A warm solution of J acidified with dil. H_2SO_4 decolourizes an aqueous solution of A.

(i) Identify A to L. **Note:** Write the chemical formulae.

Answer

A	B	C	D	E	F
$KMnO_4$	K_2MnO_4	H_2O_2	H_2O	MnO_2	$FeSO_4$
G	H	I	J	K	L
$BaSO_4$	$NaNO_3$	$[Fe(NO)]^{2+}$ (or $[Fe(H_2O)_5NO]^{2+}$)	$Na_2C_2O_4$	CaC_2O_4	$H_2C_2O_4$

(ii) Give balanced chemical equations for the following (physical states not required).
I. Formation of D from C.
II. Formation of I.
III. Formation of K.

Answer

I. $2H_2O_2 \rightarrow 2H_2O + O_2$
II. $2NO_3^- + 4H_2SO_4 + 6Fe^{2+} \rightarrow 6Fe^{3+} + 2NO + 4SO_4^{2-} + 4H_2O$ (or $NO_3^- + 3Fe^{2+} + 4H^+ \rightarrow 3Fe^{3+} + NO + 2H_2O$; or $2NaNO_3 + 6FeSO_4 + 4H_2SO_4 \rightarrow Na_2SO_4 + 3Fe_2(SO_4)_3 + 2NO + 4H_2O$)
then $Fe^{2+} + NO \rightarrow [Fe(NO)]^{2+}$ (brown)
III. $Na_2C_2O_4 + CaCl_2 \rightarrow CaC_2O_4 + 2NaCl$ (or $Ca^{2+} + C_2O_4^{2-} \rightarrow CaC_2O_4$)

(iii) Give balanced **ionic** equations for the reactions that take place when A is added to the following solutions (physical states not required).
I. an acidified solution of C
II. an aqueous solution of F acidified with dil. H_2SO_4
III. an acidified solution of J

Answer

I. $2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$
II. $MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$
III. $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$ (or $2MnO_4^- + 5H_2C_2O_4 + 6H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$)

Review.

Key clues: a 1:1:4 compound of a period-4 d-block metal with a lilac flame (K^+) and a purple solution is $KMnO_4$; the green K–Mn–O salt is K_2MnO_4 (Mn +6). The viscous liquid that is both an oxidant and a reductant and disproportionates is H_2O_2 (D = H_2O); it reduces manganate(VI) to brown MnO_2 ($MnO_4^{2-} + H_2O_2 \rightarrow MnO_2 + O_2 + 2OH^-$). Hematite is Fe_2O_3, and F must contain Fe^{2+} because it is used in the brown-ring test; a white precipitate with $BaCl_2$ that does not dissolve in acid is $BaSO_4$, so F = $FeSO_4$. A brown ring with no brown fumes from dil. H_2SO_4 means nitrate, not nitrite, and a yellow flame means Na^+. The calcium salt that gives a weak dibasic acid and whose sodium salt decolourizes warm acidified $KMnO_4$ is the oxalate. Common mistakes: writing MnO_4^- for B, $Fe_2(SO_4)_3$ or $FeCl_2$ for F, $NaNO_2$ for H, and forgetting that oxalate needs warming with permanganate.

(b) [20 marks]

Give balanced chemical equations for the reactions that take place between the following (physical states not required). State the function (oxidizing agent/reducing agent) of H_2S and SO_2 in reactions (i)–(iii).
(i) Mg(s) and H_2S(g) · H_2S: .....
(ii) Mg(s) and SO_2(g) · SO_2: .....
(iii) H_2S(g) and SO_2(g) · H_2S: ....., SO_2: .....
(iv) S(s) and conc. HNO_3(aq)

Answer

(i) $Mg + H_2S \rightarrow MgS + H_2$ · H_2S: oxidizing agent
(ii) $2Mg + SO_2 \rightarrow 2MgO + S$ (or $3Mg + SO_2 \rightarrow 2MgO + MgS$) · SO_2: oxidizing agent
(iii) $2H_2S + SO_2 \rightarrow 3S + 2H_2O$ · H_2S: reducing agent, SO_2: oxidizing agent
(iv) $S + 6HNO_3 \rightarrow H_2SO_4 + 6NO_2 + 2H_2O$

Review.

Follow the oxidation numbers. (i) H in H_2S goes from +1 to 0 (H_2), so H_2S oxidizes Mg. (ii) S in SO_2 goes from +4 to 0 (or −2 in MgS) while Mg is oxidized to +2. (iii) S goes from −2 (H_2S) and +4 (SO_2) to 0 (comproportionation): H_2S is the reductant and SO_2 the oxidant. (iv) Hot conc. HNO_3 oxidizes S (0) to H_2SO_4 (+6) and is itself reduced to NO_2 (+4), so 6 mol of HNO_3 accept the 6 electrons lost by 1 mol of S. These reactions are listed in the Resource Book under H_2S, SO_2 and HNO_3.

Read: RB U6 §4.10 · p. 160 RB U6 §4.6 · p. 141 RB U6 §4.5 · p. 136 RB U3 §3.6 · p. 105

Question 3 · Part A · structured essay

(a) [30 marks]

(i) A closed container equipped with a piston contains a given mass of an ideal gas at a constant temperature T. Give the relationship between pressure P and volume V of the gas using a mathematical expression.

Answer

PV = constant ($P \propto 1/V$), for a fixed amount of gas at constant temperature (Boyle's law); equivalently $P_1V_1 = P_2V_2$.

(ii) Show that the density d of the ideal gas in (i) above, at a constant temperature T is directly proportional to the pressure P.

Answer

Ideal gas equation: PV = nRT. With n = m/M (m = mass, M = molar mass): PV = (m/M)RT, so P = (m/V)(RT/M) = dRT/M, since d = m/V.
Therefore d = (M/RT) × P. For the given gas at constant T, M, R and T are constant, so **$d \propto P$**.

(iii) Show the variation of P with V of the system in (i) above at the two different temperatures of 300 K and 500 K, by drawing two graphs in the figure given below. Indicate clearly the temperature corresponding to each graph.
(The figure is a pair of axes: P on the vertical axis and V on the horizontal axis.)

Answer

500 K

300 K

at the same V, P(500 K) > P(300 K)

V

P

0

Both graphs are rectangular hyperbolas (PV = nRT = constant at each temperature) that approach the axes without touching them. The 500 K curve lies above (further from the origin than) the 300 K curve, because nRT is larger: at the same V, P(500 K) = (500/300) × P(300 K) = 1.67 × P(300 K). Label each curve with its temperature.

Review.

Boyle's law follows from PV = nRT with n and T fixed. Writing n = m/M gives P = dRT/M, the form used to relate density and molar mass. On a P–V plot each isotherm is a hyperbola; a higher temperature gives a larger constant nRT and so a curve further from the axes. Common mistakes: drawing straight lines, letting the curves cross or touch the axes, or putting the higher temperature curve below.

(b) [70 marks]

Depletion of $O_3(g)$ occurs according to the mechanism given below in the presence of Cl(g) and O(g) atoms,
Step 1: $O_3(g) + Cl(g) \rightarrow O_2(g) + ClO(g)$
Step 2: $ClO(g) + O(g) \rightarrow Cl(g) + O_2(g)$

(i) Write the overall reaction for the mechanism given above.

Answer

$O_3(g) + O(g) \rightarrow 2O_2(g)$ (adding steps 1 and 2 and cancelling Cl(g) and ClO(g))

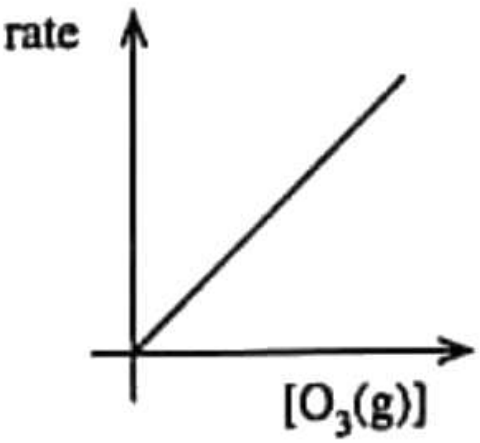
(ii) Giving reasons, identify the **catalyst** and the **intermediate product** of the above mechanism.

Answer

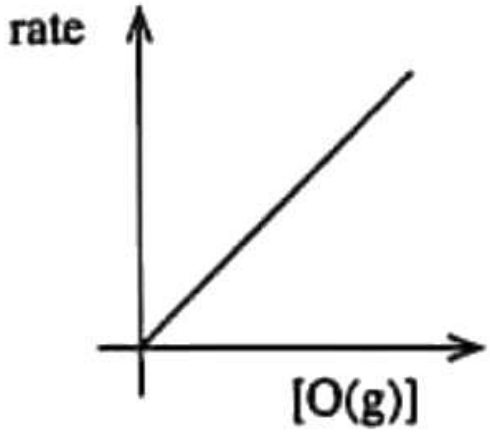
Catalyst: Cl(g)

Intermediate: ClO(g)

(iii) The following graphs were obtained from an experiment carried out in relation to the overall reaction in (i) above at temperature T. Rates and concentrations are measured in units of mol dm^{-3} s^{-1} and mol dm^{-3} respectively.



Graph 1



Graph 2

3

Graph 1 was obtained by keeping [O(g)] constant.
Graph 2 was obtained by keeping $[O_3(g)]$ constant.
I. With the help of graphs 1 and 2, deduce orders of the reaction with respect to $O_3(g)$ and O(g). What is the overall order of the reaction?

Answer

Graph 1 is a straight line through the origin, so at constant [O(g)], rate ∝ $[O_3(g)]^1$: the reaction is **first order with respect to O_3(g)**.
Graph 2 is a straight line through the origin, so at constant $[O_3(g)]$, rate ∝ $[O(g)]^1$: the reaction is **first order with respect to O(g)**.
Overall order = 1 + 1 = **2**.

II. If the rate constant of the reaction is k at temperature T, write the rate law of the reaction.

Answer

rate = $k[O_3(g)][O(g)]$

III. Derive the units of k.

Answer

k = rate/($[O_3(g)][O(g)]$); units = mol dm^{-3} s^{-1} ÷ (mol dm^{-3} × mol dm^{-3}) = **mol^{-1} dm^3 s^{-1}**

IV. In an experiment carried out at temperature T, the concentrations of O_3(g) and O(g) were 1.0×10^{-3} mol dm^{-3} and 1.0×10^{-4} mol dm^{-3} respectively. The rate of the reaction was found to be 1.0×10^{-3} mol dm^{-3} s^{-1}. Calculate the value of k.

Answer

k = rate/($[O_3(g)][O(g)]$) = 1.0×10^{-3} mol dm^{-3} s^{-1} ÷ (1.0×10^{-3} mol dm^{-3} × 1.0×10^{-4} mol dm^{-3})
k = **1.0×10^4 mol^{-1} dm^3 s^{-1}**

Review.

A catalyst is consumed in an early step and regenerated later; an intermediate is formed in one step and used up in a later one, and neither appears in the overall equation (the Resource Book uses the same Cl/ClO ozone example). Orders come from experiment, not from the overall equation: a straight line through the origin on a rate–concentration plot (other concentrations fixed) means first order. The units of k follow from the rate law: for overall order 2, mol^{-1} dm^3 s^{-1}. Common mistakes: giving O_2 or O as the intermediate, writing k without units, and dividing the exponents wrongly ($10^{-3} \div 10^{-7} = 10^4$).

Read: RB U4 §1.2 · p. 5 RB U11 §1.10 · p. 57 RB U11 §1.6 · p. 16 RB U11 §1.7 · p. 26

Question 4 · Part A · structured essay

(a) [60 marks]

A

B

C

5

10

2

4

D

E

F

G

H

I

(i) Draw the structures of A, B, C, D, E, F, G, H and I in the boxes given below.

Answer

	Structure (condensed)	Name
A	CH_2=CH–$CH(CH_3)_2$	3-methylbut-1-ene
B	CH_2=$C(CH_3)$–CH_2CH_3	2-methylbut-1-ene
C	CH_2=CH–$CH_2CH_2CH_3$	pent-1-ene
D	CH_3–CH(OH)–$CH(CH_3)_2$	3-methylbutan-2-ol (C-2 is chiral)
E	$(CH_3)_2$C(OH)–CH_2CH_3	2-methylbutan-2-ol
F	$(CH_3)_2$CH–CH_2CH_3	2-methylbutane
G	$CH_3CH_2CH_2CH_2CH_3$	pentane
H	$BrCH_2$–CH(CH_3)–CH_2CH_3	1-bromo-2-methylbutane
I	$HOCH_2$–CH(CH_3)–CH_2CH_3	2-methylbutan-1-ol

(ii) Describe a chemical test to distinguish D, E and I from one another.

Answer

Lucas test.

2

immediately

after some time

no turbidity

Review.

Reasoning: C_5H_{10} with a C=C has 2-methylbutane or pentane skeletons only. A and B give the same alkane F, so they share the branched skeleton (F = 2-methylbutane); C has the other skeleton, and the only straight-chain pentene without geometric isomers is pent-1-ene (pent-2-ene has cis/trans forms). Cold conc. H_2SO_4 followed by water and heat adds H_2O by Markovnikov's rule. Of the three methylbutenes, only 3-methylbut-1-ene gives a chiral alcohol (3-methylbutan-2-ol), so it is A; 2-methylbut-1-ene and 2-methylbut-2-ene both give achiral 2-methylbutan-2-ol. HBr with peroxide adds anti-Markovnikov: 2-methylbut-1-ene gives the primary halide $BrCH_2CH(CH_3)CH_2CH_3$, whereas 2-methylbut-2-ene would give a secondary halide, so B = 2-methylbut-1-ene. Aqueous NaOH substitutes OH for Br (S_N). In the Lucas test, ROH → RCl; the insoluble alkyl chloride causes the cloudiness, and the rate follows carbocation stability (3° > 2° > 1°). Acidified $K_2Cr_2O_7$ alone cannot separate D from I, because both are oxidized (orange → green).

(b) [40 marks]

(i) Draw the structures of the products J, K, L, M and N of the following reactions (I–V) in the given boxes.
(I) $CH_3CH(CH_3)CH_2CH_2Br$ —(alcoholic KOH)→ J
(II) C_6H_5COOH (benzoic acid) —(conc. HNO_3/conc. H_2SO_4)→ K
(III) $CH_3C(CH_3)=CH_2$ —(HBr)→ L
(IV) $CH_3COCH_2CH_3$ —(HCN)→ M
(V) $CH_3CH_2CH(CH_3)CH_2Br$ —(KCN)→ N

Answer

J: $(CH_3)_2CH–CH=CH_2$ (3-methylbut-1-ene)
K: 3-nitrobenzoic acid (m-nitrobenzoic acid) — a benzene ring carrying –COOH at C-1 and $–NO_2$ at C-3 (meta to each other)
L: $(CH_3)_3C–Br$ (2-bromo-2-methylpropane)
M: $CH_3–C(OH)(CN)–CH_2CH_3$ (2-hydroxy-2-methylbutanenitrile, the cyanohydrin)
N: $CH_3CH_2CH(CH_3)CH_2–CN$ (3-methylpentanenitrile)

(ii) Selecting from the reactions I–V, give one example each, for each type of reaction given below.
Nucleophilic addition ……
Electrophilic addition ……
Elimination reaction ……

Answer

Nucleophilic addition: **IV**
Electrophilic addition: **III**
Elimination reaction: **I**

Review.

(I) Alcoholic KOH removes HBr (elimination); the only β-carbon is the CH_2 next to CH_2Br, so a single alkene forms. (II) –COOH withdraws electrons, deactivates the ring and directs the incoming NO_2^+ to the meta position (electrophilic substitution). (III) H^+ adds to the CH_2 end, giving the more stable tertiary carbocation, which Br^- then attacks (Markovnikov, electrophilic addition). (IV) ^-CN attacks the carbonyl carbon and the alkoxide is then protonated (nucleophilic addition). (V) CN^- replaces Br^- on a primary carbon (nucleophilic substitution), adding one carbon to the chain. Reactions II and V are the substitutions, so they are not used in (ii).

Read: RB U8 §2.2 · p. 33 RB U9 §3.1 · p. 54 RB U8 §2.7 · p. 50 RB U8 §2.5 · p. 49

Answer two from each part

Essay · Paper II Parts B and C

Part B

Question 5 · Part B · essay

Given at the head of Part B: universal gas constant R = 8.314 J K^{-1} mol^{-1}; Avogadro constant N_A = 6.022 × 10^{23} mol^{-1}.

(a) [60 marks]

Consider the reaction (1) given below at a temperature of 800 °C.
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ ---------- (1)
Initially, 0.45 mol of HI(g) was introduced into a 1.0 dm^3 evacuated rigid closed container at 800 °C, and allowed to reach the equilibrium given above. It was found that 0.05 mol of $H_2(g)$ was present at equilibrium.

(i) Calculate the equilibrium constant K_{C1}, for the above equilibrium at a temperature of 800 °C.

Answer

	$H_2(g)$	$I_2(g)$	2HI(g)
Initial amount / mol	0	0	0.45
Change / mol	+0.05	+0.05	−0.10
At equilibrium / mol	0.05	0.05	0.35
Concentration / mol dm^{-3} (1.0 dm^3)	0.05	0.05	0.35

C1

2

2

2

2

49

(ii) In a separate similar evacuated container at a temperature of 800 °C, reaction (2) takes place with an equilibrium constant $K_{C2} = 1.2 \times 10^8$ mol^{-1} dm^3.
$2H_2(g) + S_2(g) \rightleftharpoons 2H_2S(g)$ ---------- (2)
When the two containers are connected together, the following reaction (3) takes place at a temperature of 800 °C.
$2I_2(g) + 2H_2S(g) \rightleftharpoons S_2(g) + 4HI(g)$ ---------- (3)
Calculate the equilibrium constant K_{C3} for the reaction (3) at a temperature of 800 °C.

Answer

Reaction (3) = 2 × (1) − (2):
2 × (1): $2H_2(g) + 2I_2(g) \rightleftharpoons 4HI(g)$, $K = K_{C1}^2$
reverse of (2): $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$, $K = 1/K_{C2}$
Adding: $2I_2(g) + 2H_2S(g) \rightleftharpoons S_2(g) + 4HI(g)$
$K_{C3} = [S_2(g)][HI(g)]^4/([I_2(g)]^2[H_2S(g)]^2) = ([HI]^2/([H_2][I_2]))^2 \times ([H_2]^2[S_2]/[H_2S]^2) = K_{C1}^2/K_{C2}$
$K_{C3} = (49)^2/(1.2 \times 10^8\ mol^{-1}\ dm^3) = 2401/(1.2 \times 10^8)$ mol dm^{-3} = **2.0×10^{-5} mol dm^{-3}**

(iii) A 1.0 dm^3 rigid closed container at a temperature of 800 °C contains an equilibrium mixture of (3) in (ii) above with 5.00×10^{-5} mol HI(g), 1.25×10^{-6} mol $S_2(g)$ and 2.50×10^{-5} mol $H_2S(g)$. Calculate the number of moles of $I_2(g)$ in the above mixture.

Answer

The volume is 1.0 dm^3, so the amounts in mol are numerically equal to the concentrations in mol dm^{-3}.
$[I_2(g)]^2 = [S_2(g)][HI(g)]^4/(K_{C3}[H_2S(g)]^2) = (1.25 \times 10^{-6})(5.00 \times 10^{-5})^4/[(2.0 \times 10^{-5})(2.50 \times 10^{-5})^2]$
$= (7.81 \times 10^{-24})/(1.25 \times 10^{-14}) = 6.25 \times 10^{-10}$ mol^2 dm^{-6}
$[I_2(g)] = 2.5 \times 10^{-5}$ mol dm^{-3}, so the amount of $I_2(g)$ = **2.5×10^{-5} mol**

(iv) An extra 2.50 × 10^{-5} mol I_2(g) was added to the equilibrium mixture in (iii) above at a temperature of 800 °C.

I. Calculate the reaction quotient (Q_C) at the moment the extra I_2(g) is added.

Answer

At that moment n(I_2) = 2.5 × 10^{-5} + 2.50 × 10^{-5} = 5.0 × 10^{-5} mol, so [I_2(g)] = 5.0 × 10^{-5} mol dm^{-3}; the other concentrations are still those in (iii).

Q_C = [S_2(g)][HI(g)]^4/([I_2(g)]^2[H_2S(g)]^2) = (1.25 × 10^{-6})(5.00 × 10^{-5})^4/[(5.0 × 10^{-5})^2(2.50 × 10^{-5})^2]
= (7.81 × 10^{-24})/(1.56 × 10^{-18}) = **5.0 × 10^{-6} mol dm^{-3}**

II. Explain the change in the equilibrium that takes place upon the addition of extra I_2(g).

Answer

Q_C (5.0 × 10^{-6} mol dm^{-3}) < K_{C3} (2.0 × 10^{-5} mol dm^{-3}), so the mixture is no longer at equilibrium. The rate of the forward reaction now exceeds the rate of the backward reaction, so a net forward reaction takes place: the equilibrium shifts to the right, as Le Chatelier's principle predicts, partly using up the added I_2. I_2(g) and H_2S(g) are consumed and S_2(g) and HI(g) are formed until Q_C again equals K_{C3}; K_{C3} itself does not change because the temperature is constant. The concentrations change in the ratio I_2 : H_2S : S_2 : HI = 2 : 2 : 1 : 4 (decrease : decrease : increase : increase).

For reference, solving 2.0 × 10^{-5} = (1.25 × 10^{-6} + x)(5.00 × 10^{-5} + 4x)^4/[(5.0 × 10^{-5} − 2x)^2(2.50 × 10^{-5} − 2x)^2] gives x ≈ 1.25 × 10^{-6} mol dm^{-3}, so at the new equilibrium [I_2] ≈ 4.75 × 10^{-5}, [H_2S] ≈ 2.25 × 10^{-5}, [S_2] ≈ 2.50 × 10^{-6} and [HI] ≈ 5.50 × 10^{-5} mol dm^{-3}.

III. Sketch the variation in the concentrations of each constituent in the mixture, with time, upon the addition of extra I_2(g).

Answer

2

new equilibrium

[HI] 5.00 → 5.50

2

2

2

HI

2

2

2

2.50 → 5.00

time

concentration (not to scale)

values ×10^{-5} mol dm^{-3}

Features to show: before the addition all four concentrations are constant (the I_2 and H_2S lines coincide at 2.5 × 10^{-5} mol dm^{-3}). At the moment of addition [I_2] rises vertically (instantly) from 2.5 × 10^{-5} to 5.0 × 10^{-5} mol dm^{-3} and then falls gradually; [H_2S] falls gradually; [S_2] and [HI] rise gradually; all four curves then level off at the new equilibrium. The fall in [I_2] equals the fall in [H_2S], and the rise in [HI] is four times the rise in [S_2] (2 : 2 : 1 : 4). In the sketch the changes are drawn larger than scale for clarity; the values are in 10^{-5} mol

dm^{-3}.

Review.

The principle tested is the equilibrium law. K_C comes from an initial–change–equilibrium table; because the container is 1.0 dm^3, moles equal concentrations. Equilibrium constants are combined by these rules: multiplying an equation by n raises K to the power n, reversing it inverts K, and adding equations multiplies their K values, so $K_{C3} = K_{C1}^2/K_{C2}$. Comparing Q_C with K_C predicts the direction of change: $Q_C < K_C$ means a net forward reaction. Common mistakes: forgetting that 0.10 mol of HI is used to make 0.05 mol of H_2; writing $K_{C3} = K_{C1}/K_{C2}$; omitting the unit of K_{C3} (mol dm^{-3}); and, in the sketch, drawing $[I_2]$ rising gradually (it jumps at once) or failing to show all four curves levelling off.

(b) [60 marks]

(i) Using the data given below, calculate ΔH°, ΔS° and ΔG° for the reaction (4) at 27 °C.
$H_2(g) + I_2(g) \rightarrow 2HI(g)$ ---------- (4)
At 27 °C: $H_2(g) + I_2(s) \rightarrow 2HI(g)$; ΔH° = 53 kJ mol^{-1}, ΔS° = 410 J K^{-1} mol^{-1}
$I_2(s) \rightarrow I_2(g)$; ΔH° = 63 kJ mol^{-1}, ΔS° = 260 J K^{-1} mol^{-1}

Answer

Reaction (4) = $[H_2(g) + I_2(s) \rightarrow 2HI(g)] - [I_2(s) \rightarrow I_2(g)]$ (Hess's law; the same applies to ΔS°).
ΔH° = 53 − 63 = **−10 kJ mol^{-1}**
ΔS° = 410 − 260 = **+150 J K^{-1} mol^{-1}**
ΔG° = ΔH° − TΔS°, with T = 27 + 273 = 300 K
ΔG° = −10 kJ mol^{-1} − (300 K × 0.150 kJ K^{-1} mol^{-1}) = −10 − 45 = **−55 kJ mol^{-1}**

(ii) Using the data given below, calculate ΔH°, ΔS° and ΔG° for the reaction (5) at 27 °C.
$2H_2S(g) \rightarrow 2H_2(g) + S_2(g)$ ---------- (5)
At 27 °C:

	ΔH_f° / kJ mol^{-1}	ΔS_f° / J K^{-1} mol^{-1}
$H_2(g)$	0	130
$S_2(g)$	127	230
$H_2S(g)$	−20	200

Answer

ΔH° = $\Sigma\Delta H_f^\circ$(products) − $\Sigma\Delta H_f^\circ$(reactants) = [2(0) + 127] − [2(−20)] = 127 + 40 = **+167 kJ mol^{-1}**
ΔS° = ΣS°(products) − ΣS°(reactants) = [2(130) + 230] − [2(200)] = 490 − 400 = **+90 J K^{-1} mol^{-1}**
ΔG° = ΔH° − TΔS° = 167 kJ mol^{-1} − (300 K × 0.090 kJ K^{-1} mol^{-1}) = 167 − 27 = **+140 kJ mol^{-1}**

(iii) Using the answers obtained in (b)(i) and (b)(ii) above, predict giving reasons whether the reaction (6) below is spontaneous or not at 27 °C.
$2I_2(g) + 2H_2S(g) \rightarrow S_2(g) + 4HI(g)$ ---------- (6)

Answer

Reaction (6) = 2 × (4) + (5): $[2H_2(g) + 2I_2(g) \rightarrow 4HI(g)] + [2H_2S(g) \rightarrow 2H_2(g) + S_2(g)]$ gives $2I_2(g) + 2H_2S(g) \rightarrow S_2(g) + 4HI(g)$.
ΔG°(6) = 2ΔG°(4) + ΔG°(5) = 2(−55) + 140 = **+30 kJ mol^{-1}**
Check: ΔH°(6) = 2(−10) + 167 = +147 kJ mol^{-1}; ΔS°(6) = 2(150) + 90 = +390 J K^{-1} mol^{-1}; ΔG°(6) = 147 − 300 × 0.390 = +30 kJ mol^{-1}.
Since ΔG° > 0 at 27 °C, reaction (6) is **not spontaneous** at 27 °C under standard conditions; the reverse reaction is spontaneous. (Because ΔH° and ΔS° are both positive, it would become spontaneous above T = ΔH°/ΔS° = 147 000/390 ≈ 377 K, assuming ΔH° and ΔS° do not change with temperature.)

Review.

Hess's law applies to ΔH°, ΔS° and ΔG° alike: when equations are added, subtracted or multiplied, these quantities are combined in the same way. The second column of the table (printed as ΔS_f°) holds standard molar entropies S°, so ΔS° = ΣS°(products) − ΣS°(reactants); an element such as $H_2(g)$ has $\Delta H_f^\circ = 0$ but a non-zero S°. Change ΔS° to kJ K^{-1} mol^{-1} before using ΔG° = ΔH° − TΔS°, with T in kelvin (300 K). A reaction is spontaneous when ΔG < 0. Common mistakes: using T = 27 instead of 300 K, mixing J and kJ, forgetting to double reaction (4) in (iii), and taking $S^\circ(H_2)$ as zero.

(c) [30 marks]

An aqueous solution of volume 1.0 dm^3 in a beaker at a temperature of 25 °C contains 2.0×10^{-2} mol of $Cl^-(aq)$ ions and 2.0×10^{-2} mol of $CrO_4^{2-}(aq)$ ions. Small portions of concentrated aqueous $AgNO_3$ solution were added **slowly** to the above solution. At 25 °C, $K_{sp}(AgCl(s)) = 1.60 \times 10^{-10}$ mol^2 dm^{-6} and $K_{sp}(Ag_2CrO_4(s)) = 8.0 \times 10^{-12}$ mol^3 dm^{-9}. Assume that there was no significant change in solution volume upon the addition of $AgNO_3(aq)$ solution.

(i) Show that AgCl precipitates first by a suitable calculation.

Answer

AgCl begins to precipitate when the ionic product $[Ag^+][Cl^-]$ exceeds $K_{sp}(AgCl)$:
$[Ag^+]$ needed = $K_{sp}(AgCl)/[Cl^-] = 1.60 \times 10^{-10}/2.0 \times 10^{-2}$ = **8.0×10^{-9} mol dm^{-3}**
Ag_2CrO_4 begins to precipitate when $[Ag^+]^2[CrO_4^{2-}]$ exceeds $K_{sp}(Ag_2CrO_4)$:
$[Ag^+]$ needed = $\sqrt{(8.0 \times 10^{-12}/2.0 \times 10^{-2})} = \sqrt{(4.0 \times 10^{-10})}$ = **2.0×10^{-5} mol dm^{-3}**
The $[Ag^+]$ needed to start precipitating AgCl (8.0×10^{-9} mol dm^{-3}) is much lower than that for Ag_2CrO_4 (2.0×10^{-5} mol dm^{-3}). So, as Ag^+ is added slowly, the ionic product of AgCl reaches its K_{sp} first, and **AgCl precipitates first**.

(ii) Calculate the concentration of $Cl^-(aq)$ ions present in the solution at the time Ag_2CrO_4 starts to precipitate.

Answer

Ag_2CrO_4 starts to precipitate when $[Ag^+] = 2.0 \times 10^{-5}$ mol dm^{-3}. No chromate has precipitated before this, and the volume is constant, so $[CrO_4^{2-}]$ is still 2.0×10^{-2} mol dm^{-3}.
At that moment the solution is saturated with AgCl: $[Cl^-] = K_{sp}(AgCl)/[Ag^+] = 1.60 \times 10^{-10}/2.0 \times 10^{-5}$ = **8.0×10^{-6} mol dm^{-3}**
Only 0.04% of the original Cl^- is left in solution, so the precipitation of AgCl is practically complete before Ag_2CrO_4 appears. This is why chromate can act as the end-point indicator when Cl^- is titrated with Ag^+.

Review.

A salt precipitates when its ionic product exceeds K_{sp}. AgCl (1 : 1) and Ag_2CrO_4 (2 : 1) are different formula types, so their K_{sp} values cannot be compared directly; work out the $[Ag^+]$ each one needs. For Ag_2CrO_4 the expression contains $[Ag^+]^2$, so a square root is needed. Common mistakes: deciding from the K_{sp} values alone ($8.0 \times 10^{-12} < 1.6 \times 10^{-10}$ wrongly suggests Ag_2CrO_4 first), forgetting the square root, and writing $K_{sp} = [2Ag^+]^2[CrO_4^{2-}]$.

Read: RB U12 §2.1 · p. 76 RB U5 §2.4 · p. 53 RB U5 §2.2 · p. 36 RB U12 §2.4 · p. 175

Question 6 · Part B · essay

(a) [90 marks]

You are provided with an aqueous solution of sodium acetate (CH_3COONa) at 25 °C.

(i) Write the equilibrium reaction for the hydrolysis of sodium acetate in aqueous medium.

Answer

CH_3COONa dissociates completely: $CH_3COONa(aq) \rightarrow CH_3COO^-(aq) + Na^+(aq)$. The acetate ion, the conjugate base of a weak acid, hydrolyses:
$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$

(ii) Write the expression for the equilibrium constant K_h of the equilibrium in (i) above.

Answer

h

3

−

3

−

2

h

(iii) If the dissociation constants for $CH_3COOH(aq)$, and $H_2O(l)$ are K_a and K_w respectively at 25 °C, show that $K_h = K_w/K_a$.

Answer

$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$; $K_a = [CH_3COO^-(aq)][H_3O^+(aq)]/[CH_3COOH(aq)]$
$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$; $K_w = [H_3O^+(aq)][OH^-(aq)]$
$K_w/K_a = [H_3O^+][OH^-] \times [CH_3COOH]/([CH_3COO^-][H_3O^+]) = [CH_3COOH][OH^-]/[CH_3COO^-] = K_h$
$\therefore$ **$K_h = K_w/K_a$**

(iv) Given that, $K_a = 1.8 \times 10^{-5}$ mol dm^{-3} and $K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6} at 25 °C, calculate the value of K_h at 25 °C.

Answer

$K_h = K_w/K_a = (1.0 \times 10^{-14}$ mol^2 dm$^{-6})/(1.8 \times 10^{-5}$ mol dm$^{-3}) =$ **5.6×10^{-10} mol dm^{-3}**

(v) A portion of 25.00 cm^3 of 0.10 mol dm^{-3} CH_3COONa solution is titrated with a solution of 0.10 mol dm^{-3} HCl. What is the volume of 0.10 mol dm^{-3} HCl required to reach the equivalence point? Calculate the pH of the solution at the equivalence point.

Answer

$CH_3COONa(aq) + HCl(aq) \rightarrow CH_3COOH(aq) + NaCl(aq)$ (1 : 1), i.e. $CH_3COO^-(aq) + H_3O^+(aq) \rightarrow CH_3COOH(aq) + H_2O(l)$
$n(CH_3COONa) = 0.10$ mol dm$^{-3} \times 25.00 \times 10^{-3}$ dm$^3 = 2.5 \times 10^{-3}$ mol = n(HCl) required
Volume of HCl = 2.5×10^{-3} mol/0.10 mol dm$^{-3} = 2.5 \times 10^{-2}$ dm$^3 =$ **25.00 cm^3**
At the equivalence point the solution holds 2.5×10^{-3} mol CH_3COOH (and NaCl, which does not hydrolyse) in 25.00 + 25.00 = 50.00 cm^3:
$[CH_3COOH] = 2.5 \times 10^{-3}$ mol/0.050 dm$^3 = 0.050$ mol dm^{-3}
$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$; with $[CH_3COO^-] = [H_3O^+]$ and the dissociation small ($0.050 - x \approx 0.050$):
$[H_3O^+]^2 = K_a \times c = 1.8 \times 10^{-5} \times 0.050 = 9.0 \times 10^{-7}$ mol^2 dm^{-6}
$[H_3O^+] = 9.5 \times 10^{-4}$ mol dm^{-3}; pH = $-\log(9.5 \times 10^{-4}) =$ **3.02 (≈ 3.0)**
(The degree of dissociation is only about 1.9%, so the approximation is valid.)

(vi) Sketch the titration curve (pH vs. volume of HCl) for the above titration in (v).

Answer

0

10

20

30

40

50

0

2

4

6

8

10

methyl orange range (3.1–4.4)

pH 8.87

a

equivalence point: 25.00 cm³, pH ≈ 3.0

Volume of 0.10 mol dm⁻³ HCl added (cm³)

pH

Key features: the starting pH is about 8.9 (0.10 mol dm^{-3} CH_3COO^-: $[OH^-] = \sqrt{(K_h \times 0.10)} = 7.5 \times 10^{-6}$ mol dm^{-3}, pOH = 5.13, pH = 8.87). The pH drops quickly at first and then falls slowly through the buffer region (CH_3COOH/CH_3COO^-), with pH = pK_a = 4.74 at 12.50 cm^3 (half-way). The equivalence point is at 25.00 cm^3, pH ≈ 3.0 (acidic, because CH_3COOH is formed). Beyond it the excess HCl lowers the pH slowly towards that of dilute HCl (about 1.5 at 50 cm^3). The pH change around the equivalence point is small, because CH_3COO^- is a very weak base ($K_b = K_h = 5.6 \times 10^{-10}$ mol dm^{-3}).

(vii) State an indicator which can be used for the titration in (v) above.

Answer

Methyl orange

(viii) Explain why it is **not** possible to titrate a 0.10 mol dm^{-3} CH_3COOH solution with a solution of 0.10 mol dm^{-3} aqueous ammonia.

Answer

CH_3COOH is a weak acid and NH_3(aq) is a weak base. Both ions of the salt formed (CH_3COO^- and NH_4^+) hydrolyse. Before the equivalence point the solution is a CH_3COOH/CH_3COO^- buffer, and after it an NH_3/NH_4^+ buffer. So there is no steep (sharp) change in pH at the equivalence point; the pH changes only gradually (for 25.00 cm^3 of acid, from about 6.1 at 24 cm^3 to about 7.9 at 26 cm^3 of NH_3, with pH ≈ 7 at the equivalence point). No indicator changes colour sharply on the addition of a drop or two of titrant, so the end point cannot be located accurately.

Review.

Salt hydrolysis and acid–base titrations (Resource Book 12 2.2). The anion of a weak acid is a base: $K_h = K_w/K_a$. When CH_3COONa is titrated with HCl, the product at the equivalence point is the weak acid CH_3COOH, so the equivalence pH is acidic. Find it from $[H_3O^+] = \sqrt{(K_a\ c)}$, using the concentration after mixing (0.050 mol dm^{-3}, not 0.10). An indicator is suitable when its colour-change range lies within the pH change around the equivalence point; for a weak acid–weak base titration there is no steep region, so no indicator works. Common mistakes: including Na^+ in the hydrolysis equation, taking the equivalence pH as 7, forgetting the dilution to 50.00 cm^3, choosing phenolphthalein, and drawing a rising curve (the pH falls because acid is being added).

(b) [60 marks]

An ideal binary liquid mixture was prepared by mixing two volatile liquids A and B at a given temperature. When the composition of the liquid phase was $X_A = 0.2$ and $X_B = 0.8$, the pressure of the vapour phase was P (X_A and X_B are mole fractions of A and B respectively in the liquid phase). When the composition of the liquid phase was changed to $X_A = 0.5$ and $X_B = 0.5$, the pressure of the vapour phase becomes (5/3)P. At this temperature, saturated vapour pressures of A and B are $P°_A$ and $P°_B$ respectively.

(i) Show that $P°_A = 5P°_B$.

Answer

For an ideal mixture, Raoult's law and Dalton's law give $P_{total} = P_A + P_B = X_A\ P°_A + X_B\ P°_B$.
$X_A = 0.2$: $P = 0.2P°_A + 0.8P°_B$ ... (1)
$X_A = 0.5$: $(5/3)P = 0.5P°_A + 0.5P°_B$ ... (2)
Substituting (1) in (2): $(5/3)(0.2P°_A + 0.8P°_B) = 0.5P°_A + 0.5P°_B$
Multiplying by 3: $P°_A + 4P°_B = 1.5P°_A + 1.5P°_B$, so $2.5P°_B = 0.5P°_A$
∴ **$P°_A = 5P°_B$**

(ii) Draw the corresponding composition - vapour pressure diagram for the mixture of A and B by showing the variations in P_A, P_B and P_{total} and label the diagram.

Answer

0.0

0.2

0.4

0.6

0.8

1.0

A

A

A

B

B

B

total

A

B

B

A

B

0

A

B

A

A

A

A

A

B

A

A

A

vapour pressure

$P_A = X_A\,P°_A$ is a straight line from 0 (pure B, $X_A = 0$) to $P°_A = 5P°_B$ (pure A, $X_A = 1$). $P_B = X_B\,P°_B$ is a straight line from $P°_B$ (pure B) to 0 (pure A). $P_{total} = P_A + P_B$ is a straight line joining $P°_B$ and $P°_A$. $P = 1.8P°_B$ (at $X_A = 0.2$) and $(5/3)P = 3.0P°_B$ (at $X_A = 0.5$) both lie on this line.

(iii) Calculate the composition of the liquid phase at the point where $P_A = P_B$.

Answer

$P_A = P_B$: $X_A\,P°_A = X_B\,P°_B = (1 - X_A)P°_B$
$X_A(5P°_B) = (1 - X_A)P°_B \rightarrow 5X_A = 1 - X_A \rightarrow 6X_A = 1$
$X_A = 1/6 \approx 0.17$ and $X_B = 5/6 \approx 0.83$ (here $P_A = P_B = (5/6)P°_B$)

Review.

Raoult's law for an ideal mixture of volatile liquids (Resource Book 12 2.6): each partial pressure is proportional to the mole fraction of that component in the liquid, so P_A, P_B and P_{total} are all straight lines against composition. Write P_{total} for both compositions and eliminate P. Common mistakes: using vapour-phase mole fractions in Raoult's law, drawing P_A and P_B starting from the wrong ends of the axis, not labelling $P°_A$ and $P°_B$, and drawing a curved total-pressure line, which applies only to non-ideal mixtures.

Read: RB U12 §2.2 · p. 118 RB U12 §2.6 · p. 216 RB U12 §2.3 · p. 167

Question 7 · Part B · essay

(a) [75 marks]

A galvanic electrochemical cell was constructed at 25 °C based on the following half - reactions (1) and (2).
$2H_2O(l) + O_2(g) + 4e \rightarrow 4OH^-(aq)$ ---------- (1); $E° = 0.40$ V
$2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$ ---------- (2); $E° = -0.83$ V

(i) Identify the anodic and cathodic half reactions of the cell.

Answer

E° of (1) (+0.40 V) is more positive than E° of (2) (−0.83 V), so (1) takes place as a reduction and (2) runs in reverse as an oxidation.
Cathode (reduction): $2H_2O(l) + O_2(g) + 4e \rightarrow 4OH^-(aq)$
Anode (oxidation): $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e$

(ii) Write the overall balanced cell reaction of the cell.

Answer

Anode reaction × 2 + cathode reaction: $2H_2(g) + 4OH^-(aq) + 2H_2O(l) + O_2(g) \rightarrow 4H_2O(l) + 4OH^-(aq)$
$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

(iii) Calculate $E°_{cell}$ of the cell at 25 °C.

Answer

$E°_{cell} = E°_{cathode} - E°_{anode}$ = 0.40 V − (−0.83 V) = **+1.23 V** (E° values are not multiplied when the half-equations are multiplied.)

(iv) The cell was operated for a duration of 600 s. During this period, 1.0 mol $H_2(g)$ was consumed.
I. Calculate the number of moles of electrons which passed through the cell.

Answer

$H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e$: 1 mol of H_2 gives 2 mol of electrons.
Moles of electrons = 1.0 mol × 2 = **2.0 mol**

II. Calculate the amount of electricity (in coulombs) generated in the cell during its operation (1 F = 96500 C mol^{-1}).

Answer

Q = n(e) × F = 2.0 mol × 96500 C mol^{-1} = **1.93×10^5 C**

III. Assuming that the current drawn from the cell is constant during the operation, calculate its value.

Answer

Q = It, so I = Q/t = 1.93×10^5 C/600 s = **3.2×10^2 A** (321.7 A)

(v) In the above galvanic electrochemical cell propane ($C_3H_8(g)$) is used instead of $H_2(g)$.
I. Write the half-cell reaction for the propane electrode assuming propane is converted to $CO_2(g)$ and $H_2O(l)$.

Answer

The propane electrode is the anode (oxidation), in the alkaline (OH^-) electrolyte:
$C_3H_8(g) + 20OH^-(aq) \rightarrow 3CO_2(g) + 14H_2O(l) + 20e$
(The oxidation number of C changes from −8/3 to +4, so 3 × 20/3 = 20 electrons are lost. Balance O with OH^- and H with H_2O, then check the charges: −20 = −20.)

II. Derive the balanced equation for the overall cell reaction by using propane instead of $H_2(g)$ in the answer given in (ii) above.

Answer

Cathode × 5: $10H_2O(l) + 5O_2(g) + 20e \rightarrow 20OH^-(aq)$
Anode: $C_3H_8(g) + 20OH^-(aq) \rightarrow 3CO_2(g) + 14H_2O(l) + 20e$
Adding: $C_3H_8(g) + 5O_2(g) + 10H_2O(l) + 20OH^-(aq) \rightarrow 3CO_2(g) + 14H_2O(l) + 20OH^-(aq)$
$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$

III. Giving reasons, state one environmental advantage of the cell which uses $H_2(g)$ over the cell that uses propane.

Answer

The only product of the H_2 cell is water, whereas the propane cell releases $CO_2(g)$, a greenhouse gas. So the H_2 cell does not add CO_2 to the atmosphere and does not contribute to global warming.

Review.

Galvanic (fuel) cells (Resource Book 13 3.3–3.4). The half-reaction with the more positive E° is the cathode (reduction), and $E°_{cell} = E°_{cathode} - E°_{anode}$; E° is not multiplied by coefficients. Faraday's laws: charge Q = n(e)F and Q = It. For propane, balance the half-equation in alkaline medium using OH^- and H_2O, and match the electrons (20) before adding it to the cathode equation. (In a real alkaline cell CO_2 would react with OH^- to form CO_3^{2-}, but the question tells you to take $CO_2(g)$ and $H_2O(l)$ as the products.) Common mistakes: multiplying E° values, taking 1 mol H_2 as 1 mol of electrons, using H^+ in an alkaline cell, and forgetting to change minutes or hours to seconds in Q = It.

(b) [75 marks]

(i) X is a d-block element that belongs to the fourth period of the Periodic Table. On reacting X with dil. HCl, the colourless solution X_1 and the gas X_2 are obtained. When X_1 is treated with dil. NH_4OH/NH_4Cl and H_2S is bubbled through the solution thereafter, the white precipitate X_3 is obtained. X_3 is soluble in dil. HCl. On addition of dil. NaOH to X_1, the gelatinous white precipitate X_4 is formed. X_4 dissolves in excess dil. NaOH and in excess dil. NH_4OH to give X_5 and X_6 respectively. Both X_5 and X_6 are colourless.
I. Identify the species X and X_1 to X_6. (Give chemical formulae) **Note**: Reasons are not required.

Answer

X	X_1	X_2	X_3	X_4	X_5	X_6
Zn	$ZnCl_2$ ($[Zn(H_2O)_6]^{2+}$)	H_2	ZnS	$Zn(OH)_2$	$[Zn(OH)_4]^{2-}$ ($Na_2[Zn(OH)_4]$)	$[Zn(NH_3)_4]^{2+}$

II. Write the electronic configuration of X.

Answer

Zn: **$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$** ($[Ar]\ 3d^{10}\ 4s^2$)

III. Explain why X_1 is colourless.

Answer

X_1 contains Zn^{2+} (as $[Zn(H_2O)_6]^{2+}$), whose configuration is $[Ar]\ 3d^{10}$. The 3d subshell is completely filled, so no d–d electron transition (promotion of a d electron to a higher-energy d orbital) is possible. No visible light is absorbed, so the solution is colourless.

IV. Write the IUPAC name of X_6.

Answer

$[Zn(NH_3)_4]^{2+}$: **tetraamminezinc(II) ion**

(ii) Y is also a d-block element that belongs to the same row as X in the Periodic Table. Y has two common oxidation numbers **n** and **m**. **m** is greater than **n**. Y^{n+} forms the pink coloured species Y_1 in aqueous solution. On treatment of the solution containing Y_1 with dil. NaOH the pink precipitate Y_2 is formed. When H_2S is bubbled through a slightly basic solution containing Y_1, the black precipitate Y_3 is obtained. The yellowish-brown species Y_4 is formed on addition of excess conc. ammonia to a solution containing Y_1. On treatment of a solution containing Y_1 with conc. HCl, the blue coloured species Y_5 is obtained. On exposure of Y_4 to air, the brownish-red species Y_6 is formed.

I. Give the values of **n** and **m**.

Answer

n = 2, m = 3

II. Identify the species Y and Y_1 to Y_6. (Give chemical formulae) **Note**: Reasons are not required.

Answer

Y	Y_1	Y_2	Y_3	Y_4	Y_5	Y_6
Co	$[Co(H_2O)_6]^{2+}$	$Co(OH)_2$	CoS	$[Co(NH_3)_6]^{2+}$	$[CoCl_4]^{2-}$	$[Co(NH_3)_6]^{3+}$

III. Write the electronic configurations of Y^{n+} and Y^{m+}.

Answer

Co^{2+}: **$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^7$** ([Ar] $3d^7$)
Co^{3+}: **$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^6$** ([Ar] $3d^6$)
(Co is [Ar] $3d^7$ $4s^2$; the 4s electrons are removed first.)

IV. Write the IUPAC name of Y_5.

Answer

$[CoCl_4]^{2-}$: **tetrachloridocobaltate(II) ion**

Review.

Qualitative chemistry of the 3d elements (Resource Book 6 4.10). A d-block metal that gives a colourless solution and H_2 with dilute HCl, a white sulfide in NH_4OH/NH_4Cl medium, and a white amphoteric hydroxide that dissolves in both excess NaOH and excess NH_3, is zinc. Pink $[Co(H_2O)_6]^{2+}$, pink $Co(OH)_2$, black CoS, blue $[CoCl_4]^{2-}$, and the air oxidation of yellowish-brown $[Co(NH_3)_6]^{2+}$ to brownish-red $[Co(NH_3)_6]^{3+}$ identify cobalt. Transition-metal ions lose their 4s electrons before 3d. IUPAC names (6 4.10.6): ligands come before the metal, Cl^- as a ligand is 'chlorido', NH_3 is 'ammine', and an anionic complex takes the '-ate' ending (cobaltate). Common mistakes: writing Co^{2+} as [Ar] $3d^5$ $4s^2$, naming $[CoCl_4]^{2-}$ without '-ate', giving Cl_2 as the gas X_2, and writing 'amine' for 'ammine'.

Read: RB U13 §3.3 · p. 250 RB U13 §3.4 · p. 261 RB U6 §4.10 · p. 160 RB U6 §4.10.6 · p. 169

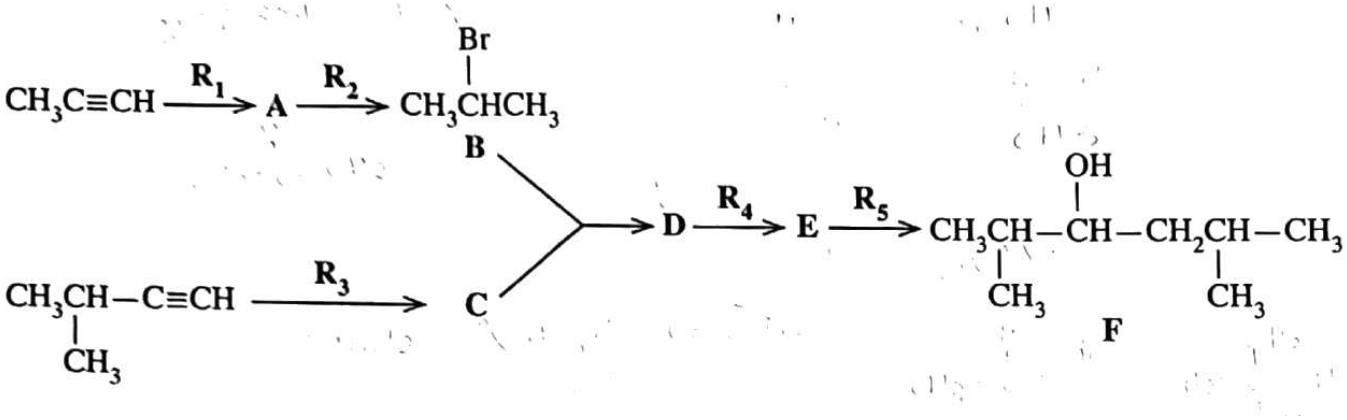
Part C

Question 8 · Part C · essay

Part C — Essay: answer two questions only (each question carries 150 marks).

(a) [60 marks]

Preparation of the compound F has been carried out using $CH_3C{\equiv}CH$ and $(CH_3)_2CHC{\equiv}CH$ according to the reaction scheme given below.



3

1

2

3

3

3

3

3

4

5

3

3

2

3

3

(i) Give the structures of the compounds A, C, D and E and the reagents R_1, R_2, R_3, R_4, and R_5.
Only the chemical substances given below should be used either **singly or as combinations** as reagents.
Chemical substances: H_2, $NaNH_2$, $NaBH_4$, $HgSO_4$, HBr, dil. H_2SO_4, Pd-$BaSO_4$/Quinoline catalyst, CH_3OH

Answer

A	C	D	E
$CH_3CH=CH_2$ (propene)	$(CH_3)_2CHC\equiv C^-\ Na^+$ (sodium salt of 3-methylbut-1-yne)	$(CH_3)_2CHC\equiv CCH(CH_3)_2$ (2,5-dimethylhex-3-yne)	$(CH_3)_2CHCOCH_2CH(CH_3)_2$ (2,5-dimethylhexan-3-one)

R_1	R_2	R_3	R_4	R_5
H_2 / Pd-$BaSO_4$ / quinoline	HBr	$NaNH_2$	dil. H_2SO_4 / $HgSO_4$	$NaBH_4$ / CH_3OH

Reaction sequence:
$CH_3C{\equiv}CH + H_2$ —(Pd-$BaSO_4$/quinoline)→ $CH_3CH{=}CH_2$ (A) (the poisoned catalyst stops the reduction at the alkene)
$CH_3CH{=}CH_2 + HBr \rightarrow CH_3CHBrCH_3$ (B) (Markovnikov addition)
$(CH_3)_2CHC{\equiv}CH + NaNH_2 \rightarrow (CH_3)_2CHC{\equiv}C^- Na^+$ (C) + NH_3 (the terminal alkyne H is acidic)
$(CH_3)_2CHC{\equiv}C^- Na^+ + CH_3CHBrCH_3 \rightarrow (CH_3)_2CHC{\equiv}CCH(CH_3)_2$ (D) + NaBr (the acetylide ion substitutes Br)
D + H_2O —($HgSO_4$/dil. H_2SO_4)→ enol → $(CH_3)_2CHCOCH_2CH(CH_3)_2$ (E) (D is symmetrical, so only one ketone forms)
E —($NaBH_4$/CH_3OH)→ $(CH_3)_2CHCH(OH)CH_2CH(CH_3)_2$ (F)

(ii) Compound F was reacted with $H^+/K_2Cr_2O_7$. When the product obtained from this reaction is reacted with 2,4-dinitrophenylhydrazine (2,4-DNP), compound G is formed. Give the structure of G.

Answer

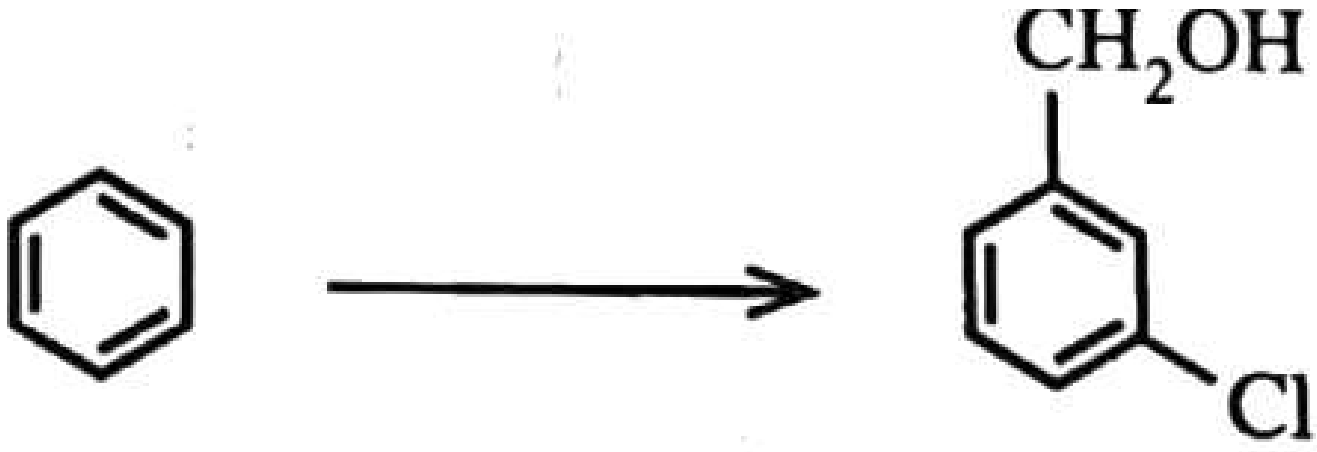
F is a secondary alcohol, so $H^+/K_2Cr_2O_7$ oxidises it back to the ketone E, $(CH_3)_2CHCOCH_2CH(CH_3)_2$. The ketone condenses with 2,4-DNP, losing H_2O:
$(CH_3)_2CHCOCH_2CH(CH_3)_2 + H_2N{-}NH{-}C_6H_3(NO_2)_2 \rightarrow (CH_3)_2CHC(=N{-}NH{-}C_6H_3(NO_2)_2)CH_2CH(CH_3)_2 + H_2O$
G = **$(CH_3)_2CH{-}C(=N{-}NH{-}Ar){-}CH_2CH(CH_3)_2$**, where Ar = 2,4-dinitrophenyl, $-C_6H_3(NO_2)_2$, with the two NO_2 groups at ring positions 2 and 4 relative to the NH. G is the orange-yellow 2,4-dinitrophenylhydrazone of 2,5-dimethylhexan-3-one.

Review.

Alkyne and carbonyl chemistry (Resource Book 8 2.2–2.3, 8 2.6, 9 3.4). Work backwards from F: its C–OH carbon was the C=O of E, which came from the C≡C of D. D is the symmetrical alkyne made by joining the isopropyl group of B to the acetylide carbon of C. Key reagent facts: Pd on $BaSO_4$ poisoned with quinoline stops hydrogenation at the alkene; HBr adds by Markovnikov's rule; $NaNH_2$ removes the acidic terminal alkyne H; the acetylide ion is a nucleophile that extends the carbon chain (with a secondary halide, elimination also competes in practice, but the scheme intends substitution); Hg^{2+}/dil. H_2SO_4 hydrates an alkyne to a ketone; $NaBH_4$ in CH_3OH reduces a ketone to a secondary alcohol. 2,4-DNP gives a C=N condensation product with C=O compounds. Common mistakes: using H_2 with an unpoisoned catalyst (gives propane), anti-Markovnikov addition (gives 1-bromopropane), using $NaBH_4$ as R_3, and putting the C=N of G on the wrong carbon.

(b) [60 marks]

(i) Show how the transformation given below can be carried out using not more than **four (04)** steps.



6

4

2

Answer

Step 1: C_6H_6 + CH_3Cl —(anhydrous $AlCl_3$)→ $C_6H_5CH_3$ + HCl (Friedel–Crafts alkylation)
Step 2: $C_6H_5CH_3$ —($H^+/KMnO_4$, heat)→ C_6H_5COOH (oxidation of the side chain)
Step 3: C_6H_5COOH + Cl_2 —(anhydrous $FeCl_3$)→ 3-ClC_6H_4COOH + HCl (–COOH is meta-directing, so Cl enters the 3-position)
Step 4: 3-ClC_6H_4COOH —(1. $LiAlH_4$/dry ether; 2. H^+/H_2O)→ 3-$ClC_6H_4CH_2OH$ (target)

(ii) Show how the transformation given below can be carried out using not more than **three (03)** steps.
CH_3CH_2OH → $CH_3CH(OH)CH_2CH_2OH$

Answer

Step 1: CH_3CH_2OH —(PCC)→ CH_3CHO (PCC stops at the aldehyde; acidified $K_2Cr_2O_7$ would oxidise on to CH_3COOH)
Step 2: $2CH_3CHO$ —(dil./aq. NaOH)→ $CH_3CH(OH)CH_2CHO$ (base-catalysed self-condensation, aldol)
Step 3: $CH_3CH(OH)CH_2CHO$ —($NaBH_4$/CH_3OH, or 1. $LiAlH_4$ 2. H^+/H_2O)→ $CH_3CH(OH)CH_2CH_2OH$ (target)

Review.

Planning syntheses: directing effects and the order of steps (Resource Book 8 2.4–2.5), side-chain oxidation, and reductions and condensations of carbonyl compounds (9 3.4–3.5). The CH_2OH and Cl are meta to each other, but CH_3 and CH_2OH are ortho/para-directing. So the carbon must be present as the meta-directing –COOH when the ring is chlorinated, and reduced to CH_2OH last. $LiAlH_4$ is needed because $NaBH_4$ does not reduce carboxylic acids. In (ii) the C_4 chain with OH on C-1 and C-3 is the reduced aldol of ethanal. Common mistakes: chlorinating toluene (gives the 2- and 4-chloro products), using $NaBH_4$ on the acid, and oxidising ethanol with acidified dichromate (gives ethanoic acid, which does not undergo aldol condensation).

(c) [30 marks]

Give the structure of the product H of the following reaction. Write the mechanism of this reaction.
$CH_3CH(CH_3)COCl$ [i.e. $(CH_3)_2CHCOCl$] —(aqueous NaOH)→ H

Answer

H = **$(CH_3)_2CHCOO^-$ Na^+** (sodium 2-methylpropanoate). Overall: $(CH_3)_2CHCOCl$ + 2NaOH → $(CH_3)_2CHCOONa$ + NaCl + H_2O
Mechanism (nucleophilic acyl substitution: addition then elimination), in outline:
$(CH_3)_2CH–C(=O)–Cl$ + HO^- → $(CH_3)_2CH–C(O^-)(OH)–Cl$ (tetrahedral intermediate) → $(CH_3)_2CH–C(=O)–OH$ + Cl^-; then $(CH_3)_2CH–COOH$ + HO^- → $(CH_3)_2CH–COO^-$ + H_2O
Step 1 (nucleophilic addition): a lone pair of HO^- attacks the electron-deficient carbonyl carbon (curly arrow from HO^- to C), and the C=O π electrons move onto oxygen (curly arrow from the C=O bond to O). This gives the tetrahedral intermediate $(CH_3)_2CH–C(O^-)(OH)–Cl$.
Step 2 (elimination): a lone pair on O^- re-forms the C=O bond, and Cl^- leaves with the C–Cl bonding pair, giving $(CH_3)_2CH–COOH$ + Cl^-.
Step 3 (acid–base): a second HO^- removes the acidic H of –COOH: $(CH_3)_2CHCOOH$ + OH^- → $(CH_3)_2CHCOO^-$ + H_2O. With Na^+, this is the sodium salt H.

Review.

Reactions of acid chlorides (Resource Book 9 3.6.1.1). As with aldehydes and ketones, the nucleophile (OH^-) first adds to the C=O group to form a tetrahedral intermediate. Unlike them, an acid chloride has a good leaving group (Cl^-), so the C=O bond re-forms and Cl^- is expelled, which is substitution overall. In aqueous NaOH the carboxylic acid formed is deprotonated, so the product is the carboxylate salt. Common mistakes: giving the free acid as the final product in excess NaOH, showing a one-step S_N2-type displacement at the carbonyl carbon, and drawing the curly arrows from the wrong atoms (arrows always start at an electron pair).

Read: RB U8 §2.3 · p. 41 RB U9 §3.4 · p. 60 RB U8 §2.5 · p. 49 RB U9 §3.6 · p. 70

Question 9 · Part C · essay

(a) [75 marks]

A and B are water soluble inorganic compounds. A is coloured while B is colourless. When aqueous solutions of A and B are mixed together, the white precipitate C and the water soluble compound D are formed. C dissolves in dil. HCl to give the gas E with a pungent smell as one of the products. When E is passed through a solution of acidified $K_2Cr_2O_7$, the solution turns green. Addition of dil. NH_4OH to an aqueous solution of A gives a green precipitate F. F dissolves in excess dil. NH_4OH to give a dark blue solution G. A black precipitate is formed when H_2S is bubbled through an aqueous solution of A to which NH_4OH/NH_4Cl has been added. On addition of $AgNO_3$(aq) to an aqueous solution of B, a white precipitate H that is soluble in dil. NH_4OH is formed. Addition of $Pb(NO_3)_2$(aq) to an aqueous solution of B gives a white precipitate I that is soluble in hot water. When dil. H_2SO_4 is added to an aqueous solution of B, a white precipitate J that is insoluble in dil. HCl is formed. B gives a green coloured flame in the flame test.

(i) Identify the species A to J. (Give chemical formulae) **Note**: Reasons are not required.

Answer

A	B	C	D	E
$NiSO_3$	$BaCl_2$	$BaSO_3$	$NiCl_2$	SO_2
F	G	H	I	J
$Ni(OH)_2$	$[Ni(NH_3)_6]^{2+}$	AgCl	$PbCl_2$	$BaSO_4$

(ii) Write balanced chemical equations for the following.
I. Formation of C and D

Answer

3

2

3

2

II. Dissolution of C in dil. HCl

Answer

3

2

2

2

Review.

Reasoning: B gives a green flame (Ba^{2+}), a white AgCl precipitate soluble in dilute ammonia, $PbCl_2$ soluble in hot water, and $BaSO_4$ insoluble in dilute HCl, so B = $BaCl_2$. A gives a green $Ni(OH)_2$ precipitate that dissolves in excess ammonia to form blue $[Ni(NH_3)_6]^{2+}$, and black NiS in NH_4OH/NH_4Cl medium, so A contains Ni^{2+}. The white Ba^{2+} salt C dissolves in dilute HCl giving a pungent gas that turns acidified dichromate green, i.e. SO_2 ($Cr_2O_7^{2-} + 3SO_2 + 2H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$), so C = $BaSO_3$ and the anion of A is SO_3^{2-}. Then D = $NiCl_2$. (Resource Book 6 4.10 for the colours of Ni compounds, 6 4.6 for SO_2 and sulfites, 6 4.2 for Ba^{2+}.) Common mistakes: taking C as $BaSO_4$ (insoluble in HCl, so no gas), or E as H_2S (it would also turn the

dichromate green, but BaS is soluble, so no white precipitate C would form), and writing G as $[Ni(NH_3)_4]^{2+}$.

(b) [75 marks]

An iron ore, X, contains FeO, Fe_2O_3 and inert substances. The following experimental procedure was used to determine the mass percentages of FeO and Fe_2O_3 in X.
A mass of 0.4800 g of X was dissolved in 10 cm^3 of concentrated acid. This solution was filtered to remove insoluble matter, and thereafter diluted to 50.00 cm^3 using distilled water. This entire diluted solution was titrated with 0.020 mol dm^{-3} $KMnO_4$ solution. The titration reading at the end point was 20.00 cm^3. The pH of the entire solution, obtained after the titration, was raised to 12. At this stage, the metal ions in solution were precipitated as their hydroxides. The precipitate was filtered and dried until a constant mass was obtained. The mass of the precipitate obtained was 0.5706 g.

(i) Write balanced chemical equations for titration and precipitation reactions.

Answer

Titration:

4

−

2+

+

2+

3+

2

Precipitation (pH 12):

3+

−

3

2+

−

2

+

−

2

+

2+

2

2

3

+

3+

2

(ii) Calculate the mass percentages of FeO and Fe_2O_3 in X.
Note: Assume that the composition does not change during drying of metal hydroxides and there is no effect from dissolved oxygen in solution.
(H = 1, O = 16, Mn = 55, Fe = 56)

Answer

FeO (from the titration):

4

−

−3

−3

3

−4

2+

−4

−3

−3

−1

30.0%

2

3

3+

2+

2

4

−

−4

−4

3

3

−3

2

3

−3

−3

−3

2

3

−3

2

3

−3

−1

2

3

50.0%

Review.

Redox titration and gravimetric analysis (Resource Book 3 3.8; 12 2.4). MnO_4^- oxidises only Fe^{2+} (1 mol MnO_4^- : 5 mol Fe^{2+}), so the titration measures the FeO alone. After the titration all the iron (from both oxides) is Fe^{3+}. The Mn^{2+} formed from the permanganate also precipitates as $Mn(OH)_2$ at pH 12, and its mass must be subtracted. The note on dissolved oxygen means $Mn(OH)_2$ is not oxidised further. (The concentrated acid must be one, such as H_2SO_4, that MnO_4^- does not oxidise; Cl^- would interfere.) Common mistakes: ignoring $Mn(OH)_2$ (0.5706/107 mol Fe gives a wrong answer), counting the Fe^{3+} formed from FeO as part of Fe_2O_3, and forgetting that 1 mol of Fe_2O_3 contains 2 mol of Fe.

Read: RB U6 §4.10 · p. 160 RB U6 §4.6 · p. 141 RB U3 §3.8 · p. 115 RB U12 §2.4 · p. 175

Question 10 · Part C · essay

(a) [50 marks]

The following questions [(i)–(v)] are based on the manufacture of sulphuric acid by the Contact Process.

(i) State the **three** raw materials used.

Answer

Sulfur

2

air

2

water

2

4

3

(ii) Write balanced chemical equations for the reactions taking place. State proper conditions where necessary.

Answer

1. Burning sulfur: **$S(s) + O_2(g) \rightarrow SO_2(g)$** (sulfur is melted at about 140 °C, filtered, and sprayed into the furnace with dry air; the SO_2 gas is cleaned of dust and ash, which would poison the catalyst)
2. Oxidation of SO_2: **$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$**, $\Delta H < 0$ — V_2O_5 catalyst, 400–450 °C, about 1 atm (1–2 atm), $SO_2 : O_2 \approx 1 : 1$ by moles (excess air), several catalyst beds with cooling between them
3. Absorption: **$SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$** (oleum) — SO_3 is absorbed in 98% H_2SO_4 at about 70 °C, not in water
4. Dilution: **$H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(l)$**

(iii) State **two** strategies used to increase the efficiency of the Contact Process.

Answer

Any two:
• Use excess air ($O_2 : SO_2 \approx 1 : 1$ instead of the stoichiometric 1 : 2) to shift the SO_2/SO_3 equilibrium to the right.
• Carry out the oxidation in four catalyst beds with heat exchangers (cooling) between them, so the heat released does not drive the exothermic equilibrium backwards. The remaining SO_2 is passed through a further bed after the SO_3 is absorbed.
• Purify the SO_2/air mixture (remove dust and ash) so that the V_2O_5 catalyst is not poisoned.
• Absorb SO_3 in 98% H_2SO_4 by counter-current flow in packed towers (large surface area), avoiding the acid mist formed with water.
• Recover the heat of the exothermic steps (e.g. to raise steam) to save energy.

(iv) State **two** principles used in the determination of the optimum conditions for the Contact Process and briefly explain each principle using a reaction you specified in part (ii) above.

Answer

Reaction: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, $\Delta H < 0$ (exothermic; 3 mol of gas → 2 mol of gas).
1. Le Chatelier's principle (position of equilibrium / yield): the forward reaction is exothermic, so a low temperature increases the equilibrium yield of SO_3. It reduces the number of gas molecules, so a high pressure favours SO_3. Excess O_2 also shifts the equilibrium to the right.
2. Rate of reaction (kinetics / collision theory): at low temperatures the rate is too slow, which lowers productivity. Raising the temperature and using a V_2O_5 catalyst increase the rate.
The optimum conditions are a compromise: 400–450 °C with V_2O_5 gives a fast enough rate with a high yield. The conversion is already about 99% at about 1 atm, so high pressure is unnecessary; it would only add cost (economic consideration).

(v) Name **two** industries which utilize sulphuric acid as a raw material.

Answer

Any two: fertilizer manufacture (superphosphate, ammonium sulfate); detergent manufacture (alkyl/aryl sulfonates); artificial fibres such as rayon, and plastics; dyes, explosives and medicines; lead–acid battery (battery acid) manufacture.

Review.

Industrial chemistry of the Contact process (Resource Book 14 1.8). The key step, $2SO_2 + O_2 \rightleftharpoons 2SO_3$, is reversible and exothermic, so the conditions balance yield (Le Chatelier) against rate (kinetics) and cost. A V_2O_5 catalyst at 400–450 °C and about 1 atm is used. SO_3 is absorbed in concentrated H_2SO_4 to form oleum, not in water, because the violent reaction with water forms an acid mist. Common mistakes: naming Fe or Pt as the catalyst (Fe is used in the Haber process), saying that a catalyst increases the yield (it only increases the rate), claiming high pressure is used, and dissolving SO_3 directly in water.

(b) [50 marks]

Gaseous compounds of carbon, nitrogen and sulphur with various oxidation numbers directly contribute to global environment issues.

(i) Name **two** non-halogenated carbon compounds and **one** nitrogen compound that directly contribute to global warming and state the oxidation numbers of C and N in these compounds.

Answer

2

4

2

(ii) State how the three compounds you named in (i) above are released to the atmosphere due to human activities.

Answer

2

4

2

(iii) Explain how the compounds you mentioned in (i) above contribute to global warming.

Answer

The Earth's surface absorbs incoming solar radiation (mainly visible and low-energy UV) and re-emits energy as infrared (IR) radiation. CO_2, CH_4 and N_2O molecules absorb this IR radiation and re-emit it in all directions, including back towards the Earth, so heat is trapped in the lower atmosphere (the greenhouse effect). These gases stay in the atmosphere for a long time. As human activities raise their concentrations, more IR radiation is retained and the average temperature of the Earth rises (enhanced greenhouse effect, i.e. global warming).

(iv) Name **two** nitrogen compounds with the oxidation numbers of N that directly contribute to photochemical smog.

Answer

Nitric oxide (nitrogen monoxide), NO

2

(v) Write balanced chemical equations for the formation of tropospheric ozone by a nitrogen compound you stated in (iv) above.

Answer

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$
$NO_2(g) + h\nu \rightarrow NO(g) + O(g)$ (photodissociation by sunlight)
$O(g) + O_2(g) \rightarrow O_3(g)$

(vi) Explain why the tropospheric ozone level reaches its maximum level in the afternoon.

Answer

NO and unburnt hydrocarbons are released mainly by vehicle traffic, especially in the morning. During the morning NO is oxidised to NO_2, both directly and by the peroxy radicals formed from the hydrocarbons. Ozone forms only through the photodissociation of NO_2, which needs sunlight. The intensity of sunlight (and the temperature) is greatest around midday and early afternoon, when the NO_2 concentration is also high, so O_3 builds up and reaches its maximum in the afternoon. In the evening the sunlight fades, O_3 is no longer produced, and it is used up by reaction with NO ($NO + O_3 \rightarrow NO_2 + O_2$), so its level falls.

(vii) State **three** water quality parameters that are affected as a result of the dissolution of oxides of nitrogen and sulphur in water bodies.

Answer

Any three: **pH** (falls, because HNO_3, H_2SO_3 and H_2SO_4 form); **electrical conductivity / total dissolved solids** (rise, because of the extra H^+, NO_3^- and SO_4^{2-} ions); **hardness** (rises, as acidic water dissolves Ca- and Mg-containing rocks); also the nitrate and sulfate content, the concentration of dissolved metal ions such as Al^{3+} and heavy-metal ions leached from soil, and dissolved oxygen (falls, e.g. through oxidation of sulfite and nitrate-driven eutrophication).

Review.

Air pollution chemistry (Resource Book 14 1.13) and water quality parameters (14 1.14). Greenhouse gases are long-lived gases that absorb IR radiation: CO_2, CH_4 and N_2O (water vapour is not counted as a cause of global warming). NO and NO_2 are too short-lived to be greenhouse gases, but they drive photochemical smog. Ozone in the troposphere comes from the photolysis of NO_2, so it needs sunlight and peaks after the morning traffic peak. Assign oxidation numbers with O = −2 and H = +1. Common mistakes: naming CO or CFCs (CFCs are halogenated, which the question excludes), giving NO_2 as the greenhouse nitrogen compound, writing 'the hole in the ozone layer' for global warming, and omitting hν in the photolysis equation.

(c) [50 marks]

The following questions are based on chemical products related to plant sources.

(i) Give relevant balanced equations to indicate the chemical changes that take place when ethanol in coconut toddy is produced by fermentation of sweet toddy.

Answer

Yeast from the air grows in sweet toddy (a sucrose solution), and its enzymes convert the sugar into ethanol:
$\mathbf{C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6}$ (sucrose → glucose + fructose; enzyme sucrase/invertase)
$\mathbf{C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2}$ (yeast enzymes, zymase; anaerobic)

(ii) Explain why it is necessary to remove free fatty acids from plant oils taken as raw materials in the production of bio-diesel.

Answer

Biodiesel is made by the transesterification of the triglycerides in the oil with methanol, using NaOH (or KOH) as the catalyst. Free fatty acids (RCOOH) react with the NaOH to form soap: RCOOH + NaOH → RCOONa + H_2O. This uses up (neutralises) the catalyst. The soap forms foam and emulsions that inhibit the catalytic action and make it difficult to separate the biodiesel and glycerol layers, so the yield and purity of the biodiesel fall. The free fatty acid content is therefore kept low (below about 2% w/w).

(iii) Explain briefly why essential oils can be extracted from plant materials by steam distillation, at a temperature which is below the boiling points of both pure water and essential oil.

Answer

Water and the essential oil are immiscible, so each exerts its own saturated vapour pressure, independent of the other and of the amounts present. By Dalton's law of partial pressures, the total vapour pressure is $P = P_{H2O} + P_{oil}$. The mixture boils when P equals atmospheric pressure. Because both liquids contribute to P, this is reached at a temperature at which each individual vapour pressure is still below atmospheric pressure, that is, below 100 °C and below the boiling point of the essential oil. The oil therefore distils over with the steam at a lower temperature, without decomposing or polymerising.

Review.

Chemical products from plant sources (Resource Book 14 1.12). Fermentation by yeast runs in two enzyme-catalysed steps: hydrolysis of sucrose, then conversion of the hexoses to ethanol and CO_2. Biodiesel is formed by base-catalysed transesterification, and free fatty acids consume the base as soap. Steam distillation works because the vapour pressures of immiscible liquids add (Dalton's law), so the mixture boils below 100 °C. Common mistakes: writing the oxidation of ethanol to acetic acid (that is what happens if toddy is left too long), forgetting the sucrose hydrolysis step, and explaining steam distillation with Raoult's law for miscible liquids.

Read: RB U14 §1.8 · p. 27 RB U14 §1.13 · p. 58 RB U14 §1.12 · p. 48 RB U14 §1.14 · p. 80

2021 · Chemistry Digital Paper

50 questions · 2 hours

MCQ · Paper I

Question 1 · Q1–30 · single answer

Select the correct statement with regard to particles associated with cathode rays observed in a cathode ray tube.

- (1)The particles are uncharged.
- (2)They travel from anode to cathode along straight lines.
- (3)Their charge to mass ratio (e/m) depends on the nature of gas and pressure inside the cathode ray tube.
- (4)Their direction of travel is affected by magnetic and electric fields.
- (5)They are not capable of ionizing the gas inside the cathode ray tube.

Answer and review

Answer **(4)** Official marking scheme

Cathode rays are streams of electrons: negatively charged, travelling from cathode to anode in straight lines, and deflected by electric and magnetic fields (this deflection is how e/m was measured). Their e/m is the same whatever the gas or pressure, and fast electrons can ionize the gas, so (1), (2), (3) and (5) are false.

RB U1 §1.1 · p. 2

Question 2 · Q1–30 · single answer

Which of the following statements is **incorrect** with regard to an energy level of an atom with principal quantum number (n), n = 3?

- (1)There are 3 sub shells associated with it.
- (2)There are 9 orbitals.
- (3)There can be a maximum of 18 electrons.
- (4)There can be a maximum of 10 electrons with angular momentum (azimuthal) quantum number (l), l = 2.
- (5)There can be a maximum of 8 electrons with magnetic quantum number (m_l), m_l = 0.

Answer and review

Answer **(5)** Official marking scheme

For n = 3: sub shells 3s, 3p, 3d (3); orbitals $n^2 = 9$; electrons $2n^2 = 18$; l = 2 is the 3d sub shell with 5 orbitals = 10 electrons. Each sub shell (s, p, d) has exactly one orbital with m_l = 0, so only 3 orbitals × 2 = 6 electrons, not 8. Statement (5) is the incorrect one.

RB U1 §1.3 · p. 17

Question 3 · Q1–30 · single answer

The **decreasing** order of the first ionization energy of the atoms H, He, Li, Be, B and Na is,

- (1)He > H > B > Be > Li > Na
- (2)He > H > Be > B > Li > Na
- (3)He > Be > H > Li > B > Na
- (4)H > He > B > Be > Li > Na
- (5)H > He > Be > B > Na > Li

Answer and review

Answer **(2)** Official marking scheme

He ($1s^2$, 2372 kJ mol^{-1}) > H (1312) > Be (899) > B (801) > Li (520) > Na (496). Two traps: Be > B because B removes a higher-energy 2p electron (the $2s^2$ subshell of Be is more stable), and Li > Na because Na's valence electron is further from the nucleus (down the group IE falls).

RB U1 §1.6 · p. 32

Question 4 · Q1–30 · single answer

The shapes of IF_4^+, IF_4^- and IF_5 are respectively,

- (1)see-saw, square planar and square pyramidal.
- (2)square planar, see-saw and square pyramidal.
- (3)tetrahedral, see-saw and trigonal bipyramidal.
- (4)see-saw, tetrahedral and square pyramidal.
- (5)tetrahedral, square planar and trigonal bipyramidal.

Answer and review

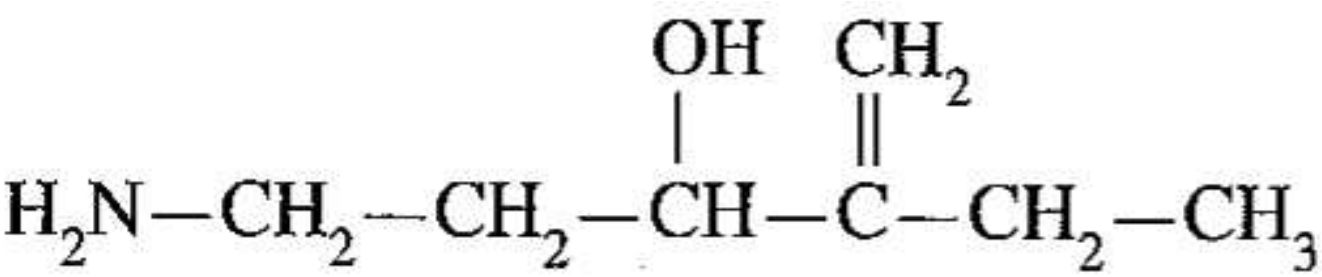
Answer **(1)** Official marking scheme

VSEPR electron pairs on I: IF_4^+ has 4 bond pairs + 1 lone pair (7 − 1 = 6 electrons on I; 4 used in bonds, one lone pair) → trigonal bipyramidal geometry, see-saw shape. IF_4^- has 4 bond pairs + 2 lone pairs → octahedral geometry, square planar shape. IF_5 has 5 bond pairs + 1 lone pair → octahedral geometry, square pyramidal shape.

RB U2 §2.3 · p. 52

Question 5 · Q1–30 · single answer

What is the IUPAC name of the following compound?



- (1)1-amino-4-ethylpent-4-en-3-ol

- (2)5-amino-2-ethylpent-1-en-3-ol
- (3)2-ethyl-3-hydroxypent-1-en-5-amine
- (4)4-ethyl-3-hydroxypent-4-en-1-amine
- (5)5-amino-2-ethyl-3-hydroxypent-1-ene

Answer and review

Answer **(2)** Official marking scheme

The compound is $H_2N–CH_2–CH_2–CH(OH)–C(=CH_2)–CH_2CH_3$. The principal functional group is –OH (alcohol outranks amine, which becomes the prefix "amino"). The main chain must contain the C–OH and the C=C: C1 = CH_2=, C2 bears the ethyl, C3 bears OH, C5 bears NH_2. The suffix gets the lowest locants as a whole (en 1, ol 3), giving 5-amino-2-ethylpent-1-en-3-ol. Options (3), (4) name it as an amine, (1) numbers wrongly, (5) leaves out the "-ol" suffix.

RB U7 §1.3 · p. 7

Question 6 · Q1–30 · single answer

Which of the following statements is correct with regard to boiling points?

- (1)N_2 has a higher boiling point than NO.
- (2)PH_3 has a higher boiling point than NH_3.
- (3)Xe has a higher boiling point than Kr.
- (4)CH_3CH_2OH has a higher boiling point than $CH_3CH_2CH_2OH$.
- (5)$(CH_3)_2CHCH_3$ (2-methylpropane) has a higher boiling point than $CH_3CH_2CH_2CH_3$.

Answer and review

Answer **(3)** Official marking scheme

Xe is larger and more polarizable than Kr, so its London forces are stronger and it boils higher (165 K vs 120 K). N_2 (non-polar) boils lower than polar NO; NH_3 hydrogen bonds, PH_3 does not; propan-1-ol (larger, H-bonding) boils higher than ethanol; the branched isomer has less surface contact than the straight-chain butane, so it boils lower.

RB U2 §2.6 · p. 79

Question 7 · Q1–30 · single answer

$M(OH)_2$ is a sparingly water soluble solid. The concentration of $M^{2+}(aq)$ in a saturated aqueous solution of $M(OH)_2$ at pH = 8.0 and at a given temperature is 1.0×10^{-6} mol dm^{-3}. The pH of a saturated aqueous solution of $M(OH)_2$ having $M^{2+}(aq)$ concentration of 1.0×10^{-4} mol dm^{-3} at this temperature is,

- (1)4.0
- (2)5.0
- (3)6.0
- (4)7.0
- (5)8.0

Answer and review

Answer **(4)** Official marking scheme

$K_{sp} = [M^{2+}][OH^-]^2$. At pH 8.0, $[OH^-] = 10^{-6}$, so $K_{sp} = 10^{-6} \times (10^{-6})^2 = 10^{-18}$ mol^3 dm^{-9}. For $[M^{2+}] = 10^{-4}$: $[OH^-]^2 = 10^{-18}/10^{-4} = 10^{-14}$, so $[OH^-] = 10^{-7}$, pOH = 7 and pH = 7.0 (at the given temperature, pK_w = 14). The trap is using $[OH^-] = 2[M^{2+}]$, which ignores that the pH is set by the solution.

RB U12 §2.4 · p. 175

Question 8 · Q1–30 · single answer

Select the correct statement.

- (1)The electron pair geometry and shape of SF_5^+ are different from each other.
- (2)The increasing order of radii of atoms/ions F^-, Mg^{2+}, Al, Cl^- and K is $F^- < Mg^{2+} < Cl^- < Al < K$.
- (3)The number of resonance structures that can be drawn for nitric acid (HNO_3) is four.
- (4)CO_3^{2-} has the longest C–O bond among the molecules/ions CO, CO_2, CO_3^{2-} and CH_3OH.
- (5)Among the molecules CH_4, $COCl_2$ and HCN, the electronegativity of the carbon atom increases in the order $CH_4 < COCl_2 < HCN$.

Answer and review

Answer **(5)** Official marking scheme

The electronegativity of carbon rises with its s character: sp^3 (CH_4) < sp^2 ($COCl_2$) < sp (HCN). Others: SF_5^+ has 5 bond pairs and no lone pair (both geometry and shape trigonal bipyramidal); the radius order should be $Mg^{2+} < F^- < Al < Cl^- < K$; HNO_3 has two resonance structures; the longest C–O bond is the single bond in CH_3OH (CO_3^{2-} has bond order 1.33).

RB U2 §2.3 · p. 52 RB U1 §1.6 · p. 32

Question 9 · Q1–30 · single answer

A

B

A

B

2

2

A

B

2

4

2

2

A

B

- (1)C_6H_5OH, CH_3OH
- (2)$C_6H_5CH_2OH$, CH_3CH_2OH

- (3)C_6H_5OH, $(CH_3)_2CHCH_2OH$
- (4)C_6H_5CHO, C_6H_5OH
- (5)CH_3CHO, $(CH_3)_2CHCH_2OH$

Answer and review

Answer **(3)** Official marking scheme

Phenol with bromine water gives a white precipitate of 2,4,6-tribromophenol, so A is C_6H_5OH. B is an alcohol that dehydrates with conc. H_2SO_4 to an alkene, which decolourises Br_2/H_2O: 2-methylpropan-1-ol gives 2-methylpropene. Option (1): CH_3OH cannot form an alkene; (2): $C_6H_5CH_2OH$ gives no precipitate with Br_2/H_2O; (4) and (5) A is an aldehyde with no white precipitate.

RB U9 §3.2 · p. 58 RB U9 §3.1 · p. 54

Question 10 · Q1–30 · single answer

The elementary reaction A(g) → B(g) + C(g) occurs in a closed rigid container at constant temperature. The initial pressure of the container when only A(g) is present was measured to be $2P_0$. The pressure of the container after two half lives of A(g) would be,

- (1)$P_0/2$
- (2)$P_0/4$
- (3)$3P_0/4$
- (4)$3P_0/2$
- (5)$7P_0/2$

Answer and review

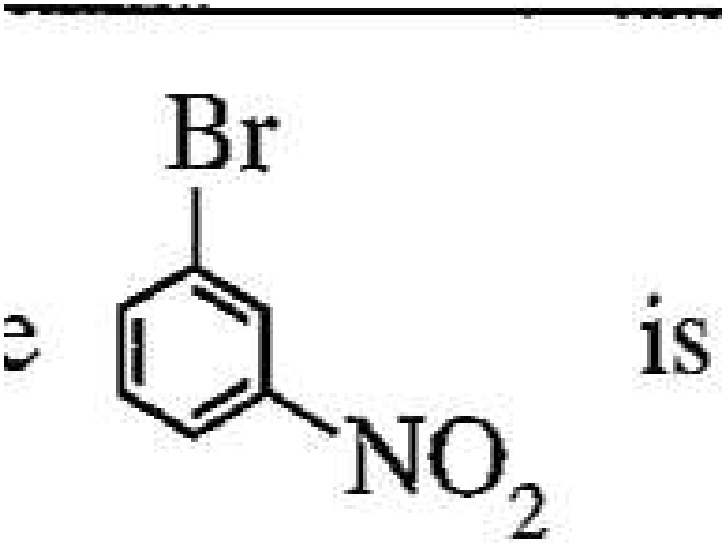
Answer **(5)** Official marking scheme

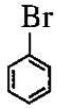
After two half lives, $P_A = 2P_0/4 = P_0/2$, so $P_0 \times 3/2$ of A has reacted: $P_B = P_C = 3P_0/2$. Total pressure = $P_0/2 + 3P_0/2 + 3P_0/2 = 7P_0/2$. The trap is giving only the pressure of A.

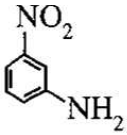
RB U11 §1.7.2 · p. 28

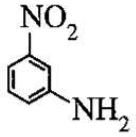
Question 11 · Q1–30 · single answer

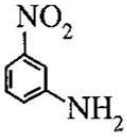
A suitable method to prepare the following compound is,

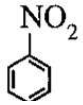


(1)  conc. HNO_3 / conc. H_2SO_4 →

(2)  (1) $NaNO_2$ / dilute HCl / 0 – 5 °C → (2) Br_2 / $FeBr_3$

(3)  (1) $NaNO_2$ / dilute HCl / 0 – 5 °C → (2) CuBr

(4)  (1) $NaNO_2$ / dilute HCl / 25 °C → (2) CuBr

(5)  Br_2 →

Options (1)–(5)

Answer and review

Answer **(3)** Official marking scheme

1-Bromo-3-nitrobenzene is made from 3-nitroaniline: diazotization with $NaNO_2$/dilute HCl at 0–5 °C gives the diazonium salt, which CuBr (Sandmeyer reaction) converts to the aryl bromide. (1) nitration of bromobenzene gives o/p products (Br is o/p directing); (2) Br_2/$FeBr_3$ cannot replace a diazonium group; (4) at 25 °C the diazonium salt decomposes; (5) nitrobenzene is strongly deactivated, so Br_2 alone (no $FeBr_3$) does not react.

RB U10 §4.3 · p. 78 RB U8 §2.5 · p. 49

Question 12 · Q1–30 · single answer

Which expression gives the correct volume (cm^3) of 70.0% (w/w) concentrated HNO_3 acid with density 1.42 g cm^{-3} required to prepare 300 cm^3 of a 0.150 mol dm^{-3} solution of HNO_3? (Relative atomic mass: H = 1, N = 14, O = 16)

- (1)(100/1.42) × (70.0/63) × (0.150/1000) × 300
- (2)(100/1.42) × (63/70.0) × (0.150/1000) × 300
- (3)(1.42/100) × (63/70.0) × (1000/0.150) × 300
- (4)(100/1.42) × (63/70.0) × (1000/0.150) × (1/300)
- (5)(1.42/100) × (70.0/63) × (0.150/1000) × 300

Answer and review

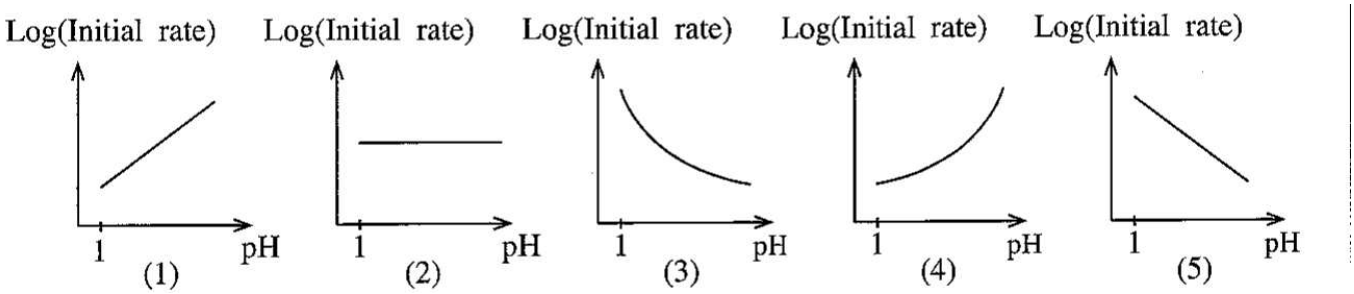
Answer **(2)** Official marking scheme

Build it step by step: moles needed = 0.150 × 300/1000; mass of HNO_3 = moles × 63; mass of concentrated acid = mass × 100/70.0; volume = mass/1.42. Multiplying gives (100/1.42) × (63/70.0) × (0.150/1000) × 300, option (2). Options (1) and (5) invert 63 and 70.0.

RB U3 §3.7 · p. 113 RB U3 §3.5 · p. 102

Question 13 · Q1–30 · single answer

The elementary reaction, $A(aq) + H_3O^+(aq) \rightarrow B^+(aq)$ occurs in an aqueous solution at constant temperature. Which of the following graphs correctly represents the relationship between Log(Initial rate) vs pH at a constant concentration of A(aq)?



Options (1)–(5), left to right

Answer and review

Answer **(5)** Official marking scheme

For an elementary reaction the rate law follows the stoichiometry: rate = $k[A][H_3O^+]$. At constant [A], $\log(\text{rate}) = \log(k[A]) + \log[H_3O^+]$ = constant − pH. Log(rate) therefore falls linearly with slope −1 as pH increases: graph (5). Graph (1) would be a rate that rises with pH; (2) would be zero-order in H_3O^+.

RB U11 §1.6 · p. 16

Question 14 · Q1–30 · single answer

An excess amount of A(g) and a small amount of B(g) are introduced into an evacuated rigid container. Then, the following elementary reactions take place at a constant temperature.
A(g) + B(g) → C(g) fast
A(g) + C(g) → 3D(g) slow
Which of the following statements is correct regarding the variation of pressure of the system with time?

- (1)Pressure remains unchanged.
- (2)Pressure increases and then becomes constant.
- (3)Pressure decreases and then becomes constant.
- (4)Pressure decreases and returns to the initial value again.
- (5)Pressure increases initially, then decreases and returns to the initial value again.

Answer and review

Answer **(4)** Official marking scheme

Step 1 (fast) turns 2 mol of gas into 1 mol, so the pressure first falls. Step 2 (slow) turns 2 mol (A + C) into 3 mol (D), so the pressure rises again. Adding the steps: B + 2A → 3D (3 mol of gas to 3 mol), so when B is used

up the total number of moles, and hence the pressure, is back at the initial value: option (4). Option (3) forgets the second step.

RB U11 §1.10 · p. 57

Question 15 · Q1–30 · single answer

The solute **A** present in volume V of an aqueous solution is extracted twice using 2V volume portions of a water immiscible organic solvent. The partition coefficient of **A** between the organic solvent and water, $[A]_{(org)}/[A]_{(aq)}$ = 4.0. The initial amount of **A** in the aqueous phase is a (mol). The amount (mol) of **A** remaining in the aqueous phase after the second extraction is,

- (1)a/2
- (2)a/9
- (3)a/18
- (4)a/25
- (5)a/81

Answer and review

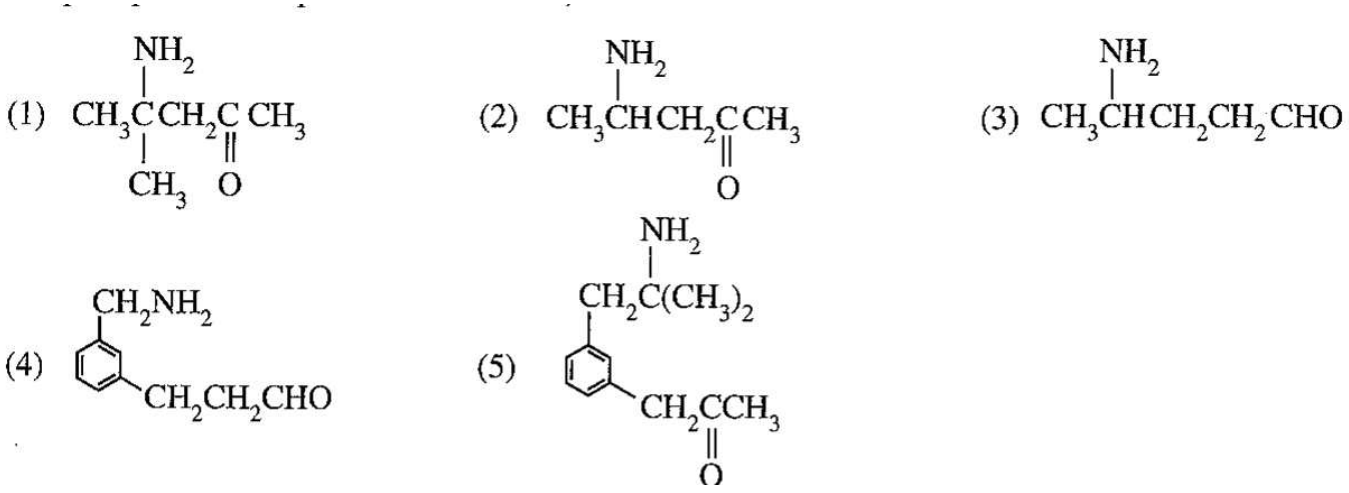
Answer **(5)** Official marking scheme

With x = amount left in water, (a − x)/2V ÷ (x/V) = 4, so (a − x)/(2x) = 4 and x = a/9 after one extraction (fraction left = V/(V + K·2V) = 1/(1 + 8) = 1/9). Each extraction repeats this factor, so after two: a × $(1/9)^2$ = a/81. The trap is a/9, which is the answer for one extraction only.

RB U12 §2.7 · p. 229

Question 16 · Q1–30 · single answer

Compound **A** reacts with $NaNO_2$/dilute HCl to give **B**. When **B** is treated with acidified aqueous $K_2Cr_2O_7$, the solution turns green. When treated with Fehling's reagent **A** did not give a brick red precipitate. Compound **A** could be,



Options (1)–(5)

Answer and review

Answer **(2)** Official marking scheme

Aliphatic primary amines react with HNO_2 ($NaNO_2$/HCl) to give alcohols (with N_2), so B is an alcohol; it turns $Cr_2O_7^{2-}$ green, so B must be a primary or secondary alcohol, and A must have no –CHO. In (2) the –$CH(NH_2)$–

becomes a secondary –CH(OH)–, which is oxidised, and A is a ketone (negative Fehling's). (1) and (5): the NH_2 is on a tertiary carbon, giving a tertiary alcohol (not oxidised); (3) and (4) contain –CHO and would give a brick-red precipitate.

RB U10 §4.1 · p. 75 RB U9 §3.1 · p. 54 RB U9 §3.4 · p. 60

Question 17 · Q1–30 · single answer

MCl_2 is a solid which is sparingly soluble in water (K_{sp} = 1.0 × 10^{-8} mol^3 dm^{-9}). Which of the following is correct regarding a saturated aqueous solution of MCl_2?

- (1)Evaporation of water from the solution increases M^{2+} and chloride ion concentrations of the solution.
- (2)Chloride ion concentration of the solution can be increased by adding NaCl(s).
- (3)The solution cannot be acidified by adding HCl.
- (4)Chloride ion concentration of the solution cannot be increased above 1.0 × 10^{-4} mol dm^{-3}.
- (5)Chloride ion concentration of the solution can be lowered by adding distilled water and maintaining the saturated condition.

Answer and review

Answer **(2)** Official marking scheme

Adding NaCl(s) adds Cl^- (common-ion effect): [Cl^-] rises while MCl_2 precipitates and [M^{2+}] falls, so (2) is correct. (1) and (5): in a saturated solution with solid present the concentrations are fixed by K_{sp} (they do not change on evaporating or adding water); (3) HCl can be added; (4) the saturated solution has [Cl^-] = 2s, where $4s^3$ = 1.0 × 10^{-8}, so s ≈ 1.4 × 10^{-3} and [Cl^-] ≈ 2.7 × 10^{-3} mol dm^{-3}, which can be exceeded by adding a soluble chloride.

RB U12 §2.4 · p. 175

Question 18 · Q1–30 · single answer

When a mass of 0.0119 g of KBr is dissolved in 500.0 cm^3 of distilled water, the K^+ composition of the solution in mol dm^{-3} and ppm (mg kg^{-1}) are respectively, (Relative atomic mass: K = 39, Br = 80; density of solution = 1.00 kg dm^{-3})

- (1)1.0 × 10^{-4} and 3.9
- (2)1.0 × 10^{-4} and 7.8
- (3)2.0 × 10^{-4} and 1.3
- (4)2.0 × 10^{-4} and 3.9
- (5)2.0 × 10^{-4} and 7.8

Answer and review

Answer **(5)** Official marking scheme

Moles of KBr = 0.0119/119 = 1.0 × 10^{-4} mol, in 0.5000 dm^3 gives 2.0 × 10^{-4} mol dm^{-3} K^+. Mass of K^+ = 1.0 × 10^{-4} × 39 = 3.9 × 10^{-3} g = 3.9 mg; mass of 500 cm^3 solution = 0.500 kg (density 1.00 kg dm^{-3}), so ppm = 3.9 mg/0.500 kg = 7.8. The traps are forgetting that the volume is 0.5 dm^3 (giving 1.0 × 10^{-4} and 3.9).

RB U3 §3.5 · p. 102

Question 19 · Q1–30 · single answer

The correct reaction relevant to the standard enthalpy of hydration of the sodium ion is,

- (1)$Na^+(g) + OH^-(aq) \rightarrow NaOH(s)$
- (2)$NaCl(g) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) + HCl(aq)$
- (3)$Na^+(g) + H_2O(l) \rightarrow Na^+(aq)$
- (4)$Na^+(g) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) + H^+(aq)$
- (5)$Na^+(g) + Cl^-(g) + H_2O(l) \rightarrow Na^+(aq) + Cl^-(aq)$

Answer and review

Answer **(3)** Official marking scheme

Enthalpy of hydration is the enthalpy change when one mole of a gaseous ion is dissolved in water to form the aqueous ion: $Na^+(g) + aq \rightarrow Na^+(aq)$, written with $H_2O(l)$ as in (3). (5) is the enthalpy of solution of NaCl from its gaseous ions (it involves both ions); (4) would also involve water ionizing.

RB U5 §2.2 · p. 36 RB U5 §2.3 · p. 51

Question 20 · Q1–30 · single answer

Which of the following is **not** a step in the chlorination of methane?

- (1)$Cl_2 \xrightarrow{(h\nu)} 2Cl\bullet$
- (2)$CH_4 + Cl\bullet \rightarrow \bullet CH_3 + HCl$
- (3)$\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\bullet$
- (4)$CH_3Cl + Cl\bullet \rightarrow \bullet CH_2Cl + HCl$
- (5)$\bullet CH_2Cl + HCl \rightarrow CH_2Cl_2 + H\bullet$

Answer and review

Answer **(5)** Official marking scheme

Free-radical chlorination has initiation (1), and propagation steps (2), (3), and (4) (further chlorination of CH_3Cl). Step (5) would produce an H atom, which is not formed in the mechanism; the real step is $\bullet CH_2Cl + Cl_2 \rightarrow CH_2Cl_2 + Cl\bullet$.

RB U8 §2.2 · p. 33

Question 21 · Q1–30 · single answer

Which of the following statements regarding the critical temperature of a real gas is correct?

- (1)It is the temperature at which the intermolecular forces can be neglected.
- (2)It is the temperature corresponding to the lowest pressure at which the gas can be liquified.
- (3)It is the temperature at which the gas is in equilibrium with its solid.
- (4)It is the highest temperature at which the gas phase and the liquid phase are in equilibrium.
- (5)It is the temperature given by the van der Waals equation at any pressure.

Answer and review

Answer **(4)** Official marking scheme

The critical temperature T_c is the highest temperature at which a gas can be liquified (above it no amount of pressure produces a liquid), i.e. the highest temperature at which liquid and gas phases coexist. Intermolecular forces are not zero at T_c; the gas–solid equilibrium is sublimation, not T_c; and the lowest pressure option mixes up the critical pressure P_c, which is the pressure needed at T_c.

RB U4 §1.5 · p. 24

Question 22 · Q1–30 · single answer

In an experiment, Mg metal was made to react with excess N_2 gas and the product obtained was reacted with H_2O. The volume of the gas evolved at standard temperature (273 K) and pressure (1.0 atm) was 672 cm^3. The mass of Mg used in the experiment is, (Assume that 1.0 mol of gas occupies a volume of 22.4 dm^3 at 273 K and 1.0 atm. Relative atomic mass: Mg = 24)

- (1)0.24 g
- (2)0.48 g
- (3)0.72 g
- (4)1.08 g
- (5)1.50 g

Answer and review

Answer **(4)** Official marking scheme

$3Mg + N_2 \rightarrow Mg_3N_2$; $Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$. Moles of NH_3 = 0.672/22.4 = 0.030 mol; so Mg_3N_2 = 0.015 mol and Mg = 3 × 0.015 = 0.045 mol; mass = 0.045 × 24 = 1.08 g. The trap is using mol Mg = mol NH_3 (0.72 g).

RB U3 §3.8 · p. 115 RB U6 §4.2 · p. 126

Question 23 · Q1–30 · single answer

The mean square speed of H_2 at absolute temperature T is equal to the mean square speed of N_2 at absolute temperature T′. Which of the following equations gives the correct relationship between T and T′? (Relative atomic mass: H = 1, N = 14)

- (1)T = T′
- (2)T = 14T′
- (3)T = T′/4
- (4)T = 7T′
- (5)T = T′/14

Answer and review

Answer **(5)** Official marking scheme

Mean square speed = 3RT/M. Equal values: $T/M(H_2) = T'/M(N_2)$, so T/2 = T′/28 and T = T′/14. The trap is using the atomic masses (1 and 14) instead of the molar masses of the molecules (2 and 28).

RB U4 §1.4 · p. 19

Question 24 · Q1–30 · single answer

A buffer solution at constant temperature contains a monobasic weak acid ($K_a = 1.00 \times 10^{-5}$ mol dm^{-3}) and its sodium salt. The concentrations of the weak acid and the sodium salt in the solution are 0.10 mol dm^{-3} each. The volume of 1.00 mol dm^{-3} weak acid that should be added to change the pH of 10.00 cm^3 of this solution by one unit, and the pH value of the solution after the addition of the weak acid are respectively,

- (1)9.00 cm^3, 4.0
- (2)9.00 cm^3, 6.0
- (3)10.00 cm^3, 4.0
- (4)10.00 cm^3, 5.0
- (5)11.00 cm^3, 4.0

Answer and review

Answer **(1)** Official marking scheme

Initial pH = pK_a = 5.0 (equal concentrations). Adding acid lowers the pH, so the new pH is 4.0, which needs [salt]/[acid] = 0.10. Amounts in 10.00 cm^3: acid 1.0 mmol, salt 1.0 mmol. Adding V cm^3 of 1.00 mol dm^{-3} acid gives 1.0/(1.0 + V) = 0.10, so V = 9.00 cm^3. Total volume cancels in the ratio.

RB U12 §2.3 · p. 167

Question 25 · Q1–30 · single answer

A gaseous discharge/production that contributes to all three environmental issues, namely, global warming, acid rain and photochemical smog is,

- (1)exhaust gas released from fossil fuel burning vehicles.
- (2)exhaust gas released from coal power plants.
- (3)gases released during repair of air conditioners and refrigerators.
- (4)gases produced from the improper discharge of municipal solid waste.
- (5)exhaust gas released from biofuel burning vehicles.

Answer and review

Answer **(1)** Official marking scheme

Vehicle exhaust from fossil fuels contains CO_2 (global warming), NO_x (acid rain and, with unburnt hydrocarbons and sunlight, photochemical smog). Coal power plants emit CO_2 and SO_2/NO_x but few hydrocarbons for smog; refrigerant gases (CFC/HFC) affect ozone and warming; waste gas (CH_4) affects warming; the official key is (1).

RB U14 §1.13 · p. 58

Question 26 · Q1–30 · single answer

Which of the following statements is **incorrect** with regard to element Lithium (Li) and its compounds?

- (1)Among the Group I elements from Li–Cs, lithium has the most negative value for electron gain energy.
- (2)Lithium forms two products when heated in air.
- (3)Considering the gases evolved, upon heating $LiNO_3$(s) produces two gases whereas Li_2CO_3(s) gives only one gas.

- (4)Among Group I elements, lithium has the weakest metallic bonding.
- (5)Lithium gives a red coloured flame in the flame test.

Answer and review

Answer **(4)** Official marking scheme

Lithium has the strongest metallic bonding in Group 1 (smallest atom, highest melting point of the group), so statement (4) is incorrect. Correct ones: Li burns in air to Li_2O and Li_3N; $4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$ (two gases) while $Li_2CO_3 \rightarrow Li_2O + CO_2$ (one gas); the flame is crimson/red.

RB U6 §4.1 · p. 122 RB U1 §1.6 · p. 32 RB U2 §2.5 · p. 78

Question 27 · Q1–30 · single answer

The number of moles of $KMnO_4$ that are required to react completely with one mole of $Fe(NO_2)_2$ in acidic medium is,
(**Note:** Neglect the loss of NO_2^− due to acidic conditions.)

- (1)3/5
- (2)4/5
- (3)1
- (4)5/4
- (5)5/3

Answer and review

Answer **(3)** Official marking scheme

Oxidations by MnO_4^− (each MnO_4^− takes 5 e^-): $Fe^{2+} \rightarrow Fe^{3+}$ gives 1 mol e^-; 2 NO_2^− → 2 NO_3^− gives 2 × 2 = 4 mol e^-. Total 5 mol e^- per mol $Fe(NO_2)_2$, hence 5/5 = 1 mol $KMnO_4$. The trap is counting only Fe^{2+} (giving 1/5).

RB U3 §3.6 · p. 105 RB U6 §4.10 · p. 160

Question 28 · Q1–30 · single answer

Which of the following statements is correct regarding water and aqueous solutions at a given temperature?

- (1)The solubility of a polar gas in water is lower than the solubility of a non polar gas in water.
- (2)Any gas undergoes ionization in an aqueous solution.
- (3)The solubility of a gas in water is proportional to its pressure.
- (4)Boiling point of water decreases with increasing pressure.
- (5)The temperature of the triple point of water increases with increasing pressure.

Answer and review

Answer **(3)** Official marking scheme

Henry's law: at constant temperature the solubility of a gas is proportional to its pressure (applies to sparingly soluble gases). Polar gases (HCl, NH_3) are generally more soluble in water; not every gas ionizes (e.g. N_2, O_2); boiling point rises with pressure; the triple point is a fixed point (611 Pa, 273.16 K) that does not change with pressure.

RB U12 §2.5 · p. 199

Question 29 · Q1–30 · single answer

Select the correct statement with regard to chromium (Cr) and its compounds.

- (1)When an aqueous solution of K_2CrO_4 is treated with dilute H_2SO_4, a colour change is not observed.
- (2)The electronegativity of Cr is greater than that of Co.
- (3)An aqueous solution of $Cr(H_2O)_6^{2+}$ when treated with excess NaOH, followed by the addition of H_2O_2 gives a yellow coloured solution.
- (4)Cr_2O_3 shows basic properties.
- (5)When H_2S gas is passed into an acidic solution of $K_2Cr_2O_7$, a clear green coloured solution is observed.

Answer and review

Answer **(3/4)** Official marking scheme

The official scheme accepts (3) or (4). Cr^{3+}(aq) (the paper's "2+" charge is a misprint) dissolves in excess NaOH as green $[Cr(OH)_4]^-$, and H_2O_2 oxidises this to yellow CrO_4^{2-}, so (3) is true. Cr_2O_3 is amphoteric (it reacts with acids as a base as well as with alkali), so (4) can also be taken as true. (1) is false: yellow CrO_4^{2-} turns orange $Cr_2O_7^{2-}$ in acid; (2) Cr (1.66) is less electronegative than Co (1.88); (5) H_2S reduces dichromate to green Cr^{3+} but also deposits a milky yellow sulfur precipitate, so the solution is not clear.

RB U6 §4.10 · p. 160 RB U1 §1.6 · p. 32

Question 30 · Q1–30 · single answer

Which of the following statements is **incorrect** regarding carboxylic acids?

- (1)The product formed by the reaction of a carboxylic acid with $LiAlH_4$ gives an alcohol upon hydrolysis.
- (2)Carbon dioxide is liberated when carboxylic acids are reacted with aqueous NaOH.
- (3)Carboxylic acids react with PCl_5 to give acid chlorides.
- (4)Methane is liberated when carboxylic acids are reacted with CH_3MgBr.
- (5)Carboxylic acids are formed when aldehydes are treated with $H^+/K_2Cr_2O_7$.

Answer and review

Answer **(2)** Official marking scheme

Carboxylic acids react with NaOH by simple neutralization, giving the carboxylate salt and water; CO_2 is released only with carbonates/hydrogen carbonates. The others are standard: $LiAlH_4$ reduces –COOH to a primary alcohol; PCl_5 gives RCOCl; CH_3MgBr acts as a base giving CH_4; aldehydes are oxidised to carboxylic acids.

RB U9 §3.5 · p. 66 RB U9 §3.4 · p. 60

Questions 31–40: response code

(1)	(2)	(3)	(4)	(5)
Only (a) and (b) are correct	Only (b) and (c) are correct	Only (c) and (d) are correct	Only (d) and (a) are correct	Any other number or combination of responses is correct

Question 31 · Q31–40 · response code

Which of the following give(s) 3-bromo-3-methylhexane as the major product when reacted with HBr?

- $CH_3CH_2CH_2C(CH_3)=CHCH_3$
- $CH_3CH_2CH_2CH(CH_3)CH=CH_2$
- $CH_3CH=CHCH(CH_3)CH_2CH_3$
- $CH_3CH_2CH_2C(CH_2CH_3)=CH_2$

Answer and review

Answer **(4)** Official marking scheme

3-Bromo-3-methylhexane is the tertiary bromide $CH_3CH_2C(Br)(CH_3)CH_2CH_2CH_3$. By Markovnikov addition, H adds to the less substituted alkene carbon and Br to the more substituted one: (a) (3-methylhex-2-ene) and (d) (2-ethylpent-1-ene) both place Br on the tertiary carbon bearing CH_3 and the ethyl/propyl groups. (b) and (c) are alkenes whose double bond carbons are both secondary and give secondary bromides (2-bromo-3-methylhexane; 2- and 3-bromo-4-methylhexane) as the major products. Only (a) and (d): code (4).

RB U8 §2.2 · p. 33

Question 32 · Q31–40 · response code

Which of the following statements is/are correct regarding products related to plant sources?

- Essential oils contain complex mixtures of volatile constituents of plants.
- Biodiesel is produced from volatile plant oils.
- Methanol is not used in the production of biodiesel.
- Ethanol produced by fermentation of plant materials is regarded as a renewable energy source.

Answer and review

Answer **(4)** Official marking scheme

Essential oils are volatile plant extracts (steam distillation), so (a) is true; ethanol from fermentation of plant sugars is renewable, so (d) is true. Biodiesel is made by transesterification of non-volatile vegetable oils/fats (triglycerides) with methanol (or ethanol) and a catalyst, so (b) and (c) are false. Only (a) and (d): code (4).

RB U14 §1.12 · p. 48

Question 33 · Q31–40 · response code

On which of the following factor/factors does the electrode potential of the electrode $M^{2+}(aq)/M(s)$ depend?

- Surface area of M(s)
- Concentration of $M^{2+}(aq)$
- Temperature
- Volume of $M^{2+}(aq)$ solution

Answer and review

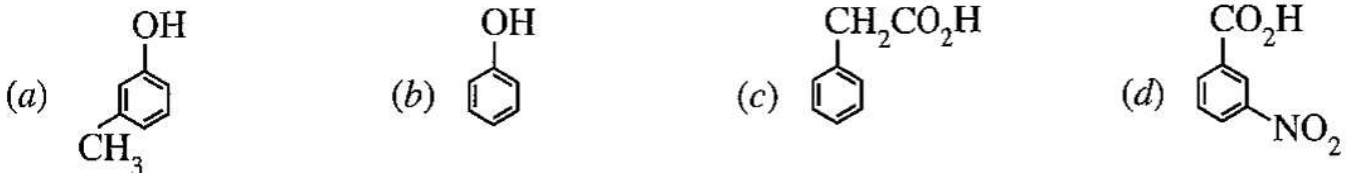
Answer **(2)** Official marking scheme

From the Nernst equation, $E = E° + (RT/2F)\ \ln[M^{2+}]$, the potential depends on the concentration of $M^{2+}(aq)$ (an intensive quantity) and on the temperature (through RT/F and E°). The surface area of the metal and the volume of the solution are extensive properties that do not change the potential. Only (b) and (c): code (2).

RB U13 §3.2 · p. 238 RB U13 §3.3 · p. 250

Question 34 · Q31–40 · response code

Which of the following give(s) CO_2 when treated with aqueous Na_2CO_3?



Compounds (a)–(d), left to right

- (a)
- (b)
- (c)
- (d)

Answer and review

Answer **(3)** Official marking scheme

Na_2CO_3 releases CO_2 only from acids stronger than carbonic acid ($pK_a \approx 6.4$): carboxylic acids such as (c) phenylacetic acid and (d) 3-nitrobenzoic acid ($pK_a \approx 4$) do so. Phenols (a) (methylphenol, $pK_a \approx 10$) and (b) (phenol, $pK_a \approx 10$) are weaker acids than H_2CO_3 and only dissolve (giving the phenoxide and HCO_3^-) without evolving CO_2. Only (c) and (d): code (3).

RB U9 §3.5 · p. 66 RB U9 §3.3 · p. 59

Question 35 · Q31–40 · response code

Which of the following statements is/are **always** correct regarding an aqueous solution of a weak electrolyte?

- When conducting an electric current, the fraction of the current carried by the anion is greater than the fraction of the current carried by the cation.
- The conductivity of the anion is greater than the conductivity of the cation.
- Only a small percentage of molecules of the weak electrolyte is dissociated into ions.
- The fraction of molecules of the weak electrolyte dissociated increases with dilution.

Answer and review

Answer **(5)** Official marking scheme

Only (d) is always true: by Ostwald's dilution law the degree of dissociation α rises as the solution is diluted. (a) and (b) depend on which ion is more mobile (for CH_3COOH the cation H^+ carries more current); (c) is not always true because a weak electrolyte can be largely dissociated at high dilution. With only (d) correct the answer is "any other combination": code (5).

RB U13 §3.1 · p. 234

Question 36 · Q31–40 · response code

Which of the following statements is/are correct regarding the relationship between global environmental issues and volatile halogenated hydrocarbons?

- CFC, HCFC and HFC all three contribute to global warming.
- CFC contributes to ozone layer depletion by producing chlorine radicals in the troposphere.
- HFC contributes to ozone layer depletion by producing chlorine radicals in the stratosphere.
- Both CFC and HCFC contribute to ozone layer depletion by producing chlorine radicals in the stratosphere.

Answer and review

Answer **(4)** Official marking scheme

CFCs, HCFCs and HFCs are all greenhouse gases (a). CFCs and HCFCs contain chlorine and are photolysed by UV in the stratosphere to give Cl• radicals that destroy ozone (d); (b) is false because the radicals are produced in the stratosphere, not the troposphere; HFCs contain no chlorine so (c) is false. Only (a) and (d): code (4).

RB U14 §1.13 · p. 58

Question 37 · Q31–40 · response code

Which of the following statements is/are correct with regard to the two allotropes of carbon, namely, graphite and diamond?

- Carbon atoms in diamond are tetrahedrally surrounded by four other carbon atoms to give a three-dimensional lattice.
- Because graphite is composed of two-dimensional layers held together by weak van der Waals forces (secondary interactions), it acts as a good lubricant.
- Diamond is a good conductor of heat and electricity.
- Graphite has a considerably higher melting point than diamond.

Answer and review

Answer **(1)** Official marking scheme

(a) and (b) are standard: diamond is a rigid sp^3 network, graphite has sp^2 layers that slide over each other. (c) is false: diamond conducts heat well but is an electrical insulator (no delocalised electrons). (d) is false: both are giant covalent solids with extremely high melting points, with no considerable difference. Only (a) and (b): code (1).

RB U6 §4.4 · p. 133

Question 38 · Q31–40 · response code

Which of the following statements is/are correct regarding gases?

- Molecules move at different speeds in a sample of a real gas whereas all the molecules move at the same speed in a sample of an ideal gas.
- Ideal gases can be liquified at extremely high pressures.
- The Maxwell-Boltzmann speed distribution curve of an ideal gas is symmetric about the maximum point.
- The compressibility factor of a real gas depends on pressure.

Answer and review

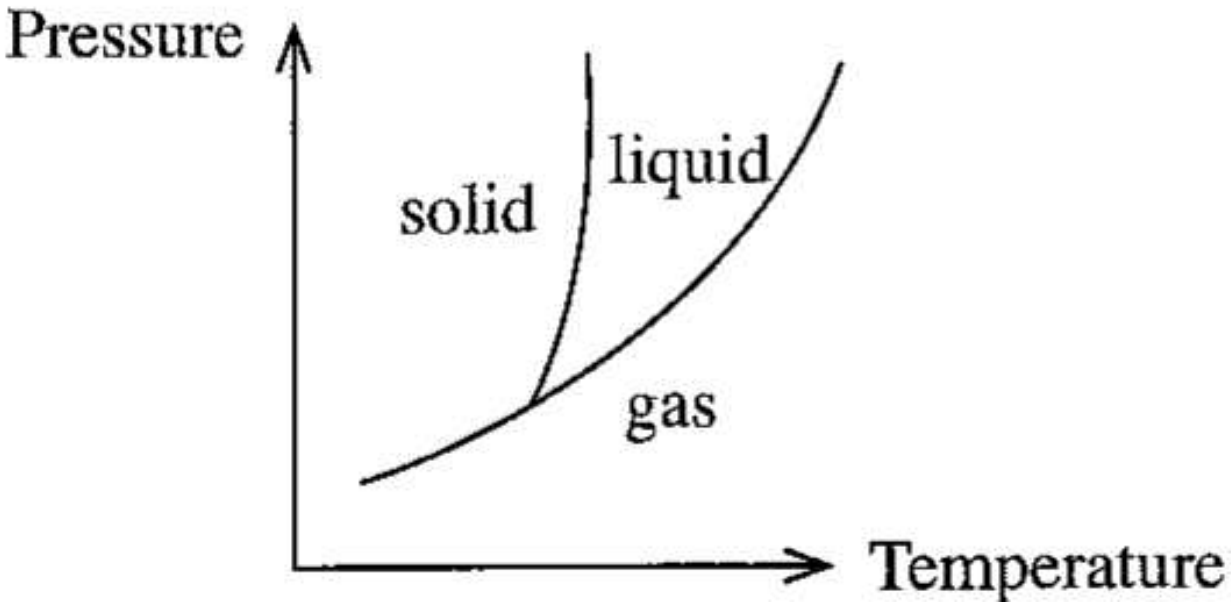
Answer **(5)** Official marking scheme

Only (d) is correct: Z = PV/nRT of a real gas changes with pressure (and temperature). (a) is false because molecules of an ideal gas also have a spread of speeds (Maxwell–Boltzmann); (b) an ideal gas has no intermolecular forces and can never be liquified; (c) the distribution is skewed with a long tail to high speeds. Only one statement is correct, so code (5).

RB U4 §1.4 · p. 19 RB U4 §1.5 · p. 24

Question 39 · Q31–40 · response code

Which of the following statements is/are correct regarding the phase diagram of a pure substance given below?



- The number of molecules in a unit volume is always higher in the gas phase than in the liquid phase.
- The liquid phase and the gas phase never co-exist at the same temperature.
- The solid phase and the gas phase never co-exist at the same pressure.
- When the system is at the triple point, the rate at which the gas is converted to the liquid is equal to the rate at which the liquid is converted to the gas.

Answer and review

Answer **(5)** Official marking scheme

Only (d) is correct: at the triple point all three phases are in dynamic equilibrium, so the forward and reverse rates for every pair of phases are equal. (a) is false: a liquid is far denser than its gas; (b) false: liquid and gas co-exist at every point on the vaporization curve (and at each temperature up to T_c); (c) false: solid and gas co-exist along the sublimation curve. Code (5).

RB U12 §2.5 · p. 199

Question 40 · Q31–40 · response code

Which of the following statements is/are correct regarding the given industrial processes?

- Sea water can be used directly as a raw material in the extraction of Mg by the Dow process.

- In the production of NaOH, the use of membrane cells is more environmentally friendly than the use of mercury cells.
- The efficiency of the Solvay process used to produce Na_2CO_3 can be increased by cooling the ammonification tower.
- Rh metal is used as a catalyst in the production of H_2SO_4 by the contact process.

Answer and review

Answer **(2)** Official marking scheme

(b) is correct: mercury cells release toxic mercury, whereas membrane cells do not. (c) is correct: dissolving NH_3 in brine is exothermic and NH_3 is more soluble in the cold, so the tower is cooled. (a) is false: sea water is first treated with lime (CaO/$Ca(OH)_2$) to precipitate $Mg(OH)_2$, which is then converted to $MgCl_2$ for electrolysis; (d) false: the contact process catalyst is V_2O_5 (or Pt), not Rh. Only (b) and (c): code (2).

RB U14 §1.2 · p. 6 RB U14 §1.5 · p. 18 RB U14 §1.8 · p. 27

Questions 41–50: statement pairs

Response	First statement	Second statement
(1)	True	True, and correctly explains the first statement
(2)	True	True, but does not explain the first statement correctly
(3)	True	False
(4)	False	True
(5)	False	False

Question 41 · Q41–50 · statement pair

Statement 1

When an acidic solution of MnO_4^− is treated with H_2O_2, it turns colourless with the evolution of O_2, whereas, an acidic solution of Fe^{2+} on treatment with H_2O_2 turns yellow-brown.

Statement 2

H_2O_2 can act as an oxidizing agent as well as a reducing agent in acidic medium.

Answer and review

Answer **(1)** Official marking scheme

MnO_4^− is reduced to colourless Mn^{2+} while H_2O_2 is oxidised to O_2 (H_2O_2 as reductant); Fe^{2+} is oxidised to yellow-brown Fe^{3+} while H_2O_2 is reduced to H_2O (oxidant). Both observations arise from the dual redox behaviour in the second statement, so both are true and (2) explains (1).

RB U6 §4.6 · p. 141 RB U6 §4.10 · p. 160

Question 42 · Q41–50 · statement pair

Statement 1

Energy of a gas in a closed rigid container with thermally insulated walls remains constant.

Statement 2

Both energy and matter of an isolated system do not exchange with the surroundings.

Answer and review

Answer **(1)** Official marking scheme

A rigid container permits no work (ΔV = 0) and insulated walls permit no heat exchange, so ΔU = q + w = 0 and the energy stays constant. This is exactly the definition of an isolated system (no exchange of energy or matter), so the second statement is true and explains the first.

RB U5 §2.1 · p. 31

Question 43 · Q41–50 · statement pair

Statement 1

Cl_2 gas undergoes disproportionation on reaction with water giving HOCl(aq) and HCl(aq).

Statement 2

HOCl has the highest oxidizing ability among the oxoacids of chlorine.

Answer and review

Answer **(2)** Official marking scheme

In $Cl_2 + H_2O \rightleftharpoons HOCl + HCl$, chlorine goes from 0 to +1 (HOCl) and −1 (HCl): disproportionation, so P1 is true. P2 is also true (oxidizing ability falls HOCl > $HClO_2$ > $HClO_3$ > $HClO_4$), but a high oxidizing power of HOCl is not the reason Cl_2 disproportionates, so P2 does not explain P1.

RB U6 §4.7 · p. 149

Question 44 · Q41–50 · statement pair

Statement 1

When a catalyst is added, the position of equilibrium of a reversible reaction changes.

Statement 2

A catalyst always increases the rate of the forward reaction more than the rate of the reverse reaction.

Answer and review

Answer **(5)** Official marking scheme

A catalyst lowers the activation energy of both the forward and reverse reactions by the same amount, so both rates increase by the same factor, K_c is unchanged and the equilibrium position does not shift (the equilibrium is just reached faster). Both statements are false.

RB U11 §1.9 · p. 54 RB U12 §2.1 · p. 76

Question 45 · Q41–50 · statement pair

Statement 1

RC≡CMgBr can be prepared by the reaction between RC≡CH and methylmagnesium bromide.

Statement 2

The alkyl group of a Grignard reagent can react as a base.

Answer and review

Answer **(1)** Official marking scheme

The terminal alkyne C–H is acidic enough for the strongly basic CH_3^− of CH_3MgBr to remove it: RC≡CH + CH_3MgBr → RC≡CMgBr + CH_4. Because the Grignard alkyl group acts as a base here, both statements are true and the second explains the first.

RB U8 §2.7 · p. 50 RB U8 §2.3 · p. 41

Question 46 · Q41–50 · statement pair

Statement 1

Reaction of HCN with any aldehyde gives a product containing a chiral carbon atom.

Statement 2

A carbon atom joined to four different groups is called a chiral carbon atom.

Answer and review

Answer **(4)** Official marking scheme

P2 is the definition of a chiral (stereogenic) carbon, so it is true. P1 is false: methanal (HCHO) gives $HOCH_2CN$, whose carbon carries two H atoms and is not chiral. Every other aldehyde RCHO gives RCH(OH)CN, with four different groups, but "any aldehyde" includes HCHO.

RB U9 §3.4 · p. 60 RB U7 §1.4 · p. 21

Question 47 · Q41–50 · statement pair

Statement 1

The main by-product in the production of Na_2CO_3 by the Solvay process is $CaCl_2$.

Statement 2

CaO is used to regenerate NH_3 in the Solvay process.

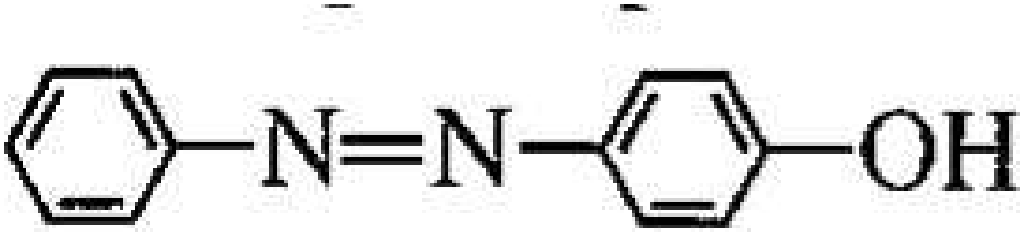
Answer and review

Answer **(1)** Official marking scheme

CaO (from limestone) forms $Ca(OH)_2$, which reacts with NH_4Cl: $2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3 + 2H_2O$. NH_3 is recycled and $CaCl_2$ is the by-product, so both statements are true and the second explains the first.

RB U14 §1.5 · p. 18

Question 48 · Q41–50 · statement pair



Statement 1

Benzenediazonium chloride reacts with phenol in the presence of aqueous NaOH to give the following compound,

Statement 2

Diazonium ions can react as electrophiles.

Answer and review

Answer **(1)** Official marking scheme

In alkaline solution phenol is present as the electron-rich phenoxide ion, which is attacked at the 4-position by the electrophilic diazonium ion ($C_6H_5N_2^+$), a coupling reaction giving the azo dye 4-hydroxyazobenzene. Both statements are true, and the electrophilic character of the diazonium ion explains the reaction.

RB U10 §4.3 · p. 78

Question 49 · Q41–50 · statement pair

Statement 1

When strong acids are titrated with aqueous ammonia, a neutral solution is not obtained at the equivalence point.

Statement 2

NH_4^+ reacts with water forming H_3O^+.

Answer and review

Answer **(1)** Official marking scheme

At the equivalence point the solution contains only NH_4^+ (the conjugate acid of a weak base), which hydrolyses: $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$. The solution is therefore acidic (pH < 7, not 7), so both statements are true and the second explains the first. Methyl orange/methyl red is the suitable indicator.

RB U12 §2.2 · p. 118

Question 50 · Q41–50 · statement pair

Statement 1

Atomic oxygen is an essential factor for the formation of ozone in the atmosphere.

Statement 2

Atomic oxygen in the atmosphere is produced only by decomposition of molecular oxygen.

Answer and review

Answer **(3)** Official marking scheme

$O\bullet + O_2 + M \rightarrow O_3 + M$, so P1 is true. P2 is false because atomic oxygen is also produced by photolysis of NO_2 ($NO_2 + h\nu \rightarrow NO + O\bullet$) in the troposphere, which is how ozone forms in photochemical smog; the "only" makes the statement wrong.

RB U14 §1.13 · p. 58

Structured essay · answer all four

SEQ · Paper II Part A

Question 1 · Part A · structured essay

(a) [24 marks]

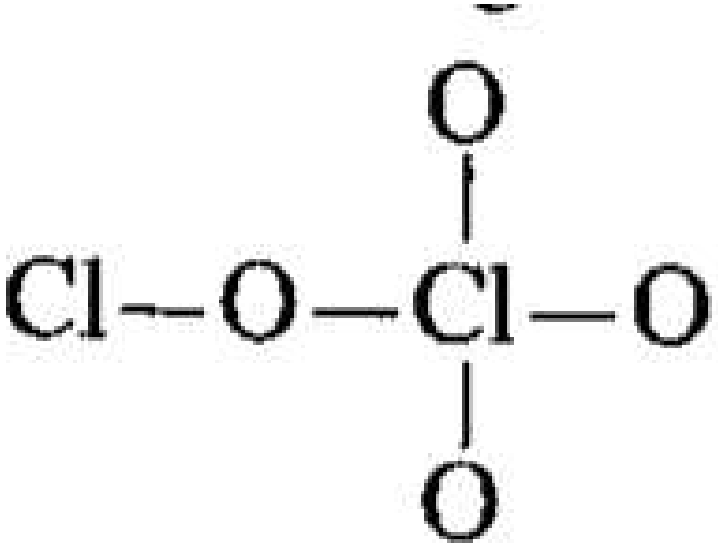
State whether the following statements are true or false on the dotted lines. Reasons are not required.
(i) Rules related to polarizing power of cations and polarizability of anions predict that the melting point of KBr is higher than that of LiI.
(ii) The electron gain energy of Be is positive.
(iii) The spacing between two adjacent lines in a given series of the atomic spectrum of hydrogen decreases gradually in the direction of decreasing wavelengths.
(iv) The de Broglie wavelength associated with the N_2 molecule is shorter than the de Broglie wavelength of the O_2 molecule when travelling at the same velocity.
(v) The effective nuclear charge (Z_{eff}) felt by a valence electron of C is greater than the effective nuclear charge felt by a valence electron of N.
(vi) All C–O bonds in carbonic acid (H_2CO_3) are equal in length.

Answer

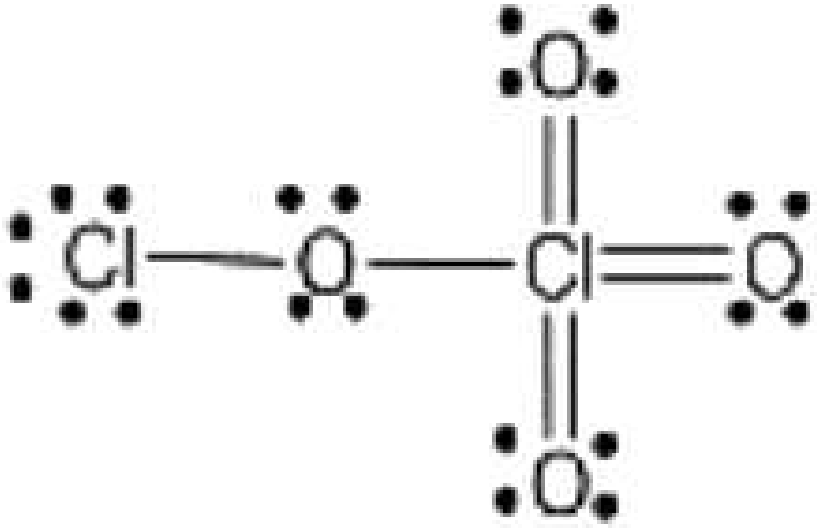
(i) True (ii) True (iii) True (iv) False (v) False (vi) False (04 marks × 6 = 24 marks) · 1(a): 24 marks

(b) [54 marks]

(i) Draw the **most** acceptable Lewis dot-dash structure for the molecule Cl_2O_4. Its skeleton is given below.



Answer



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4

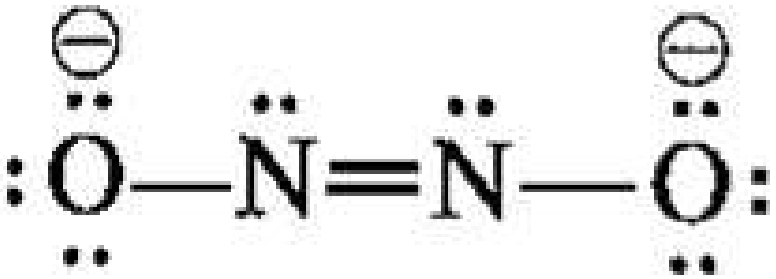
Cl–O–Cl(=O)(=O)=O: the first Cl is bonded to the bridging O by a single bond (Cl with three lone pairs, O with two lone pairs); the second Cl carries three Cl=O double bonds (each terminal O with two lone pairs) in addition to the single bond to the bridging O. (06 marks)

(ii) Give the oxidation states of the two chlorine atoms in the structure drawn in (i) above. The chlorine atoms are labelled as follows: Cl^1–O–Cl^2(–O)(–O)–O.

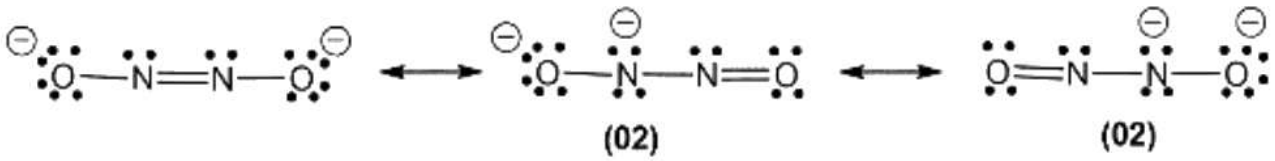
Answer

Cl^1: +I (+1); Cl^2: +VII (+7) (01 + 01)

(iii) The **most** stable Lewis dot-dash structure for the ion $N_2O_2^{2-}$ is shown below. Draw **two** additional Lewis dot-dash structures (resonance structures) for this ion.



Answer



(02) (02)

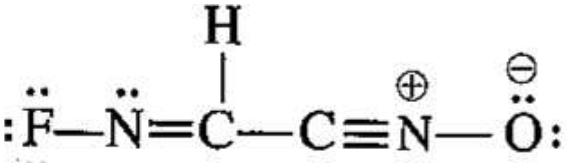
2

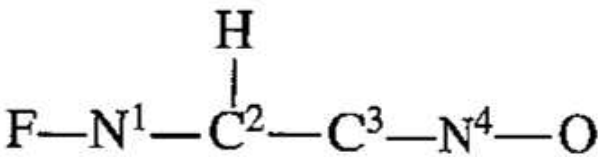
2

2–

Two further resonance structures (lone pairs as shown in the figure): O^{-}–N^{-}–N=O (negative charges on one terminal O and on the adjacent N; N=O double bond at the other end) and O=N–N^{-}–O^{-} (the mirror image). (02 + 02)

(iv) Complete the given table based on the Lewis dot-dash structure and its labelled skeleton given below. Rows: I. VSEPR pairs around the atom; II. electron pair geometry around the atom; III. shape around the atom; IV. hybridization of the atom. Columns: N^1, C^2, C^3, N^4.





Answer

	N^1	C^2	C^3	N^4
I. VSEPR pairs around the atom	3	3	2	2
II. electron pair geometry	trigonal planar	trigonal planar	linear	linear
III. shape around the atom	angular / V	trigonal planar	linear	linear
IV. hybridization	sp^2	sp^2	sp	sp

(01 mark × 16 = 16 marks)

Parts (v) to (viii) are based on the Lewis dot-dash structure given in part (iv) above. Labelling of atoms is as in part (iv).

(v) Identify the atomic/hybrid orbitals involved in the formation of σ bonds between the two atoms given below.

I. N^1–F II. N^1–C^2 III. C^2–H IV. C^2–C^3 V. C^3–N^4 VI. N^4–O

Answer

I. N^1 sp^2; F 2p or sp^3
II. N^1 sp^2; C^2 sp^2
III. C^2 sp^2; H 1s
IV. C^2 sp^2; C^3 sp
V. C^3 sp; N^4 sp
VI. N^4 sp; O 2p or sp^3 (01 mark × 12 = 12 marks)

(vi) Identify the atomic orbitals involved in the formation of π bonds between the two atoms given below.

I. N^1–C^2 II. C^3–N^4

Answer

I. N^1 2p; C^2 2p
II. C^3 2p; N^4 2p (first π bond) and C^3 2p; N^4 2p (second π bond) (01 mark × 6 = 06 marks)

(vii) State the approximate bond angles around N^1, C^2, C^3 and N^4 atoms.

Answer

N^1 (118° ± 1); C^2 (120° ± 1); C^3 (180° ± 1); N^4 (180° ± 1) (01 mark × 4 = 04 marks)

(viii) Arrange the atoms N^1, C^2, C^3 and N^4 in the **increasing** order of electronegativity.

Answer

$C^2 < C^3 < N^1 < N^4$ (04 marks) · 1(b): 54 marks

(c) [22 marks]

(i) A laser emits photons of wavelength 695 nm.
I. To which region of the electromagnetic spectrum do these photons belong?
II. Calculate the energy of a mole of these photons in kJ mol^{-1}. Velocity of light c = 3.00×10^8 m s^{-1}; Planck constant h = 6.63×10^{-34} J s

Answer

I. Visible region (02)
II. Energy of a photon, $E = h\nu = hc/\lambda$ (01)
Energy of a mole of photons = $(hc/\lambda) \times N_A$ (N_A = Avogadro constant) (01)
= 6.63×10^{-34} (J s) × 3.00×10^8 (m s^{-1}) × 6.022×10^{23} (mol^{-1}) / 695×10^{-9} (m) (03 + 01)
= 172 kJ mol^{-1} (02)
Note: marks can be awarded for combining steps. h = 6.626×10^{-34} J s is accepted.

(ii) A molecule of formula AX_3 has **three** A–X σ bonds. Here, A and X represent symbols of elements and A is the central atom. Name the molecular shape(s) possible for AX_3 in I and II given below.
I. if AX_3 is polar
II. if AX_3 is non-polar
III. Give **one** example each, for the shapes stated by you in I and II above. (**Note:** Molecular formulae are required.)

Answer

I. AX_3 polar: T shape, trigonal pyramidal (02 + 02)
II. AX_3 non-polar: trigonal planar
III. Examples (any one for each shape): T shape – ClF_3, BrF_3, IF_3 (02); trigonal pyramidal – NH_3, PH_3, NCl_3, PCl_3 (02); trigonal planar – BF_3, BCl_3, BBr_3, BI_3 (02) · 1(c): 22 marks

Review.

Part (a) tests polarization (Fajans' rules: small, highly charged cation and large anion give more covalent character, so LiI melts lower than KBr), the positive electron gain energy of Be (full 2s subshell), Rydberg-series convergence (lines get closer at shorter wavelength), de Broglie $\lambda = h/mv$ (lighter N_2 has the longer λ), Z_{eff} increasing across a period (N > C) and resonance in H_2CO_3 (C=O is shorter than the two C–O single bonds). Part (b): draw Lewis structures with formal charges minimised (expanded octet at Cl^{+7}), then use VSEPR pairs → geometry → hybridization: N^1 (bonds to F and C, one double bond, one lone pair) is sp^2 and bent; C^3 and N^4 are sp. The $C^3 \equiv N^4$ triple bond is one σ and two π (2p–2p) bonds. Common mistakes: counting a lone pair as a bond when finding hybridization, forgetting the second π bond of the triple bond, and ordering electronegativity without noting that sp carbon (C^3) is more electronegative than sp^2 carbon (C^2). Part (c): $E_{mol} = N_A\, hc/\lambda$ = 172 kJ mol^{-1} (695 nm is visible, red); AX_3 shapes are trigonal planar (non-polar), trigonal pyramidal and T-shaped (polar). Common mistakes: forgetting N_A, leaving λ in nm and the answer in J.

Read: RB U2 §2.4 · p. 75 RB U1 §1.6 · p. 32 RB U1 §1.3 · p. 17 RB U2 §2.1 · p. 44 RB U2 §2.3 · p. 52 RB U1 §1.2 · p. 13

Question 2 · Part A · structured essay

(a) [35 marks]

A

s

A

2

A

A

Answer

K (05)

(ii) Write the complete electronic configuration of **A**.

Answer

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$ (05)

(iii) Name the gas evolved in the reaction of **A** with water.

Answer

Hydrogen or H_2 (05)

(iv) What is the colour given by **A** in the flame test?

Answer

Lilac (violet) (05)

(v) Write the balanced chemical equation for the reaction of **A** with excess $O_2(g)$.

Answer

$K + O_2 \rightarrow KO_2$ (05)

(vi) Is the first ionization energy of **A** higher or lower than that of the element in the same group and the period above it in the Periodic Table? Briefly explain your answer.

Answer

Lower (02)
When going down the group, the change in effective nuclear charge (or Z_{eff}) for the outermost / last electron is negligible. (01)
However, atom size increases. (01)
Therefore, the attraction of the outer electron to the nucleus decreases. (01)
Note: (vi) Award marks for the reasoning only if "lower" is written.

(vii) Give the chemical formula of the compound of **A** in Sylvite.

Answer

KCl (05) · 2(a): 35 marks

(b) [25 marks]

B

X

Y

X

Y

p

X

Y

X

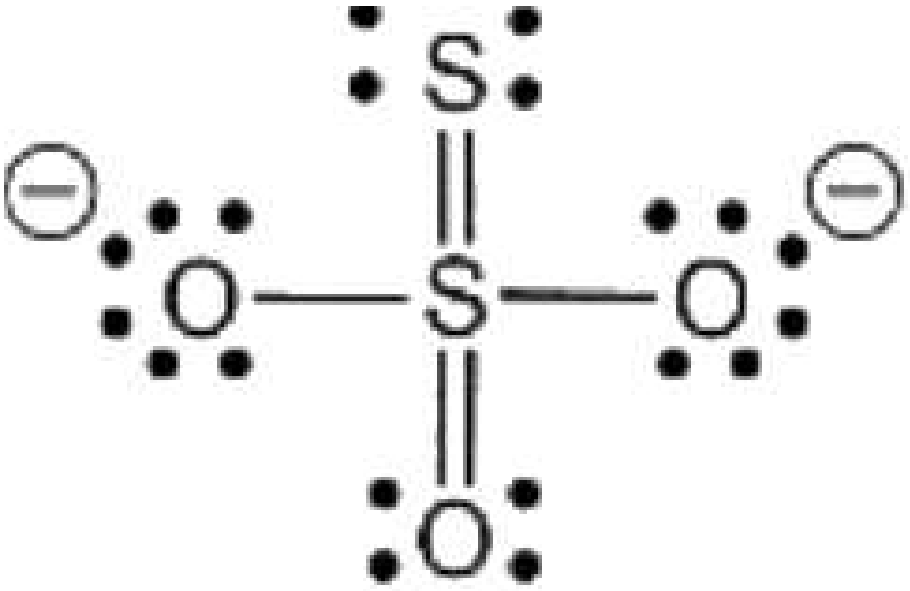
B

Answer

$S_2O_3^{2-}$ (05)

(ii) Draw the Lewis dot-dash structure of **B**.

Answer



2

3

2−

Central S bonded to the terminal S by a double bond (S has two lone pairs) and to the two O atoms: one O by a double bond and the other two O atoms by single bonds, each of the single-bonded O atoms carrying three lone pairs and a negative charge (see figure). (05)

(iii) Give the oxidation state of the central atom of **B**.

Answer

+4 (05)

(iv) Give a chemical test to identify **B**. (**Note:** Observation(s) is/are also required.)

Answer

Test	Observation
1. Add dil. H_2SO_4	Colourless gas with a pungent smell and colloidal sulfur precipitate (or milky solution)
2. Add $Pb(OAc)_2$	White precipitate which turns black on heating
3. Add $AgNO_3$	White precipitate which turns black on standing / heating

(02)

(03)

(v) Write the chemical formula for the compound which has **A** as the cation and **B** as the anion.

Answer

$K_2S_2O_3$ (05) · 2(b): 25 marks

(c) [10 marks]

C

C

A

p

B

+

C

Answer

KIO_3 (10) · 2(c): 10 marks

(d) [30 marks]

D

C

D

Answer

D = KI (05)

II. Write the balanced **ionic** equation for the reaction that takes place.

Answer

IO_3^−(aq) + $5I^-$(aq) + $6H^+$(aq) → $3I_2$(aq) + $3H_2O$(l) (10)

(ii) On addition of an excess of a solution containing **B**, to the reddish-brown solution obtained in (i) above, the reddish-brown solution becomes colourless. Write the balanced **ionic** equation for the reaction that takes place.

Answer

I_2 + $2S_2O_3^{2-}$ → $S_4O_6^{2-}$ + $2I^-$ (05)

(iii) The concentration of a solution containing **B** can be determined by volumetric analysis utilizing the reactions in (i) and (ii) above. State an indicator which can be used and give the expected colour change at the end point.

Answer

Indicator: starch (05)
Colour change: blue / dark blue / blue-violet to colourless (05) · 2(d): 30 marks

Review.

Part (a): group 1 metal that ignites with water and forms a superoxide on burning in excess O_2 is K (Na gives the peroxide, Li the oxide); K is lilac in the flame and occurs as KCl in sylvite; first ionization energy falls down a group because the outer electron is further from the nucleus while Z_{eff} barely changes. Part (b): X and Y are in the same group with X less electronegative, so X = S and Y = O; the 2:3 ratio and the pungent gas (SO_2) from S with hot conc. H_2SO_4 give $S_2O_3^{2-}$. Taking the central S–terminal S bond as S to S, the central S is +4 (as in the scheme); do not quote the average value +2. In acid, thiosulfate gives SO_2 and colloidal sulfur. Part (c): the yellow AgI, insoluble in concentrated NH_3, shows iodine, so C is KIO_3. Part (d): iodate oxidizes iodide in acid to iodine (iodate–iodide reaction), and thiosulfate reduces iodine to tetrathionate, which is the basis of iodometric titrations with starch added near the end point (blue to colourless). Common mistakes: writing KIO_4, giving +2 (the average) instead of +4 for the central S, unbalanced ionic equations and forgetting the $6H^+$.

Read: RB U6 §4.1 · p. 122 RB U6 §4.6 · p. 141 RB U6 §4.7 · p. 149 RB U3 §3.6 · p. 105 RB U3 §3.8 · p. 115

Question 3 · Part A · structured essay

(a) [50 marks]

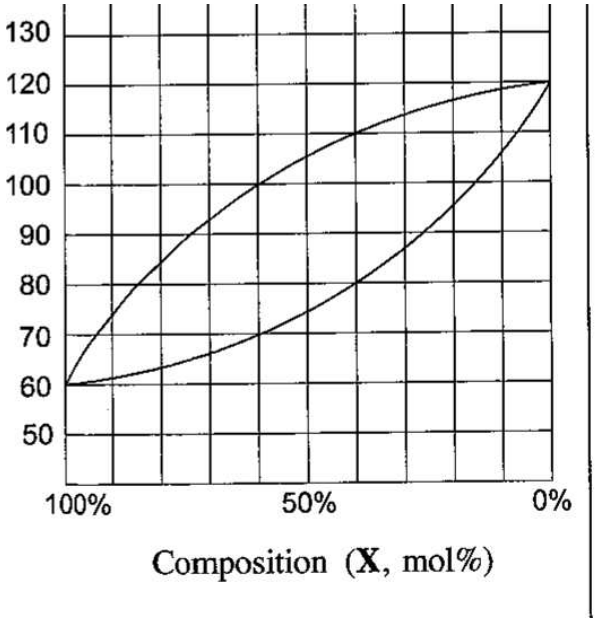
X

Y

5

X

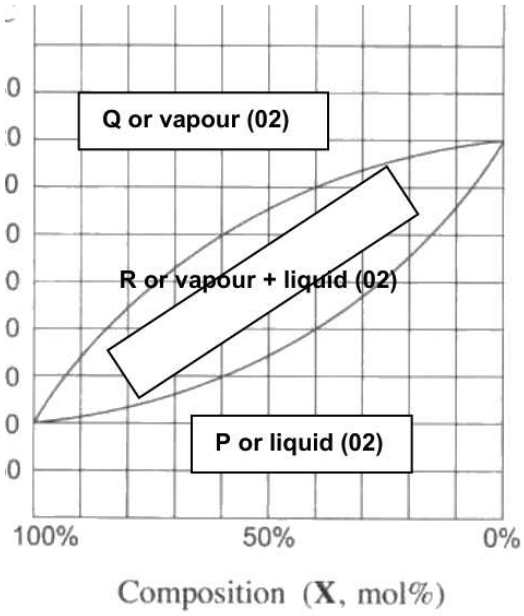
Y



Temperature (°C) against composition (X, mol%); the horizontal axis runs from 100% X on the left to 0% X on the right

(i) Indicate the following regions on the phase diagram by writing the letters P, Q, R.
P – region where only the liquid phase is present
Q – region where only the vapour phase is present
R – region where the liquid phase and the vapour phase are in equilibrium

Answer



Scheme: regions of the phase diagram

Q (vapour only): the region above the upper curve (02); R (liquid + vapour): the lens-shaped region between the two curves (02); P (liquid only): the region below the lower curve (02)

(ii) Give the boiling points of pure **X** and pure **Y**.

Answer

X = 60 °C; Y = 120 °C (02 + 01) × 2

(iii) What is the temperature at which a liquid mixture of **X** and **Y** containing 40 mol% of **X** begins to boil?

Answer

80 °C (02 + 01)

(iv) What is the lowest temperature at which a mixture of **X** and **Y** containing 60 mol% of **X** is completely converted to vapour?

Answer

100 °C (02 + 01)

(v) Calculate the saturated vapour pressure of **X** at the temperature of 100 °C.

Answer

$P_X^{\circ}g = P_X^{\circ}0\ x_X^{\circ}l$ (03)
$P_X^{\circ}g = P^{total}\ x_X^{\circ}g$ (03)
Therefore, $P_X^{\circ}0 = P^{total}\ x_X^{\circ}g / x_X^{\circ}l$ (03)
$P_X^{\circ}0 = 1 \times 10^5$ Pa × 60 / 15 (05 + 01)
$P_X^{\circ}0 = 4.0 \times 10^5$ Pa (04 + 01)

(vi) In a separate experiment, a mixture containing **X** and **Y** was allowed to reach equilibrium in a **closed rigid** container at temperature T. It was then found that the liquid phase in equilibrium with the vapour phase contained 0.10 mol of **X** and 0.10 mol of **Y**. Saturated vapour pressures of **X** and **Y** at this temperature are 4.0×10^5 Pa and 2.0×10^5 Pa, respectively. Using Raoult law, calculate the partial pressures of **X** and **Y**.

Answer

P_X = 0.1 mol × 4.0×10^5 Pa / (0.1 mol + 0.1 mol) (02 + 01)
P_X = 2.0×10^5 Pa (02 + 01)
P_Y = 0.1 mol × 2.0×10^5 Pa / (0.1 mol + 0.1 mol) (02 + 01)
P_Y = 1.0×10^5 Pa (02 + 01) · 3(a): 50 marks
(The printed scheme writes "P_X" in the last line, a misprint for P_Y.)

(b) [50 marks]

The concentration of an aqueous solution of acetic acid (solution **Z**) was determined by titrating with an aqueous solution of NaOH. A volume of 12.50 cm^3 of solution **Z** required 25.00 cm^3 of NaOH solution of concentration 0.050 mol dm^{-3} to reach the end point.
(i) Calculate the concentration of acetic acid in solution **Z**.

Answer

$[CH_3COOH(aq)]$ = 25.00 cm^3 × 0.05 mol dm^{-3} / 12.50 cm^3 (02 + 01)
= 0.10 mol dm^{-3} (02 + 01)

(ii) Calculate the pH value of solution **Z**. Acid dissociation constant of acetic acid (K_a) at the temperature at which the experiment was carried out is 1.80×10^{-5} mol dm^{-3}.

Answer

$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$ (02) or $CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$
Initial concentration of acetic acid = C; fraction dissociated = α (or amount dissociated = x). [Physical states are required for K_a]
$K_a = [H^+(aq)][CH_3COO^-(aq)] / [CH_3COOH(aq)]$ or $K_a = [H_3O^+(aq)][CH_3COO^-(aq)] / [CH_3COOH(aq)]$ (02)
$K_a = C\alpha C\alpha / C(1-\alpha)$ or $K_a = x^2 / (C-x)$ (02) [if this is not written but the calculation is done correctly, award 02 marks for the calculation]
Since $\alpha << 1$ or $x << C$ (02)
pH calculation (do not deduct marks if physical states are not given):
$[H^+(aq)] = \sqrt{(K_a\ C)} = \sqrt{(1.80 \times 10^{-5}}$ mol $dm^{-3} \times 0.1$ mol $dm^{-3})$ (02)
$[H^+(aq)]$ = 0.00134 mol dm^{-3} (02)
$pH = -\log[H_3O^+(aq)$ / 1.0 mol $dm^{-3}]$ or $-\log[H^+(aq)$ / 1.0 mol $dm^{-3}]$ (02)
pH = 2.87 (02)
Alternate answer: $-\log[H^+(aq)] = ½(-\log(K_a\ c))$ (02); $pH = ½(-\log(1.8 \times 10^{-5} \times 0.1))$ (04); pH = 2.87 (02)

(iii) To another portion (100.00 cm^3) of solution **Z**, 0.200 g of pure solid NaOH was added and dissolved. Calculate the pH value of this solution assuming that the volume and the temperature of the solution remain unchanged. [Relative atomic mass: Na = 23, O = 16, H = 1]

Answer

Amount of CH_3COOH in 100.00 cm^3 of solution = 1.0×10^{-2} mol (02)
Amount of NaOH added = 0.005 mol (02)
Amount of CH_3COOH left in the medium (after reacting with NaOH) = 5.00×10^{-3} mol (02)
Therefore, in solution (do not deduct marks if physical states are not given): $[CH_3COOH(aq)]$ = 0.05 mol dm^{-3} (02); $[CH_3COONa(aq)]$ = 0.05 mol dm^{-3} (02)
pH calculation: $[H^+(aq)] = K_a\ [CH_3COOH(aq)] / [CH_3COO^-(aq)]$ (02) = 1.80×10^{-5} mol $dm^{-3} \times 0.050$ mol dm^{-3} / 0.050 mol dm^{-3} (02) = 1.80×10^{-5} mol dm^{-3}; pH = 4.74 (02)
Alternate answer (Henderson): $pH = pK_a + \log([CH_3COO^-(aq)] / [CH_3COOH(aq)])$ (02); $pH = -\log(1.8 \times 10^{-5}) + \log(0.05/0.05)$ (02); pH = 4.74 (02)
(The printed scheme shows 1.80×10^5 in the substitution line, a misprint for 10^{-5}.)

(iv) Does the solution described in (iii) above behave as a buffer solution? Explain your answer.

Answer

The solution in (iii) above behaves as a buffer solution. (02)
The solution contains a weak acid and the sodium salt of its conjugate base. (02 + 02)

(v) In a separate experiment, 0.800 g of pure solid NaOH was dissolved in a 100.00 cm^3 volume of solution **Z**. Does this solution behave as a buffer solution? Explain your answer using a suitable calculation. Assume that the volume and temperature of the solution remain unchanged.

Answer

The amount of CH_3COOH in 100.00 cm^3 = 0.01 mol
The amount of NaOH added = 0.02 mol (02)
Solution does not contain CH_3COOH (or CH_3COOH has reacted completely) (02)
Solution does not behave as a buffer solution (02) · 3(b): 50 marks

Review.

Part (a): in an ideal solution at equilibrium, Raoult's law gives $P_X = P_X\text{^}0\ x_X^{liquid}$, while Dalton's law gives $P_X = P_{total}\ x_X^{vapour}$; at 100 °C the tie line reads x_X (liquid) = 15% and x_X (vapour) = 60%, so $P_X\text{^}0 = 1.0 \times 10^5 \times 60/15 = 4.0 \times 10^5$ Pa. In (vi) the liquid mole fractions are both 0.5, so $P_X = 2.0 \times 10^5$ Pa and $P_Y = 1.0 \times 10^5$ Pa. Read the lens correctly: the lower curve is the boiling (liquid) curve and the upper curve the dew (vapour) curve; commonest errors are swapping the two curves and using the vapour composition in Raoult's law. Part (b): $C = 25.00 \times 0.050 / 12.50 = 0.10$ mol dm^{-3}; for a weak acid $[H^+] = \sqrt{(K_a\ C)} = 1.34 \times 10^{-3}$, pH = 2.87. NaOH 0.200 g = 0.0050 mol neutralizes half of the 0.010 mol acid, giving equal CH_3COOH and CH_3COO^- (0.05 mol dm^{-3} each) so $pH = pK_a$ = 4.74; this is a buffer. 0.800 g = 0.020 mol exceeds 0.010 mol, so all the acid is consumed and excess OH^- remains, and the solution is not a buffer. Common mistakes: using the Henderson equation without checking that both buffer components are present and forgetting that the volume is 100.00 cm^3 in both cases.

Read: RB U12 §2.6 · p. 216 RB U12 §2.5 · p. 199 RB U12 §2.2 · p. 118 RB U12 §2.3 · p. 167

Question 4 · Part A · structured essay

(a) [56 marks]

A

B

C

5

11

B

A

C

A

B

C

D

E

F

5

12

D

E

F

F

D

E

G

H

G

H

3

A

B

C

D

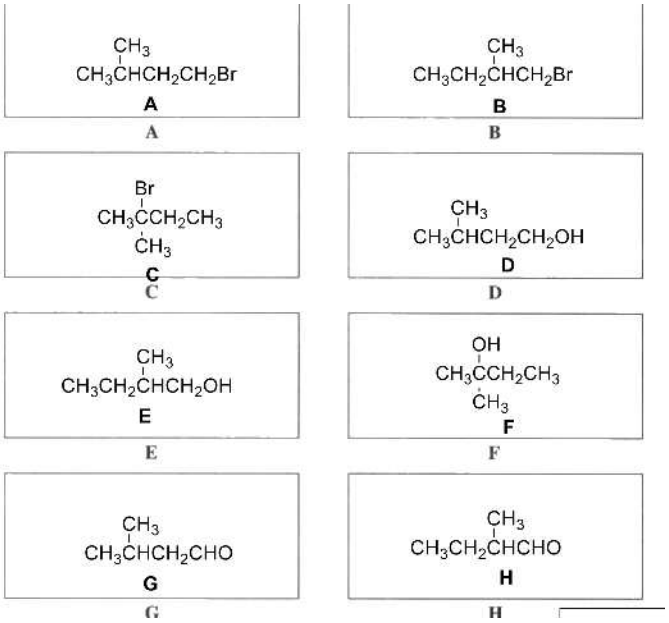
E

F

G

H

Answer



Scheme: structures of A to H

A

3

2

2

2

B

3

2

3

2

C

3

2

2

3

D

3

2

2

2

E

3

2

3

2

F

3

2

2

3

G

3

2

2

H

3

2

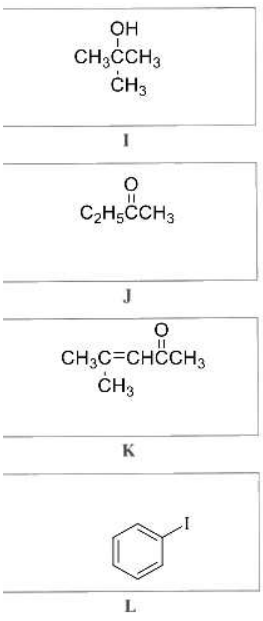
3

(07 marks × 8 = 56 marks) · 4(a): 56 marks

(b) [24 marks]

Draw the structures of the products **I**, **J**, **K** and **L** of the following reactions, in the given boxes.
(i) CH_3COOCH_3 → (1) CH_3MgBr (excess) / dry ether; (2) H^+ / H_2O → **I**
(ii) $C_2H_5C{\equiv}CH$ → dilute H_2SO_4 / Hg^{2+} → **J**
(iii) CH_3COCH_3 → (1) aqueous NaOH; (2) H^+ / Δ → **K**
(iv) benzenediazonium chloride ($C_6H_5N_2{\hat{}}+Cl^-$) → KI → **L**

Answer



Scheme: structures of I, J, K and L

I

3

3

J

2

5

3

K

3

2

3

L

6

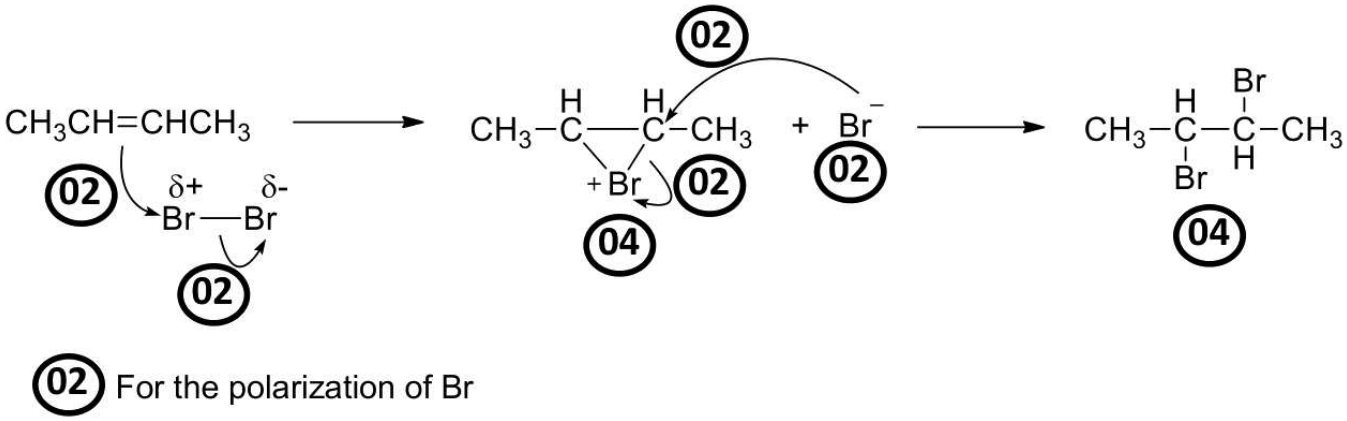
5

(06 marks × 4 = 24 marks) · 4(b): 24 marks

(c) [20 marks]

Give the mechanism and the structure of the product formed for the reaction between $CH_3CH=CHCH_3$ and Br_2/CCl_4.

Answer



Scheme: mechanism of bromine addition to but-2-ene

Electrophilic addition: the π electrons of C=C attack the $Br^{\delta+}$ of the polarized Br–Br molecule (curved arrows from the π bond to $Br^{\delta+}$ and from the Br–Br bond to $Br^{\delta-}$), giving a cyclic bromonium ion CH_3–CH–CH–CH_3 (bridged by Br^+) and Br^-. The Br^- then attacks one of the carbons of the bromonium ion from the opposite side, opening the ring to give $CH_3CHBrCHBrCH_3$ (2,3-dibromobutane). Marks: polarization of Br–Br (02); arrow from π bond (02); arrow from Br–Br bond (02); bromonium ion (04) and Br^- (02); attack of Br^- (02); product (04); 4(c): 20 marks

Review.

Part (a): optical activity of B requires a chiral carbon, so B = 1-bromo-2-methylbutane; A and C are positional isomers (the Br on a different carbon), A = 1-bromo-3-methylbutane (primary, gives an aldehyde G with PCC) and C = 2-bromo-2-methylbutane (tertiary: its alcohol F resists PCC). Both aldehydes G and H give a 2,4-DNP

precipitate and Tollens' silver mirror. Part (b): (i) an ester reacts with excess Grignard reagent twice, giving a tertiary alcohol (2-methylpropan-2-ol); (ii) hydration of a terminal alkyne with Hg^{2+}/H^{+} follows Markovnikov addition, giving the methyl ketone; (iii) aldol condensation of propanone, followed by dehydration, gives the α,β-unsaturated ketone; (iv) the diazonium group is replaced by I with KI. Part (c): bromine adds to an alkene by electrophilic addition through a bromonium ion, with anti stereochemistry; draw curved arrows from the π bond and from the Br–Br bond. Common mistakes: forgetting the intermediate ion, showing a carbocation instead of the bridged ion, and drawing a ketone for G or H.

Read: RB U7 §1.4 · p. 21 RB U8 §2.6 · p. 49 RB U9 §3.1 · p. 54 RB U9 §3.4 · p. 60 RB U8 §2.2 · p. 33 RB U10 §4.3 · p. 78

Answer two from each part

Essay · Paper II Parts B and C

Part B

Question 5 · Part B · essay

−1

−1

A

23

−1

(a) [75 marks]

(i) A gas mixture containing CH_4, C_2H_6 and excess O_2 was introduced into an evacuated closed rigid container. The volume of the container was 8.314×10^{-3} m^3. The pressure of the container at 400 K was 4.80×10^6 Pa. Calculate the total number of moles of gases in the container. Assume that all the gases behave ideally and that there is no reaction at this temperature.

Answer

Using pV = nRT (05)
At 400 K, $n_1 = (4.8 \times 10^6 \text{ Pa} \times 8.314 \times 10^{-3} \text{ m}^3)/(8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 400 \text{ K})$ (04 + 01)
n_1 = **12.0 mol** (04 + 01)

(ii) All the hydrocarbons in the container were completely combusted by increasing the temperature of the container to 800 K. The pressure of the container after the combustion reactions at 800 K was 1.00×10^7 Pa. Calculate the total number of moles of gases in the container after combustion. Assume that H_2O is present as a gas under these conditions.

Answer

At 800 K, $n_2 = (1.0 \times 10^7 \text{ Pa} \times 8.314 \times 10^{-3} \text{ m}^3)/(8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 800 \text{ K})$ (04 + 01)
n_2 = **12.5 mol** (04 + 01) (the scheme prints this as "n_1 = 12.5 mol")

(iii) Write balanced chemical equations (giving physical states, at 800 K) for the combustion reactions of the gases given below.
I. $CH_4(g)$
II. $C_2H_6(g)$

Answer

I. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ (05)
II. $2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(g)$ (05)

(iv) Only one of the two hydrocarbons above contributes to the change in the number of moles of gases before and after combustion.
Calculate the number of moles of this hydrocarbon initially introduced into the container.

Answer

The hydrocarbon that contributes to the change of the number of moles before and after the combustion is C_2H_6 (05) ($CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$: 3 mol of gas → 3 mol of gas, no change; $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$: 9 mol → 10 mol).
Number of moles increased after combustion = 12.5 − 12.0 = 0.5 mol
The amount of C_2H_6 introduced initially = 0.5 mol × 2 = **1.0 mol** (04 + 01)
Alternate answer (iv) and (v): Let the initial moles be $CH_4 = n_1$, $C_2H_6 = n_2$, $O_2 = 2n_1 + (7/2)n_2 + n_{excess}$. After combustion: $CO_2 = n_1 + 2n_2$, $H_2O = 2n_1 + 3n_2$, $O_2 = n_{excess}$ (the scheme's list prints the final O_2 as $2n_1 + 7/2\ n_2 + n_{excess}$, a slip; its equation (2) correctly uses n_{excess}). Before combustion: $12.0 = n_1 + n_2 + 2n_1 + (7/2)n_2 + n_{excess}$ (1). After combustion: $12.5 = n_1 + 2n_2 + 2n_1 + 3n_2 + n_{excess}$ (2). (2) − (1): $0.5 = ½n_2$, so n_2 = **1.0 mol** (05) + (04 + 01)

(v) The container was then cooled to 300 K and the water was removed. Then the pressure of the container was 2.10×10^6 Pa.
Calculate the following.
I. Total number of moles of H_2O produced
II. Number of moles of H_2O produced from the combustion of C_2H_6
III. Number of moles of H_2O produced from the combustion of CH_4
IV. Number of moles of O_2 introduced initially into the container

Answer

Amount (moles) of gases after removing water: $n_3 = (2.1 \times 10^6\ Pa \times 8.314 \times 10^{-3}\ m^3)/(8.314\ J\ mol^{-1}\ K^{-1} \times 300\ K)$ (04 + 01); n_3 = **7.0 mol** (04 + 01)
I. The amount of water formed = (12.5 − 7.0) mol = **5.5 mol** (04 + 01) (the scheme prints "12.7 − 7.0", a slip for 12.5 − 7.0)
II. Water from the combustion of C_2H_6 = 1.0 mol × 6/2 = **3.0 mol** (04 + 01)
III. Water from the combustion of CH_4 = (5.5 − 3.0) mol = **2.5 mol** (04 + 01)
IV. The amount of O_2 introduced initially = 12.0 mol − (1.0 + amount of CH_4 introduced) = 12.0 mol − (1.0 + 2.5/2) mol = **9.75 mol** (04 + 01)
Alternate answer: $n_1 + 2n_2 + n_{excess}$ = 7.0 mol (04 + 01) and 7.0 mol (04 + 01); from (2), $n_1 = ½(12.5 - (n_1 + 2n_2 + 3n_2 + n_{excess})) = ½(12.5 - 10.0)$ mol = 1.25 mol. I. Total water = $2n_1 + 3n_2 = (2 \times 1.25 + 3 \times 1.0)$ mol = 5.5 mol (04 + 01); II. water from $C_2H_6 = 3n_2$ = 3.0 mol (04 + 01); III. water from $CH_4 = 2n_1$ = 2.5 mol (04 + 01); IV. O_2 introduced initially = (12.0 − (1.25 + 1.0)) mol = 9.75 mol (04 + 01). · 5(a): 75 marks

Review.

Principle: the ideal gas equation applied to a rigid container (V constant) at three states, and mole balance through the reaction stoichiometry (U4 §1.2, Dalton's law §1.3). Method: n = pV/RT gives 12.0, 12.5 and 7.0 mol; CH_4 burns with no change in moles (3 → 3) so the 0.5 mol rise comes only from C_2H_6 ($2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$: 9 → 10, so Δn = 0.5 per 1 mol of C_2H_6, i.e. 1.0 mol C_2H_6 gives 0.5 mol rise). Water removed = 12.5 − 7.0 = 5.5 mol. Check: CO_2 3.25 + O_2 left 3.75 = 7.0 mol. Common mistakes: using the wrong temperature for n, forgetting that H_2O is a gas at 800 K but is removed at 300 K, and mixing up 'moles of C_2H_6 reacting' with '0.5 mol increase'.

(b) [75 marks]

(i) Using a **thermochemical cycle** and the data given, calculate the standard enthalpy change for the reaction given below.
$4CH_4(g) + O_2(g) \rightarrow 2C_2H_6(g) + 2H_2O(g)$

	ΔH_f° (kJ mol^{-1})	S° (J mol^{-1} K^{-1})
$CH_4(g)$	−74.8	186.3
$C_2H_6(g)$	−84.7	229.6
$CO_2(g)$	−393.5	213.7
$H_2O(g)$	−214.8	188.8
C(s), graphite	0.0	5.7
$O_2(g)$	0.0	205.1
$H_2(g)$	0.0	130.7

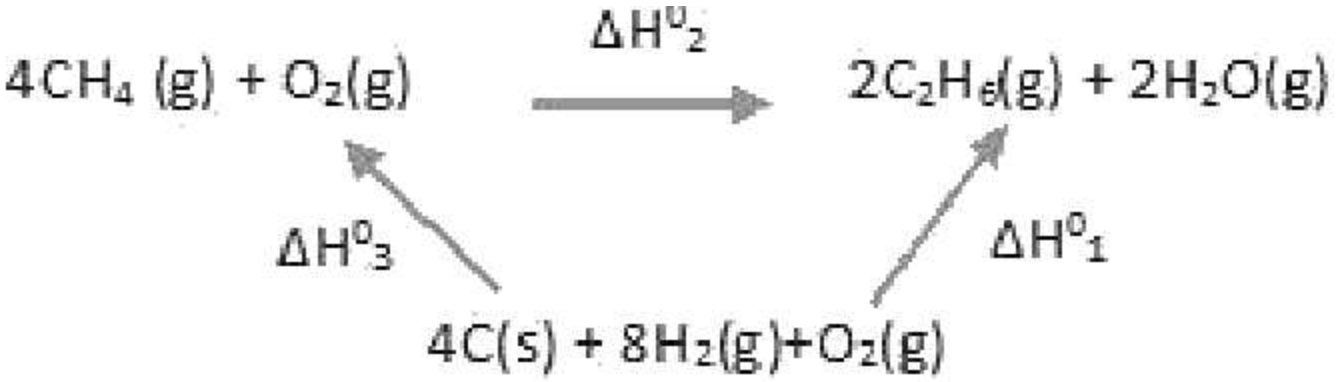
Answer

For the thermochemical cycle: for the correct species, correct stoichiometry and correct physical state (02 marks × 7 = 14)

$\Delta H_2^\circ = \Delta H_1^\circ - \Delta H_3^\circ$ (03)

Or $\Delta H_2^\circ = \Sigma\ \Delta H^\circ$(products) $- \Sigma\ \Delta H^\circ$(reactants) (06) (06) (06) (02)

$\Delta H_2^\circ = [-84.7 \times 2 - 214.8 \times 2 - (-74.8 \times 4)]$ kJ mol^{-1} = **−299.8 kJ mol^{-1}** (03 + 01)



1

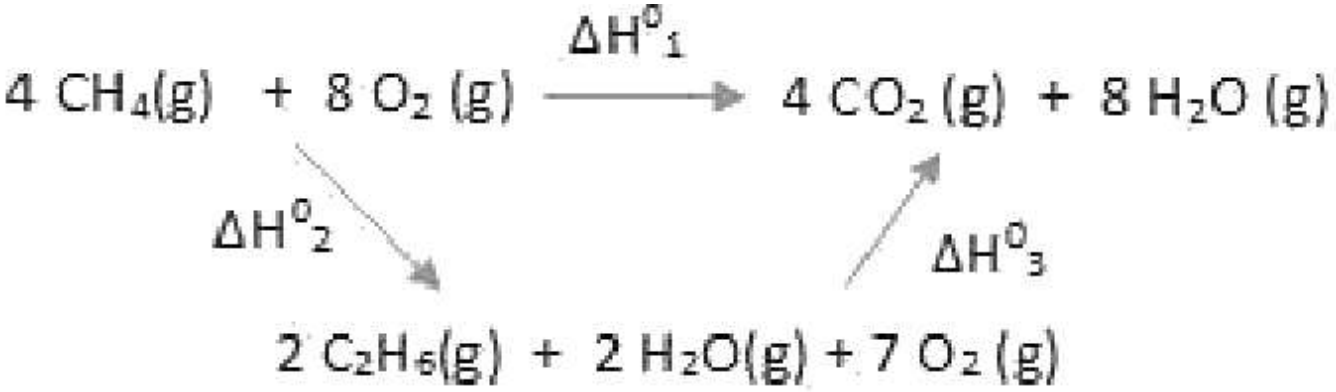
3

Alternate thermodynamic cycle

2

2

(02 marks × 7 = 14)



2

2

$\Delta H_1^\circ = (-393.5 \times 4 - 214.8 \times 8 - (-74.8 \times 4 + 0 \times 8))$ kJ $mol^{-1} = -2993.2$ kJ mol^{-1} (02 each)
$\Delta H_3^\circ = ((-393.5 \times 4 - 214.8 \times 8) - (-84.7 \times 2 - 214.8 \times 2 - 0 \times 7))$ kJ $mol^{-1} = -2693.4$ kJ mol^{-1}
$\Delta H_2^\circ = \Delta H_1^\circ - \Delta H_3^\circ$ (03) = $(-2993.2 - (-2693.4))$ kJ mol^{-1} = **-299.8 kJ mol^{-1}** (03 + 01)

(ii) Calculate the standard entropy change for the reaction in (b)(i) above.

Answer

$\Delta S^\circ = \Sigma\ S^\circ$(products) $- \Sigma\ S^\circ$(reactants) (04)
$\Delta S^\circ = (229.6 \times 2 + 188.8 \times 2 - (186.3 \times 4 + 205.1 \times 1))$ J mol^{-1} K^{-1} (02) (02) (02) (02) (01) = **-113.5 J mol^{-1} K^{-1}** (02 + 01) (the scheme prints 186.2 for $S^\circ(CH_4)$, but the question gives 186.3 and −113.5 follows from 186.3)

(iii) Calculate the standard Gibbs energy change (ΔG°) for the reaction in (b)(i) above at 500 K.

Answer

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (04)
$= -299.8$ kJ $mol^{-1} - (500$ K $\times (-113.5 \times 10^{-3})$ kJ mol^{-1} $K^{-1})$ (04 + 01)
= **-243.05 kJ mol^{-1}** (02 + 01)

(iv) State, giving reasons, whether increase in temperature favours the reaction in (b)(i) above. Assume that the enthalpy change and entropy change are independent of temperature.

Answer

Increasing temperature does not favour the forward reaction. (03) (Or: increasing temperature makes the Gibbs energy change less negative.)
Because the reaction has a negative change in entropy. (03)
[If the sign of the entropy change is incorrect, but the prediction agrees with the sign of the entropy change, award 06 marks.] 5(b): 75 marks

Review.

Principle: Hess's law ($\Delta H^\circ = \Sigma\ \Delta H_f^\circ$(products) $- \Sigma\ \Delta H_f^\circ$(reactants), elements 0) and $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (U5 §2.2 and §2.4). Method: $\Delta H^\circ = 2(-84.7) + 2(-214.8) - 4(-74.8) = -299.8$ kJ mol^{-1}; $\Delta S^\circ = 2(229.6) + 2(188.8) - 4(186.3) - 205.1 = -113.5$ J K^{-1} mol^{-1}; $\Delta G^\circ(500\ K) = -299.8 + 500 \times 0.1135 = -243.05$ kJ mol^{-1}. Because ΔS° is negative, $-T\Delta S^\circ$ becomes more positive as T rises, so ΔG° becomes less negative and higher temperature disfavours the reaction (exothermic, fewer gas moles: 5 → 4). Common mistakes: not converting ΔS° to kJ before combining with ΔH°, wrong sign on ΔG°, and forgetting that $H_2O(g)$ has the ΔH_f° value given here (the data are as printed in the question, not textbook values).

Read: RB U4 §1.2 · p. 5 RB U5 §2.2 · p. 36 RB U5 §2.4 · p. 53 RB U4 §1.3 · p. 16

Question 6 · Part B · essay

(a) [80 marks]

(i) Consider the reversible reaction a A(aq) ⇌ b B(aq) + c C(aq) that occurs in the aqueous medium. Considering that both forward and reverse steps are elementary reactions, write expressions for the rate of the forward reaction (R_1) and the rate of the reverse reaction (R_2). Rate constants for the forward reaction and the reverse reaction are k_1 and k_2, respectively.

Answer

$R_1 = k_1$[A(aq)]^a (05 + 01)
$R_2 = k_2$[B(aq)]^b[C(aq)]^c (05 + 01) (the scheme prints "R = k [B(aq)]^b [C(aq)]^c")

(ii) Write the relationship between R_1 and R_2 at equilibrium.

Answer

At equilibrium, $R_1 = R_2$ (05)

(iii) Write down the expression for equilibrium constant K_C. Also give the relationship between K_C, k_1 and k_2.

Answer

K_C = [B(aq)]^b[C(aq)]^c/[A(aq)]^a (05 + 01) [expression 05 marks, physical states 01 mark]
$K_C = k_1/k_2$ (05)

(iv) To study the above equilibrium, three experiments were carried out at a constant temperature. In these experiments, different amounts of A, B and C were mixed, and the system was allowed to reach equilibrium. The following data were obtained at equilibrium.

Experiment Number	Concentration at equilibrium (mol dm^{-3})		
[A]	[B]	[C]	
1	1.0×10^{-1}	1.0×10^{-2}	1.0×10^{-3}
2	1.0×10^{-2}	1.0×10^{-3}	1.0×10^{-3}
3	1.0×10^{-2}	1.0×10^{-2}	1.0×10^{-5}

Answer

$K_C = (1.0 \times 10^{-2})^b (1.0 \times 10^{-3})^c/(1.0 \times 10^{-1})^a$ ... (1) (06)
$K_C = (1.0 \times 10^{-3})^b (1.0 \times 10^{-3})^c/(1.0 \times 10^{-2})^a$ ... (2) (06)
$K_C = (1.0 \times 10^{-2})^b (1.0 \times 10^{-5})^c/(1.0 \times 10^{-2})^a$ ... (3) (06)

II. Prove that a = b = 2c using these relationships.

Answer

From (1)/(2): $1 = 10^b/10^a$ (05), so $10^a = 10^b$, a = b (05)
From (2)/(3): $1 = 10^{2c}/10^b$ (05), so $10^b = 10^{2c}$
Therefore a = b = 2c (05)
Alternate answer 1: $K_C = 10^{-2b-3c+a}$ ... (4) (04); $K_C = 10^{-3b-3c+2a}$ ... (5) (04); $K_C = 10^{-2b-5c+2a}$ ... (6) (04). Taking logs: log $K_C = -2b - 3c + a$ (7); $= -3b - 3c + 2a$ (8); $= -2b - 5c + 2a$ (9). (4)/(5) or (7) − (8): a = b (04); (5)/(6) or (8) − (9): a = 2c (04). Therefore a = b = 2c.
Alternate answer 2: $K_C = (0.01)^b(0.001)^c(0.1)^{-a}$ (4); $K_C = (0.001)^b(0.001)^c(0.01)^{-a}$ (5); $K_C = (0.01)^b(0.00001)^c(0.01)^{-a}$ (6). (1)/(2): $1 = 10^b \times 10^{-a}$, so $10^a = 10^b$, a = b (05) + (05); (1)/(3): $1 = 10^{2c} \times 10^{-a}$, so a = 2c (05) + (05). Therefore a = b = 2c.

III. Using the smallest integers for the stoichiometric coefficients a, b and c, calculate the value of the equilibrium constant, K_C of the above reaction.

Answer

Using the smallest set of integers, a = 2, b = 2, c = 1
$K_C = (1.0 \times 10^{-2}$ mol $dm^{-3})^2 (1.0 \times 10^{-3}$ mol $dm^{-3})^1/(1.0 \times 10^{-1}$ mol $dm^{-3})^2$ ((02 + 01) × 3 = 09)
K_C = **1.0×10^{-5} mol dm^{-3}** (04 + 01) · 6(a): 80 marks

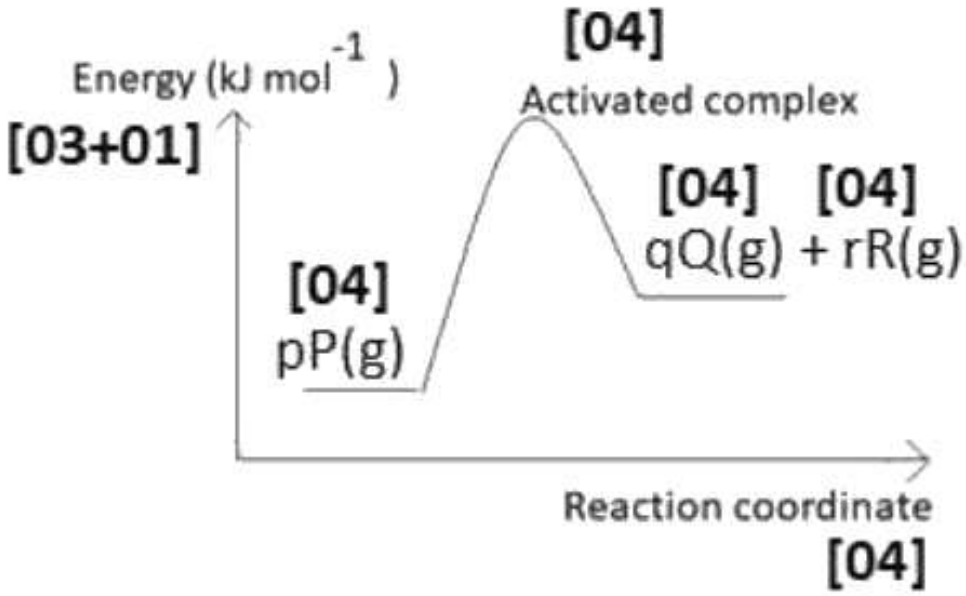
Review.

Principle: at equilibrium of an elementary reversible reaction the forward and reverse rates are equal, so $K_C = k_1/k_2$ (U12 §2.1; rate laws, U11 §1.6). Method: dividing the K_C expressions for different experiments cancels K_C and leaves a power-of-ten equation: (1)/(2) gives a = b and (2)/(3) gives b = 2c, so the smallest integers are 2A ⇌ 2B + C, with $K_C = (10^{-2})^2(10^{-3})/(10^{-1})^2 = 1.0 \times 10^{-5}$ mol dm^{-3} (check with experiment 2: $10^{-6} \times 10^{-3}/10^{-4} = 10^{-5}$). Common mistakes: writing the units of K_C wrongly (here Δn = +1 so mol dm^{-3}), forgetting that rate exponents equal stoichiometric coefficients only because the steps are elementary, and not simplifying powers of ten correctly.

(b) [70 marks]

Consider the reaction, p P(g) ⇌ q Q(g) + r R(g) that takes place in gas phase.
(i) The enthalpy change and activation energy of the forward reaction, p P(g) → q Q(g) + r R(g) are 50.0 kJ mol^{-1} and 90.0 kJ mol^{-1}, respectively. Draw the labelled energy diagram (the graph of energy vs reaction coordinate) for this reaction. Show the positions of P, Q and R by marking them on the energy diagram. Also, mark the position of the activated complex as 'activated complex' on it.

Answer



Energy diagram: pP(g) at lower energy, activated complex at the peak, qQ(g) + rR(g) higher than the reactants

The scheme marks: axes labelled, with Energy (kJ mol^{-1}) on the y-axis (03 + 01) and Reaction coordinate on the x-axis (04); pP(g) (04); activated complex (04); qQ(g) + rR(g) at a higher level than pP(g) (04 + 04). The forward reaction is endothermic (ΔH = +50.0 kJ mol^{-1}) and the peak lies 90.0 kJ mol^{-1} above P.

(ii) Calculate the activation energy for the reverse reaction.

Answer

E_a(reverse) = (90.0 − 50.0) kJ mol^{-1} (05 + 01) = **40.0 kJ mol^{-1}** (04 + 01)

(iii) Explain the effect of increasing temperature on the equilibrium constant of this reaction.

Answer

When the temperature is increased, the equilibrium constant is increased (05) because the reaction has a positive change in enthalpy (it is endothermic) (05). When the temperature is increased, the rate constant of the forward reaction is increased more than the rate constant of the reverse reaction. (05)

(iv) Explain the effect of a catalyst
I. on the rates of forward and reverse reactions.

II. on the equilibrium constant.

Answer

I. Increases the rate of the forward reaction (05) and the rate of the reverse reaction (05) by the same factor (extent). (05)
II. The value of the equilibrium constant is not changed. (05)
Alternate answer: I. It provides a new pathway for the reaction with higher rate constants for forward and reverse reactions (05). The ratio between the two rate constants does not change (05). Rate constants of the forward and reverse reactions are increased by the same factor (extent). (05) II. The value of the equilibrium constant is not changed. (05) · 6(b): 70 marks

Review.

Principle: an energy profile shows $\Delta H = E_a(\text{forward}) - E_a(\text{reverse})$, a catalyst lowers both activation energies equally, and K depends only on temperature through ΔH (van 't Hoff / Le Chatelier) (U11 §1.8, §1.9; U12 §2.1). Method: $E_a(\text{reverse}) = 90.0 - 50.0 = 40.0$ kJ mol^{-1}; an endothermic reaction has K increasing with T because $k_{forward}$ (larger E_a) rises faster than $k_{reverse}$. A catalyst gives a lower-energy pathway, raising $k_{forward}$ and $k_{reverse}$ by the same factor, so $K = k_1/k_2$ is unchanged and equilibrium is reached faster. Common mistakes: drawing products below reactants for an endothermic reaction, putting the activated complex at 50 rather than 90 kJ above P, and saying a catalyst shifts the equilibrium or changes ΔH.

Read: RB U12 §2.1 · p. 76 RB U11 §1.6 · p. 16 RB U11 §1.8 · p. 53 RB U11 §1.9 · p. 54

Question 7 · Part B · essay

(a) [75 marks]

You are provided with the three metal rods L, M, N and the three solutions L^{2+} (1.0 mol dm^{-3}), M^{2+} (1.0 mol dm^{-3}), N^{2+} (1.0 mol dm^{-3}). When the metal N is dipped in the solution of M^{2+} ions, M^{2+} is reduced to M, whereas when N is dipped in the solution of L^{2+} ions, L^{2+} does not get reduced to L.
(i) Giving reasons arrange the three metals, L, M and N in the increasing order of their reducing ability.

Answer

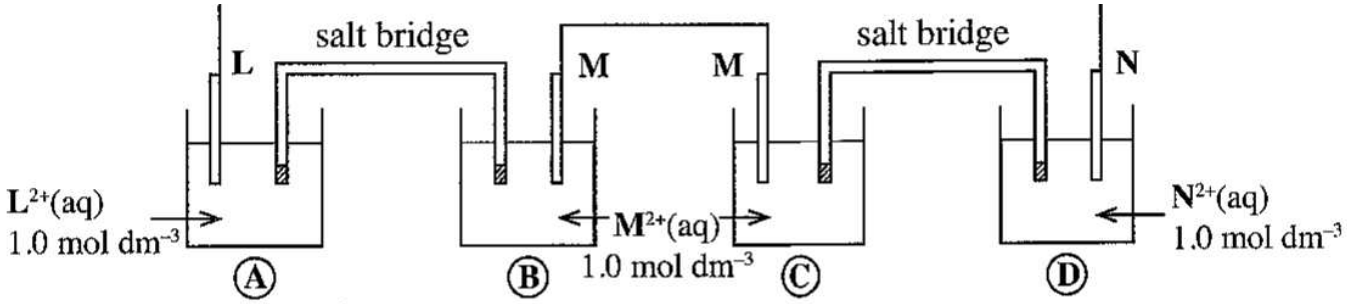
$N(s) + M^{2+}(aq) \rightarrow N^{2+}(aq) + M$ is spontaneous. Reducing ability N > M, or [$E°_{N^{2+}/N} < E°_{M^{2+}/M}$] (05)
$N(s) + L^{2+}(aq) \rightarrow N^{2+}(aq) + L$ is not spontaneous. Reducing ability L > N, or [$E°_{L^{2+}/L} < E°_{N^{2+}/N}$] (05)
Increasing order of reducing ability: **M < N < L** (05) (or increasing order of oxidizing ability L < N < M)

(ii) Electromotive forces of the two electrochemical cells prepared using $L^{2+}(aq)/L(s)$ electrode and each of the other two electrodes are +0.30 V and +1.10 V. Using this information and your answer to (i) above, calculate $E°_{M^{2+}(aq)/M(s)}$ and $E°_{N^{2+}(aq)/N(s)}$. ($E°_{L^{2+}(aq)/L(s)} = -0.80$ V)

Answer

Out of the two cells one has $E_{cell} = 0.30$ V and the other has $E_{cell} = 1.10$ V. The highest E_{cell} is between the $L^{2+}(aq)/L$ and $M^{2+}(aq)/M$ electrodes; the lowest E_{cell} is between the $L^{2+}(aq)/L$ and $N^{2+}(aq)/N$ electrodes.
$E°_{M^{2+}(aq)/M} - E°_{L^{2+}(aq)/L} = 1.10$ V (05); $E°_{M^{2+}(aq)/M} = 1.10 - 0.80$ V = **0.30 V** (05)
$E°_{N^{2+}(aq)/N} - E°_{L^{2+}(aq)/L} = 0.30$ V (05); $E°_{N^{2+}(aq)/N} = 0.30 + (-0.80)$ V = **−0.50 V** (05)
Alternate answer: Based on the order of reducing ability, L^{2+}/L should be the anode in both cells. $E°_{cathode} - E°_{L^{2+}/L} = 1.10$ V, so $E°_{cathode} = 1.10 - 0.80 = 0.3$ V (05); $E°_{cathode} - E°_{L^{2+}/L} = 0.3$ V, so $E°_{cathode} = 0.3 - 0.80 = -0.5$ V (05). Therefore $E°_{M^{2+}/M} = 0.3$ V (05) and $E°_{N^{2+}/N} = -0.5$ V (05).

(iii) You are provided with the following arrangement, where a potentiometer (P) is connected between the metal rods L and N.



2+

2+

2+

I. Calculate the potentiometer reading.
II. Write the electrode reactions that occur at each of the electrodes (A), (B), (C) and (D) separately when the potentiometer is removed and L and N are connected by a conductor.

Answer

I. Potentiometer reading P = $E°_{cell}(1) + E°_{cell}(2)$ (05)
= $(E°_{M^{2+}(aq)/M} - E°_{L^{2+}(aq)/L}) + (E°_{N^{2+}(aq)/N} - E°_{M^{2+}(aq)/M})$ (05)
= $E°_{N^{2+}(aq)/N} - E°_{L^{2+}(aq)/L}$ (05) = −0.50 V − (−0.80 V) = **0.30 V** (05)
II. Electrode reactions when a current is drawn:
Electrode (A): L(s) → $L^{2+}(aq) + 2e$ (05)
Electrode (B): $M^{2+}(aq) + 2e \rightarrow M(s)$ (05)
Electrode (C): M(s) → $M^{2+}(aq) + 2e$ (this line is missing from the printed scheme, which gives 05 marks each for A, B and D and totals 75; it follows from the arrangement, since M at B is reduced and M at C is oxidised)
Electrode (D): $N^{2+}(aq) + 2e \rightarrow N(s)$ (05) · 7(a): 75 marks

Review.

Principle: a spontaneous displacement shows the more strongly reducing metal; cell emf = $E°_{cathode} - E°_{anode}$; emfs of cells in series add, so the intermediate M electrodes cancel (U13 §3.2, §3.3). Method: N reduces M^{2+} so N is a stronger reducer than M; N does not reduce L^{2+}, so L is stronger still: M < N < L, hence E° (M) > E° (N) > E° (L). Emfs 1.10 V (L with M) and 0.30 V (L with N) give $E°_M$ = +0.30 V and $E°_N$ = −0.50 V. Potentiometer reading = $E°_N - E°_L$ = 0.30 V. With a conductor, the most reducing metal L is the anode (oxidation) and N^{2+} is reduced at D. Common mistakes: reversing the cell emf direction, adding the potentials of the two intermediate M electrodes instead of letting them cancel, and writing reductions at the anode.

(b) [75 marks]

The following questions are based on the element manganese (Mn).
(i) Write the complete electronic configuration of Mn.

Answer

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$ (03)

(ii) Write **three** common oxidation states of Mn.

Answer

+2, +3, +4, +7 (any three) (02 × 3)

(iii) When $MnSO_4 \cdot H_2O$ is dissolved in water, solution P is obtained.
I. State the colour of solution P.

II. Give the chemical formula and the IUPAC name of the species responsible for this colour.

Answer

I. Very pale pink / pale pink / colourless (03)
II. $[Mn(H_2O)_6]^{2+}(aq)$ (03); hexaaquamanganese(II) ion (03)

(iv) What would you observe when
I. dilute NaOH is added to solution P?
II. the mixture from (iv)(I) above is exposed to air?
III. conc. HCl is added to the mixture from (iv)(I) above?

Answer

I. White / cream precipitate (03)
II. Brown precipitate or blackish-brown precipitate (03)
III. Yellow / greenish-yellow solution (03)

(v) Give the chemical formulae of **five** oxides of Mn, and write the oxidation state of Mn in each. State the nature of each of the oxides as basic, weakly basic, amphoteric, weakly acidic, acidic.

Answer

Oxide	Oxidation state	Nature
MnO	+2	basic
Mn_2O_3	+3	weakly basic
MnO_2	+4	amphoteric
MnO_3	+6	weakly acidic
Mn_2O_7	+7	acidic

(02 × 3 for each oxide)

(vi) Give the chemical formula of the most common oxoanion of Mn.

Answer

MnO_4^− (03)

(vii) Give balanced ionic half equations to indicate how the oxoanion given by you in (vi) above behaves as an oxidizing agent in acidic and basic media.

Answer

Acidic: MnO_4^−(aq) + $8H^+(aq)$ + 5e → $Mn^{2+}(aq)$ + $4H_2O(l)$ (06)
Alkaline: MnO_4^−(aq) + $2H_2O(l)$ + 3e → $MnO_2(s)$ + $4OH^-(aq)$ (06)

(viii) State **one** use of $MnSO_4$ in the analysis of water quality parameters.

Answer

Determination of dissolved O_2 in water samples (03) · 7(b): 75 marks

Review.

Principle: 3d-block chemistry of Mn: variable oxidation states, the pale pink $[Mn(H_2O)_6]^{2+}$, $Mn(OH)_2$ oxidising in air, acidic character rising with oxidation state, and $KMnO_4$ as an oxidant (U6 §4.10, §4.10.6; Winkler DO method, U14 §1.14). Method: Mn^{2+} + OH^- gives white $Mn(OH)_2$, which is oxidised by O_2 to brown $MnO(OH)_2$ / MnO_2; conc. HCl dissolves the brown Mn(IV) compound (it is reduced by Cl^-, forming Cl_2 and

chloro-manganese species), giving a yellow/greenish-yellow solution. Oxides become more acidic as Mn's oxidation state rises (MnO basic to Mn_2O_7 acidic). Common mistakes: writing $Mn^{2+}(aq)$ as strongly coloured, giving MnO_4^− products that do not balance in charge (check: acidic $8H^+ - 1 + 5e^-$: +8 − 1 − 5 = +2 ✓), and confusing the two reduction products of permanganate (Mn^{2+} in acid, MnO_2 in base).

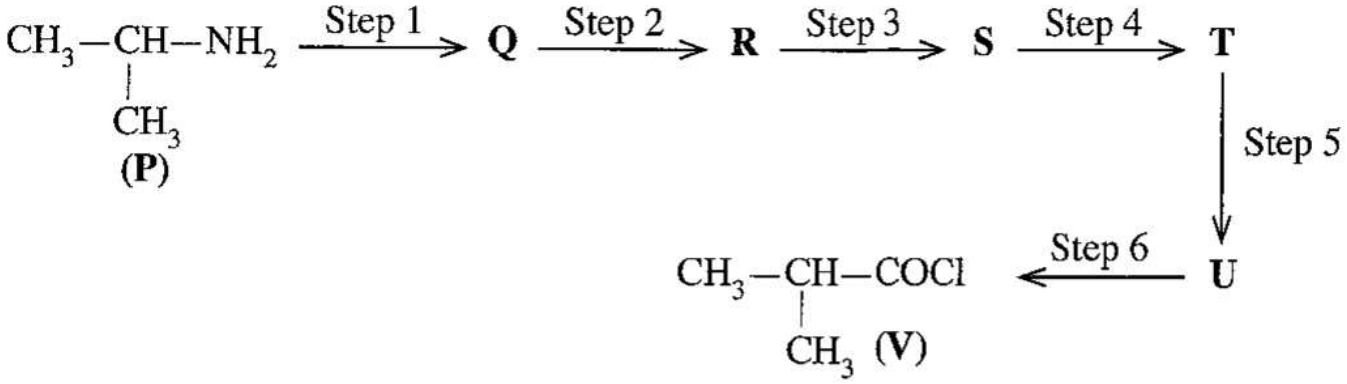
Read: RB U13 §3.2 · p. 238 RB U13 §3.3 · p. 250 RB U6 §4.10 · p. 160 RB U6 §4.10.6 · p. 169

Part C

Question 8 · Part C · essay

(a) [65 marks]

Compound P was converted to compound V using the reaction scheme given below.



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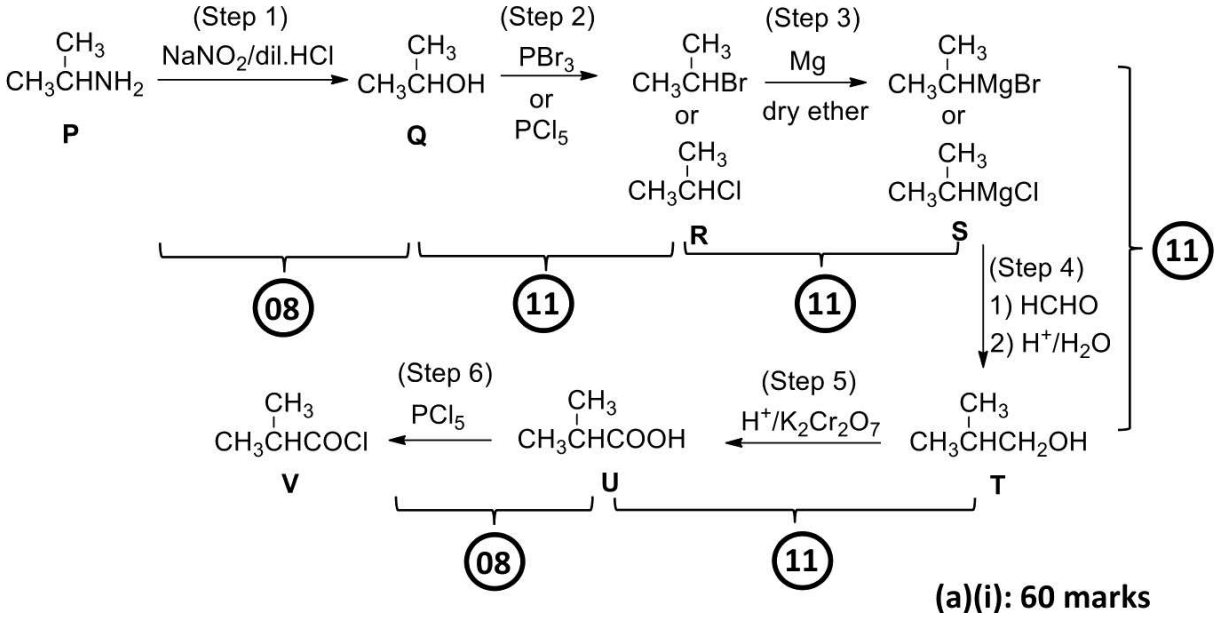
3

(i) Complete the above reaction sequence by drawing the structures of compounds Q, R, S, T and U and writing the reagents for steps 1–6 selected only from those given in the list below.
List of reagents: HCHO, Mg/dry ether, $H^+/K_2Cr_2O_7$, PCl_5, PBr_3, $NaNO_2$/dilute HCl, H^+/H_2O
(Note: The reaction of a compound with a Grignard reagent and the hydrolysis of the resultant magnesium alkoxide should be considered as **one step** in the above reaction sequence.)

Answer

Step 1: $NaNO_2$/dil. HCl → Q = $CH_3CH(CH_3)OH$ (propan-2-ol) (08)
Step 2: PBr_3 or PCl_5 → R = $(CH_3)_2CHBr$ or $(CH_3)_2CHCl$ (11)
Step 3: Mg/dry ether → S = $(CH_3)_2CHMgBr$ or $(CH_3)_2CHMgCl$ (11)
Step 4: (1) HCHO; (2) H^+/H_2O → T = $(CH_3)_2CHCH_2OH$ (2-methylpropan-1-ol) (11)
Step 5: $H^+/K_2Cr_2O_7$ → U = $(CH_3)_2CHCOOH$ (2-methylpropanoic acid) (11)
Step 6: PCl_5 → V = $(CH_3)_2CHCOCl$ (08) · (a)(i): 60 marks
*In Step 4 the student may have misinterpreted the instruction given in the note in the question and written HCHO and H^+/H_2O without showing the sequence 1 and 2 (the scheme allows this).

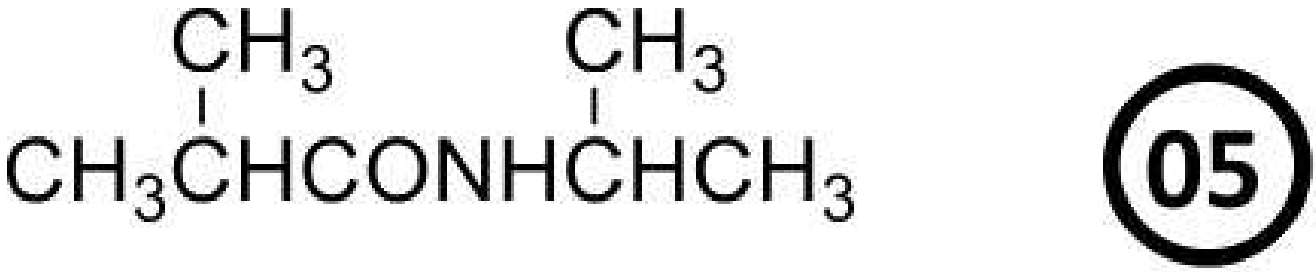


Scheme answer: structures Q, R, S, T, U and reagents for steps 1–6 with mark allocation

(ii) Draw the structure of the product formed when compounds P and V react with each other.

Answer

$(CH_3)_2CH–CO–NH–CH(CH_3)_2$ (N-isopropyl-2-methylpropanamide, an amide) (05) · (a)(ii): 05 marks · 8(a): 65 marks



Amide formed from P and V

Review.

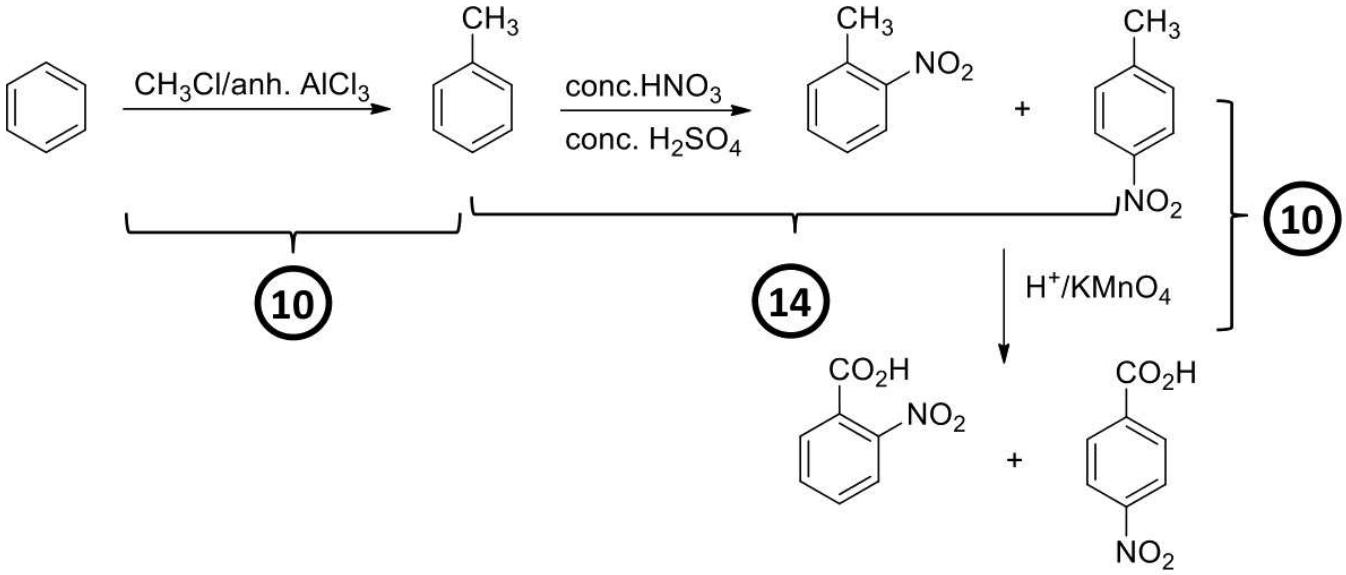
Principle: amine → diazotisation-type conversion to alcohol → alkyl halide → Grignard reagent → one-carbon chain extension with HCHO to a primary alcohol → oxidation to carboxylic acid → acid chloride; amine + acid chloride → amide (U10 §4.3, U8 §2.7, U9 §3.1, §3.6). Method: HCHO adds to R–MgX to give $R–CH_2OMgX$, hydrolysed to the primary alcohol RCH_2OH, which $K_2Cr_2O_7/H^+$ oxidises to the acid; PCl_5 converts the acid to the acid chloride. The product of P with V is the amide formed by nucleophilic acyl substitution. Common mistakes: using $H^+/K_2Cr_2O_7$ too early (it would convert Q to a ketone), using PCl_5/PBr_3 where the alcohol must first be made, forgetting that the Grignard + HCHO + H^+/H_2O is one step, and giving an ammonium salt rather than an amide.

(b) [65 marks]

(i) Propose a method to prepare a mixture of o-nitrobenzoic acid and p-nitrobenzoic acid from benzene using not more than **three** (03) steps.

Answer

Benzene → (CH_3Cl/anhyd. $AlCl_3$) → toluene (10) → (conc. HNO_3/conc. H_2SO_4) → o-nitrotoluene + p-nitrotoluene (14) → ($H^+/KMnO_4$) → o-nitrobenzoic acid + p-nitrobenzoic acid (10) · (b)(i): 34 marks

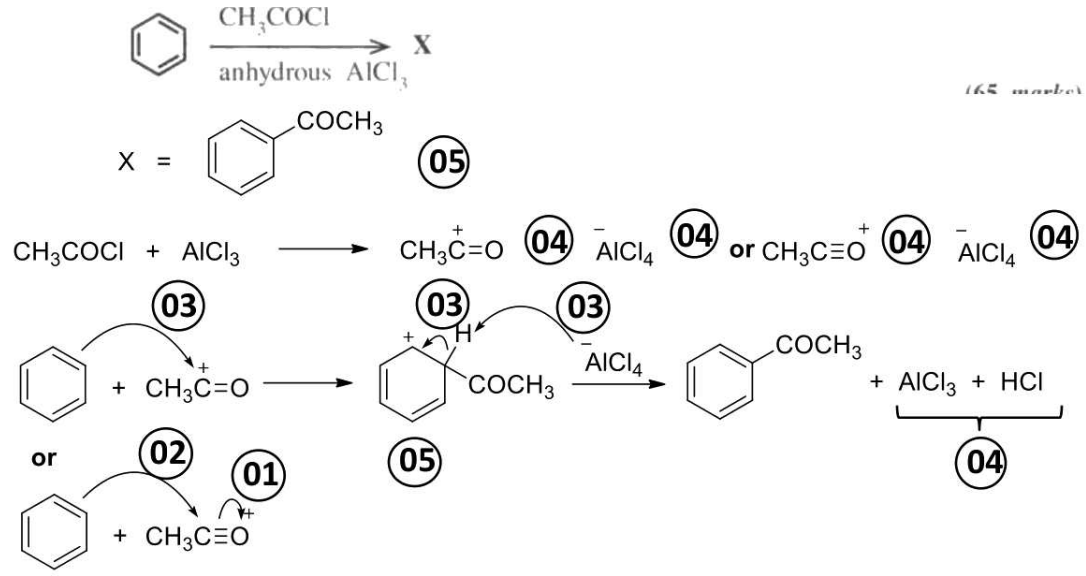


Benzene → toluene → o- and p-nitrotoluene → o- and p-nitrobenzoic acids

(ii) Give the structure of the product X and the mechanism of the following reaction: benzene → (CH_3COCl, anhydrous $AlCl_3$) → X

Answer

X = acetophenone ($C_6H_5COCH_3$) (05)
Formation of the electrophile: $CH_3COCl + AlCl_3 \rightarrow CH_3C^+{=}O$ (04) + $AlCl_4{\wedge}-$ (04) (or $CH_3{-}C{\equiv}O^+$ (04) + $AlCl_4{\wedge}-$ (04))
Attack of the benzene ring on the acylium ion (curved arrow from the ring to C^+) (03) (or, for $CH_3{-}C{\equiv}O^+$, arrows (02) + (01)); formation of the carbocation (σ-complex) intermediate (05); $AlCl_4{\wedge}-$ removes H^+ from the ring (curved arrows) (03) + (03) to give $C_6H_5COCH_3 + AlCl_3 + HCl$ (04) · (b)(ii): 31 marks · 8(b): 65 marks



Friedel–Crafts acylation mechanism

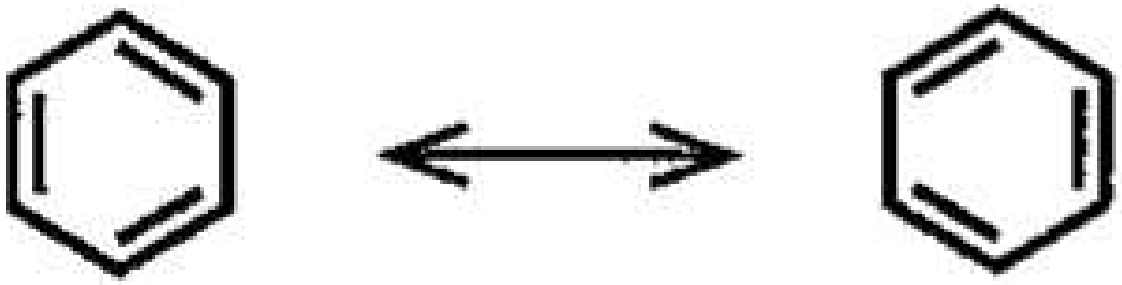
Review.

Principle: electrophilic aromatic substitution; Friedel–Crafts alkylation then acylation of the ring (U8 §2.4, §2.5). Method: a $-CH_3$ group directs ortho/para, and nitration gives o- and p-nitrotoluene; the methyl group is then oxidised to –COOH (a nitro-substituted ring survives). The order matters: nitrating benzoic acid would give the meta isomer, so the CH_3 group is introduced first and oxidised last. In (ii) $AlCl_3$ converts CH_3COCl

into the acylium ion CH_3CO^+, the electrophile, and is regenerated at the end. Common mistakes: nitrating before alkylating (nitrobenzene does not undergo Friedel–Crafts), oxidising before nitrating (the –COOH group is meta-directing), and omitting the σ-complex or the regeneration of $AlCl_3$.

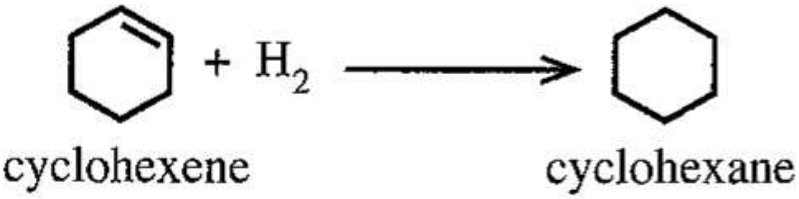
(c) [20 marks]

The structure of benzene is represented as the resonance hybrid of the following two hypothetical six membered cyclic structures (cyclohexatriene).



The two hypothetical cyclohexatriene (Kekulé) structures

Using the standard enthalpy data of hydrogenation given below, show that benzene is more stable than hypothetical 'cyclohexatriene'.



$\Delta H^\circ = -120 \text{ kJ mol}^{-1}$

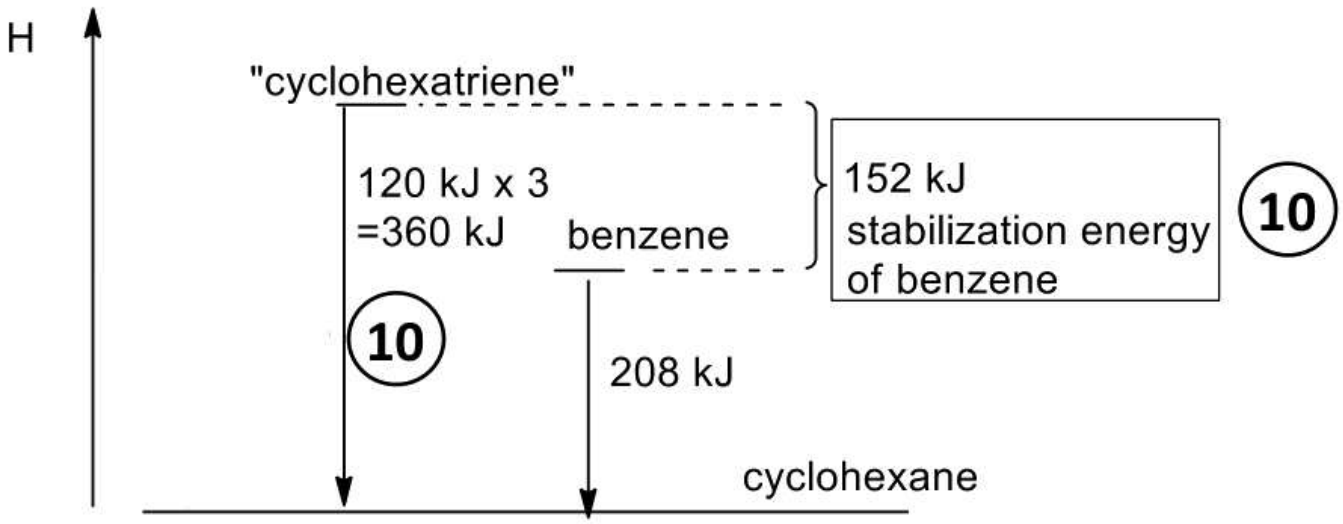
2

−1

Benzene + $3H_2$ → cyclohexane, $\Delta H^\circ = -208 \text{ kJ mol}^{-1}$

Answer

Standard enthalpy of hydrogenation of cyclohexene = -120 kJ mol^{-1}
Expected enthalpy of hydrogenation of hypothetical 'cyclohexatriene' = $-120 \times 3 \text{ kJ mol}^{-1} = -360 \text{ kJ mol}^{-1}$ (10)
Standard enthalpy of hydrogenation of benzene = -208 kJ mol^{-1}
Stabilization energy of benzene = -152 kJ mol^{-1} (benzene is 152 kJ mol^{-1} more stable) (10)
OR by an enthalpy diagram: 'cyclohexatriene' at the top, 120 × 3 = 360 kJ down to cyclohexane; benzene 208 kJ above cyclohexane; 152 kJ stabilization energy of benzene (10 + 10).
NB. 10 marks for calculating the expected enthalpy of hydrogenation of 'cyclohexatriene'; 10 marks for stating or indicating the stabilization of benzene. These 10 marks can be awarded even if the stabilization energy is not calculated but is indicated by a statement such as: hydrogenation of both benzene and 'cyclohexatriene' (with $3H_2$) gives cyclohexane; however, benzene (releases less energy, i.e. is more stable).
8(c): 20 marks



Enthalpy diagram: cyclohexatriene, benzene and cyclohexane

Review.

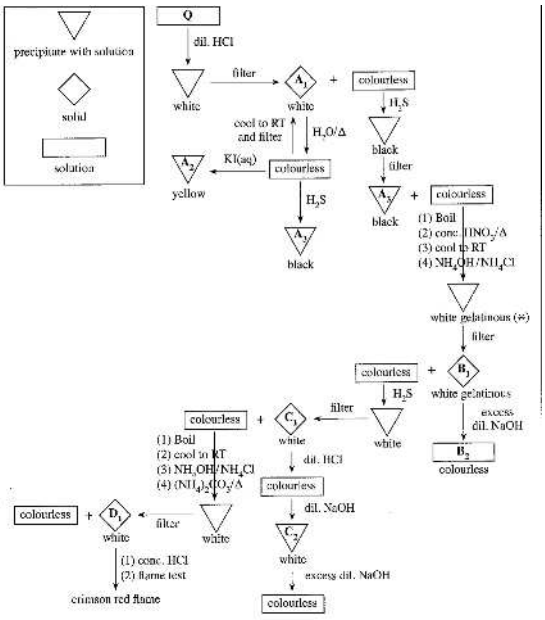
Principle: delocalisation (resonance) stabilises benzene, and the stabilisation energy is the difference between the enthalpy of hydrogenation expected for three isolated C=C bonds and the measured value (U8 §2.4). Method: 3 × (−120) = −360 kJ mol^{-1} expected; measured −208 kJ mol^{-1}; difference 152 kJ mol^{-1}, so benzene is more stable than the hypothetical localised cyclohexatriene. Common mistakes: forgetting the factor of 3, subtracting in the wrong direction (the answer is a stabilisation, not a destabilisation), and quoting the sign of the energy incorrectly.

Read: RB U10 §4.3 · p. 78 RB U8 §2.7 · p. 50 RB U9 §3.6 · p. 70 RB U8 §2.4 · p. 44

Question 9 · Part C · essay

(a) [75 marks]

The following question is based on the qualitative analysis of cations. An aqueous solution Q contains **four** cations of metals A, B, C and D. Q is subjected to the reactions given in the scheme below. The symbols given in the box are used to represent precipitates with solutions, solids and solutions. (Note: RT – room temperature)



1

2

3

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2

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1

(i) A_1, A_2, A_3, B_1, B_2, C_1, C_2 and D_1 are compounds/species of the four cations A, B, C and D. Identify A_1, A_2, A_3, B_1, B_2, C_1, C_2 and D_1.
(Note: Write **only** chemical formulae. Chemical equations and reasons are **not** required.)

Answer

$A_1 = PbCl_2$; $A_2 = PbI_2$; $A_3 = PbS$; $B_1 = Al(OH)_3$; $B_2 = NaAlO_2$ or AlO_2^− or $[Al(OH)_4]^-$ or $Na[Al(OH)_4]$; $C_1 = ZnS$; $C_2 = Zn(OH)_2$; $D_1 = SrCO_3$ (08 marks × 8 = 64 marks)

(ii) Give a reason for the use of NH_4OH/NH_4Cl as a reagent when obtaining the white gelatinous precipitate (∗).

Answer

NH_4OH is added to precipitate the Group III ions (Fe^{3+}, Al^{3+} and Cr^{3+}) as hydroxides. (02) Then, the hydroxides of Group IV metal ions (Zn^{2+}, Mn^{2+}, Co^{2+} and Ni^{2+}) may also precipitate together with the hydroxides of Group III metal ions. (02)
NH_4Cl is added to reduce the concentration of OH^- (common ion effect) (02), or: addition of NH_4Cl shifts the equilibrium position of $NH_4OH(aq) \rightleftharpoons NH_4$^+(aq) + $OH^-(aq)$ so that the concentration of OH^- is reduced.
The K_{sp} of hydroxides of Group IV metal ions is greater than those of the Group III metal ions. (02)
This allows Fe^{3+}, Al^{3+} and Cr^{3+} hydroxides to be precipitated while the hydroxides of Zn^{2+}, Mn^{2+}, Co^{2+} and Ni^{2+} remain in solution. (03) · (11 marks)
Alternate answer: NH_4OH is added to precipitate Al^{3+} as the hydroxide (02). However, then both Zn^{2+} and Al^{3+} can be precipitated as their hydroxides (02). NH_4Cl is added to reduce the concentration of OH^- (common ion effect) (02) (or it shifts the equilibrium $NH_4OH \rightleftharpoons NH_4$^+ + OH^- so that $[OH^-]$ is reduced). K_{sp} of $Zn(OH)_2$ > $Al(OH)_3$ (02). Therefore precipitation of $Zn(OH)_2$ can be prevented by using NH_4Cl/NH_4OH (03) · (11 marks) · 9(a): 75 marks

Review.

Principle: group separation of cations by sulfides and hydroxides under controlled $[S^{2-}]$ and $[OH^-]$, using K_{sp} and the common-ion effect (U12 §2.4; reactions of the cations, U6 §4.10). Method: Q + dil. HCl precipitates $PbCl_2$ (A_1: white, dissolves in hot water; the hot filtrate gives yellow PbI_2 with KI and black PbS with H_2S). The filtrate + H_2S in acid gives black PbS (A_3). After boiling off H_2S, oxidising with conc. HNO_3 (oxidising any Fe^{2+} to Fe^{3+}), NH_4OH/NH_4Cl precipitates white gelatinous $Al(OH)_3$ (B_1), which dissolves in excess NaOH to $[Al(OH)_4]^-$ (B_2). The filtrate + H_2S (in the ammoniacal medium) gives white ZnS (C_1), which dissolves in dil. HCl and then gives white $Zn(OH)_2$ (C_2) with dil. NaOH, soluble in excess (zincate). The final filtrate + $(NH_4)_2CO_3$ gives white $SrCO_3$ (D_1), which gives a crimson-red flame with conc. HCl. Common mistakes: writing $Zn(OH)_2$ instead of ZnS for C_1, confusing the white gelatinous precipitate with $Zn(OH)_2$, and not giving a reason involving both the common-ion effect and the K_{sp} difference between Group III and Group IV hydroxides.

(b) [75 marks]

A mixture X contains only aluminium sulfide (Al_2S_3) and ferric sulfide (Fe_2S_3). The following procedure was carried out to calculate the mass percentages of Al_2S_3 and Fe_2S_3 in X.
When a mass **m** of mixture X was heated at high temperature under H_2 gas, Al_2S_3 remains unchanged but Fe_2S_3 was converted to iron (Fe) metal. The final mass obtained was 0.824 g.
When another mass **m** of mixture X was heated at high temperature in air, both Al_2S_3 and Fe_2S_3 decomposed, giving SO_2 gas. This SO_2 gas was bubbled through a solution of H_2O_2 and oxidized to H_2SO_4 acid, which is the only product. When this entire solution was titrated with a standard 1.00 mol dm^{-3} NaOH solution in the presence of phenolphthalein indicator, the burette reading was 36.00 cm^3.
(Relative atomic mass: Al = 27, S = 32, Fe = 56)
(i) Write the balanced chemical equation for the reaction of Fe_2S_3 with hydrogen gas.

Answer

$Fe_2S_3 + 3H_2 \rightarrow 2Fe + 3H_2S$ (04)

(ii) Write the balanced chemical equation for the reaction of SO_2 with H_2O_2 to give H_2SO_4.

Answer

$SO_2 + H_2O_2 \rightarrow H_2SO_4$ (04)

(iii) Calculate the mass percentages of Al_2S_3 and Fe_2S_3 in mixture X.

Answer

$2Al_2S_3 + 9O_2 \rightarrow 2Al_2O_3 + 6SO_2$, or $Al_2S_3 : SO_2 = 1 : 3$ (03)
$2Fe_2S_3 + 9O_2 \rightarrow 2Fe_2O_3 + 6SO_2$, or $Fe_2S_3 : SO_2 = 1 : 3$ (03)
$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$, or $H_2SO_4 : NaOH = 1 : 2$ (03)
Molar mass of $Al_2S_3 = (27 \times 2) + (32 \times 3) = 150$ (02); molar mass of $Fe_2S_3 = (56 \times 2) + (32 \times 3) = 208$ (02) (the scheme prints 218 here, but uses 208 in all the working)
Let the masses of Al_2S_3 and Fe_2S_3 be m_1 and m_2. Mass of Fe from Fe_2S_3 after heating under $H_2 = (m_2/208) \times 56 \times 2$ (04)
Total mass after heating under H_2: $m_1 + (m_2/208) \times 56 \times 2 = 0.824$ g ... [1] (08)
Heating in air: moles of H_2SO_4 from $Al_2S_3 = (m_1/150) \times 3$ (04); from $Fe_2S_3 = (m_2/208) \times 3$ (04); total = $(m_1/150) \times 3 + (m_2/208) \times 3$ (04)
Moles of NaOH = $(1/1000) \times 36$ (02); moles of H_2SO_4 from titration = $(1/1000) \times (36/2) = 18 \times 10^{-3}$ (02)
$3m_1/150 + 3m_2/208 = 18 \times 10^{-3}$ ... [2] (08)
Solving [1] and [2]: $m_1/50 + 3m_2/208 = 0.018$ [3]; [3] × 50: $m_1 + 150m_2/208 = 0.900$ [4]; [4] − [1]: $150m_2/208 - 112m_2/208 = 0.900 - 0.824$, so m_2 = **0.416 g** (02); $m_1 = 0.824 - 0.416 \times 112/208$ = **0.600 g** (02)
% $Al_2S_3 = 0.600/(0.416 + 0.600) \times 100\%$ = **59.06% (or 59%)** (04); % $Fe_2S_3 = 100 - 59.06$ = **40.94% (or 41%)** (04)
Alternate answer 01: let the moles of $Al_2S_3 = n_1$ and $Fe_2S_3 = n_2$. $150n_1 + 112n_2 = 0.824$ [1] (08); $3n_1 + 3n_2 = 0.018$ [2] (08) ($n(H_2SO_4)$ from $Al_2S_3 = 3n_1$ (04), from $Fe_2S_3 = 3n_2$ (04), total (04); n(NaOH) = 36/1000 (02); $n(H_2SO_4) = 18 \times 10^{-3}$ (02)). [2] × 50: $150n_1 + 150n_2 = 0.9$ [3]; [3] − [1]: $38n_2 = 0.076$, $n_2 = 0.002$ mol (02); $3n_1 + 3 \times 0.002 = 0.018$, $n_1 = 0.004$ mol (02). Mass of $Al_2S_3 = 0.004 \times 150 = 0.600$ g; mass of $Fe_2S_3 = 0.002 \times 208 = 0.416$ g; % Al_2S_3 = 59.06% or 59% (04); % Fe_2S_3 = 40.94% or 41% (04).
Alternate answer 02: let the mass of Al_2S_3 in the 0.824 g be m. $n_{Fe} = (0.824 - m)/56$ mol (06); $n_{Fe2S3} = ½(0.824 - m)/56$ mol (06) [1]; $n_{SO2} = 3 \times m/150 + 3 \times ½(0.824 - m)/56$ mol (10); n(NaOH) = 36/1000 mol (02); $n(H_2SO_4) = 18 \times 10^{-3}$ mol (02); so $3 \times m/150 + 3 \times ½(0.824 - m)/56 = 0.018$ [2] (10). Then $m/150 + (0.824 - m)/112 = 0.006$; $112m + 150(0.824 - m) = 0.006 \times 150 \times 112$; $38m = 22.8$, $m = m_{Al2S3} = 0.60$ g (02); $n_{Fe2S3} = ½(0.824 - 0.60)/56 = 0.002$ mol; $m_{Fe2S3} = 0.002 \times 208 = 0.416$ g (02); % Al_2S_3 = 59.06% or 59% (04); % Fe_2S_3 = 40.94% or 41% (04).

(iv) If the above titration is carried out using methyl orange as the indicator instead of phenolphthalein, would there be a change in the burette reading? Explain your answer.

Answer

No (02)
Because this is a strong acid – strong base titration (02), so the colour-change pH intervals of methyl orange and phenolphthalein both fall within the vertical region of the titration curve. (02) · 9(b): 75 marks

Review.

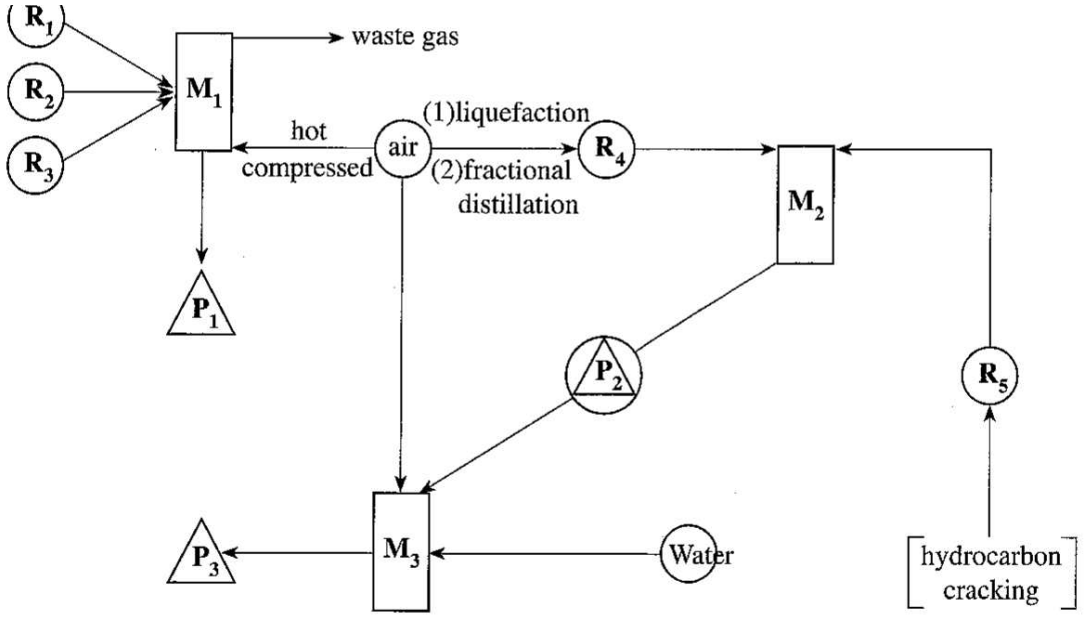
Principle: stoichiometry of two linked experiments giving two simultaneous equations (U3 §3.8), and acid–base indicator choice for a strong acid–strong base titration (U12 §2.2). Method: one equation from the mass after H_2 reduction ($m_1 + 112m_2/208 = 0.824$) and one from the $SO_2 \rightarrow H_2SO_4$ titration ($3m_1/150 + 3m_2/208 = 0.018$); solving gives 0.600 g Al_2S_3 and 0.416 g Fe_2S_3, i.e. 59.06% and 40.94%. Check: $0.600 + 0.416 \times 112/208 = 0.824$ g and $3(0.004 + 0.002) = 0.018$ mol. Common mistakes: using the Fe_2S_3 molar mass 218 (it is 208), forgetting that Fe_2S_3 loses its sulfur on reduction (2 mol Fe_2S_3, 416 g, leaves 4 mol Fe, 224 g; equivalently 208 g Fe_2S_3 leaves 112 g Fe), forgetting that 1 mol H_2SO_4 needs 2 mol NaOH, and wrongly saying the indicator changes the end point for a strong acid–strong base titration.

Read: RB U6 §4.10 · p. 160 RB U12 §2.4 · p. 175 RB U3 §3.8 · p. 115

Question 10 · Part C · essay

(a) [50 marks]

The following flow chart shows the industrial extraction/production of three important elements/compounds P_1, P_2 and P_3. There is evidence to show that our ancestors produced P_1 thousands of years ago. P_1 is used as a catalyst in M_2. P_3 is used in the manufacture of explosives.



1

2

3

1

1

4

2

5

2

2

3

3

(i) Name the manufacturing processes M_2 and M_3. (e.g.: Manufacture of Na_2CO_3 is named as Solvay process.)

Answer

M_2 – Manufacture of NH_3 by the Haber process (02)
M_3 – Manufacture of HNO_3 by the Ostwald process (02)

(ii) Identify the process M_1 and name the main constituent of its waste gas.

Answer

M_1 – extraction of Fe (iron) (02); waste gas: N_2 gas (02)

(iii) Give the common names of the raw materials R_1, R_2 and R_3 used in M_1.
(Note: R_1 functions as a reducing agent as well as an energy source in M_1; R_2 is a naturally occurring source which can be used to obtain P_1.)

Answer

R_1 – coke (02); R_2 – iron ore / hematite (02); R_3 – limestone (02)

(iv) Write a balanced chemical equation for the role of R_1 as a reducing agent in M_1 process.

Answer

As a reducing agent: $FeO(s) + C(s) \rightarrow Fe(l) + CO(g)$ (02)
Or $CO_2(g) + C(s) \rightarrow 2CO(g)$
Or $2FeO(s) + C(s) \rightarrow 2Fe(l) + CO_2(g)$

(v) Identify R_4 and R_5.

Answer

R_4 – $N_2(g)$ (02); R_5 – $H_2(g)$ (02)

(vi) Give balanced chemical equations for reactions taking place in the processes M_1, M_2 and M_3. Appropriate conditions (temperature, pressure, catalysts, etc.) must be stated as required.
(Note: For the M_1 process, give only the reactions showing the conversion of R_2 to P_1.)

Answer

1

2

3

3

4

2

2

3

3

4

2

(02)

3

4

2

(02)

2

2

(02)

2

2

2

3

(02)

(01)

(01)

(01)

2

2

3

(01)

3

3

2

2

(01)

(01)

(02)

2

2

(02)

2

2

2

3

(02)

(vii) Give **two** uses each of P_1, P_2 and P_3 (**other than** what is indicated in the flow chart or given in the question).

Answer

P_1 (Fe): to make alloy steel / construction industry to provide strength to structures / machinery and tool manufacture (01 × 2)
P_2 (NH_3): production of fertilizers / production of nylon / in the petroleum industry to neutralize acids in crude oil constituents / water and waste water treatment / as a refrigerant / to prevent coagulation of rubber (01 × 2)
P_3 (HNO_3): manufacture of fertilizer / in industries which require nitrates such as KNO_3 in explosive manufacture and $AgNO_3$ in photography / to clean surfaces when welding metals / aqua regia (01 × 2)

(viii) State whether the M_2 process would be favoured at very high temperatures. Explain your answer using ΔH, ΔS and ΔG.

Answer

The reaction is exothermic, ΔH is negative (−ve). The number of gaseous moles decreases, so ΔS is negative (−ve) (01).
According to ΔG = ΔH − TΔS: when ΔS is negative, the −TΔS term is positive (01). As temperature increases, the positive term overrides the negative term, making ΔG positive (01). Therefore the process is not favoured at high temperature. (01) · 10(a): 50 marks

Review.

Principle: industrial chemistry of iron (blast furnace), ammonia (Haber) and nitric acid (Ostwald), and the Gibbs-energy criterion ΔG = ΔH − TΔS (U14 §1.10, §1.6; U5 §2.4). Method: identify the processes from the clues (P_1 = Fe, a catalyst in the Haber process; $R_4 = N_2$ from liquefied air; $R_5 = H_2$ from hydrocarbon cracking; $P_2 = NH_3$; $P_3 = HNO_3$ for explosives). In the blast furnace, coke gives CO, which reduces Fe_2O_3 stepwise; the waste gas is mostly N_2 from the hot air blast. For the Haber process, ΔH < 0 and ΔS < 0, so ΔG becomes positive at high T, and a compromise temperature (400–500 °C) with catalyst and high pressure is used. Common mistakes: omitting conditions, writing NH_3 oxidation to NO_2 directly, and arguing from Le Chatelier alone without ΔG = ΔH − TΔS as the question requires.

(b) [50 marks]

The following questions are based on photochemical smog and water pollution.
(i) State the major types of gaseous chemical pollutants and conditions that are required for the formation of photochemical smog.

Answer

NO_x (NO or NO_2), volatile hydrocarbons (VOC), sunlight/solar radiation, temperature above 15 °C (02 × 4)

(ii) State why the strength of photochemical smog is low in the morning and evening.

Answer

The intensity of solar radiation is low during the morning and evening. (03) Therefore photochemical smog is weak in the morning and evening.

(iii) Using balanced chemical equations, explain how ozone is formed in the lower atmosphere due to photochemical smog.

Answer

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$
$NO_2(g) \rightarrow NO(g) + O(g)$ (sunlight)
$O(g) + O_2(g) \rightarrow O_3(g)$ (03 × 3)

(iv) State **four** major products (excluding ozone) of photochemical smog.

Answer

PAN (peroxyacetyl nitrate); PBN (peroxybenzoyl nitrate); short-chain (volatile) aldehydes; particles (particulate matter) (02 × 4)

(v) State **three** free radicals produced during the formation of photochemical smog.

Answer

OH• (hydroxyl radical), ROO• (peroxy radical), R• (alkyl radical), RO• (alkoxy radical), O• (oxygen radical), NO (any three) (02 × 3)

(vi) Many countries now promote the use of electric vehicles. State how the use of electric vehicles affect the formation of photochemical smog.

Answer

Electric vehicles do not release ingredients for photochemical smog. (02) Therefore, electric vehicles contribute to the reduction of photochemical smog (or no photochemical smog from them).

(vii) State an environmental problem, other than photochemical smog, that could ease due to the use of electric vehicles.

Answer

Global warming / acid rain (03)

(viii) A ship carrying the following chemicals sank in the sea.
Na_2HPO_4, HNO_3, $Pb(CH_3COO)_2$
State an effect from each chemical on the water quality parameters of the water surrounding the ship, by the release of the above chemicals.

Answer

PO_4^{3-}, NO_3^− – reduction of the dissolved oxygen level (nutrients cause eutrophication and algal growth)
HNO_3 – increases the acidity / decreases the pH
Pb^{2+} – increases the heavy metal level (lead level) of the sea water (03 × 3) · 10(b): 50 marks

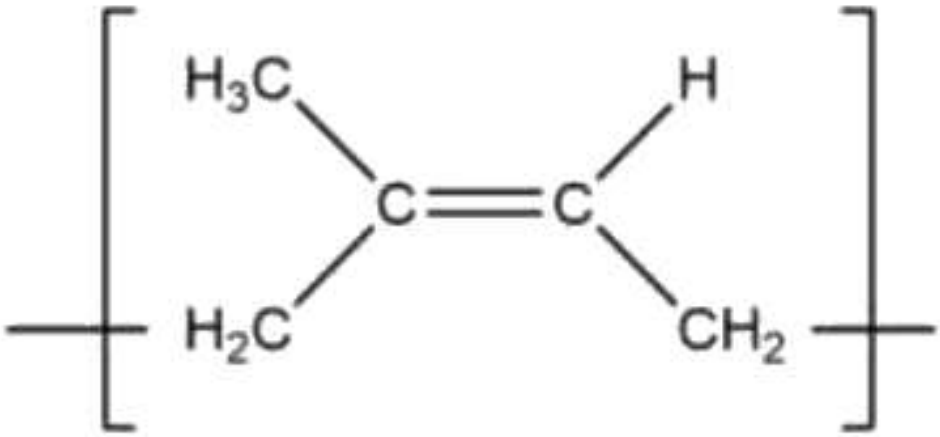
Review.

Principle: photochemical smog forms when NO_x and VOCs react in sunlight; water-quality parameters respond to nutrients, acids and heavy metals (U14 §1.13, §1.14). Method: NO from engines is oxidised to NO_2, whose photolysis gives O, and O + O_2 gives O_3; VOCs and radicals (OH•, RO_2•) give PAN, aldehydes and particles. Smog peaks around midday when sunlight is strongest. Phosphate and nitrate raise nutrient (eutrophication) and lower dissolved oxygen, HNO_3 lowers pH, and Pb^{2+} adds toxic heavy metal. Common mistakes: forgetting sunlight and VOCs as conditions, giving ozone formation without the NO_2 photolysis step, and naming effects (e.g. 'pollution') instead of the specific water-quality parameter.

(c) [50 marks]

The following questions are based on natural rubber and additives used for polymer related products.
(i) Sketch the repeating unit of natural rubber.

Answer



Repeating unit of natural rubber (cis-1,4-polyisoprene)

–[CH_2–$C(CH_3)$=CH–CH_2]– with the cis arrangement about the C=C bond (H_3C and the –CH_2– of the chain on the same side) (10)

(ii) Give a compound that can be used to prevent coagulation of natural rubber latex.

Answer

NH_3 solution (04)

(iii) State a compound that can be used to coagulate natural rubber latex and explain how it acts.

Answer

Acids such as acetic/formic acid. (04) H^+ can neutralize the COO^- groups, making the surface of the rubber particles neutral. The particles can then combine together and become a mass. (02 × 4 = 08)

(iv) Briefly state how the 'vulcanization' of natural rubber is carried out.

Answer

Rubber is heated with 1–3% sulfur. (03 × 3 = 09)

(v) State **two** types of substances used to increase the efficiency of vulcanization.

Answer

Organic catalysts (accelerators); catalyst promoters or ZnO (03 × 2 = 06)

(vi) Give **three** properties, which can be enhanced by adding additives to polymer products.

Answer

Increase flexibility; decrease flammability; increase mechanical and/or physical strength (any three) (03 × 3 = 09) · 10(c): 50 marks

Review.

Principle: natural rubber is cis-1,4-polyisoprene, stabilised as latex by NH_3, coagulated by acid (which removes the negative charge on the protein/fatty-acid coating), and cross-linked with sulfur bridges on vulcanization to give a harder, more elastic, less sticky material (U14 §1.11). Method: recall the isoprene repeat unit, the role of NH_3 (keeps the latex alkaline so the particles stay charged), acid (H^+ neutralises COO^- and the particles aggregate), and sulfur plus accelerators/ZnO. Common mistakes: drawing trans-polyisoprene (gutta-percha), using a base to coagulate, and stating that vulcanization uses oxygen or more than a few percent sulfur.

Read: RB U14 §1.10 · p. 33 RB U14 §1.6 · p. 21 RB U14 §1.13 · p. 58 RB U14 §1.14 · p. 80

2020 · Chemistry Digital Paper

50 questions · 2 hours

MCQ · Paper I

Question 1 · Q1–30 · single answer

Consider the following discoveries made with regard to the atomic structure.

I. Positive rays inside a cathode ray tube
II. Radioactivity by certain types of nuclei

The two scientists who discovered the above stated I and II respectively, are,

- (1)J. J. Thomson and Henry Becquerel
- (2)Eugen Goldstein and Robert Millikan
- (3)Henry Becquerel and Eugen Goldstein
- (4)J. J. Thomson and Ernest Rutherford
- (5)Eugen Goldstein and Henry Becquerel

Answer and review

Answer **(5)** Official marking scheme

Positive (canal) rays in a discharge tube were discovered by Eugen Goldstein (1886), and natural radioactivity by Henri Becquerel (1896). The traps are the other famous names: Thomson (electron, cathode rays), Millikan (charge of the electron) and Rutherford (nucleus).

RB U1 §1.1 · p. 2

Question 2 · Q1–30 · single answer

The number of electrons in the manganese atom (Mn, Z = 25) that have quantum numbers l = 0 and $m_l = -1$ respectively, are,

- (1)6 and 4
- (2)8 and 12
- (3)8 and 5
- (4)8 and 6
- (5)10 and 5

Answer and review

Answer **(3)** Official marking scheme

Mn: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$. l = 0 means s electrons: 1s, 2s, 3s, 4s = 2 + 2 + 2 + 2 = 8. $m_l = -1$ is found in one orbital of each p subshell and one d orbital: 2p (2 e) + 3p (2 e) + 3d (1 e, since the five 3d electrons occupy five different orbitals by Hund's rule) = 5. Trap: counting all p electrons (12) or all d electrons.

RB U1 §1.3 · p. 17 RB U1 §1.4 · p. 23

Question 3 · Q1–30 · single answer

M

3

M

- (1)2
- (2)13
- (3)14
- (4)15
- (5)16

Answer and review

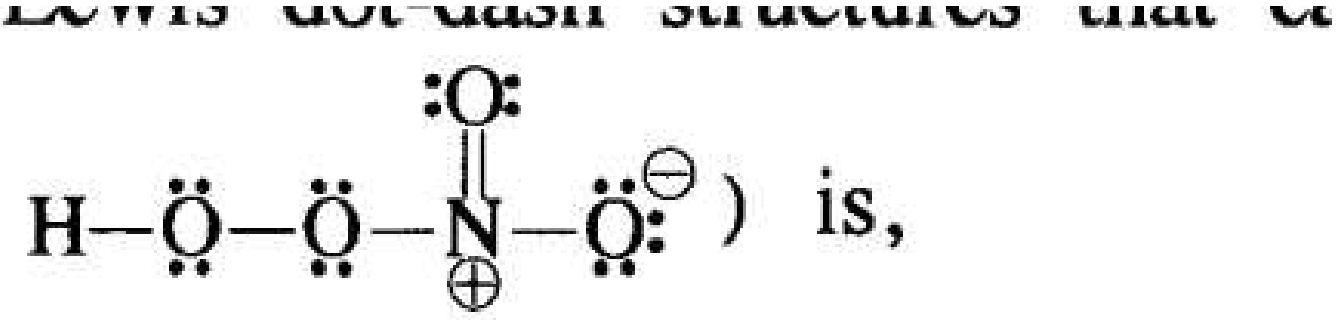
Answer **(4)** Official marking scheme

MCl_3 has a net dipole only if its shape is unsymmetrical. Group 13 (BCl_3) is trigonal planar, three equal bond dipoles cancel, non-polar. Group 15 (NCl_3) is trigonal pyramidal because of the lone pair on N, so the bond dipoles do not cancel: polar. Group 2 (Be) and 14 (C) and 16 (O) do not form MCl_3 as stable covalent molecules.

RB U2 §2.3 · p. 52

Question 4 · Q1–30 · single answer

The number of **unstable** Lewis dot-dash structures that can be drawn for the peroxynitric acid molecule (formula HNO_4, structure shown below) is,



- (1)1
- (2)2
- (3)3
- (4)4
- (5)5

Answer and review

Answer **(2)** Official marking scheme

The given structure (N^+ carrying =O and one O^-) obeys the octet rule, and its equivalent partner (the two terminal oxygens swapped) is equally good, so these are the stable resonance forms. The Resource Book's rules for relative stability of Lewis/resonance structures (octet rule obeyed, minimum formal-charge separation, positive charge not on a very electronegative atom such as O, no like charges on adjacent atoms) are used to decide which other drawings are unstable. The official key is 2; the main trap is counting the

equivalent stable forms as "unstable".

RB U2 §2.1 · p. 44 RB U2 §2.3 · p. 52

Question 5 · Q1–30 · single answer

The IUPAC name of the given compound is,

$HO–CH_2–CH(CH_3)–C(=O)–CH=CH–Br$

- (1)1-bromo-4-methyl-5-hydroxypent-1-en-3-one
- (2)5-bromo-1-hydroxy-2-methylpent-4-en-3-one
- (3)1-bromo-5-hydroxy-4-methylpent-1-en-3-one
- (4)5-bromo-2-methyl-3-oxopent-4-en-1-ol
- (5)1-bromo-4-methyl-3-oxopent-1-enol

Answer and review

Answer **(All)** Official marking scheme

The official scheme gives full credit for any response (All). Working: the principal characteristic group is the ketone (suffix –one), on the 5-carbon chain; numbering from either end gives C=O locant 3, so the lower locant for the double bond decides: numbering from the Br end gives en = 1. Substituents in alphabetical order: bromo (1), hydroxy (5), methyl (4): 1-bromo-5-hydroxy-4-methylpent-1-en-3-one, which is option (3). Options (1) is not alphabetical; (2) and (4) number from the wrong end; (5) treats the ketone as an enol.

RB U7 §1.3 · p. 7

Question 6 · Q1–30 · single answer

The **decreasing** order of radii of the species O, O^{2-}, F, F^-, S^{2-}, Cl^- is,

- (1)$S^{2-} > Cl^- > O^{2-} > F^- > O > F$
- (2)$S^{2-} > Cl^- > O^{2-} > F^- > F > O$
- (3)$Cl^- > S^{2-} > O^{2-} > F^- > O > F$
- (4)$Cl^- > S^{2-} > F^- > O^{2-} > O > F$
- (5)$S^{2-} > Cl^- > O^{2-} > O > F^- > F$

Answer and review

Answer **(1)** Official marking scheme

Anions are larger than their atoms. Third-period anions (S^{2-} 184 pm, Cl^- 181 pm) exceed second-period anions (O^{2-} 140 pm, F^- 133 pm); $S^{2-} > Cl^-$ because it has fewer protons for the same 18 electrons, and $O^{2-} > F^-$ for the same reason (10 electrons). The neutral atoms are smaller, and O (66 pm) > F (64 pm) because Z_{eff} increases across the period. Traps: reversing O and F, or putting an atom above an anion.

RB U1 §1.6 · p. 32

Question 7 · Q1–30 · single answer

A rigid-closed container contains n_1 moles of an ideal gas at temperature T_1 (K) and pressure P_1 (Pa). When an additional amount of the gas was inserted into the container, the new temperature and pressure were T_2 and P_2, respectively. The total number of moles of the gas now in the container is,

- (1)n_1T_1P_1 / (T_2P_2)
- (2)n_1T_1P_2 / (T_2P_1)
- (3)T_2P_2 / (n_1T_1P_1)
- (4)n_1T_2P_2 / (T_1P_1)
- (5)n_1T_2P_1 / (T_1P_2)

Answer and review

Answer **(2)** Official marking scheme

The container is rigid, so V is constant. Initially n_1 = P_1V/(RT_1); finally n_2 = P_2V/(RT_2). Dividing, n_2/n_1 = P_2T_1/(P_1T_2), so n_2 = n_1T_1P_2/(T_2P_1). Trap: inverting the temperature or pressure ratio.

RB U4 §1.2 · p. 5

Question 8 · Q1–30 · single answer

The total number of electrons exchanged in the reaction of the oxidation of ethanol (C_2H_5OH) to acetic acid (CH_3COOH) using acidic $K_2Cr_2O_7$ solution is,

- (1)6
- (2)8
- (3)10
- (4)12
- (5)14

Answer and review

Answer **(3)** Official marking scheme

Possible error in the official key.

3

C

2

3

3

2

7

2−

+

3+

2

2

5

2

7

2−

+

3

3+

2

RB U3 §3.1 · p. 88 RB U3 §3.6 · p. 105 RB U9 §3.1 · p. 54

Question 9 · Q1–30 · single answer

Which compound of the following, can undergo aldol condensation, when reacted with aqueous NaOH?

- (1)CH_3COOH
- (2)CH_3COOCH_3
- (3)$HCOOCH_3$
- (4)CH_3CH_2CHO
- (5)$(CH_3)_3CCHO$

Answer and review

Answer **(4)** Official marking scheme

Aldol condensation needs an aldehyde or ketone with an α-hydrogen, so that base can form the enolate. CH_3CH_2CHO has α-H (on CH_2). $(CH_3)_3CCHO$ has no α-H. The acid and the esters react with NaOH by neutralisation or hydrolysis instead.

RB U9 §3.4 · p. 60

Question 10 · Q1–30 · single answer

AX(s), A_2Y(s) and AZ(s) are sparingly soluble salts in water having K_{sp} values of 1.6×10^{-9}, 3.2×10^{-11} and 9.0×10^{-12}, respectively at 25 °C. Which of the following shows the order of the three saturated solutions of these salts in decreasing concentration of cation A^+(aq), at 25 °C?

- (1)AX(s) > A_2Y(s) > AZ(s)
- (2)A_2Y(s) > AX(s) > AZ(s)
- (3)AX(s) > AZ(s) > A_2Y(s)
- (4)A_2Y(s) > AZ(s) > AX(s)
- (5)AZ(s) > A_2Y(s) > AX(s)

Answer and review

Answer **(2)** Official marking scheme

AX: $[A^+] = \sqrt{(1.6 \times 10^{-9})} = 4.0 \times 10^{-5}$ mol dm^{-3}. A_2Y: $K_{sp} = (2s)^2 s = 4s\text{^}3 = 3.2 \times 10^{-11}$, $s = 2.0 \times 10^{-4}$, so $[A^+] = 2s = 4.0 \times 10^{-4}$. AZ: $[A^+] = \sqrt{(9.0 \times 10^{-12})} = 3.0 \times 10^{-6}$. Order A_2Y > AX > AZ. Trap: comparing K_{sp} values directly or forgetting that A_2Y gives two A^+ per formula unit.

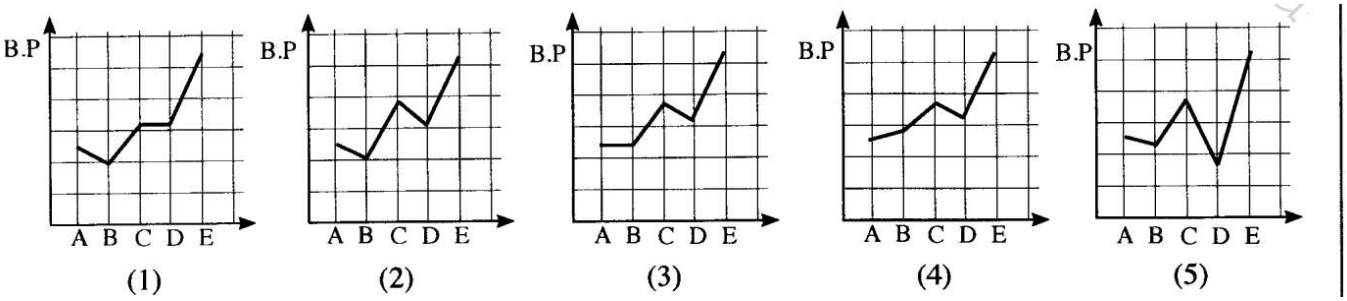
RB U12 §2.4 · p. 175

Question 11 · Q1–30 · single answer

Consider the following compounds.

	A	B	C	D	E
Compound	$CH_3CH_2CH_2CH_2CH_2CH_3$	$CH_3C(CH_3)_2CH_2CH_3$	$CH_3CH_2CH_2CH_2CHO$	$CH_3C(CH_3)_2CHO$	$CH_3CH_2CH_2CH_2CH_2OH$
Relative molecular mass	86	86	86	86	88

Variation of boiling points (B.P) of these compounds is best shown by,



Answer and review

Answer **(2)** Official marking scheme

Boiling points: B (2,2-dimethylbutane, compact, only London forces) 50 °C < A (hexane) 69 °C < D (2,2-dimethylpropanal, polar C=O but compact) 77 °C < C (pentanal, polar and unbranched) 103 °C < E (pentan-1-ol, hydrogen bonding) 138 °C. So from A to E: down at B, up at C (large rise), down at D, up to the highest at E, which is graph (2). Branching lowers b.p.; dipole–dipole (C=O) raises it; H-bonding raises it most.

RB U2 §2.6 · p. 79 RB U9 §3.4 · p. 60

Question 12 · Q1–30 · single answer

The **increasing** order of covalent character of the chemical species NaCl, Na_2S, KF and KCl is,

- (1)KF < NaCl < KCl < Na_2S
- (2)KCl < NaCl < KF < Na_2S
- (3)KF < KCl < NaCl < Na_2S
- (4)Na_2S < NaCl < KCl < KF
- (5)KF < Na_2S < NaCl < KCl

Answer and review

Answer **(3)** Official marking scheme

By Fajans' rules covalent character increases with a more polarizing (smaller, more highly charged) cation and a more polarizable (larger, more highly charged) anion. K^+ is larger than Na^+, so potassium salts are less covalent than sodium salts with the same anion: KCl < NaCl. F^- is small and hard to polarize, so KF is the most ionic; S^{2-} is large and doubly charged, so Na_2S is the most covalent. Order: KF < KCl < NaCl < Na_2S.

RB U2 §2.4 · p. 75

Question 13 · Q1–30 · single answer

Standard combustion enthalpies of $H_2(g)$, C(s) and $CH_3OH(l)$ at 298 K are -286 kJ mol^{-1}, -393 kJ mol^{-1} and -726 kJ mol^{-1}, respectively. Enthalpy of vaporization of $CH_3OH(l)$ is $+37$ kJ mol^{-1}. Enthalpy of formation (kJ mol^{-1}) of one mole of **gaseous** CH_3OH at 298 K is,

- (1)-276
- (2)-239
- (3)-202
- (4)$+84$
- (5)$+202$

Answer and review

Answer **(3)** Official marking scheme

Formation of $CH_3OH(l)$: $C(s) + 2H_2(g) + ½O_2(g) \rightarrow CH_3OH(l)$. $\Delta H_f = \Delta H_c(C) + 2\Delta H_c(H_2) - \Delta H_c(CH_3OH) = -393 + 2(-286) - (-726) = -239$ kJ mol^{-1}. Converting liquid to gas absorbs 37 kJ mol^{-1}: $-239 + 37 = -202$ kJ mol^{-1}. Trap: stopping at -239 (option 2, the liquid) or forgetting the factor 2 for H_2.

RB U5 §2.2 · p. 36

Question 14 · Q1–30 · single answer

Phosphorous can be prepared in an electric furnace as given by the following balanced chemical equation.

$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow 6CaSiO_3 + 10CO + P_4$

When 620 g of $Ca_3(PO_4)_2$, 180 g of SiO_2 and 96 g of C were reacted, 50 g of P_4 were obtained. Under these conditions, the limiting reagent (reagent that is completely consumed) and percentage yield of P_4 respectively are, (C = 12, O = 16, Si = 28, P = 31, Ca = 40)

- (1)$Ca_3(PO_4)_2$ and 80.7%
- (2)SiO_2 and 80.7%
- (3)C and 50.4%
- (4)SiO_2 and 40.3%
- (5)C and 25.2%

Answer and review

Answer **(2)** Official marking scheme

Moles: $Ca_3(PO_4)_2 = 620/310 = 2.0$; $SiO_2 = 180/60 = 3.0$; $C = 96/12 = 8.0$. Divide by the coefficients: $2.0/2 = 1.0$; $3.0/6 = 0.50$; $8.0/10 = 0.80$. The smallest is SiO_2, the limiting reagent. P_4 formed (theoretical) $= 3.0 \times (1/6) = 0.50$ mol $= 0.50 \times 124 = 62$ g. Yield $= 50/62 \times 100 = 80.7\%$. Trap: choosing the reagent with the smallest number of moles ($Ca_3(PO_4)_2$ here is 2 mol, SiO_2 3 mol) without dividing by coefficients.

RB U3 §3.8 · p. 115

Question 15 · Q1–30 · single answer

Consider the following two equilibria occurring in two separate rigid-closed containers under the same conditions.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $K_{P1} = 3.0 \times 10^{-4}$

$NH_3(g) + H_2S(g) \rightleftharpoons NH_4HS(g)$; $K_{P2} = 8.0 \times 10^{-4}$

Under these conditions K_p for the equilibrium $2H_2S(g) + N_2(g) + 3H_2(g) \rightleftharpoons 2NH_4HS(g)$ is,

- (1)5.76×10^{-12}
- (2)7.2×10^{-10}
- (3)1.92×10^{-8}
- (4)3.40×10^{-6}
- (5)3.75×10^{-2}

Answer and review

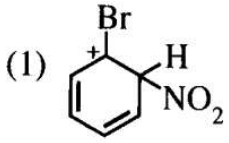
Answer **(All)** Official marking scheme

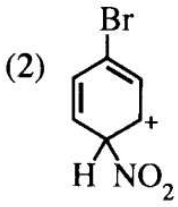
The official scheme gives full credit for any response (All), because none of the options matches the correct value. Working: the target equation = (equilibrium 1) + 2 × (equilibrium 2), so $K_p = K_{P1} \times (K_{P2})^2 = 3.0 \times 10^{-4} \times (8.0 \times 10^{-4})^2 = 1.92 \times 10^{-10}$. Option (3) has the right digits but the exponent −8. When equations are added the K values multiply; when an equation is multiplied by 2, K is squared.

RB U12 §2.1 · p. 76

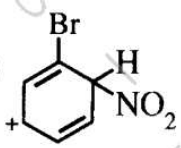
Question 16 · Q1–30 · single answer

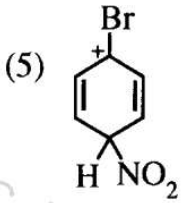
Consider the nitration reaction of bromobenzene. Resonance stabilized carbocation intermediates are formed during this reaction. Which of the following is **not** a resonance structure of these intermediates?

(1) 

(2) 

(3)

(4) 

(5) 

Answer and review

Answer **(3)** Official marking scheme

In the arenium ion the carbon that bears H and NO_2 is sp^3, and the + charge is delocalised over the ring carbons that are ortho and para to that sp^3 carbon. Structures (1), (2), (4) and (5) satisfy this (some of them put + on the C–Br carbon, which Br can stabilise with a lone pair). Structure (3) is wrong because the sp^3 carbon carries H and Br while NO_2 is on a neighbouring ring carbon: the substituent pattern is not that of an intermediate formed by NO_2^+ attack, and Br and NO_2 cannot be moved by resonance (only electrons move).

RB U8 §2.4 · p. 44 RB U8 §2.5 · p. 49

Question 17 · Q1–30 · single answer

A reaction which is non-spontaneous at room temperature and 1 atm pressure becomes spontaneous at high temperature at the same pressure. Which of the following is correct for this reaction at room temperature? (Assume that ΔH and ΔS do not change with temperature and pressure.)

Options are given as (ΔG, ΔH, ΔS):

- (1)ΔG positive, ΔH positive, ΔS positive
- (2)ΔG positive, ΔH negative, ΔS negative

- (3)ΔG positive, ΔH negative, ΔS positive
- (4)ΔG negative, ΔH positive, ΔS negative
- (5)ΔG negative, ΔH negative, ΔS negative

Answer and review

Answer **(1)** Official marking scheme

Non-spontaneous at room temperature means ΔG > 0. ΔG = ΔH − TΔS becomes negative only at high T if the −TΔS term grows more negative, so ΔS > 0; for ΔG to be positive at low T, ΔH must be positive. So ΔG +, ΔH +, ΔS + (option 1). Options (2) and (3) have negative ΔH: with ΔS negative the reaction gets less favourable on heating (opposite behaviour), and with ΔS positive it would be spontaneous at all temperatures. Options (4) and (5) give negative ΔG at room temperature, contradicting the data.

RB U5 §2.4 · p. 53

Question 18 · Q1–30 · single answer

The de Broglie wavelength of a neutron travelling with a velocity v is λ. If the kinetic energy E (E = ½mv^2) of this neutron is increased four times, the new de Broglie wavelength would be,

- (1)λ/2
- (2)λ/4
- (3)2λ
- (4)4λ
- (5)16λ

Answer and review

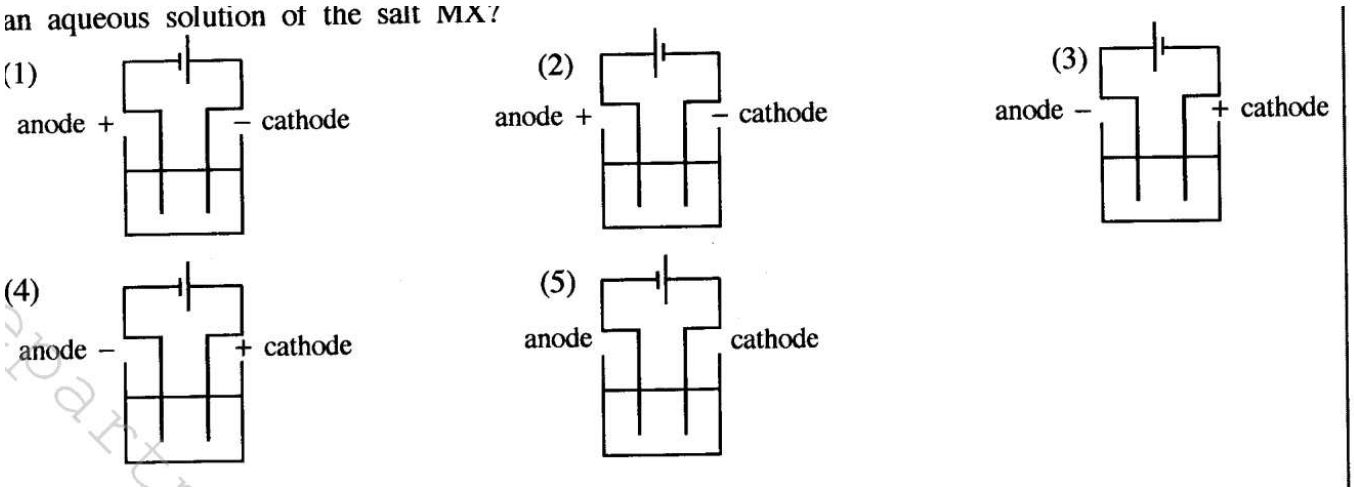
Answer **(1)** Official marking scheme

λ = h/mv and E = ½mv^2, so v ∝ √E and λ ∝ 1/√E. Increasing E four times doubles v (√4 = 2), so λ becomes λ/2. Trap: using λ ∝ 1/E (λ/4).

RB U1 §1.2 · p. 13

Question 19 · Q1–30 · single answer

Which of the following correctly shows the electrolytic cell constructed for the electrolysis of an aqueous solution of the salt MX?



Answer and review

Answer **(2)** Official marking scheme

In an electrolytic cell the external source makes the anode positive (oxidation occurs there) and the cathode negative (reduction occurs there). In a cell symbol the longer line is the positive terminal, so the long line must be on the side connected to the anode. Only diagram (2) has the anode labelled + and joined to the long (positive) plate of the battery, with the cathode − joined to the short plate. (1) has the labels right but the battery reversed; (3) and (4) label the electrodes with the galvanic-cell polarity; (5) gives no polarity.

RB U13 §3.4 · p. 261

Question 20 · Q1–30 · single answer

Which of the following statements is correct regarding the reaction between a carboxylic acid and an alcohol to give an ester?

- (1)The overall reaction is a nucleophilic addition reaction of a carbonyl compound.
- (2)It is a reaction in which the alcohol acts as a nucleophile.
- (3)It is a reaction which occurs with the cleavage of the O–H bond of the carboxylic acid.
- (4)It is a reaction which occurs with the cleavage of the C–O bond of the alcohol.
- (5)It is an acid-base reaction.

Answer and review

Answer **(2)** Official marking scheme

Esterification (Fischer) is a nucleophilic acyl substitution: the lone pair on the alcohol oxygen attacks the (protonated) carbonyl carbon, so the alcohol is the nucleophile. Overall the OH of the acid (C–OH bond) is replaced by OR, so it is substitution, not simple addition (1), the C–O bond cleaved is that of the acid, not of the alcohol (4), and the O–H of the alcohol loses its proton (3 is wrong). It is not an acid-base reaction (5).

RB U9 §3.5 · p. 66 RB U9 §3.6 · p. 70

Question 21 · Q1–30 · single answer

Decomposition of 1 mol of $CH_3OH(l)$ occurs at high temperatures as follows.

$CH_3OH(l) \rightarrow CO(g) + 2H_2(g)$; $\Delta H = +128$ kJ

Which of the following is **incorrect** for the above reaction? (H = 1, C = 12, O = 16)

- (1)The heat absorbed when 1 mol of $CH_3OH(g)$ is decomposed is less than 128 kJ.
- (2)Enthalpy of $CO(g) + 2H_2(g)$ is higher than the enthalpy of $CH_3OH(l)$.
- (3)128 kJ of heat is released when 1 mol of CO(g) is formed.
- (4)128 kJ of heat is absorbed during the decomposition of a mole of reactant.
- (5)128 kJ of heat is absorbed when 32 g of products are formed.

Answer and review

Answer **(3)** Official marking scheme

ΔH is positive, so the reaction is endothermic and 128 kJ is **absorbed**, not released, when 1 mol CO forms (3 is incorrect). (1) is true because $CH_3OH(g)$ is already higher in enthalpy than the liquid by the heat of vaporization. (2) products are higher in enthalpy (ΔH > 0). (4) is the definition for 1 mol of reactant. (5) 1 mol

CO + 2 mol H_2 = 28 + 4 = 32 g of products for 128 kJ.

RB U5 §2.2 · p. 36

Question 22 · Q1–30 · single answer

Identify the **incorrect** statement from the following.

- (1)Electron gain energy of nitrogen [N(g)] is positive.
- (2)Dilution of $BiCl_3$(aq) solution with water gives a white precipitate.
- (3)H_2S gas can act both as an oxidizing agent and a reducing agent.
- (4)The effective nuclear charge (Z*) felt by a valence electron in He is less than 2.
- (5)Aluminium is inert towards N_2 gas even when heated to a high temperature.

Answer and review

Answer **(4/5)** Official marking scheme

The official scheme accepts (4) or (5). Statement (5) is clearly incorrect: Al reacts with N_2 at high temperature to give AlN ($2Al + N_2 \rightarrow 2AlN$). (1) is true (N: +134 kJ mol^{-1}, half-filled p^3 subshell); (2) is true ($BiCl_3 + H_2O \rightarrow BiOCl\downarrow + 2HCl$); (3) is true ($S^{2-}$ in H_2S can be oxidised; H^+ can be reduced by active metals). Statement (4) is also credited by the scheme, although Z* for He is about 1.7 by Slater's rules (so the statement itself is true); the Resource Book only states that $Z_{eff} < Z$. Option (5) is therefore the safest choice.

RB U1 §1.6 · p. 32 RB U6 §4.5 · p. 136 RB U6 §4.3 · p. 131

Question 23 · Q1–30 · single answer

The concentration of a dilute aqueous solution of a weak acid HA is C mol dm^{-3} and its acid dissociation constant is K_a at 298 K. Which of the following expressions gives the pH of the solution at 298 K?

- (1)$pH = ½pK_a - ½\log C$
- (2)$pH = -½pK_a - ½\log C$
- (3)$pH = -½pK_a + ½\log C$
- (4)$pH = -½pK_a - ½\log (1/C)$
- (5)$pH = ½pK_a - ½\log (1/C)$

Answer and review

Answer **(1)** Official marking scheme

For a weak acid $[H^+] = \sqrt{(K_aC)}$ (dissociation negligible). $pH = -\log[H^+] = -½\log K_a - ½\log C = ½pK_a - ½\log C$. Check: for 0.1 mol dm^{-3} acid with $pK_a = 5$, pH = 2.5 + 0.5 = 3. Trap: sign errors; note $\log(1/C) = -\log C$, so (5) is really $½pK_a + ½\log C$, which is wrong.

RB U12 §2.2 · p. 118

Question 24 · Q1–30 · single answer

The strength of a H_2O_2 solution can be expressed as the volume of O_2 produced at standard temperature and pressure (STP). For example, a litre of 20 **volume strength** H_2O_2 solution will produce 20 litres of O_2 gas at STP ($2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$). (Assume that 1 mole of gas has 22.4 litres volume at STP.)

A bottle labelled **X** contains H_2O_2 solution. When 25.0 cm^3 of solution **X** was titrated with 1.0 mol dm^{-3} $KMnO_4$ in the presence of dilute H_2SO_4 the volume required to reach the end point was 25.0 cm^3. The volume strength of solution **X** is,

- (1)15
- (2)20
- (3)25
- (4)28
- (5)30

Answer and review

Answer **(All)** Official marking scheme

The official scheme gives full credit for any response (All). Working: $2MnO_4$^− + $5H_2O_2$ + $6H^+$ → $2Mn^{2+}$ + $5O_2$ + $8H_2O$. n(MnO_4^−) = 1.0 × 0.0250 = 0.0250 mol; n(H_2O_2) = 0.0250 × 5/2 = 0.0625 mol in 25.0 cm^3, so [H_2O_2] = 2.5 mol dm^{-3}. 1 dm^3 of solution decomposes to give 2.5/2 = 1.25 mol O_2 = 1.25 × 22.4 = 28 dm^3 at STP, i.e. 28 volume strength, option (4). The unusually concentrated 1.0 mol dm^{-3} $KMnO_4$ is a likely reason all responses were credited.

RB U3 §3.8 · p. 115 RB U6 §4.6 · p. 141

Question 25 · Q1–30 · single answer

$M(OH)_2$(s) is a sparingly water soluble salt formed by the reaction between M^{2+}(aq) and OH^-(aq) ions at 298 K. The solubility (mol dm^{-3}) of $M(OH)_2$(s) in water at pH = 5 is, ($K_{sp\ M(OH)2}$ = 4.0 × 10^{-36} at 298 K).

- (1)√2 × 10^{-18}
- (2)2 × 10^{-18}
- (3)1 × 10^{-18}
- (4)∛2 × 10^{-12}
- (5)1 × 10^{-12}

Answer and review

Answer **(All)** Official marking scheme

The official scheme gives full credit for any response (All), because the correct value is not among the options. Working: at pH 5, [H^+] = 10^{-5} so [OH^-] = 10^{-9} mol dm^{-3} (fixed by the buffer/pH). K_{sp} = [M^{2+}][OH^-]^2, so solubility = [M^{2+}] = 4.0 × 10^{-36}/(10^{-9})^2 = 4.0 × 10^{-18} mol dm^{-3}. The pure-water value (4s^3 = 4.0 × 10^{-36}, s = 1 × 10^{-12}) is option (5), the trap for those who ignore the pH.

RB U12 §2.4 · p. 175

Question 26 · Q1–30 · single answer

Which of the following correctly denotes the standard galvanic cell constructed by using a standard hydrogen electrode, a standard Mg-electrode and a salt-bridge at 298 K?

- (1)Mg(s) | Mg^{2+}(aq, 1.00 mol dm^{-3}) || H^+(aq, 1.00 mol dm^{-3}) | H_2(g) | Pt(s)
- (2)Pt(s) | H_2(g) | H^+(aq, 1.00 mol dm^{-3}) || Mg^{2+}(aq, 1.00 mol dm^{-3}) | Mg(s)
- (3)Mg(s), Mg^{2+}(aq, 1.00 mol dm^{-3}) || H^+(aq, 1.00 mol dm^{-3}) | H_2(g) | Pt(s)
- (4)Mg(s) | Mg^{2+}(aq, 1.00 mol dm^{-3}) || H^+(aq, 1.00 mol dm^{-3}), H_2(g) | Pt(s)

- (5)Pt(s), $H_2(g)$ | H^+(aq, 1.00 mol dm^{-3}) || Mg^{2+}(aq, 1.00 mol dm^{-3}), Mg(s)

Answer and review

Answer **(1)** Official marking scheme

Mg ($E° = -2.37$ V) is a stronger reducing agent than H_2 (0.00 V), so Mg is oxidised and is the anode. By convention the anode (oxidation) is written on the left, the salt bridge is ||, the cathode (reduction) on the right, and a phase boundary is written as |. In the cell Mg(s) | Mg^{2+} || H^+ | $H_2(g)$ | Pt(s) the H^+ solution and H_2 gas are separate phases. Options (2) and (5) put the hydrogen electrode on the left (anode); (3) and (4) use commas incorrectly for different phases.

RB U13 §3.3 · p. 250

Question 27 · Q1–30 · single answer

The following procedure was carried out at 298 K to determine the distribution coefficient K_D of a monobasic organic acid between dichloromethane and water. 50.00 cm^3 of a 0.20 mol dm^{-3} aqueous solution of acid were mixed vigorously with 10.00 cm^3 of dichloromethane and the two layers were allowed to separate. Thereafter, the dichloromethane layer in the bottom of the flask was drained out. 10.00 cm^3 of 0.02 mol dm^{-3} NaOH(aq) solution were required to neutralize the acid remaining in the aqueous layer. (Assume that the acid does not dimerize in the organic phase.) K_D of the acid between **dichloromethane and water** at 298 K is,

- (1)0.05
- (2)0.25
- (3)4.00
- (4)20.00
- (5)245.00

Answer and review

Answer **(5)** Official marking scheme

Acid initially = 50.00 × 0.20 = 10.00 mmol. Acid left in water (the whole aqueous layer is titrated) = 10.00 × 0.02 = 0.20 mmol, so $[acid]_{aq}$ = 0.20/50.00 = 0.0040 mol dm^{-3}. Acid in dichloromethane = 10.00 − 0.20 = 9.80 mmol in 10.00 cm^3, so $[acid]_{DCM}$ = 0.98 mol dm^{-3}. K_D = [DCM]/[water] = 0.98/0.0040 = 245. Traps: using amounts instead of concentrations, or inverting the ratio (water/DCM = 0.0041).

RB U12 §2.7 · p. 229

Question 28 · Q1–30 · single answer

A reaction $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$ occurs in a rigid-closed container at a given temperature. After a certain time, it was found that the rate of the reaction with respect to consumption of $C_2H_4(g)$ was x mol dm^{-3} s^{-1}. Which of the following shows the rates of consumption of $O_2(g)$, formation of $CO_2(g)$ and formation of $H_2O(g)$ respectively, during that time?

Rates are in mol dm^{-3} s^{-1}, listed in the order $O_2(g)$, $CO_2(g)$, $H_2O(g)$.

- (1)3/x, 2/x, 2/x
- (2)x, x, x
- (3)x/3, x/2, x/2
- (4)1/x, 1/x, 1/x

- (5)3x, 2x, 2x

Answer and review

Answer **(5)** Official marking scheme

Rates follow the stoichiometric coefficients: $-d[C_2H_4]/dt = -(1/3)d[O_2]/dt = (1/2)d[CO_2]/dt = (1/2)d[H_2O]/dt = x$. So O_2 is consumed at 3x, and CO_2 and H_2O are each formed at 2x. Options with x in the denominator are dimensionally wrong; dividing by the coefficients (3) is the reverse operation.

RB U11 §1.3 · p. 9

Question 29 · Q1–30 · single answer

Consider the following reaction occurring in a rigid-closed container at temperature T.

$M(g) + Q(g) \rightarrow R(g) + Z(g)$

The rate of reaction doubled when the concentration of **M** was doubled. The rate of reaction is 5.00×10^{-4} mol dm^{-3} s^{-1} when the concentrations of **M** and **Q** are 1.0×10^{-5} mol dm^{-3} and 2.0 mol dm^{-3} respectively. The rate constant of the reaction under these conditions is,

- (1)2.5×10^{-4} s^{-1}
- (2)12.5 s^{-1}
- (3)25 s^{-1}
- (4)50 s^{-1}
- (5)500 s^{-1}

Answer and review

Answer **(4)** Official marking scheme

Doubling [M] doubles the rate, so the reaction is first order in M. All the answer choices have units of s^{-1}, which means the overall order is one, so the order in Q is zero (rate = k[M]). k = rate/[M] = $5.00 \times 10^{-4}/1.0 \times 10^{-5} = 50$ s^{-1}. Trap: treating Q as first order gives 25 (option 3), but that would have units dm^3 mol^{-1} s^{-1}, not s^{-1}.

RB U11 §1.6 · p. 16

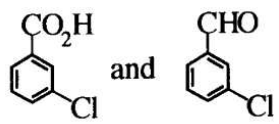
Question 30 · Q1–30 · single answer

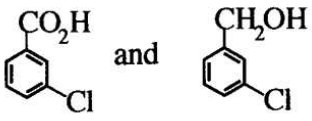
Consider the following reaction scheme.

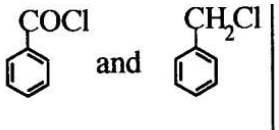
benzoic acid (a benzene ring bearing CO_2H) —($Cl_2/AlCl_3$)→ **P** —(1. $LiAlH_4$, 2. H^+/H_2O)→ **Q**

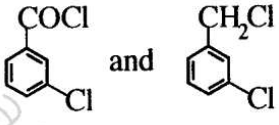
P

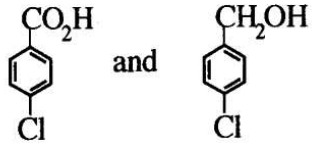
Q

(1) 

(2) 

(3) 

(4) 

(5) 

Answer and review

Answer **(2)** Official marking scheme

–CO_2H is a deactivating, meta-directing group, so chlorination with $Cl_2/AlCl_3$ gives 3-chlorobenzoic acid (P). $LiAlH_4$ reduces a carboxylic acid to the primary alcohol (not an aldehyde), so Q is 3-chlorobenzyl alcohol, with the aryl C–Cl bond untouched. Option (2) is the only one with meta Cl and $CO_2H \rightarrow CH_2OH$. (1) stops at CHO; (3) and (4) involve acid chlorides, not formed by $Cl_2/AlCl_3$; (5) has para Cl.

RB U8 §2.5 · p. 49 RB U9 §3.5 · p. 66

Questions 31–40: response code

(1)	(2)	(3)	(4)	(5)
Only (a) and (b) are correct	Only (b) and (c) are correct	Only (c) and (d) are correct	Only (d) and (a) are correct	Any other number or combination of responses is correct

Question 31 · Q31–40 · response code

Which of the following statement/s is/are correct with regard to 3d-block elements and their compounds?

- Among the 3d-block elements, Sc is not considered as a transition element.
- The radii of atoms (Sc to Cu) decrease from left to right.
- $[Ni(NH_3)_6]^{2+}$ is blue in colour whereas $[Zn(NH_3)_4]^{2+}$ is colourless.
- The IUPAC name of K_2NiCl_4 is dipotassium tetrachloronickelate(II).

Answer and review

Answer **(5)** Official marking scheme

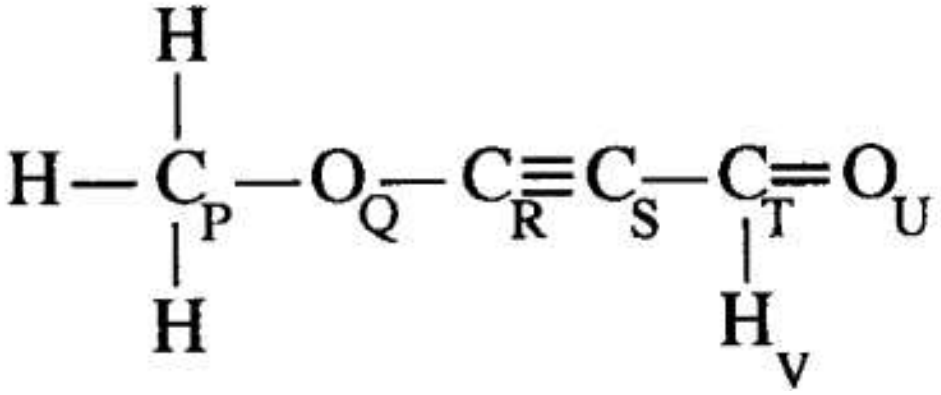
(a) is true: Sc forms only Sc^{3+} ($3d^0$), so it has no partly filled d subshell in any common ion. (c) is true: Ni^{2+} (d^8) complex is blue-violet while Zn^{2+} (d^{10}) gives colourless complexes. (d) is true: anionic complex, ligand chloro, Ni(II), so tetrachloronickelate(II), with the cation named first. (b) is not strictly true because the radii fall to Ni and then rise slightly at Cu. Hence (a), (c), (d) are correct, which is none of the listed pairs: code (5).

RB U6 §4.10 · p. 160 RB U6 §4.10.6 · p. 169

Question 32 · Q31–40 · response code

Which statement/s is/are correct regarding the following molecule?

are correct regarding the following mole



- Atoms labelled P, Q, R and S lie on a straight line.
- Atoms labelled Q, R, S and T lie on a straight line.
- Atoms labelled R, S, T, U and V lie on the same plane.
- Atoms labelled R, S, T and U lie on a straight line.

Answer and review

Answer **(2)** Official marking scheme

Q (the ether O) is bonded to P and R and is bent (sp^3 O), so P–Q–R is not linear: (a) false. R and S are sp carbons, so the atoms attached to the C≡C unit (Q and T) lie on the same line as R and S: (b) true. T is sp^2 (trigonal planar) with S, U and V attached, and R lies on the S–T axis, so R, S, T, U, V are all in one plane: (c) true. T–U makes about 120° with the S–T axis, so R, S, T, U are not collinear: (d) false. Only (b) and (c): code (2).

RB U2 §2.3 · p. 52

Question 33 · Q31–40 · response code

0.01 moles of $N_2(g)$, 0.10 moles of $H_2(g)$ and 0.40 moles of $NH_3(g)$ were inserted into a 1.0 dm^3 rigid-closed container and allowed to reach equilibrium at 500 K as given below.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $K_C = 2.0 \times 10^2$ mol^{-2} dm^6

Which of the following statement/s is/are correct for the changes in the system from the initial stage to equilibrium? Q_C is the reaction quotient.

- Initially $Q_C > K_C$; $NH_3(g)$ starts to produce $N_2(g)$ and $H_2(g)$ and the system reaches equilibrium.
- Initially $Q_C < K_C$; $NH_3(g)$ starts to produce $N_2(g)$ and $H_2(g)$ and the system reaches equilibrium.
- Initially $Q_C < K_C$; $N_2(g)$ and $H_2(g)$ react to form $NH_3(g)$ and the system reaches equilibrium.
- Initially $Q_C > K_C$; $N_2(g)$ and $H_2(g)$ react to form $NH_3(g)$ and the system reaches equilibrium.

Answer and review

Answer **(5)** Official marking scheme

Volume = 1.0 dm^3, so concentrations equal the moles. $Q_C = [NH_3]^2/([N_2][H_2]^3) = (0.40)^2/(0.01 \times 0.10^3) = 0.16/(1.0 \times 10^{-5}) = 1.6 \times 10^4 > K_C = 2.0 \times 10^2$. When $Q_C > K_C$ the net reaction runs backwards: NH_3 decomposes to N_2 and H_2 until equilibrium. Only (a) is correct, which is not one of the listed pairs: code (5).

RB U12 §2.1 · p. 76

Question 34 · Q31–40 · response code

Which of the following statement/s regarding the reaction between compound **P** and HCl to form an alkyl halide is/are correct?

P

3

3

2

- The major product is 2-chloro-2-methylbutane.
- A secondary carbocation is formed as an intermediate in this reaction.
- In one of the steps of the reaction, the HCl bond is cleaved to give a chlorine radical (Cl•).
- In one of the steps of the reaction, a nucleophile reacts with a carbocation.

Answer and review

Answer **(4/5)** Official marking scheme

The official scheme accepts (4) or (5). Working: P is 2-methylbut-2-ene. H^+ adds to the CH carbon (Markovnikov), giving the **tertiary** carbocation $(CH_3)_2C^+–CH_2CH_3$, which is captured by Cl^- (a nucleophile) to give 2-chloro-2-methylbutane. So (a) and (d) are true, (b) is false (tertiary, not secondary carbocation) and (c) is false (HCl breaks heterolytically; this is electrophilic addition, not a radical reaction). The true pair (d, a) is code (4); code (5) is also credited by the scheme.

RB U8 §2.2 · p. 33

Question 35 · Q31–40 · response code

A binary liquid mixture prepared by mixing two liquids in a closed evacuated container at a given temperature shows a negative deviation from Roult's Law. Which of the following statement/s is/are correct for this system?

- Total vapour pressure of the mixture is less than the expected total vapour pressure should it behave as an ideal mixture.
- Heat is released when the mixture is formed.
- Number of molecules in the vapour phase of the mixture is greater than the expected number of molecules should it behave as an ideal mixture.
- Heat is absorbed when the mixture is formed.

Answer and review

Answer **(1)** Official marking scheme

Negative deviation arises when A–B attractions are stronger than A–A and B–B attractions. Molecules then escape less easily, so the vapour pressure is lower than the ideal value (a) and fewer molecules are present in the vapour (c is false); forming stronger interactions releases heat, $\Delta H_{mix} < 0$ (b), so (d) is false. (a) and (b): code (1).

RB U12 §2.6 · p. 216

Question 36 · Q31–40 · response code

Which of the following statement/s is/are correct with regard to CFC, HCFC and HFC?

- Both classes of compounds CFC and HCFC have the ability to produce chlorine free radicals in the upper atmosphere (stratosphere).
- Both classes of compounds HFC and HCFC have the ability to produce chlorine free radicals in the upper atmosphere (stratosphere).
- All three classes of compounds CFC, HCFC and HFC are strong greenhouse gases.
- All three classes of compounds CFC, HCFC and HFC contribute significantly to ozone layer depletion.

Answer and review

Answer **(5)** Official marking scheme

Only compounds that contain chlorine release Cl• on photolysis by stratospheric UV, so CFCs and HCFCs do (a true) but HFCs (no Cl) do not, so they do not deplete ozone (b and d false). All three classes absorb infrared strongly and are potent greenhouse gases (c true). The correct set is (a) and (c), which is not among the listed pairs: code (5).

RB U14 §1.13 · p. 58

Question 37 · Q31–40 · response code

Which of the following statement/s is/are correct with regard to halogens, noble gases and their compounds?

- Hypochlorous ion disproportionates rapidly in acidic solutions.
- Xe forms a series of compounds with F_2 gas, among which XeF_4 has a square planar geometry.
- Among the hydrogen halides, HF has the highest bond dissociation energy per mole.
- Boiling points of halogens increase down the group as a result of increasing strength of London forces.

Answer and review

Answer **(3/5)** Official marking scheme

The official scheme accepts (3) or (5). (a) is false: in acid HOCl is the more stable species, and disproportionation of ClO^- ($3ClO^- \rightarrow ClO_3\text{^}- + 2Cl^-$) is favoured under basic conditions. (b) XeF_2, XeF_4, XeF_6 form with F_2, and XeF_4 (4 bond pairs, 2 lone pairs) is square planar: true. (c) H–F is the strongest H–X bond (about 565 kJ mol^{-1}): true. (d) Larger, more polarisable halogen molecules have stronger London forces: true. The fully correct set is (b), (c), (d), code (5); code (3) (c, d) is also credited.

RB U6 §4.7 · p. 149 RB U6 §4.8 · p. 152 RB U2 §2.6 · p. 79

Question 38 · Q31–40 · response code

Which of the following statement/s is/are correct regarding the Daniell cell when it operates at room temperature? ($E°_{cell} = +1.10$ V)

- Net electron flow occurs from Zn to Cu.
- The equilibrium $Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s)$ shifts to the right.
- A liquid-junction potential is created due to the presence of a salt-bridge.
- The equilibrium $Cu^{2+}(aq) + 2e \rightleftharpoons Cu(s)$ shifts to the right.

Answer and review

Answer **(4)** Official marking scheme

In the spontaneous Daniell cell Zn is oxidised (anode) and Cu^{2+} is reduced (cathode). Electrons flow through the external wire from Zn to Cu (a true). At the Zn electrode $Zn^{2+} + 2e \rightleftharpoons Zn$ shifts to the **left** (b false), while at the Cu electrode $Cu^{2+} + 2e \rightleftharpoons Cu$ shifts to the right (d true). The salt bridge is used to **minimise** the liquid-junction potential, not to create one (c false). (a) and (d): code (4).

RB U13 §3.3 · p. 250

Question 39 · Q31–40 · response code

Which of the following statement/s is/are correct for ideal gases and real gases at constant temperature?

- At very high pressures, the volume of a real gas is higher than that of an ideal gas.
- At high pressures, real gases tend to behave as ideal gases.
- At very high pressures, the volume of a real gas is lower than that of an ideal gas.
- At low pressures, real gases tend to behave as ideal gases.

Answer and review

Answer **(4)** Official marking scheme

At very high pressure the molecules are packed closely, their own volume is no longer negligible and repulsions dominate (Z > 1), so the real gas occupies a **larger** volume than the ideal gas (a true, c false). At high pressure gases deviate strongly (b false); at low pressure the molecules are far apart and intermolecular forces and molecular volume are negligible, so the gas behaves ideally (d true). (d) and (a): code (4).

RB U4 §1.5 · p. 24

Question 40 · Q31–40 · response code

Which of the following statement/s is/are correct regarding some industrial processes?

- The first two steps involved in the manufacture of Na_2CO_3 by Solvay Process are endothermic.
- The presence of Mg^{2+}, Ca^{2+} and SO_4^{2-} ions in brine, hinders the production of NaOH using the membrane cell method.
- The first step involved in the manufacture of nitric acid by Ostwald method is the oxidation of NH_3 gas using O_2 in air in the presence of a catalyst to give NO_2 gas.
- High temperature and low pressure conditions are employed in the manufacture of NH_3 gas using Haber-Bosch process.

Answer and review

Answer **(5)** Official marking scheme

Only (b) is correct. (a) false: the first two steps, ammonification of brine (dissolving NH_3) and carbonation (formation of NH_4HCO_3), are both exothermic, so the towers are cooled. (b) true: Mg^{2+}, Ca^{2+} and SO_4^{2-} must be removed from the brine, otherwise they foul the membrane (precipitating $Mg(OH)_2$, $Ca(OH)_2$, $CaSO_4$) and damage the cell. (c) false: the first step gives NO ($4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$), which is later oxidised to NO_2. (d) false: the exothermic reaction with a decrease in moles of gas uses high pressure (about 200 atm) and a moderate temperature (about 450 °C) as a compromise. A single correct statement is not a listed pair: code (5).

RB U14 §1.5 · p. 18 RB U14 §1.2 · p. 6 RB U14 §1.6 · p. 21

Questions 41–50: statement pairs

Response	First statement	Second statement
(1)	True	True, and correctly explains the first statement
(2)	True	True, but does not explain the first statement correctly
(3)	True	False
(4)	False	True
(5)	False	False

Question 41 · Q41–50 · statement pair

Statement 1

Among the oxides of Cr and Mn, CrO and MnO are acidic, while CrO_3 and Mn_2O_7 are basic.

Statement 2

The acidic/basic nature of the oxides of Cr and Mn is dependant on the oxidation number of the metal.

Answer and review

Answer **(4)** Official marking scheme

The first statement is false: it is reversed. Low oxidation states give basic oxides (CrO, MnO), the intermediate ones are amphoteric (Cr_2O_3), and the highest oxidation states give acidic oxides (CrO_3, Mn_2O_7, which give H_2CrO_4 and $HMnO_4$). The second statement is true: acidity increases with the oxidation number of the metal (more covalent M–O bonding). So the first is false and the second is true: response (4).

RB U6 §4.10 · p. 160

Question 42 · Q41–50 · statement pair

Statement 1

An acidic buffer solution can be prepared by mixing a weak acid HA(aq) with its sodium salt NaA(aq).

Statement 2

When $OH^-(aq)$ or $H^+(aq)$ ions are added to a buffer solution, the added amounts of $OH^-(aq)$ or $H^+(aq)$ are removed through the reactions; $OH^-(aq) + HA(aq) \rightarrow A^-(aq) + H_2O(l)$ and $H^+(aq) + A^-(aq) \rightarrow HA(aq)$ respectively.

Answer and review

Answer **(1/2)** Official marking scheme

The official scheme accepts (1) or (2). Both statements are true. A weak acid with its conjugate base (salt) is an acidic buffer, and the second statement gives the mechanism by which HA removes added OH^- and A^- removes added H^+. Whether this is regarded as "explaining" the first statement is debatable (it explains how the buffer works, not why this mixture is called an acidic buffer, which depends on pH < 7), so both (1) and (2) are credited.

RB U12 §2.3 · p. 167

Question 43 · Q41–50 · statement pair

Statement 1

Essential oils can be extracted from plants by steam distillation at a temperature below 100 °C.

Statement 2

At the temperature at which a mixture of essential oil and water boils, the total vapour pressure of the system is less than the atmospheric pressure.

Answer and review

Answer **(3)** Official marking scheme

The first statement is true: the essential oil is immiscible with water, so the total vapour pressure is the sum of the two vapour pressures, $P = P_{oil} + P_{water}$, and the mixture boils below 100 °C. The second statement is false: a liquid (or mixture) boils when its total vapour pressure **equals** the atmospheric pressure, not when it is less. Response (3).

RB U14 §1.12 · p. 48 RB U12 §2.5 · p. 199 RB U12 §2.6 · p. 216

Question 44 · Q41–50 · statement pair

Statement 1

At a given temperature and pressure the molar volumes of two different ideal gases are different from each other.

Statement 2

At 0 °C temperature and 1 atm pressure, the molar volume of an ideal gas is 22.4 $dm^3\ mol^{-1}$.

Answer and review

Answer **(4)** Official marking scheme

By Avogadro's law, equal volumes of any ideal gases at the same T and P contain the same number of moles, so the molar volume $V_m = RT/P$ is the same for all ideal gases: the first statement is false. At 273.15 K and 1 atm, $V_m = 0.08206 \times 273.15/1 = 22.4\ dm^3\ mol^{-1}$: the second statement is true. Response (4).

RB U4 §1.2 · p. 5

Question 45 · Q41–50 · statement pair

Statement 1

All compounds having a C=C bond show diastereoisomerism.

Statement 2

Any two isomers which are not mirror images of each other are diastereoisomers.

Answer and review

Answer **(5)** Official marking scheme

Both statements are false. A C=C bond gives geometric (cis/trans, E/Z) diastereoisomers only when each carbon of the double bond carries two different groups (e.g. $CH_2{=}CH_2$ and $(CH_3)_2C{=}CH_2$ show none). Diastereoisomers are **stereoisomers** that are not mirror images; "any two isomers" also includes structural (constitutional) isomers such as butan-1-ol and butan-2-ol, which are not diastereoisomers. Response (5).

RB U7 §1.4 · p. 21

Question 46 · Q41–50 · statement pair

Statement 1

Hydrogenation of benzene is more difficult than hydrogenation of alkenes.

Statement 2

Addition of hydrogen to benzene results in the loss of aromatic stabilization.

Answer and review

Answer **(1)** Official marking scheme

The delocalised π system of benzene gives it extra (aromatic) stability, about 150 kJ mol^{-1} (resonance energy). Hydrogenation destroys this delocalisation, so it needs more severe conditions (high pressure, Ni catalyst and heat) than a simple alkene. Both statements are true and the second explains the first: response (1).

RB U8 §2.4 · p. 44 RB U8 §2.2 · p. 33

Question 47 · Q41–50 · statement pair

Statement 1

The reaction that takes place between SO_3 gas and water in the production of sulphuric acid is endothermic.

Statement 2

SO_3 gas reacts with concentrated H_2SO_4 to give oleum.

Answer and review

Answer **(4)** Official marking scheme

The first statement is false: the reaction $SO_3 + H_2O \rightarrow H_2SO_4$ is highly exothermic (it gives a mist of acid), which is why it is not carried out directly in industry. The second statement is true: in the Contact process SO_3 is absorbed in 98% H_2SO_4 to give oleum, $H_2S_2O_7$, which is then diluted with water. Response (4).

RB U14 §1.8 · p. 27

Question 48 · Q41–50 · statement pair

Statement 1

Reaction between ammonia and an alkylhalide gives a mixture of primary, secondary and tertiary amines and a quaternary ammonium salt.

Statement 2

Primary, secondary and tertiary amines can react as nucleophiles.

Answer and review

Answer **(1)** Official marking scheme

NH_3 attacks the alkyl halide (S_{N2}) to give a primary amine. The amine still has a lone pair on N and is itself a nucleophile, so it attacks another molecule of RX to give the secondary amine, then the tertiary amine and finally the quaternary ammonium salt $R_4N\hat{}+X^-$. Both statements are true and the second explains the first: response (1).

RB U10 §4.1 · p. 75 RB U8 §2.6 · p. 49

Question 49 · Q41–50 · statement pair

Statement 1

If P + Q → R is a first order reaction with respect to the reactant P, the graph of rate against concentration of P gives a straight line passing through the origin.

Statement 2

Initial rate of a first order reaction is independent of the concentration of reactant(s).

Answer and review

Answer **(3)** Official marking scheme

For first order in P, rate = k[P] (the order in Q does not alter this when [Q] is held constant), which is a straight line through the origin: the first statement is true. The second statement is false: for a first order reaction the rate is directly proportional to the concentration, so the initial rate changes when the concentration changes (it is the rate constant, and the half-life, that are independent of concentration). Response (3).

RB U11 §1.6 · p. 16

Question 50 · Q41–50 · statement pair

Statement 1

On a sunny day, strong photochemical smog can be seen in a city with heavy traffic congestion.

Statement 2

Photochemical smog is caused entirely by scattering of solar radiation by small particles and water droplets that are emitted by vehicle exhaust systems.

Answer and review

Answer **(3)** Official marking scheme

The first statement is true: vehicle exhaust supplies NO_x and hydrocarbons, which react in strong sunlight (UV) to form O_3, PAN and aldehydes. The second statement is false: photochemical smog is caused by **photochemical reactions** producing secondary pollutants, not "entirely" by scattering of light by particles and droplets. Response (3).

RB U14 §1.13 · p. 58

Structured essay · answer all four

SEQ · Paper II Part A

Question 1 · Part A · structured essay

(a) [24 marks]

Write the answers to the questions given below.
(i) Of the three ions Na^+, Mg^{2+} and F^-, which one has the **smallest** ionic radius?

Answer

Mg^{2+} (04 marks)

(ii) Of the three elements C, N and O, which one has the **highest** second ionization energy?

Answer

O (04 marks)

(iii) Of the three compounds H_2O, HOCl and OF_2, which one has the **most** electronegative oxygen atom?

Answer

OF_2 (04 marks)

(iv) Of the three elements Be, C and N, which one will liberate energy when an electron is added to its atom [$Y(g) + e \rightarrow Y^-(g)$; Y = Be, C, N] in the gaseous state?

Answer

C (04 marks)

(v) Of the three ionic compounds NaF, KF and KBr, which one has the **highest** solubility in water?

Answer

KF or KBr (04 marks)

(vi) Of the three compounds HCHO, CH_3F and H_2O_2, which one has the **strongest** intermolecular forces?

Answer

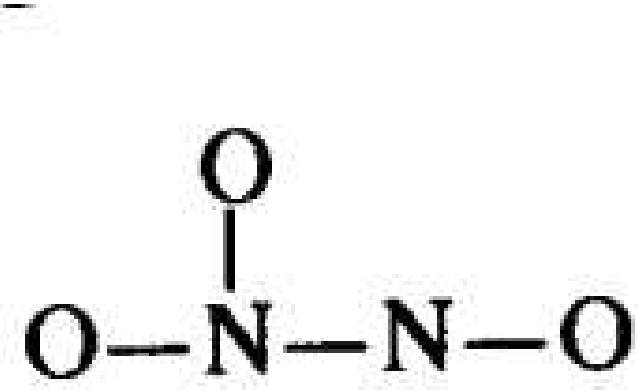
H_2O_2 (04 marks × 6 = 24 marks) · 1(a): 24 marks

Review.

(i) Mg^{2+} has the largest nuclear charge (+12) for the same 10 electrons, so it is the smallest isoelectronic ion. (ii) Removing the second electron from O (O^+, $2p^3$ half-filled) is hardest; N^+ ($2p^2$) and C^+ ($2p^1$) lose theirs more easily. (iii) The two electronegative F atoms pull electron density from O in OF_2, making O the most electronegative here (O is attached to atoms of higher electronegativity). (iv) Be ($2s^2$, full) and N ($2p^3$, half-filled) have positive (endothermic) electron gain enthalpies; C ($2p^2 \rightarrow 2p^3$) releases energy. (v) NaF has a high lattice energy that makes it much less soluble; KF and KBr are both very soluble (the scheme accepts either). (vi) H_2O_2 forms extensive hydrogen bonds; HCHO and CH_3F have only dipole–dipole forces (no O–H or N–H/F–H bond, so no hydrogen bonding). Common error: choosing HCHO or CH_3F for (vi) because of polarity alone.

(b) [56 marks]

(i) Draw the **most** acceptable Lewis dot-dash structure for the ion, $N_2O_3^{2-}$. Its skeleton is given below.



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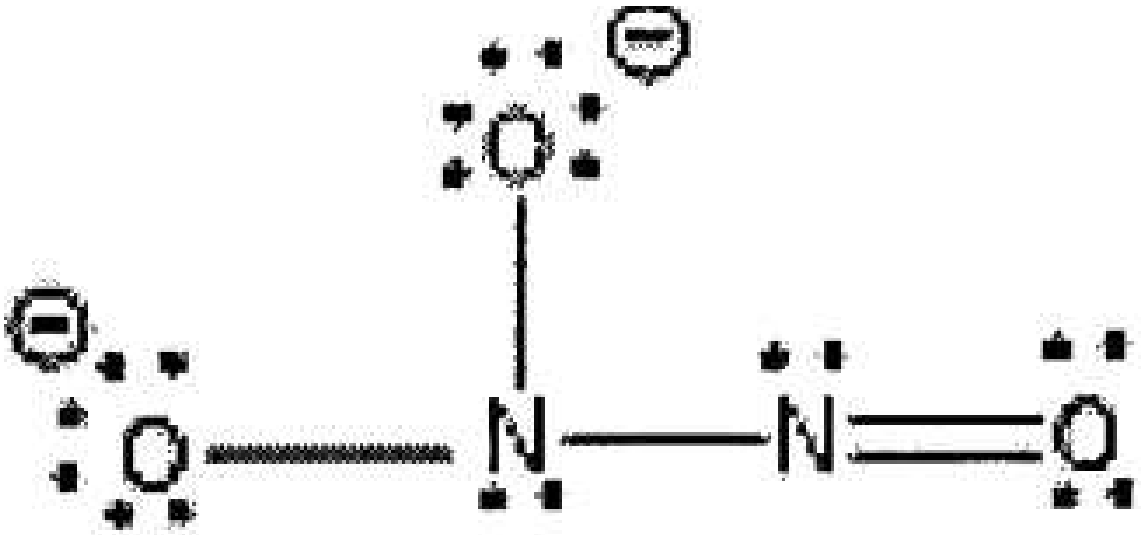
2−

Answer

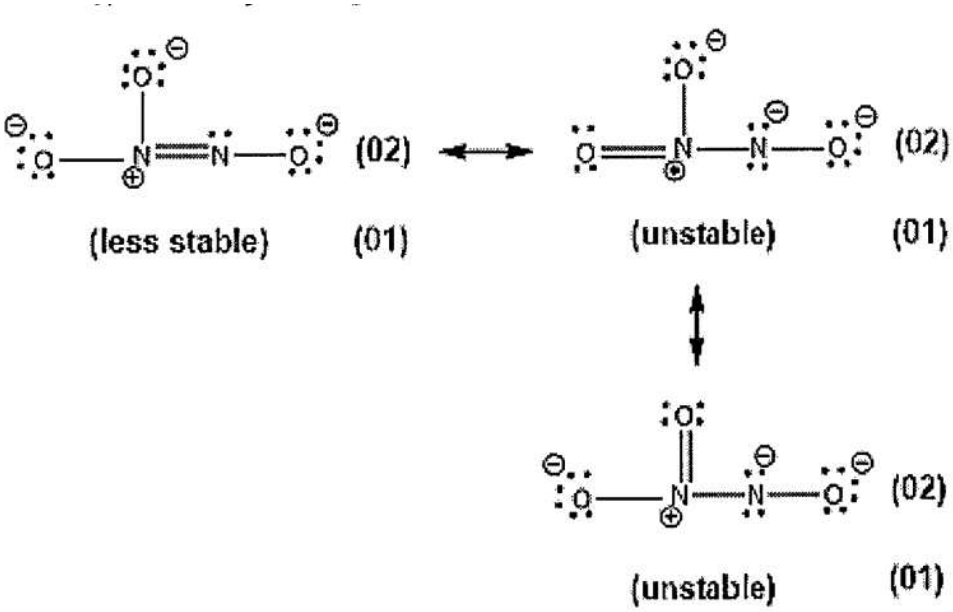


Most acceptable Lewis structure

Each of two O atoms bonded singly to the first N carries a negative charge (O^-) and has three lone pairs; N–N single bond; the other N is doubly bonded to the terminal O (N=O). Formal charges on both N atoms are zero. (06 marks)

(ii) Draw **three** more Lewis structures (resonance structures) for this ion. Indicate the relative stabilities of the structures drawn by you, when compared with the most acceptable structure drawn in (i) above, by writing 'less stable' or 'unstable' under these structures.

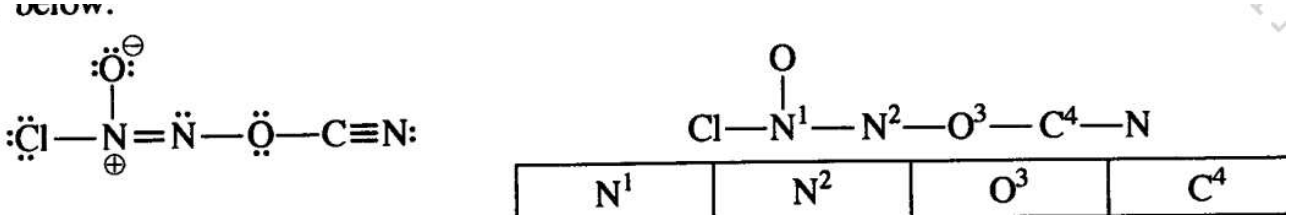
Answer



Resonance structures

(1) O^-–N^+(–O^-)=N–O^- (N^1 carries +1, N^1=N^2 double bond, N^2–O^- single bond): **less stable** (02 + 01)
(2) O=N^+(–O^-)–N^-–O^- (double bond from N^1 to one O; N^2 carries −1): **unstable** (02 + 01)
(3) the same as (2) with the double bond to the other O on N^1: **unstable** (02 + 01)
(02 + 01) × 3 = 09 marks

(iii) Complete the given table based on the Lewis dot-dash structure (Cl–N^1(O^-)=N^2–O^3–C^4≡N, with N^1 carrying a formal positive charge) and its labelled skeleton below (Cl–N^1(O)–N^2–O^3–C^4–N).



Lewis structure and labelled skeleton

Answer

	N^1	N^2	O^3	C^4
VSEPR pairs around the atom	3	3	4	2
electron pair geometry around the atom	trigonal planar	trigonal planar	tetrahedral	linear
shape around the atom	trigonal planar	angular / V	angular / V	linear
hybridization of the atom	sp^2	sp^2	sp^3	sp

(01 mark × 16 = 16 marks)

Parts (iv) to (vii) are based on the Lewis dot-dash structure given in part (iii) above. Labelling of atoms is as in part (iii).

(iv) Identify the atomic / hybrid orbitals involved in the formation of σ bonds between the two atoms given below.

I. Cl–N^1 II. N^1–O III. N^1–N^2 IV. N^2–O^3 V. O^3–C^4 VI. C^4–N

Answer

I. Cl: 3p **or** sp^3; N^1: sp^2
II. N^1: sp^2; O: 2p **or** sp^3
III. N^1: sp^2; N^2: sp^2
IV. N^2: sp^2; O^3: sp^3
V. O^3: sp^3; C^4: sp
VI. C^4: sp; N: 2p **or** sp (01 mark × 12 = 12 marks)

(v) Identify the atomic orbitals involved in the formation of π bonds between the two atoms given below.

I. N^1–N^2 II. C^4–N

Answer

I. N^1: 2p; N^2: 2p
II. (two π bonds) C^4: 2p, N: 2p; and C^4: 2p, N: 2p (01 mark × 6 = 06 marks)

(vi) State the approximate bond angles around N^1, N^2, O^3 and C^4 atoms.

Answer

N^1: 120° ± 1; N^2: 115°–118°; O^3: 104° ± 1; C^4: 180° ± 1 (01 mark × 4 = 04 marks)

(vii) Arrange the atoms N^1, N^2, O^3 and C^4 in the **increasing** order of electronegativity.

Answer

$C^4 < N^2 < N^1 < O^3$ (03 marks) · 1(b): 56 marks

Review.

Method: for each atom count σ-bond pairs plus lone pairs (VSEPR pairs); this gives the electron-pair geometry and hybridization (2 → sp, 3 → sp^2, 4 → sp^3); lone pairs are then removed to describe the shape. Each double bond has one σ and one π bond (π from side-on 2p–2p overlap) and a triple bond has one σ and two π bonds. N^2 has one lone pair, so its shape is angular with an angle a little below 120° (115°–118°); O^3 has two lone pairs (≈104°). Electronegativity increases with s-character and with positive formal charge, hence the scheme's order puts N^1 (formal charge +1) above N^2. Common mistakes: forgetting the formal charges when drawing the best structure, counting π bonds as σ bonds, and giving the shape as 'tetrahedral' instead of 'angular' for O^3.

(c) [20 marks]

Consider the following information.
I. The atoms A and B combine to form a heterodiatomic molecule AB that has a σ bond. This is represented as A–B.
II. The electronegativity of A is less than that of B ($X_A < X_B$). X = electronegativity of the atom.
III. The inter-nuclear distance between A and B atoms ($d_{A–B}$) of the AB molecule is given by the following equation.
$d_{A–B} = r_A + r_B - c(X_B - X_A)$ (r = atomic radius, c = 9 pm)
Note: d and r are measured in picometres (pm). (1 pm = 10^{-12} m)
Based on the above information, answer the following questions.
(i) What is the name used to identify the type of σ bond between A and B?

Answer

Polar covalent bond (03 marks)

(ii) Show how fractional charges (δ+ and δ−) are located in the molecule AB.

Answer

$A^{\delta+}$–$B^{\delta-}$ (03 marks)

(iii) Write the equation to calculate the dipole moment (μ) of molecule AB and show its direction.

Answer

$\mu = d_{AB} \times \delta$ **or** $\mu = q\ r$; direction shown by an arrow from A towards B (A→B), or A+→B (crossed arrow, positive end at A). (01 + 01 marks)

(iv) Calculate the percentage of ionic character of the H–F bond in the HF molecule using the data given below.
Inter-nuclear distance of H_2 ($d_{H–H}$) = 74 pm Electronegativity of F = 4.0
Inter-nuclear distance of F_2 ($d_{F–F}$) = 144 pm Dipole moment of HF = 6.0×10^{-30} C m
Electronegativity of H = 2.1 Charge of an electron = 1.6×10^{-19} C

Answer

$\mu = d_{HF} \times \delta\ (H^{\delta+}\text{–}F^{\delta-})$
$r_H = d_{H2}/2 = 74/2 = 37$ pm (02)
$r_F = d_{F2}/2 = 144/2 = 72$ pm (02)
$d_{HF} = 37 + 72 - 9(4.0 - 2.1)$ (01) $= 109 - 9 \times 1.9 = 91.9$ pm (02)
$\mu = d_{HF} \times \delta$: 6.0×10^{-30} C m $= \delta \times 91.9 \times 10^{-12}$ m (01)
$\delta = 6.0 \times 10^{-30} / 91.9 \times 10^{-12} = 0.65 \times 10^{-19}$ C (02)
% ionic character $= (0.65 \times 10^{-19} / 1.6 \times 10^{-19}) \times 100$ (01) = **40.6 %** (01)
OR
$r_H = 37$ pm (02), $r_F = 72$ pm (02); $d_{HF} = 37 + 72 - 9(4.0 - 2.1)$ (01) $= 91.9$ pm (02)
$\mu_{ionic} = 1.6 \times 10^{-19}$ C $\times 91.9 \times 10^{-12}$ m $= 147.04 \times 10^{-31}$ C m (03)
% ionic character $= (6 \times 10^{-30} / 147.04 \times 10^{-31}) \times 100$ (01) = **40.8 %** (01) · 1(c): 20 marks

Review.

Principle: a bond between atoms of different electronegativity is polar covalent, with partial charges δ+ and δ−; the dipole moment is $\mu = \delta \times d$. The bond length is estimated by the Schomaker–Stevenson-type relation given, $d = r_A + r_B - c(\Delta X)$. Percentage ionic character = (observed μ / μ if the bond were 100 % ionic, i.e. one full electronic charge separated by d) × 100 = δ/e × 100. Check: d = 91.9 pm, $\mu_{ionic} = 1.47 \times 10^{-29}$ C m, $6.0 \times 10^{-30}/1.47 \times 10^{-29} = 40.8$ %; the δ-first route gives 40.6 % because of rounding (both accepted). Common mistakes: using $d_{H–H}$ and $d_{F–F}$ directly instead of the radii (half the bond length), omitting the electronegativity correction, and not converting pm to m.

Read: RB U1 §1.6 · p. 32 RB U2 §2.1 · p. 44 RB U2 §2.3 · p. 52 RB U2 §2.4 · p. 75 RB U2 §2.6 · p. 79

Question 2 · Part A · structured essay

(a) [50 marks]

A, B, C and D are chlorides of p-block elements. These elements have atomic numbers less than 20. A description of the products (P_1–P_9) formed when A is reacted with a limited amount of water and B, C and D are reacted with excess water are given below.

Compound	Product	Description of products
A	P_1	a compound with a covalent network structure
P_2	a strong monobasic acid	
B	P_3	a gas that turns red litmus blue
P_4	a compound with bleaching properties	
C	P_5	a tribasic acid
P_6	a strong monobasic acid	
D	P_7	a gas that turns acidic $KMnO_4$ solution colourless
P_8	a colloidal solid	
P_9	a strong monobasic acid	

Answer

A: $SiCl_4$ B: NCl_3 C: PCl_5 D: SCl_2 (04 marks × 4 = 16 marks)

(ii) Give balanced chemical equations for the reactions of A, B, C and D with water to give products P_1 to P_9.

Answer

$SiCl_4 + 2H_2O \rightarrow SiO_2$ (P_1) + 4HCl (P_2) (05)
$NCl_3 + 3H_2O \rightarrow NH_3$ (P_3) + 3HOCl (P_4) (05)
$PCl_5 + 4H_2O \rightarrow H_3PO_4$ (P_5) + 5HCl (P_6) (05)
$2SCl_2 + 2H_2O \rightarrow SO_2$ (P_7) + S (P_8) + 4HCl (P_9) (05)
Note: award marks if correct balanced equations are given. (05 marks × 4 = 20 marks)

(iii) Write balanced chemical equations for the following reactions.
I. P_1 with NaOH(aq)
II. P_3 with Mg
III. P_7 with acidic $K_2Cr_2O_7$

Answer

I. $SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$ (04)
II. $3Mg + 2NH_3 \rightarrow Mg_3N_2 + 3H_2$ (04)
III. $3(SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e)$; $Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$
Overall: $3SO_2 + Cr_2O_7^{2-} + 2H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$ (06)
If only half reactions are given, part marks (02 + 02). (14 marks) · 2(a): 50 marks

(b) [50 marks]

A student is provided with bottles labelled P, Q, R, S, T and U containing aqueous solutions of $Al_2(SO_4)_3$, H_2SO_4, $Na_2S_2O_3$, $BaCl_2$, $Pb(Ac)_2$ and KOH (not in order). Some useful observations for their identification on mixing two solutions at a time are given below. (Ac – acetate ion)

	Solutions mixed	Observations
I	T + R	a clear colourless solution
II	P + R	a white precipitate
III	T + S	a gelatinous white precipitate
IV	U + R	a white precipitate
V	P + Q	a white precipitate, turns black on heating
VI	P + U	a white precipitate, dissolves on heating

Answer

P: $Pb(Ac)_2$ Q: $Na_2S_2O_3$ R: H_2SO_4 S: $Al_2(SO_4)_3$ **or** KOH T: KOH **or** $Al_2(SO_4)_3$ U: $BaCl_2$ (05 marks × 6 = 30 marks)

(ii) Give balanced chemical equations for each of the reactions I to VI. (Note: indicate precipitates as ↓)

Answer

I. $2KOH + H_2SO_4 \rightarrow K_2SO_4 + 2H_2O$ **or** $Al_2(SO_4)_3 + H_2SO_4 \rightarrow$ no reaction (03)
II. $Pb(Ac)_2 + H_2SO_4 \rightarrow PbSO_4\downarrow + 2HAc$ (03)
III. $6KOH + Al_2(SO_4)_3 \rightarrow 2Al(OH)_3\downarrow + 3K_2SO_4$ (03)
IV. $BaCl_2 + H_2SO_4 \rightarrow BaSO_4\downarrow + 2HCl$ (03)
V. formation of white precipitate: $Pb(Ac)_2 + Na_2S_2O_3 \rightarrow PbS_2O_3\downarrow + 2NaAc$ (03)
turning black on heating: $PbS_2O_3 + H_2O \rightarrow PbS\downarrow + H_2SO_4$ (02)
VI. $Pb(Ac)_2 + BaCl_2 \rightarrow PbCl_2\downarrow + Ba(Ac)_2$ (03)
Note: precipitates have to be shown by ↓ or as (s); if not, deduct 01 mark. (20 marks) · 2(b): 50 marks

Review.

Part (a): the hydrolysis of covalent chlorides of p-block elements is the key: $SiCl_4$ gives hydrated SiO_2 (network solid) and HCl; PCl_5 gives H_3PO_4 (tribasic) and HCl; NCl_3 hydrolyses to NH_3 (turns red litmus blue) and HOCl (bleaching), because in NCl_3 the N–Cl bond is polarised $N^{\delta-}$–$Cl^{\delta+}$ (N and Cl have similar electronegativity and N has the lone pair), so water gives NH_3 and HOCl rather than HCl; SCl_2 disproportionates (S(+2) → S(+4) and S(0)) to SO_2 (decolourises acidic $KMnO_4$), colloidal S and HCl. P_3 (NH_3) reacts with hot Mg to form Mg_3N_2; SiO_2 is an acidic oxide that dissolves in NaOH; SO_2 is oxidised to sulphate by dichromate (orange to green Cr^{3+}). Part (b): start with unique observations: a precipitate that turns black on heating = lead thiosulfate → PbS, which fixes P and Q; a gelatinous white precipitate with an excess-soluble hydroxide = $Al(OH)_3$, which fixes T/S (KOH and $Al_2(SO_4)_3$); R must be H_2SO_4 because it gives white precipitates with both P ($PbSO_4$) and U ($BaSO_4$). $PbCl_2$ dissolves on heating, which confirms VI. Common mistakes: writing $Pb(Ac)_2$ + $Na_2S_2O_3$ directly to PbS at the white-precipitate stage, balancing errors in the dichromate redox equation (check: 6e on each side), and omitting ↓ (1 mark deducted).

Read: RB U6 §4.9 · p. 155 RB U6 §4.5 · p. 136 RB U6 §4.6 · p. 141 RB U3 §3.6 · p. 105

Question 3 · Part A · structured essay

(a) [60 marks]

A saturated aqueous solution of a sparingly soluble salt $AB_2(s)$ was prepared by stirring an excess amount of $AB_2(s)$ in 1.0 dm^3 of distilled water at 25 °C. The amount of $A^{2+}(aq)$ ions present in this saturated aqueous solution was found to be 2.0×10^{-3} mol.
(i) Write the equilibrium related to the dissolution of $AB_2(s)$ in the above system at 25 °C.

Answer

$AB_2(s) \rightleftharpoons A^{2+}(aq) + 2B^{-}(aq)$ (05 marks)

(ii) Write the expression for the equilibrium constant for the equilibrium written in (i) above at 25 °C.

Answer

$K_{sp} = [A^{2+}(aq)][B^{-}(aq)]^2$ (05 marks)
($K_c = [A^{2+}(aq)][B^{-}(aq)]^2 / [AB_2(s)]$: if only K_c is given, award 03 marks.)

(iii) Calculate the value of the equilibrium constant stated in (ii) above at 25 °C.

Answer

$[A^{2+}(aq)] = 2.0 \times 10^{-3}$ mol dm^{-3} (04 + 01)
$[B^{-}(aq)] = 2[A^{2+}(aq)] = 4.0 \times 10^{-3}$ mol dm^{-3} (04 + 01)
$K_{sp} = 2.0 \times 10^{-3}$ mol $dm^{-3} \times (4.0 \times 10^{-3}$ mol $dm^{-3})^2$ (05)
$K_{sp} =$ **3.2×10^{-8} mol^3 dm^{-9}** (05)

(iv) Another saturated aqueous solution of AB_2 was prepared by stirring an excess amount of $AB_2(s)$ in 2.0 dm^3 of distilled water at 25 °C. Giving reasons, predict the value of the equilibrium constant for this system.

Answer

$K_{sp} = 3.2 \times 10^{-8}$ mol^3 dm^{-9} (05)
K_{sp} is a constant at constant temperature (05)
and does not depend on the volume (05)

(v) A small amount of the strong electrolyte NaB(s) is added to a saturated aqueous solution of AB_2 at 25 °C. Giving reasons, predict whether the concentration of $A^{2+}(aq)$ is increased or decreased.

Answer

Common ion $B^-(aq)$ is added (05)
∴ more $AB_2(s)$ is formed to keep the K_{sp} constant **or** the reverse reaction takes place (05)
$[A^{2+}(aq)]$ **decreases** (05) · 3(a): 60 marks

Review.

Principle: for a sparingly soluble salt the solubility product $K_{sp} = [A^{2+}][B^-]^2$ (the solid has unit activity and is left out), and K_{sp} depends only on temperature. Method for (iii): the stoichiometry gives $[B^-] = 2[A^{2+}]$, so $K_{sp} = s(2s)^2 = 4s^3 = 4(2.0 \times 10^{-3})^3 = 3.2 \times 10^{-8}$ mol^3 dm^{-9}. Doubling the volume of water doubles the amount dissolved but not the concentrations, so K_{sp} is unchanged. Adding NaB raises $[B^-]$ and, by Le Chatelier's principle (common-ion effect), the equilibrium shifts left and $[A^{2+}]$ falls. Common mistakes: including $[AB_2(s)]$ in the expression, forgetting to square $[B^-]$ or to double it, and omitting units.

(b) [40 marks]

In an aqueous solution, propanoic acid (C_2H_5COOH) ionizes as given below.
$C_2H_5COOH(aq) + H_2O(l) \rightleftharpoons C_2H_5COO^-(aq) + H_3O^+(aq)$
At 25 °C, K_a (propanoic acid) $= 1.0 \times 10^{-5}$
(i) Write the expression for the equilibrium constant for the above reaction at 25 °C.

Answer

$K_a = [C_2H_5COO^-(aq)][H_3O^+(aq)] / [C_2H_5COOH(aq)]$ (05 marks)

(ii) 100.0 cm^3 of an aqueous solution of $C_2H_5COOH(aq)$ was prepared by dissolving 0.74 cm^3 of C_2H_5COOH in distilled water at 25 °C. Calculate the pH of the solution at 25 °C. (C = 12; O = 16; H = 1; consider the density of C_2H_5COOH as 1.0 g cm^{-3})

Answer

mass of $C_2H_5COOH = 0.74$ cm^3 $\times$ 1.00 g cm^{-3} = 0.74 g
moles of C_2H_5COOH in 100 cm^3 = 0.74 g / 74 g mol^{-1} = 0.01 mol (05)
∴ $[C_2H_5COOH(aq)] = 0.10$ mol dm^{-3} (05)
Equilibrium: initial 0.10, 0, 0; change −x, +x, +x; at equilibrium 0.10 − x, x, x (mol dm^{-3}) (05)
$K_a = x \cdot x / (0.10 - x) = 1.0 \times 10^{-5}$ (02)
$x^2/0.10 = 1.0 \times 10^{-5}$ (0.10 − x ≈ 0.10) (03)
$x^2 = 1.0 \times 10^{-6}$
$x = 1.0 \times 10^{-3}$ mol dm^{-3} $= [H_3O^+(aq)]$ (05)
$pH = -\log[H_3O^+(aq)] = -\log(1.0 \times 10^{-3})$ (05)
pH = 3.0 (05)
Note: students may take −log of both sides of $K_a = [C_2H_5COO^-][H_3O^+]/[C_2H_5COOH]$ and calculate the pH; award marks appropriately. 3(b): 40 marks

Review.

Principle: a weak acid ionizes only slightly, so $[H^+] = \sqrt{(K_a\ c)}$ when x << c. Method: molar mass of C_2H_5COOH = 74 g mol^{-1}; 0.74 g = 0.010 mol in 0.100 dm^3 gives 0.10 mol dm^{-3}; $[H^+] = \sqrt{(1.0 \times 10^{-5} \times 0.10)} = 1.0 \times 10^{-3}$ mol dm^{-3}, so pH = 3.0 (x is 1 % of 0.10, so the approximation is valid). Common mistakes: not converting 0.74 cm^3 to a mass with the density, forgetting that the final volume is 100 cm^3 (concentration in mol dm^{-3}), and using the concentration of the acid directly as $[H^+]$ (that would give pH 1).

Read: RB U12 §2.4 · p. 175 RB U12 §2.2 · p. 118 RB U3 §3.8 · p. 115

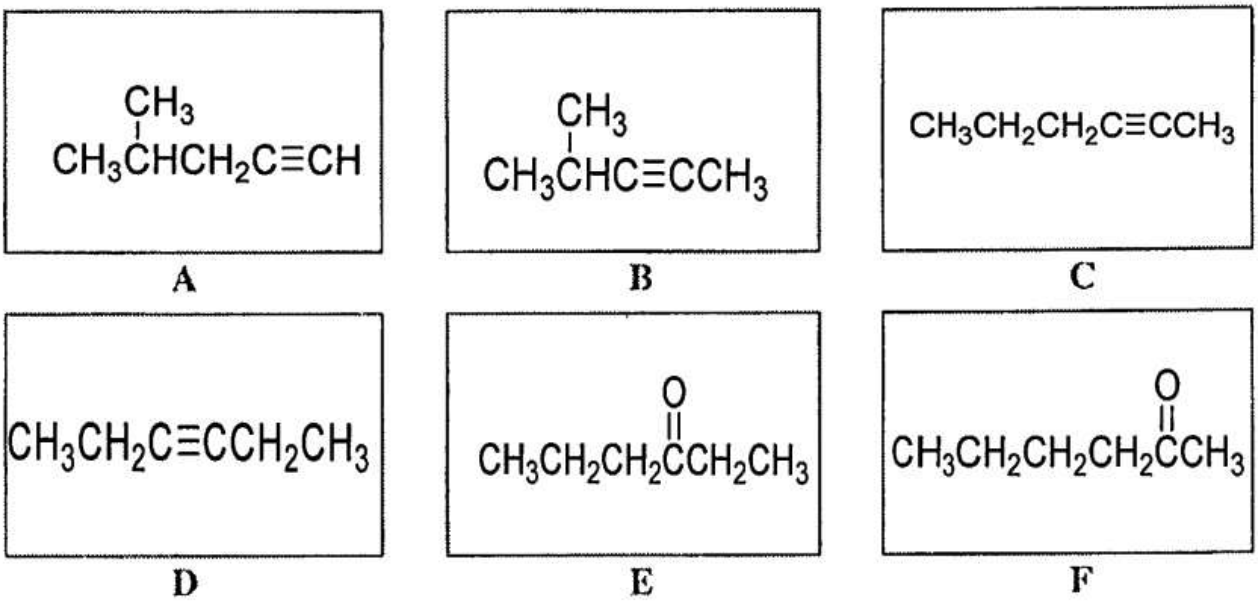
Question 4 · Part A · structured essay

(a) [60 marks]

A, B, C and D are structural isomers having the molecular formula C_6H_{10}. None of them show optical isomerism. All four isomers, A, B, C and D when treated with $HgSO_4$/dil. H_2SO_4 give products which react with 2,4-dinitrophenylhydrazine (2,4-DNP) to give coloured precipitates. Only A gives a precipitate with ammoniacal $AgNO_3$. A has only one position isomer, which is B. B is a chain isomer of C. C reacts with $HgSO_4$/dil. H_2SO_4 to give two products E and F. D reacts with $HgSO_4$/dil. H_2SO_4 to give only one product, which is E.

(i) Draw the structures of A, B, C, D, E and F in the boxes given below.

Answer



Structures of A–F

A: $CH_3CH(CH_3)CH_2C{\equiv}CH$ (4-methylpent-1-yne)
B: $CH_3CH(CH_3)C{\equiv}CCH_3$ (4-methylpent-2-yne)
C: $CH_3CH_2CH_2C{\equiv}CCH_3$ (hex-2-yne)
D: $CH_3CH_2C{\equiv}CCH_2CH_3$ (hex-3-yne)
E: $CH_3CH_2CH_2C(=O)CH_2CH_3$ (hexan-3-one)
F: $CH_3CH_2CH_2CH_2C(=O)CH_3$ (hexan-2-one) (06 marks × 6 = 36 marks)

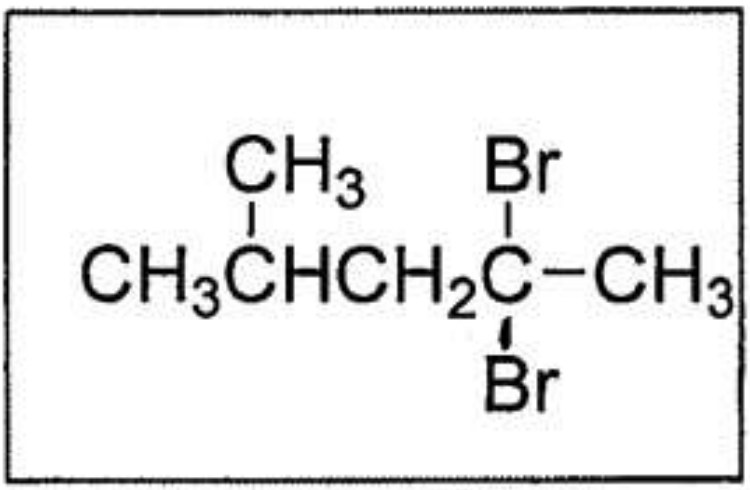
(ii) Which of the compounds A, B, C and D gives a product that does not show diastereoisomerism when reacted separately with H_2 / Pd-$BaSO_4$ / quinoline?

Answer

A, i.e. $CH_3CH(CH_3)CH_2C{\equiv}CH$ (or the appropriate letter A identifying the correct structure) (05 marks)

(iii) Draw, in the box given below, the structure of the product G obtained when A is reacted with excess HBr.

Answer



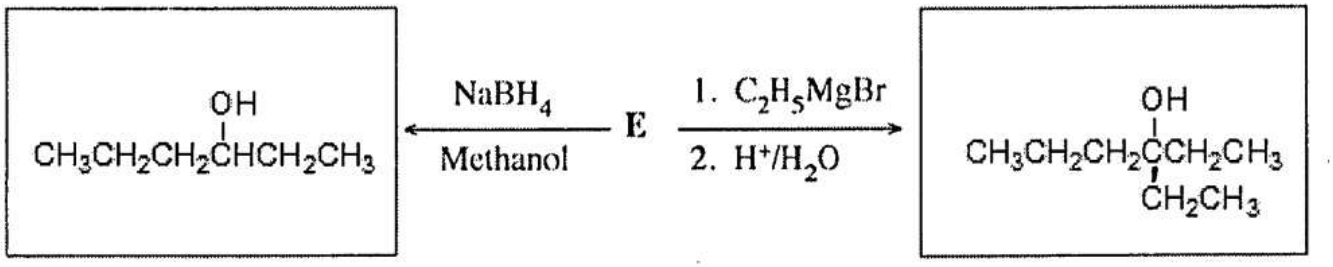
G

Product G

G: $CH_3CH(CH_3)CH_2C(Br)_2CH_3$ (2,2-dibromo-4-methylpentane) (05 marks)

(iv) Draw the structures of products X and Y obtained in the following reactions of E, in the appropriate boxes.
E → X with $NaBH_4$ / methanol; E → Y with 1. C_2H_5MgBr, 2. H^+/H_2O.
Name a test to distinguish between X and Y.

Answer



Products X and Y

X: $CH_3CH_2CH_2CH(OH)CH_2CH_3$ (hexan-3-ol) Y: $CH_3CH_2CH_2C(OH)(CH_2CH_3)CH_2CH_3$ (3-ethylhexan-3-ol) (05 × 2 = 10 marks)
Test to distinguish X and Y: Lucas test **or** anhydrous $ZnCl_2$ / conc. HCl **or** $H^+/K_2Cr_2O_7$ **or** $H^+/KMnO_4$ (04 marks) · 4(a): 60 marks

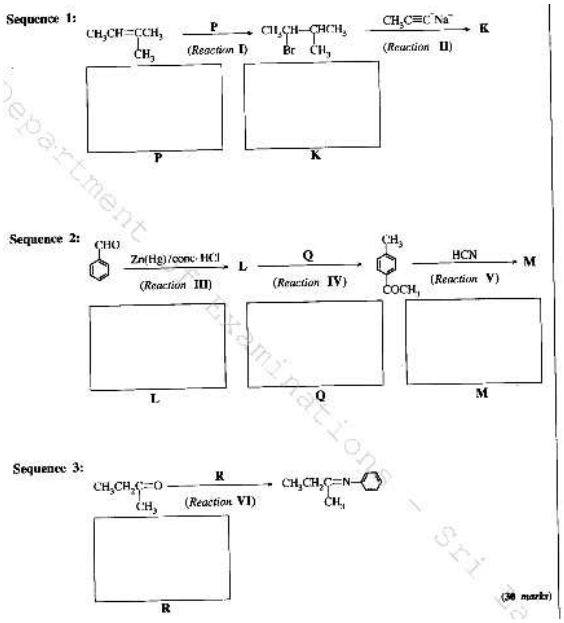
Review.

Principle: $HgSO_4$/dil. H_2SO_4 hydrates an alkyne (Markovnikov) to an enol that tautomerises to a ketone, which gives an orange 2,4-DNP precipitate; only a terminal alkyne (≡C–H) forms a silver acetylide precipitate with ammoniacal $AgNO_3$, so A is terminal. A and B are position isomers of the same carbon skeleton (the triple bond moves), B and C are chain isomers (branched vs straight), and C (unsymmetrical, hex-2-yne) gives two ketones while the symmetrical D (hex-3-yne) gives only one (E). H_2/Pd-$BaSO_4$/quinoline (Lindlar-type) stops at the cis-alkene; B, C and D give cis-alkenes (with cis/trans stereoisomers possible in the product), while the terminal alkyne A gives a terminal alkene with no geometric isomerism. Excess HBr adds Markovnikov twice, to give the geminal dibromide G. $NaBH_4$ reduces the ketone E to the secondary alcohol X; the Grignard reagent adds to give the tertiary alcohol Y after hydrolysis. The Lucas reagent gives turbidity immediately with the tertiary alcohol Y but only slowly (on warming) with the secondary alcohol X. Common mistakes:

placing the keto group wrongly in E/F, forgetting that C gives two ketones and D only one, and giving a test that does not separate secondary from tertiary alcohols.

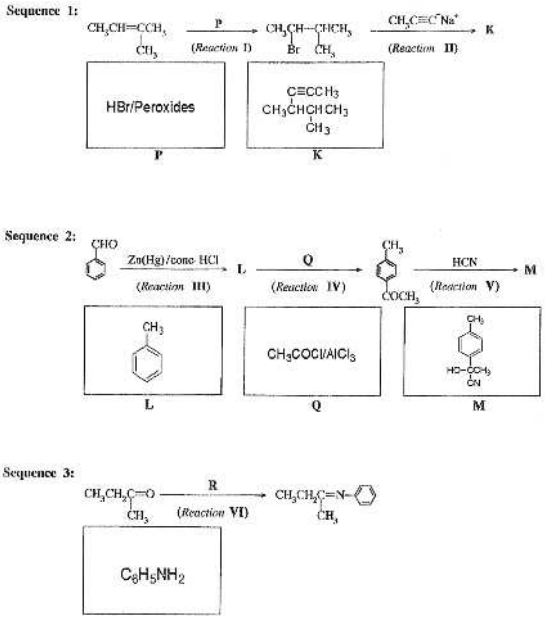
(b) [40 marks]

(i) Complete the following three reaction sequences by drawing structures of compounds K, L and M and giving the reagents/catalysts P, Q and R in the boxes given below.
Sequence 1: $(CH_3)_2C{=}CHCH_3$ → [P, Reaction I] → $CH_3CH(Br)CH(CH_3)CH_3$ → [$CH_3C{\equiv}C^-Na^+$, Reaction II] → K
Sequence 2: benzaldehyde (C_6H_5CHO) → [Zn(Hg)/conc. HCl, Reaction III] → L → [Q, Reaction IV] → 4-methylacetophenone (p-$CH_3C_6H_4COCH_3$) → [HCN, Reaction V] → M
Sequence 3: $CH_3CH_2C(=O)CH_3$ → [R, Reaction VI] → $CH_3CH_2C(CH_3){=}N{-}C_6H_5$



Reaction sequences 1 to 3

Answer



Compounds and reagents

P: HBr / peroxides (05)
K: $CH_3CH(C{\equiv}CCH_3)CH(CH_3)CH_3$ (05)
L: toluene ($C_6H_5CH_3$) (05)

Q: CH_3COCl / $AlCl_3$ (05)
M: p-$CH_3C_6H_4$–C(OH)(CH_3)CN (the cyanohydrin) (05)
R: $C_6H_5NH_2$ (aniline) (05) (05 × 6 = 30 marks)

(ii) Selecting from the reactions I–VI, give one (01) example for each of the following types of reactions.
Nucleophilic addition
Nucleophilic substitution

Answer

Nucleophilic addition: Reaction V (05)
Nucleophilic substitution: Reaction II (05) (05 × 2 = 10 marks) · 4(b): 40 marks

Review.

Sequence 1: HBr with peroxides adds in an anti-Markovnikov (free-radical) manner, putting Br on the less substituted carbon of $(CH_3)_2C{=}CHCH_3$ (Markovnikov addition would give the tertiary bromide); the propynide ion then displaces Br^- from the secondary halide (S_{N2} type nucleophilic substitution) to give K. Sequence 2: the Clemmensen reduction (Zn(Hg)/conc. HCl) converts –CHO to –CH_3, and Friedel–Crafts acylation ($CH_3COCl/AlCl_3$) puts the acetyl group para to the activating methyl group; HCN adds to the C=O of the ketone (nucleophilic addition) to give the cyanohydrin M. Sequence 3: a ketone reacts with a primary amine (aniline) to form an imine (Schiff base) by addition–elimination. Common mistakes: using HBr alone for Reaction I, and naming Reaction VI as nucleophilic addition (it is addition–elimination, condensation).

Read: RB U8 §2.3 · p. 41 RB U9 §3.4 · p. 60 RB U7 §1.4 · p. 21 RB U9 §3.1 · p. 54 RB U8 §2.2 · p. 33 RB U8 §2.7 · p. 50

Answer two from each part

Essay · Paper II Parts B and C

Part B

Question 5 · Part B · essay

Scheme note: PHYSICAL STATES ARE NECESSARY.

−1

−1

A

23

−1

(a) [75 marks]

A compound $XY_2Z_2(g)$ undergoes dissociation when heated to temperatures above 300 K as given below: $XY_2Z_2(g) \rightleftharpoons XY_2(g) + Z_2(g)$ (on heating). A sample of 7.5 g of $XY_2Z_2(g)$ was placed in an evacuated 1.00 dm^3 rigid-closed container and the temperature was raised to 480 K. Molar mass of $XY_2Z_2(g)$ is 150 g mol^{-1}. Use the approximate value of 4000 J mol^{-1} for RT at 480 K. Assume ideal gas behaviour for all gases.
(i) Calculate the number of moles of $XY_2Z_2(g)$ in the container before dissociation.

Answer

7.5 g/150 g mol^{-1} = **5.0×10^{-2} mol** (05) · 5(a)(i): 05 marks

(ii) When the above system reaches equilibrium at 480 K, the total number of moles in the container was found to be 7.5×10^{-2} mol. Calculate the number of moles of $XY_2Z_2(g)$, $XY_2(g)$ and $Z_2(g)$ in the equilibrium mixture at 480 K.

Answer

$XY_2Z_2(g) \rightleftharpoons XY_2(g) + Z_2(g)$
Initial: 0.05, 0, 0 mol (05)
Change: −x, +x, +x
At equilibrium: 0.05 − x, x, x (05)
Total number of moles = $0.05 + x = 7.5 \times 10^{-2}$ mol (05)
$x = 2.5 \times 10^{-2}$ mol (05)
$XY_2(g) = Z_2(g) = 2.5 \times 10^{-2}$ mol (05)
$XY_2Z_2(g) = 5.0 \times 10^{-2} - 2.5 \times 10^{-2} = 2.5 \times 10^{-2}$ mol (05) · 5(a)(ii): 30 marks

(iii) Calculate the equilibrium constant K_c for the above reaction at 480 K.

Answer

$K_c = [XY_2(g)][Z_2(g)]/[XY_2Z_2(g)]$ (05)
Each concentration = 2.5×10^{-2} mol/1.00 $dm^3 = 2.5 \times 10^{-2}$ mol dm^{-3} (05)
$K_c = (2.5 \times 10^{-2}$ mol $dm^{-3} \times 2.5 \times 10^{-2}$ mol $dm^{-3})/(2.5 \times 10^{-2}$ mol $dm^{-3})$ (05)
K_c = 2.5 × 10^{-2} mol dm^{-3} (05) · 5(a)(iii): 20 marks

(iv) Calculate K_p for the equilibrium at 480 K.

Answer

$K_p = K_c(RT)^{\Delta n}$ (05); $\Delta n = 1$ (05)
$K_p = 2.5 \times 10^{-2}$ mol $dm^{-3} \times 4 \times 10^3$ J mol^{-1} (05) (= 25 mol $m^{-3} \times 4000$ J mol^{-1})
K_p = 1.0 × 10^5 Pa (05)
Alternative: total moles at equilibrium = 7.5×10^{-2} mol; $P_{total} = (7.5 \times 10^{-2}$ mol × 4×10^3 J $mol^{-1})/(1.0 \times 10^{-3}$ $m^3) = 3.0 \times 10^5$ Pa. The moles of $XY_2Z_2(g)$, $XY_2(g)$ and $Z_2(g)$ are each 2.5×10^{-2} mol, so each mole fraction = 1/3 and $P_i = X_{iPtotal}$: $P_{XY2Z2} = P_{XY2} = P_{Z2} = 1.0 \times 10^5$ Pa. $K_p = P_{XY2(g)}\ P_{Z2(g)}/P_{XY2Z2(g)}$ = **1.0 × 10^5 Pa** (20) · 5(a)(iv): 20 marks · 5(a): 75 marks

Review.

Principle: an equilibrium-table (ICE) treatment of a gas-phase dissociation in a rigid container, then the link between K_c and K_p. Method: moles initially = mass/M; the increase in total moles equals the amount dissociated (x); divide moles by the 1.00 dm^3 volume for concentrations; $K_p = K_c(RT)^{\Delta n}$ with Δn = (moles of gaseous products − moles of gaseous reactant) = 1. Take care with units: K_c is in mol dm^{-3}, so to get K_p in Pa convert to mol m^{-3} (× 1000) before multiplying by RT in J mol^{-1}; the check by partial pressures (P = nRT/V, then K_p from P_i) gives the same value. Common mistakes: using 7.5×10^{-2} mol as the amount of reactant left, forgetting that $\Delta n = 1$, and leaving K_p in mixed units.

(b) [75 marks]

For the reaction $XY_2Z_2(g) \rightarrow XY_2(g) + Z_2(g)$ described in (a), Gibbs free energies (G) at 480 K for $XY_2Z_2(g)$, $XY_2(g)$ and $Z_2(g)$ are −60 kJ mol^{-1}, −76 kJ mol^{-1} and −30 kJ mol^{-1}, respectively.
(i) Calculate ΔG (in kJ mol^{-1}) for the reaction at 480 K.

Answer

$\Delta G_{rxn} = G_{products} - G_{reactants}$ (05) = [(−76) + (−30)] − (−60) = **−46 kJ mol^{-1}** (04 + 01)
Note: no marks if $\Delta G°_{rxn}$ is written. 5(b)(i): 10 marks

(ii) The magnitude of ΔS of the above reaction is 150 J K^{-1} mol^{-1} at 480 K. Calculate ΔH for the reaction at 480 K by using the appropriate sign (− or +) of ΔS.

Answer

ΔS must be positive (the number of gaseous moles is higher in the products) (05)
ΔG = ΔH − TΔS (05)
$-46\ kJ\ mol^{-1} = \Delta H - 480\ K \times 150 \times 10^{-3}\ kJ\ K^{-1}\ mol^{-1}$ (04 + 01)
$\Delta H = -46\ kJ\ mol^{-1} + 72\ kJ\ mol^{-1}$
$\Delta H = +26\ kJ\ mol^{-1}$ (04 + 01) · 20 marks for this sub-question (5 + 15 in the scheme's headings 5(b)(ii) and 5(b)(iii))

(iii) By using the sign (− or +) of ΔH obtained in (ii), explain whether this reaction is exothermic or endothermic.

Answer

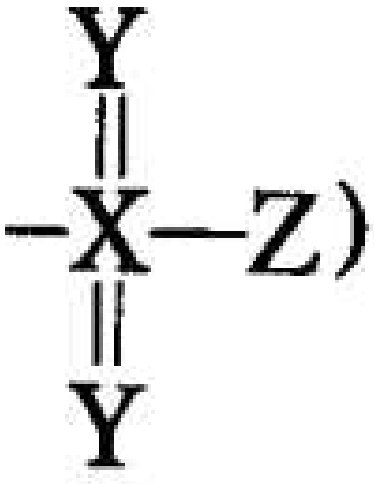
The reaction is endothermic (05) because ΔH is positive (05) · 10 marks (printed in the scheme under the heading 5(b)(iv))

(iv) Deduce the enthalpy difference for the formation of $XY_2Z_2(g)$ from $XY_2(g)$ and $Z_2(g)$ at 480 K.

Answer

This is the reverse of the dissociation reaction, so **$\Delta H = -26\ kJ\ mol^{-1}$** (09 + 01) · 10 marks (printed in the scheme under the heading 5(b)(v))

(v) If the bond enthalpy of the X–Z bond in $XY_2Z_2(g)$ is +250 kJ mol^{-1}, calculate the bond enthalpy of the Z–Z bond. (Assume that $XY_2Z_2(g)$ has the structure shown: Z–X–Z with a double-bonded Y on each side of X.)



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Answer

$\Delta H_{rxn} = \Delta H_{bonds\ formed} - \Delta H_{bonds\ broken}$ (05)
$\Delta H_{rxn} = \Delta H_{Z-Z} - 2\Delta H_{X-Z}$ (05)
$26\ kJ\ mol^{-1} = \Delta H_{Z-Z} - 2 \times 250\ kJ\ mol^{-1}$
$\Delta H_{Z-Z} = 526\ kJ\ mol^{-1}$ (04 + 01)
(OR students may solve through an appropriate thermochemical cycle.) 15 marks (printed in the scheme under the heading 5(b)(vi))

(vi) If liquid XY_2Z_2 is used instead of gaseous XY_2Z_2, giving reasons, explain whether the value of ΔH obtained for the reaction $XY_2Z_2(l) \rightarrow XY_2(g) + Z_2(g)$ is equal to, or higher or lower than ΔH obtained in (ii).

Answer

Higher

(05)

2

2

2

2

(05) · 5(b)(vi): 25 marks (with the bond-enthalpy part above) · 5(b): 75 marks

Review.

Principle: ΔG = ΣG(products) − ΣG(reactants) and ΔG = ΔH − TΔS (Gibbs energy and entropy), Hess's law, bond enthalpies. Method: ΔG = −46 kJ mol^{-1}; one mole of gas gives two moles of gas, so ΔS is positive; ΔH = ΔG + TΔS = +26 kJ mol^{-1}, so the dissociation is endothermic and the reverse (formation) has ΔH = −26 kJ mol^{-1}; liquid → gas vaporisation adds an endothermic step, so ΔH is higher for the liquid. Issue in the official answer to (v): the official working equates +26 with ΔH_{Z-Z} − 2 × 250, giving 526 kJ mol^{-1}. For the dissociation (ΔH = +26) two X–Z bonds are broken and one Z–Z bond is formed, so ΔH = 2(250) − ΔH_{Z-Z} and ΔH_{Z-Z} = 474 kJ mol^{-1}; the printed formula "bonds formed − bonds broken" has the opposite sign convention to the Resource Book (ΔH = Σ bonds broken − Σ bonds formed). The official 526 is kept as the scheme answer, but check the sign convention if you use it. Common mistakes: writing ΔG° for a non-standard calculation (the scheme gives no marks), using J and kJ together in TΔS, and forgetting the sign change for the reverse reaction.

Read: RB U12 §2.1 · p. 76 RB U4 §1.2 · p. 5 RB U5 §2.4 · p. 53 RB U5 §2.2 · p. 36

Question 6 · Part B · essay

Scheme note: PHYSICAL STATES ARE NECESSARY.

(a) [90 marks]

Consider the reaction given below occurring in a closed container at a given temperature T: $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$
(i) Write three expressions for the rate of reaction relevant to each of the compounds appearing in the reaction.

Answer

Rate = $-\Delta[N_2O_5(g)]/2\Delta t = \Delta[NO_2(g)]/4\Delta t = \Delta[O_2(g)]/\Delta t$ (05) · 6(a)(i): 05 marks

(ii) This reaction was carried out at temperature T with an initial concentration of 0.10 mol dm^{-3} of $N_2O_5(g)$. It was found that 40% of the initial amount was decomposed after a period of 400 s.
I. Calculate the average rate of decomposition of $N_2O_5(g)$ in this time interval.

Answer

Decomposed amount = 0.10 mol dm^{-3} × 40/100 = 4.0 × 10^{-2} mol dm^{-3} (05)
Remaining concentration after 400 s = 6.0 × 10^{-2} mol dm^{-3} (05)
Average rate = −(0.06 − 0.10) mol dm^{-3}/(400 − 0) s = **1.0 × 10^{-4} mol dm^{-3} s^{-1}** (05)

II. Calculate average rates of formation of $NO_2(g)$ and $O_2(g)$.

Answer

$\Delta[N_2O_5(g)]/2\Delta t = \Delta[NO_2(g)]/4\Delta t$, so $\Delta[NO_2(g)]/\Delta t = 2 \times 1.0 \times 10^{-4} =$ **2.0×10^{-4} mol dm^{-3} s^{-1}** (02)
$\Delta[O_2(g)]/\Delta t = -\Delta[N_2O_5(g)]/2\Delta t =$ **5.0×10^{-5} mol dm^{-3} s^{-1}** (03) · 6(a)(ii): 20 marks

(iii) In another experiment, initial rates were measured for this reaction at 300 K and the results are given below: $[N_2O_5(g)]$/mol dm^{-3}: 0.01, 0.02, 0.03; initial rate/mol dm^{-3} s^{-1}: 6.930×10^{-5}, 1.386×10^{-4}, 2.079×10^{-4}. Derive the rate law for the reaction at 300 K.

Answer

When the concentration was increased two and three times, the rate increased two and three times, respectively (05); therefore the reaction is first order (05).
Rate law: **Rate = k[$N_2O_5(g)$]** (05)
(OR $R_1/R_2 = 1/2$ when $[N_2O_5]$ is halved, so the reaction is first order.) 6(a)(iii): 15 marks

(iv) Another experiment was carried out at 300 K with an initial concentration of 0.64 mol dm^{-3} of $N_2O_5(g)$. It was found that the concentration of $N_2O_5(g)$ which remained after a period of 500 s was 2.0×10^{-2} mol dm^{-3}.
I. Calculate the half-life ($t_{½}$) of the reaction at 300 K.

Answer

Order of concentration change = $0.64/2.0 \times 10^{-2} = 32 = (2)^5$ (05)
Fraction of initial $N_2O_5(g)$ remaining = $(½)^5$ (05)
That is, 5 half-lives passed to reach this concentration (05)
$t_{½}$ = 500 s/5 = **100 s** (05)

II. Calculate the rate constant of the reaction at 300 K.

Answer

From (iii): Rate = k[$N_2O_5(g)$]; 6.93×10^{-5} mol dm^{-3} s^{-1} = k × 0.01 mol dm^{-3} (05); **k = 6.93×10^{-3} s^{-1}** (04 + 01)
OR the reaction is first order, so $t_{½} = 0.693/k$ (05); k = 0.693/100 s = **6.93×10^{-3} s^{-1}** (05) · 6(a)(iv): 30 marks

(v) This reaction proceeds through a mechanism involving the following elementary steps. Step 1: $N_2O_5(g) \rightleftharpoons NO_3(g) + NO_2(g)$: Fast. Step 2: $NO_3(g) + NO_2(g) \rightarrow 2NO_2(g) + O(g)$: Slow. Step 3: $N_2O_5(g) + O(g) \rightarrow 2NO_2(g) + O_2(g)$: Fast. Show that the above mechanism is consistent with the rate law of the reaction.

Answer

From Step 2 (the slow step): Rate = k[$NO_3(g)$][$NO_2(g)$] (05)
For Step 1 (equilibrium): $K_{eq} = [NO_3(g)][NO_2(g)]/[N_2O_5(g)]$ (05), so $K_{eq}[N_2O_5(g)] = [NO_3(g)][NO_2(g)]$
$\therefore$ Rate = k $K_{eq}[N_2O_5(g)] = k'[N_2O_5(g)]$ (05)
This is a first-order rate law, which agrees with the rate law derived experimentally. (05) · 6(a)(v): 20 marks · 6(a): 90 marks

Review.

Principle: rate expressions with stoichiometric coefficients, rate law from initial-rate data, half-life of a first-order reaction, and the rate-determining-step method for a mechanism. Method: divide each Δ[ ]/Δt by its coefficient (so the rate of NO_2 formation = 2 × the rate of N_2O_5 loss, and the rate of O_2 formation = ½ × the rate of N_2O_5 loss); for a first-order reaction the half-life is constant, so 0.64 → 0.02 mol dm^{-3} is five half-lives ($0.64/2^5 = 0.02$), and $k = 0.693/t_{½}$; in the mechanism, an intermediate (NO_3) in the slow step is replaced using the fast pre-equilibrium. Common mistakes: forgetting the coefficients (giving NO_2 the same rate as N_2O_5), using the stoichiometric coefficient as the order, and writing the rate law from the overall equation.

(b) [60 marks]

An ideal binary-liquid mixture was prepared by mixing two liquids A and B in a closed evacuated container at temperature T. After establishing the equilibrium at temperature T, partial pressures of A and B in the vapour phase are P_A and P_B, respectively. At temperature T, the saturated vapour pressures of A and B are $P°_A$ and $P°_B$, respectively. Mole fractions of A and B in solution are X_A and X_B, respectively.
(i) Show that $P_A = P°_{AXA}$. (Consider that the rates of vaporization and condensation are equal at equilibrium.)

Answer

Consider the vapour–liquid equilibrium of an ideal solution of components A and B. As the rate of evaporation equals the rate of condensation at equilibrium:
A(l) ⇌ A(g) (1) (05)
r_v and r_c are the rates of vaporization and condensation of component A. From (1): $r_v = k[A(l)] = k_1X_A$ (05), where X_A is the mole fraction of A in solution.
Likewise, $r_c = k'[A(g)] = k_2P_A$ (05) (written r′_v in the scheme), where P_A is the partial pressure of A in the vapour phase.
At equilibrium $r_v = r_c$: $k_2P_A = k_1X_A$ (05)
∴ $P_A = (k_1/k_2)X_A$ or $P_A = kX_A$ (05)
When $X_A = 1$, $P_A = P°_A$ = saturated vapour pressure of A, ∴ $k = P°_A$ (05)
∴ **$P_A = P°_{AXA}$** (05) · 6(b)(i): 35 marks

(ii) In the above system at 300 K, the total pressure was 5.0×10^4 Pa. The saturated vapour pressures of pure A and B at 300 K are 7.0×10^4 Pa and 3.0×10^4 Pa, respectively.
I. Calculate the mole fraction of A in the liquid phase of the equilibrium mixture.

Answer

$P_{total} = P_A + P_B$ (05) $= X_{AP}°_A + X_{BP}°_B = X_{AP}°_A + (1 - X_A)P°_B$ (05)
∴ $X_A = (P_{total} - P°_B)/(P°_A - P°_B)$ (05) $= (5 \times 10^4 - 3 \times 10^4)/(7 \times 10^4 - 3 \times 10^4) =$ **½** (05)

II. Calculate the vapour pressure of A in the equilibrium mixture.

Answer

$P_A = P°_{AXA} = ½ \times 7 \times 10^4$ Pa = **3.5×10^4 Pa** (05) · 6(b)(ii): 25 marks · 6(b): 60 marks

Review.

Principle: Raoult's law derived from the equality of rates of vaporization and condensation, and Dalton's law of partial pressures for an ideal solution. Method: $P_{total} = X_{AP}°_A + (1 - X_A)P°_B$, which rearranges to $X_A = (P_{total} - P°_B)/(P°_A - P°_B) = 0.5$; then $P_A = 0.5 \times 7.0 \times 10^4 = 3.5 \times 10^4$ Pa (and $P_B = 1.5 \times 10^4$ Pa, which sums to 5.0×10^4 Pa). Common mistakes: using the vapour-phase mole fraction in Raoult's law (which needs the liquid-phase X_A), and presenting the derivation without stating that $k = P°_A$ comes from the limiting case $X_A = 1$.

Read: RB U11 §1.3 · p. 9 RB U11 §1.7.2 · p. 28 RB U11 §1.10 · p. 57 RB U12 §2.6 · p. 216

Question 7 · Part B · essay

Scheme note: PHYSICAL STATES ARE NECESSARY.

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(a) [75 marks]

(i) To compare the properties of Electrolytic and Galvanic cells, copy and complete the following table using the given terms. Terms: anode, cathode, positive, negative, spontaneous, non-spontaneous.

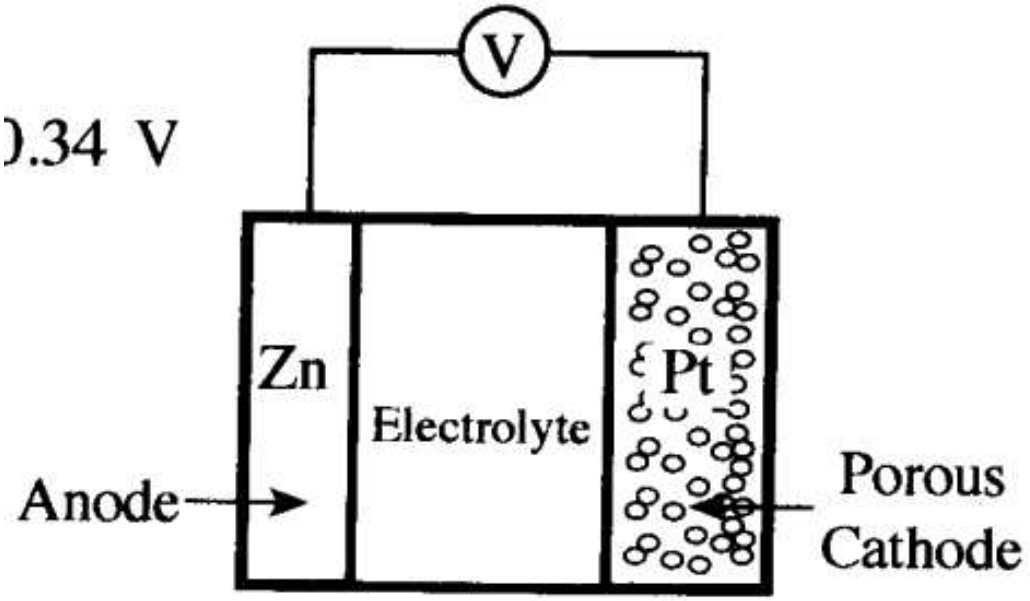
		Electrolytic cell	Galvanic cell
A.	Oxidation half-reaction takes place at		
B.	Reduction half-reaction takes place at		
C.	Sign of $E°_{cell}$		
D.	Electron flow	From ..... to	From ..... to .....
E.	Spontaneity of the cell reaction		

Answer

		Electrolytic cell	Galvanic cell
A.	Oxidation half-reaction takes place at	Anode	Anode
B.	Reduction half-reaction takes place at	Cathode	Cathode
C.	Sign of $E°_{cell}$	−ve (negative)	+ve (positive)
D.	Electron flow	From anode to cathode	From anode to cathode
E.	Spontaneity of the cell reaction	Non-spontaneous	Spontaneous

(2 × 10 = 20 marks) · 7(a)(i): 20 marks

(ii) An electrochemical cell was constructed at 300 K by using a Zn(s) anode, an aqueous alkaline electrolyte and a porous Pt cathode which facilitates the collection of oxygen $O_2(g)$ from air as shown below. As the cell operates ZnO(s) is produced. You are given that $E°_{ZnO(s)|Zn(s)|OH^-(aq)} = -1.31$ V and $E°_{O2(g)|OH^-(aq)} = +0.34$ V; Zn = 65 g mol^{-1}, O = 16 g mol^{-1} and 1 F = 96 500 C.



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I. Write the half-reactions occurring at anode and cathode.

Answer

Anode: $Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e$ (05)
Cathode: $O_2(g) + 2H_2O(l) + 4e \rightarrow 4OH^-(aq)$ (05)

II. Write the overall cell reaction.

Answer

$2Zn(s) + O_2(g) \rightarrow 2ZnO(s)$ (05)

III. Calculate the cell potential $E°_{cell}$ at 300 K.

Answer

$E°_{cell} = E°_R - E°_L = E°_{cathode} - E°_{anode}$ (05) = 0.34 V − (−1.31 V) = **1.65 V** (04 + 01)

IV. State the direction of migration of $OH^-(aq)$ ions between the electrodes.

Answer

From the anode to the cathode (from the Zn electrode to the oxygen electrode). (05)

V. When the cell operates for a period of 800 s at 300 K, 2 mol of $O_2(g)$ are consumed.
A. Calculate the number of moles of electrons passing through the cell.

Answer

2 mol $O_2(g)$ × (4 mol e/1 mol $O_2(g)$) = **8 moles of electrons** (05)

B. Calculate the mass of ZnO(s) formed.

Answer

Mass of ZnO(s) = (8 mol e × 96 500 C/1 mol e × 800 s) × (1 mol e/96 500 C) × (2 mol ZnO/4 mol e) × (81 g/1 mol ZnO) (05) = **324 g** (04 + 01)
OR mass of ZnO = 4 mol × 81 g mol^{-1} (05) = 324 g (04 + 01)

C. Calculate the current passing through the cell.

Answer

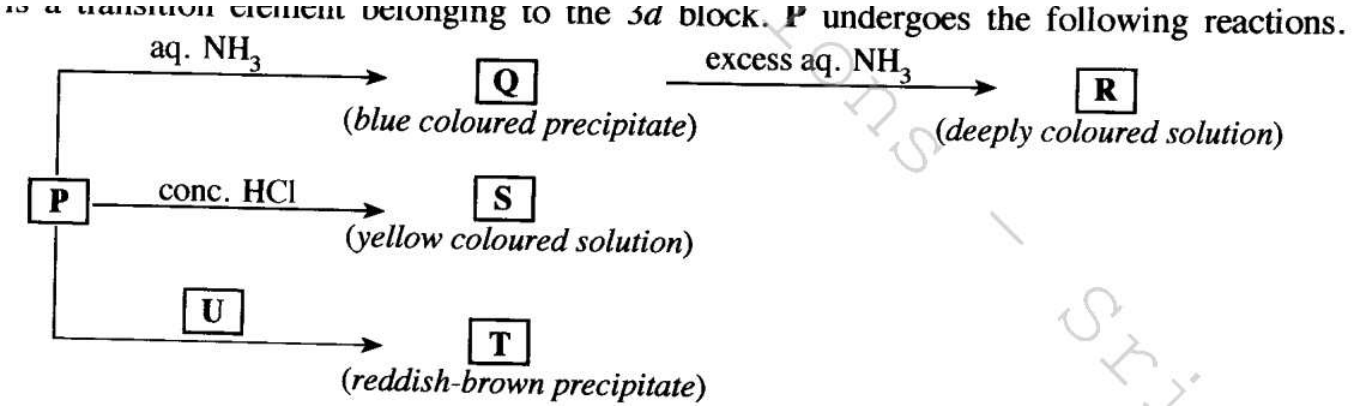
I = q/t (05) = (8 mol e × 96 500 C/1 mol e)/800 s = **965 A** (05) · 7(a)(ii): 55 marks · 7(a): 75 marks

Review.

Principle: the common features of galvanic and electrolytic cells, standard cell potential from electrode potentials, and Faraday's laws. Method: oxidation is always at the anode and reduction at the cathode, electrons always flow anode → cathode in the external circuit, and $E°_{cell} = E°_{cathode} - E°_{anode}$ (+1.65 V here, so the cell is spontaneous); the cathode half-reaction uses 4 e per O_2, so 2 mol O_2 corresponds to 8 mol e, 4 mol ZnO (4 × 81 = 324 g) and I = Q/t = 8 × 96 500/800 = 965 A. Anions (OH^-) migrate towards the anode through the electrolyte to balance charge as OH^- is consumed there and produced at the cathode. Common mistakes: mixing up the anode/cathode signs between the two cell types, using 2 e per O_2, and forgetting that ZnO is 81 g mol^{-1} (not 65).

(b) [75 marks]

A coloured complex ion P is formed when the salt $M(NO_3)_n$ is dissolved in distilled water. M is a transition element belonging to the 3d block. P undergoes the following reactions (see the figure: P with aq. NH_3 gives Q (blue coloured precipitate), which with excess aq. NH_3 gives R (deeply coloured solution); P with conc. HCl gives S (yellow coloured solution); P with U gives T (reddish-brown precipitate)). T and U are coordination compounds each containing four elements. P, R and S are complex ions.



Reaction scheme of the complex ion P

(i) Identify the metal M. Give the oxidation state of M in complex ion P.

Answer

M = Cu (10); oxidation state: +2 (or Cu^{2+}) (03) · 7(b)(i): 13 marks

(ii) Give the value of n in $M(NO_3)_n$.

Answer

n = 2 (03)

(iii) Write the complete electronic configuration of M in complex ion P.

Answer

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$ (03)

(iv) Write the chemical formulae of P, Q, R, S, T and U.

Answer

P: $[Cu(H_2O)_6]^{2+}$ (04)
Q: $Cu(OH)_2$ (04)
R: $[Cu(NH_3)_4]^{2+}$ (04)
S: $[CuCl_4]^{2-}$ (04)
T: $Cu_2[Fe(CN)_6]$
U: $K_4[Fe(CN)_6]$ (7(b)(iv): 16 marks)

(v) Give the IUPAC names of P, R, S, T and U.

Answer

P: hexaaquacopper(II) ion (03)
R: tetraamminecopper(II) ion (03)
S: tetrachloridocuprate(II) ion (03)
T: copper hexacyanoferrate(II)
U: potassium hexacyanoferrate(II) (7(b)(v): 12 marks)

(vi) What is the colour of P?

Answer

Pale blue (04)

(vii) What would you expect to observe in I and II given below?
I. When H_2S gas is passed into an acidic solution containing P at room temperature
II. When the mixture obtained in I above is heated with dilute HNO_3 after the removal of dissolved H_2S

Answer

I. A black precipitate (06)
II. A pale blue solution (04); the solution is turbid / a pale yellow, milky or white precipitate (sulfur) (02)
OR a turbid pale blue solution (06) · 7(b)(vii): 12 marks

(viii) Briefly describe a method with the aid of balanced chemical equations for determining the concentration of M^{n+} present in an aqueous solution, using the following chemicals: KI, $Na_2S_2O_3$ and starch.

Answer

Add excess KI (01) to an aqueous solution of volume V_1 cm^3 containing M^{n+} (01). Here $M^{n+} = Cu^{2+}$. Titrate the liberated I_2 (01) with $Na_2S_2O_3$ whose concentration is known (M mol dm^{-3}) (01) with starch as the indicator (01).
$2Cu^{2+} + 2I^- \rightarrow 2Cu^+ + I_2$ (1) (01)
$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$ (2) (01)
$2Cu^{2+} + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2Cu^+$ (3) (02)
OR $2Cu^{2+} + 4I^- \rightarrow 2CuI\downarrow + I_2$ (1a) (01); $I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$ (2a) (01); $2Cu^{2+} + 4I^- + 2S_2O_3^{2-} \rightarrow 2CuI\downarrow + S_4O_6^{2-} + 2I^-$ (3a) (02)
Note: if the correct overall equation is given, award the part marks for the half equations as well.
From (3) or (3a): $Cu^{2+} \equiv S_2O_3^{2-}$ (01)
Let the burette reading of $S_2O_3^{2-}$ be V_2 cm^3 (01)
Moles of $S_2O_3^{2-} = V_2M/1000$ (01); therefore moles of $Cu^{2+} = V_2M/1000$ (01)
Therefore $[Cu^{2+}] = (V_2M/1000) \times (1000/V_1)$ (01) = $\mathbf{MV_2/V_1}$ **mol** $\mathbf{dm^{-3}}$ (01)
Note: the above explanation could be given in words. 7(b)(viii): 15 marks · 7(b): 75 marks

Review.

Principle: the chemistry of copper(II) (aqua, hydroxide, ammine and chlorido complexes; reaction with hexacyanoferrate(II)) and iodometric titration. Method: the pale blue $[Cu(H_2O)_6]^{2+}$ gives a blue $Cu(OH)_2$

precipitate with a little NH_3, which dissolves in excess to give the deep blue $[Cu(NH_3)_4]^{2+}$; conc. HCl gives yellow $[CuCl_4]^{2-}$; $K_4[Fe(CN)_6]$ gives reddish-brown $Cu_2[Fe(CN)_6]$; H_2S gives black CuS, which dissolves in hot dil. HNO_3 (sulfur is deposited). Cu^{2+} oxidises I^- to I_2, which is titrated with standard thiosulfate (starch added near the end point), the mole ratio Cu^{2+} : $S_2O_3^{2-}$ being 1 : 1. Common mistakes: writing the oxidation state of copper as +1, wrong ligand numbers (6 H_2O, 4 NH_3, 4 Cl^-), naming errors (ammine has two m's; "cuprate" for the anionic complex), and omitting the starch/end-point detail.

Read: RB U13 §3.3 · p. 250 RB U13 §3.4 · p. 261 RB U13 §3.2 · p. 238 RB U6 §4.10.6 · p. 169 RB U6 §4.10 · p. 160

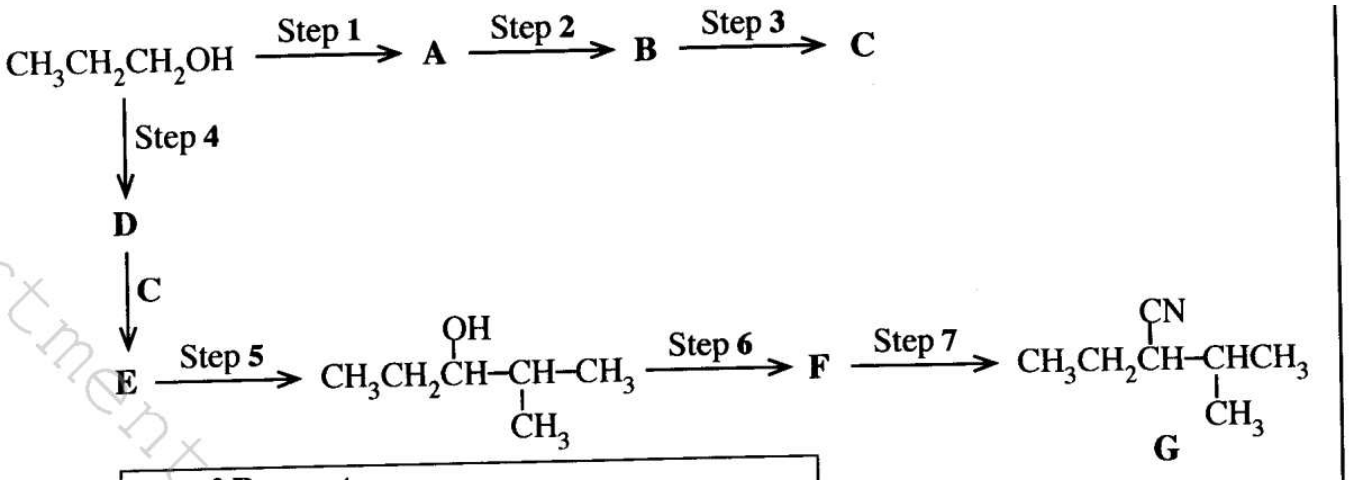
Part C

Question 8 · Part C · essay

Scheme note: PHYSICAL STATES ARE NECESSARY.

(a) [76 marks]

(i) Given below is a reaction scheme for the synthesis of compound G using $CH_3CH_2CH_2OH$ as the only organic starting compound. Complete the reaction scheme by drawing the structures of compounds A, B, C, D, E and F and writing the appropriate reagents for steps 1 – 7, selected only from those given in the list.
List of Reagents: HBr, PBr_3, pyridiniumchlorochromate (PCC), Mg/dry ether, KCN, conc. H_2SO_4, dil. H_2SO_4



3

2

2

Answer

Compounds:

3

2

3

3

3

2

3

2

3

2

3

2

3

2

3

2

Reagents:

2

4

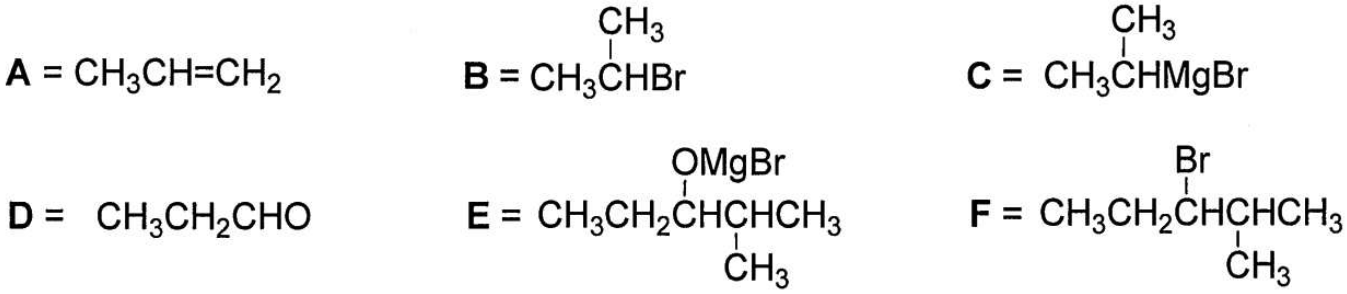
2

4

3

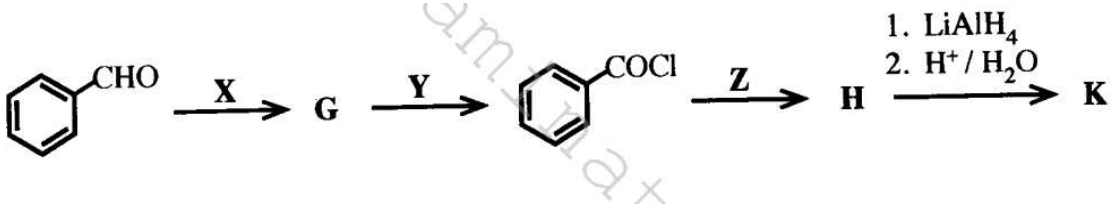
(04 × 13 = 52 marks) · 8(a)(i): 52 marks

Compounds, A – F



Structures of A – F (scheme)

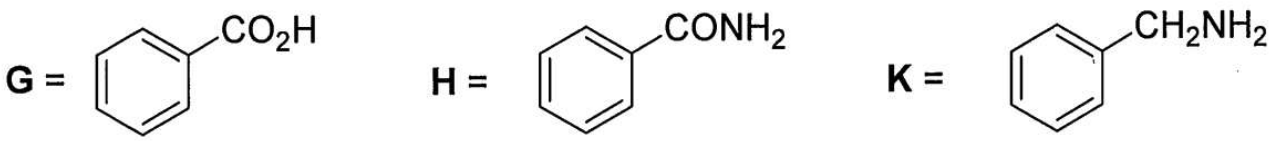
(ii) Consider the following series of reactions. Draw the structures of compounds G, H and K. Give the reagents X, Y and Z. Benzaldehyde —X→ G —Y→ benzoyl chloride (C_6H_5COCl) —Z→ H —(1. $LiAlH_4$; 2. H^+/H_2O)→ K. Note that K gives benzyl alcohol ($C_6H_5CH_2OH$) when reacted with $NaNO_2$/dil. HCl.



Reaction series from benzaldehyde

Answer

G = benzoic acid, $C_6H_5CO_2H$; H = benzamide, $C_6H_5CONH_2$; K = benzylamine, $C_6H_5CH_2NH_2$.
X = $H^+/K_2Cr_2O_7$ (or $H^+/KMnO_4$, or H^+/CrO_3); Y = PCl_5 or PCl_3; Z = NH_3. (04 × 6 = 24 marks) · 8(a)(ii): 24 marks · 8(a): 76 marks



Reagents

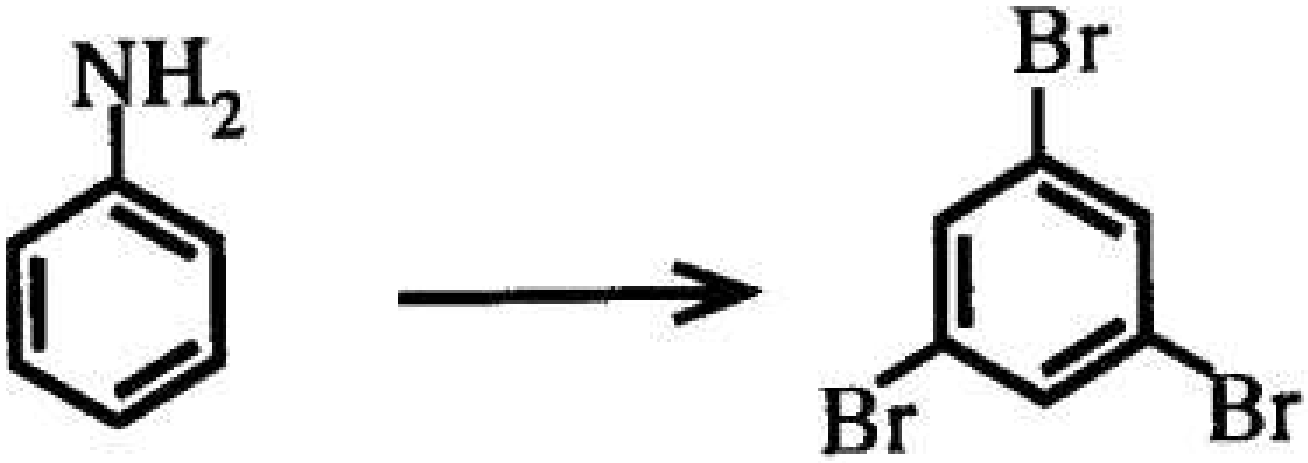
Structures of G, H and K (scheme)

Review.

Principle: building a carbon skeleton with a Grignard reagent, and interconversion of carboxylic acid derivatives. Method for (i): dehydrate propan-1-ol (conc. H_2SO_4) to propene; Markovnikov addition of HBr gives 2-bromopropane, which with Mg in dry ether gives the Grignard reagent C; propan-1-ol is oxidised only to the aldehyde propanal with PCC (D); C adds to the carbonyl group of D to give the magnesium alkoxide E, which dil. H_2SO_4 hydrolyses to the secondary alcohol; PBr_3 replaces OH with Br (F) and KCN (nucleophilic substitution) gives the nitrile G. For (ii): oxidise the aldehyde to benzoic acid, make the acid chloride with PCl_5 (or PCl_3), then the amide with NH_3; $LiAlH_4$ reduces the amide to the amine, and a primary aliphatic amine with $NaNO_2$/dil. HCl gives the alcohol (via the unstable diazonium ion). Common mistakes: using HBr (instead of PBr_3) for step 6, choosing an acidic reagent for step 3, and forgetting that PCC stops at the aldehyde.

(b) [40 marks]

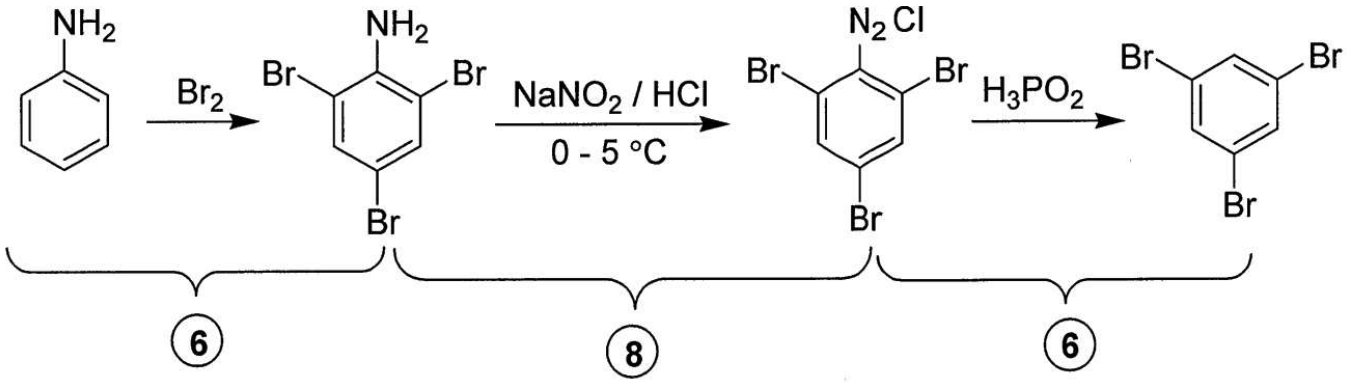
(i) Show how the following conversion could be carried out in not more than three steps: aniline ($C_6H_5NH_2$) → 1,3,5-tribromobenzene.



The required conversion

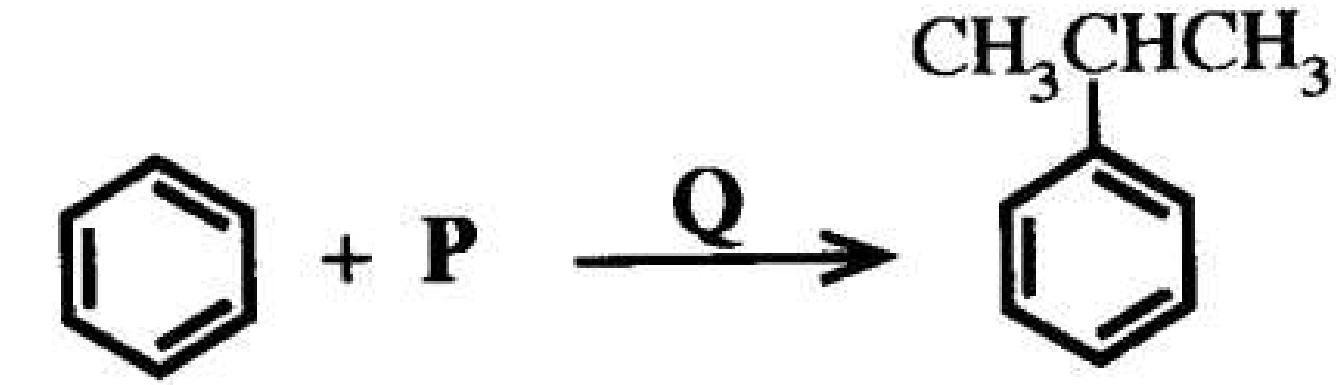
Answer

Step 1: Br_2 gives 2,4,6-tribromoaniline (06)
Step 2: $NaNO_2$/HCl at 0 – 5 °C gives the 2,4,6-tribromobenzenediazonium chloride (08)
Step 3: H_3PO_2 replaces the diazonium group by H, giving 1,3,5-tribromobenzene (06) · 8(b)(i): 20 marks



Three-step route (scheme)

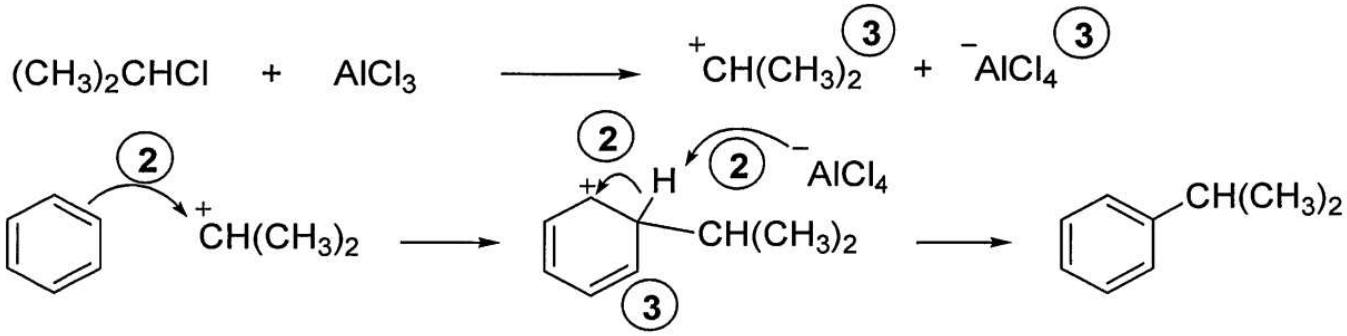
(ii) Consider the following reaction: benzene + P —Q→ isopropylbenzene ($C_6H_5CH(CH_3)_2$). Identify the chemical substances P and Q necessary to carry out this reaction. Write the mechanism of this reaction.



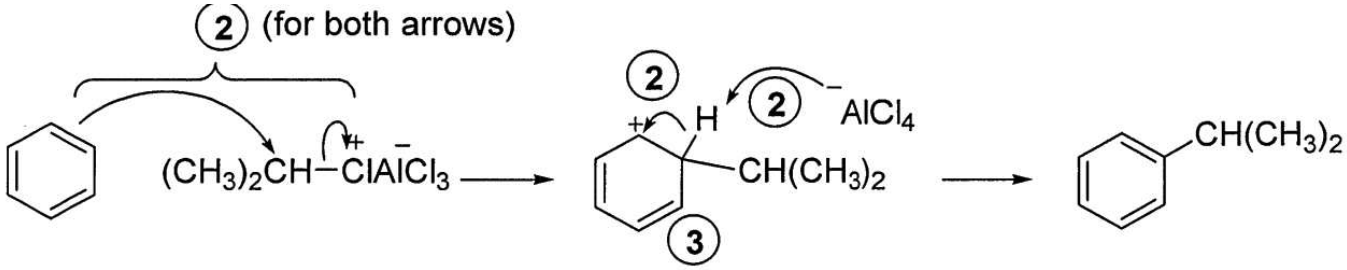
The reaction

Answer

P and Q: $(CH_3)_2CHCl$ + $AlCl_3$ (05)
Mechanism (electrophilic substitution, Friedel–Crafts alkylation): $(CH_3)_2CHCl$ + $AlCl_3$ → ^+$CH(CH_3)_2$ + ^−$AlCl_4$ (03 + 03); the π electrons of benzene attack the carbocation (curved arrow) (02) giving the carbocation (arenium) intermediate with the H and $CH(CH_3)_2$ on the same ring carbon (03); $AlCl_4$^− removes H^+ (curved arrow) (02) to give isopropylbenzene, $C_6H_5CH(CH_3)_2$ (and regenerates $AlCl_3$ and HCl). (Intermediates 03 × 3 = 09; arrows 02 × 3 = 06)
Alternative answer: if the student has written the electrophile as the R–Cl molecule polarised by coordination to $AlCl_3$, only the marks for the last two steps may be awarded: both arrows (02), then the arenium intermediate (02 + 03), then removal of H^+ by $AlCl_4$^− (02) = 09 marks. The electrophile may be written as $(CH_3)_2CH^{\delta+}$–Cl···$^{\delta-}AlCl_3$ (with + / − or δ+ / δ− on the polarised complex). 8(b)(ii): 20 marks · 8(b): 40 marks



Mechanism (scheme)



02+02+02+03 = 09

Alternative electrophile (scheme)

Review.

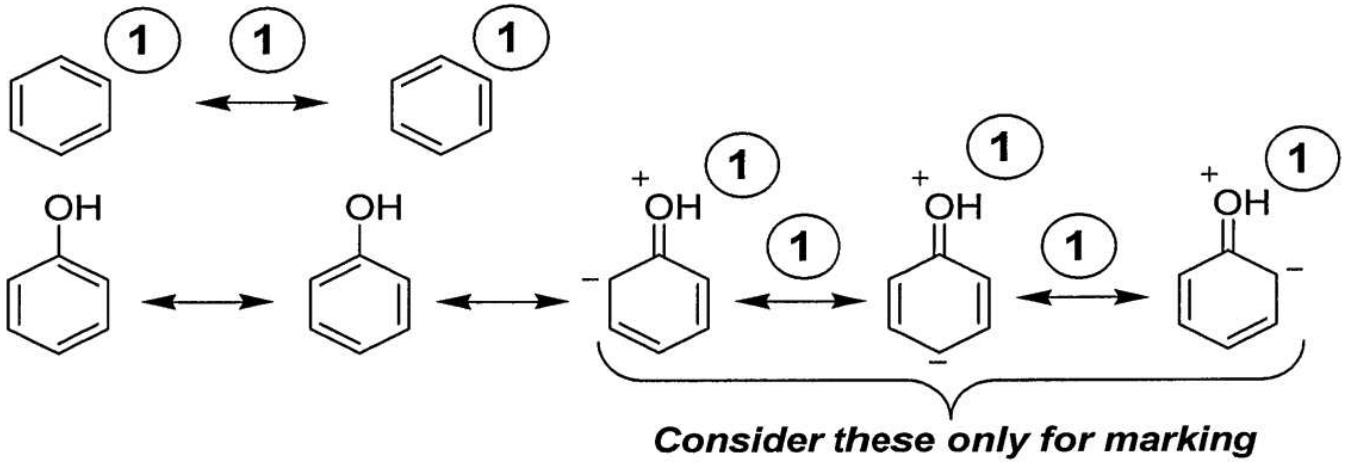
Principle: electrophilic aromatic substitution; the directing/activating effects of NH_2, and diazonium chemistry; Friedel–Crafts alkylation. Method for (i): the strongly activating NH_2 group directs Br to positions 2, 4 and 6; replacing N_2^+ by H (H_3PO_2) leaves bromines at positions 1,3,5 — a pattern that cannot be made by direct bromination of benzene. For (ii): $AlCl_3$ generates the electrophile (isopropyl cation, or the polarised R–Cl···$AlCl_3$ complex); loss of H^+ restores aromaticity. Common mistakes: drawing curved arrows from the carbocation to the benzene ring, omitting the $AlCl_4$^− step, and using H_2O instead of H_3PO_2 (which gives a phenol).

(c) [34 marks]

(i) Explain why phenol is more reactive in electrophilic substitution reactions than benzene, by considering their resonance hybrids.

Answer

Structures of benzene and phenol can be illustrated as follows: two Kekulé structures for benzene (01 + 01 + 01 for the double-headed arrow) and the resonance structures of phenol, including the three structures in which the oxygen carries a + charge and the ring carbons at the 2-, 4- and 6- positions carry a − charge (Resonance structures and double-headed arrows: 01 × 8 = 08).
The benzene ring in phenol is electron rich compared with benzene (04) due to the delocalization (04) of a lone pair of electrons on the oxygen atom over the benzene ring of phenol (04), so the ring is more reactive towards electrophiles than benzene itself. (04 × 3 = 12) · 8(c)(i): 20 marks

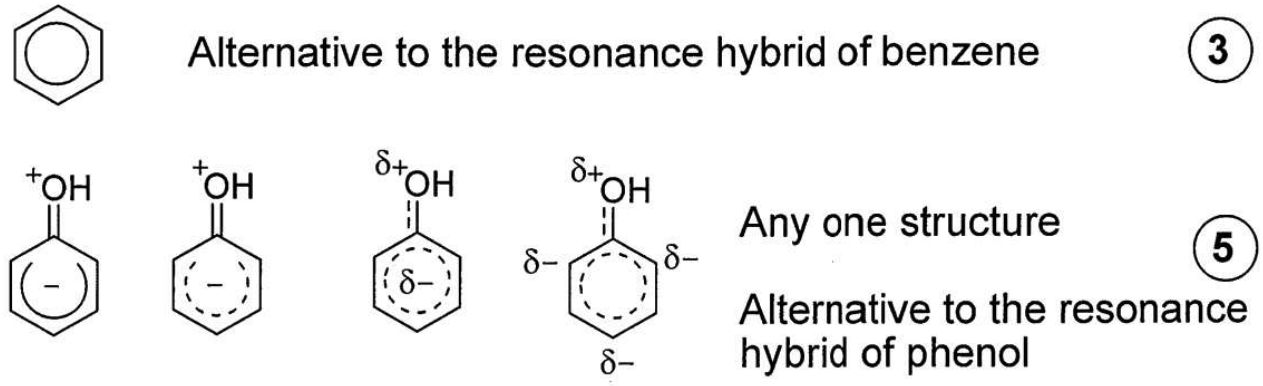


Resonance structures of benzene and phenol (scheme)

OR (resonance hybrids):

(03)

(05)



Alternative: resonance hybrids (scheme)

(ii) Illustrate the difference in reactivity between phenol and benzene as given in (i) above by means of a suitable reaction.

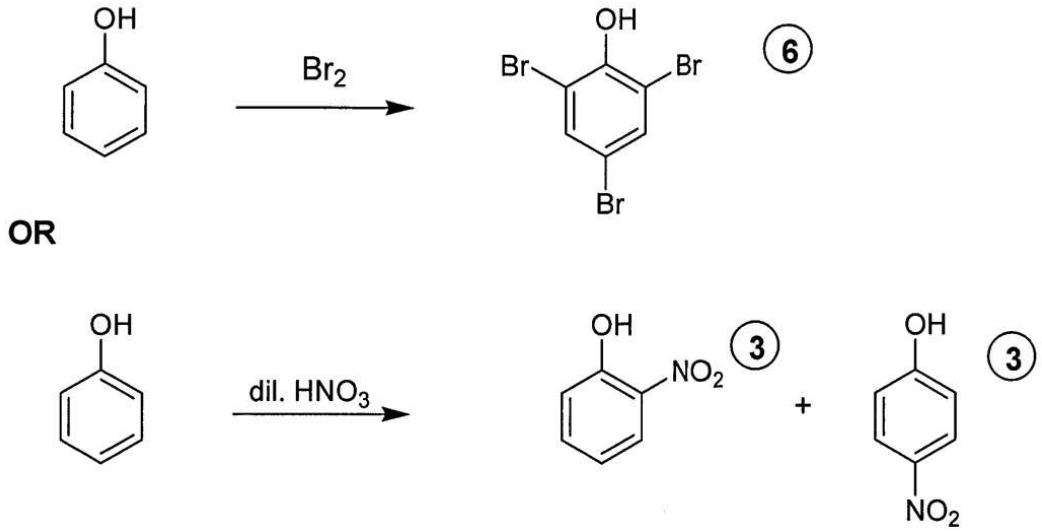
Answer

Phenol reacts with bromine at room temperature / decolorizes bromine / gives a white precipitate with bromine water. Benzene does not react with bromine at room temperature / does not decolorize bromine / does not give a white precipitate with bromine water. (04 × 2 = 08)
OR benzene reacts with bromine (only) in the presence of a Lewis catalyst, whereas the reaction of phenol with bromine occurs even in the absence of a Lewis catalyst.
OR nitration of phenol takes place at room temperature / at 20 °C / without heating with dilute HNO_3 (20% HNO_3), while benzene does not react with dilute HNO_3. 8(c)(ii): 08 marks

(iii) Draw the structure(s) of product(s) you described in the reaction in (ii) above.

Answer

Phenol + Br_2 → 2,4,6-tribromophenol (white precipitate) (06)
OR phenol + dil. HNO_3 → 2-nitrophenol + 4-nitrophenol (03 + 03) · 8(c)(iii): 06 marks · 8(c): 34 marks



Products (scheme)

Review.

Principle: the +M (mesomeric) electron donation of the OH lone pair activates the ring and directs substitution to the ortho and para positions (Resource Book: phenol as an activated aromatic ring). Method:

draw the three charge-separated resonance forms of phenol (− charge at C-2, C-4, C-6) and show the lone pair of oxygen delocalised into the ring; the higher electron density makes the ring react with Br_2 without a Lewis-acid catalyst (white precipitate of 2,4,6-tribromophenol with bromine water) and with dilute HNO_3. Common mistakes: stating "OH is electron-withdrawing so the ring is more reactive", drawing the + charge on carbon, and forgetting the double-headed arrows between resonance structures (each carries a mark).

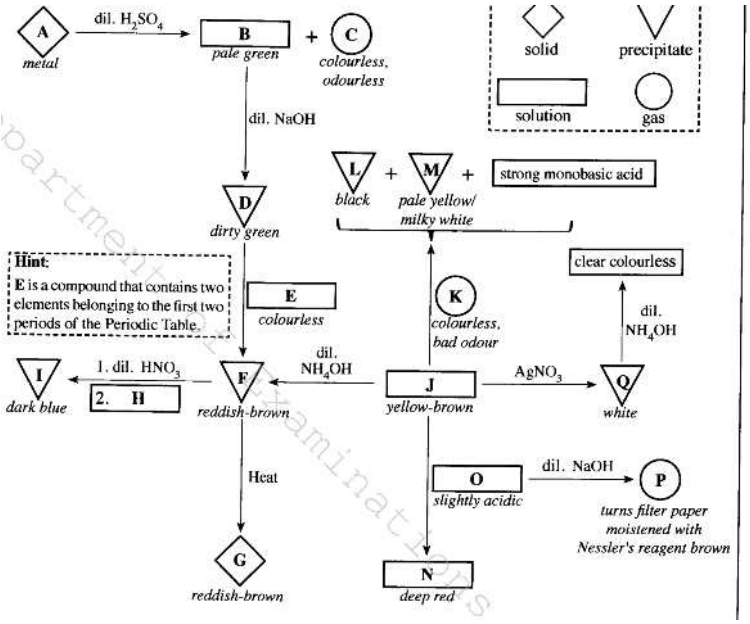
Read: RB U8 §2.7 · p. 50 RB U9 §3.1 · p. 54 RB U9 §3.5 · p. 66 RB U9 §3.6 · p. 70 RB U10 §4.1 · p. 75 RB U10 §4.3 · p. 78 RB U8 §2.4 · p. 44 RB U9 §3.2 · p. 58

Question 9 · Part C · essay

Scheme note: PHYSICAL STATES ARE NECESSARY.

(a) [75 marks]

(i) Write the chemical formulae of the substances A – Q given in the flow chart below. (Note: Chemical equations and reasons are not expected for the identification of substances A – Q.) The symbols given in the box (dash lines) are used to represent solids, precipitates, solutions and gases (diamond = solid, inverted triangle = precipitate, rectangle = solution, circle = gas). Hint: E is a compound that contains two elements belonging to the first two periods of the Periodic Table.



Flow chart (A – Q)

Answer

A: Fe
B: $FeSO_4$ (or $[Fe(H_2O)_6]SO_4$, or $[Fe(H_2O)_6]^{2+}$)
C: H_2
D: $Fe(OH)_2$
E: H_2O_2
F: $Fe(OH)_3$
G: Fe_2O_3
H: $K_4[Fe(CN)_6]$
I: $Fe_4[Fe(CN)_6]_3$ (or $KFe[Fe(CN)_6]$)
J: $FeCl_3$
K: H_2S
L: FeS
M: S (or S_8)
N: $Fe(SCN)_3$ (or $[Fe(SCN)(H_2O)_5]^{2+}$, or $[Fe(SCN)]^{2+}$)
O: NH_4SCN
P: NH_3
Q: AgCl
(04 marks × 17 = 68 marks) · 9(a)(i): 68 marks

(ii) Write the complete electronic configuration of A.

Answer

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$ (02)

(iii) State the function of E in the conversion of D to F. Give the relevant balanced chemical equations for the stated function.

Answer

E (H_2O_2): oxidizing agent (02)
$2[Fe(OH)_2 + H_2O \rightarrow Fe(OH)_3 + H^+ + e]$
$H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O$
Overall: $2Fe(OH)_2 + H_2O_2 \rightarrow 2Fe(OH)_3$ (03)
OR $2(Fe^{2+} \rightarrow Fe^{3+} + e)$; $H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O$; overall $2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O$ (03)
(Half-reactions: 01 each if written.) 9(a)(ii) and (iii): 07 marks · 9(a): 75 marks

Review.

Principle: qualitative analysis of iron(II) and iron(III) (colours of $Fe(OH)_2$, $Fe(OH)_3$, Prussian blue, thiocyanato complex), with the hint that E = H_2O_2. Method: Fe + dil. H_2SO_4 gives pale green $FeSO_4$ (B) and colourless odourless H_2 (C); NaOH gives dirty-green $Fe(OH)_2$ (D), which H_2O_2 oxidises to reddish-brown $Fe(OH)_3$ (F), giving Fe_2O_3 on heating (G); F with HCl gives yellow-brown $FeCl_3$ (J); H_2S reduces Fe^{3+} to Fe^{2+}, giving S (milky) and, with NaOH, FeS (black); $K_4[Fe(CN)_6]$ gives dark-blue Prussian blue with Fe^{3+} (I); NH_4SCN (O) gives deep-red $Fe(SCN)_3$ (N); NaOH on NH_4SCN releases NH_3 (P) that turns Nessler's paper brown; $AgNO_3$ gives white AgCl (Q). Common mistakes: confusing $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$, and writing the electronic configuration of Fe with 4s before 3d.

(b) [75 marks]

The solid X contains only Cu_2S and CuS. The following procedure was used to determine the percentage of Cu_2S in X. **Procedure:** A 1.00 g portion of solid X was treated with 100.00 cm^3 of 0.16 mol dm^{-3} $KMnO_4$ in dilute H_2SO_4 medium. This reaction gave Mn^{2+}, Cu^{2+} and $SO_4{}^{2-}$ as products. Thereafter, the excess $KMnO_4$ in this solution was titrated with 0.15 mol dm^{-3} Fe^{2+} solution. The volume required for the titration was 35.00 cm^3.

(i) Write the balanced ionic equations for the reactions taking place in the above procedure.

Answer

2

4

+

2+

(03)

2−

2

4

2−

+

(03)

+

2−

2

2+

4

2−

+

4

+

2+

2

(03)

+

2−

4

+

2+

4

2−

2+

2

(05)

2

4

+

2+

4

2−

2+

2

4

2−

2

4

2−

+

4

+

2+

2

2−

4

+

4

2−

2+

2

(05)

4

+

4

2+

2

2+

4

2−

2+

4

2+

3+

(03)

4

+

2+

2

2+

4

+

2+

3+

2

(05) · 9(b)(i): 27 marks

OR (separating the ions):

+

4

+

2+

(03)

4

+

2+

2

(03)

+

4

+

2+

2+

2

(05)

2−

4

(03 + 05)

2+

4

(03 + 05)

Note: if only the overall reaction is written correctly, award the marks due to the half reactions as well.

(ii) Based on the answers to (i) above, determine the molar ratio between, I. Cu_2S and $KMnO_4$, II. CuS and $KMnO_4$, III. Fe^{2+} and $KMnO_4$.

Answer

I. Cu_2S : MnO_4^− = 1 : 2
II. CuS : MnO_4^− = 5 : 8
III. Fe^{2+} : MnO_4^− = 5 : 1 (05 × 3) · 9(b)(ii): 15 marks

(iii) Calculate the percentage by weight of Cu_2S in X. (Cu = 63.5, S = 32)

Answer

Let the number of moles of Cu_2S and CuS be n_1 and n_2 respectively in the 1.0 g of X.
Molar mass of Cu_2S = (2 × 63.5) + 32 = 159 (02); molar mass of CuS = 63.5 + 32 = 95.5 (02)
$159n_1 + 95.5n_2 = 1.0$ (9) (02)
Moles of Fe^{2+} reacted = (0.15/1000) × 35.0 (02)
Moles of excess MnO_4^− = (0.15/1000) × 35.0 × ⅕ (02)
Moles of MnO_4^− reacted with Cu_2S and CuS = (0.16/1000) × 100.0 − (0.15/1000) × 35.0 × ⅕ (02) = 0.016 − 0.001 (02) = 0.015 mol (02)
Based on the molar ratios: $2n_1 + (8/5)n_2 = 0.015$ (10) (02)
(9) + (10): $2n_1 + (8/5)(1 − 159n_1)/95.5 = 0.015$ (02)
$2 × 5 × 95.5n_1 + 8(1 − 159n_1) = 0.015 × 95.5 × 5$ (02)
$955n_1 + 8 − 1272n_1 = 7.1625$; $317n_1 = 0.84$; $n_1 = 0.0027$ (02)
Weight of Cu_2S = 0.0027 × 159 g = 0.43 g (02); % Cu_2S = (0.43/1.0) × 100 (02) = **43%** (03) · 9(b)(iii): 33 marks
OR (second method, same first steps): Moles of Fe^{2+} = (0.15/1000) × 35.0 (02); moles of MnO_4^− remaining = (0.15/1000) × 35.0 × ⅕ (02); moles of MnO_4^− added = (0.16/1000) × 100.0 (02); moles reacted with Cu_2S and CuS = 0.016 − 0.001 = 0.015 mol (02 + 02 + 02). Let the masses of Cu_2S and CuS be p and q: p + q = 1.0 g (9a) (02); M(Cu_2S) = 159 (02), M(CuS) = 95.5 (02); $2p/159 + 8q/(95.5 × 5) = 0.015$ (10a) (02); substituting q = 1 − p: $2p × 5 × 95.5 + 8 × 159(1 − p) = 0.015 × 5 × 159 × 95.5$ (02); $955p − 1272p = 1138.84 − 1272$ (02); $317p = 133.16$, p = 0.42 (02); % Cu_2S = 0.42/1.0 × 100 (02) = **42%** (03)
OR (third method): moles of MnO_4^− added = 0.016 (02); moles of Fe^{2+} reacted = 0.005 (02); moles of MnO_4^− remaining = 0.001 (02); moles reacted = 0.015 (02); $159n_1 + 95.5n_2 = 1$ (1) (02 + 02 + 02 + 02); moles of $Cu^+ = 2n_1$, so MnO_4^− reacted with $Cu^+ = 2n_1/5$; moles of $S^{2−} = n_1 + n_2$, so MnO_4^− reacted with $S^{2−} = 8(n_1 + n_2)/5$ (02); total MnO_4^− reacted = $(10n_1 + 8n_2)/5 = 0.015$ (02), i.e. $10n_1 + 8n_2 = 0.075$ (2) (02); (1) × 8 − (2) × 95.5: $1272n_1 − 955n_1 = 8 − 7.14$ (02); $317n_1 = 0.86$ (02); mass of Cu_2S = (0.86/317) × 159 g (02 + 02); % Cu_2S = **43%** (03) · 9(b)(iii): 33 marks · 9(b): 75 marks

Review.

Principle: redox titration with back-titration, where MnO_4^- (reduced to Mn^{2+}) oxidises Cu(I) to Cu(II) and sulfide to sulfate, and Fe^{2+} is used to determine the excess; two unknowns need two simultaneous equations (mass and moles of MnO_4^-). Method: MnO_4^- used = 0.016 − (0.15 × 0.035)/5 = 0.016 − 0.00105 = 0.01495 mol (the scheme rounds the excess to 0.001, giving 0.015 mol); with $159n_1 + 95.5n_2 = 1.00$ and $2n_1 + 1.6n_2$ = (moles MnO_4^- used) one gets $n_1 \approx 0.0027$ mol of Cu_2S, i.e. about 43% (the scheme gives 43% in two of its methods and 42% in the mass-based method because of rounding; with 0.015 mol exactly the value is 42.0% and with 0.01495 mol it is 43.2%, so 42–43% should be accepted). Common mistakes: forgetting that Cu_2S contains two Cu^+ (so a total of 10 electrons per Cu_2S, not 8), taking Fe^{2+} : MnO_4^- as 1 : 1, and using the mole ratio of S^{2-} alone for Cu_2S.

Read: RB U6 §4.10 · p. 160 RB U6 §4.6 · p. 141 RB U3 §3.8 · p. 115 RB U3 §3.6 · p. 105

Question 10 · Part C · essay

Scheme note: PHYSICAL STATES ARE NECESSARY.

(a) [50 marks]

The following questions are based on the properties of titanium dioxide (TiO_2) and its manufacture carried out by the "Chloride Process".
(i) Name the raw materials used in this process.

Answer

Rutile (02); coke (02); Cl_2 (02); O_2 (02) · 10(a)(i): 08 marks

(ii) Briefly describe the manufacturing process of TiO_2 giving balanced chemical equations where applicable.

Answer

Chlorination:

(02)

(02)

2

2

(03)

(02)

2

4

(03)

OR

2

2

4

2

(06)

(02 × 3)

4

4

(02)

Oxidation:

4

2

4

2

2

2

(03)

2

(02) · 10(a)(ii): 19 marks

(iii) State three properties of TiO_2 and give one use each, relevant to each property.

Answer

White colour – as a pigment in paint, plastic goods and paper
High refractive index – as a pigment
Chemically inert – as a pigment in medicine and toothpaste
Prevents the reach of UV rays to skin – to produce substances that prevent sunburn
Any three properties (02 × 3 = 06); one use for each property (02 × 3 = 06) · 10(a)(iii): 12 marks

(iv) If you were to consider establishing a TiO_2 manufacturing plant in Sri Lanka, state three requirements that need to be fulfilled.

Answer

Any three (02 × 3 = 06): availability of raw material; capital; labour force; technology; storage conditions; minimizing environmental pollution; transport facilities; waste product management. 10(a)(iv): 06 marks

(v) Does the manufacturing process described in (ii) above contribute to global warming? Justify your answer.

Answer

Yes (02). CO_2 is produced and given out to the environment in the oxidation of coke (03) · 10(a)(v): 05 marks · 10(a): 50 marks

Review.

Principle: industrial production of TiO_2 from rutile by the chloride process, and the environmental/economic factors of siting an industry. Method: chlorination of rutile with coke and Cl_2 at about 900 °C gives volatile $TiCl_4$ (CO_2 is released), which is condensed, purified and oxidised with O_2 to give pure TiO_2 with Cl_2 recycled. Common mistakes: writing the oxidation step with the wrong state of $TiCl_4$, omitting recycling of Cl_2, and giving a use that does not match the stated property.

(b) [50 marks]

Currently, global warming due to change in greenhouse effect is significantly greater than that before the industrial revolution.
(i) Explain briefly what is meant by greenhouse effect.

Answer

Heating of the earth (01) by infrared-absorbing gases (01) in the atmosphere by trapping energy (IR radiation) (02) re-radiated from the earth's surface (02) · 10(b)(i): 06 marks

(ii) Identify the major environmental problem that occurs due to global warming.

Answer

Climate change (03)

(iii) State two main natural gases that contribute to global warming.

Answer

CO_2, CH_4 and N_2O – any two (03 + 03)

(iv) Explain briefly how microorganisms contribute to the release of the gases you stated in (iii).

Answer

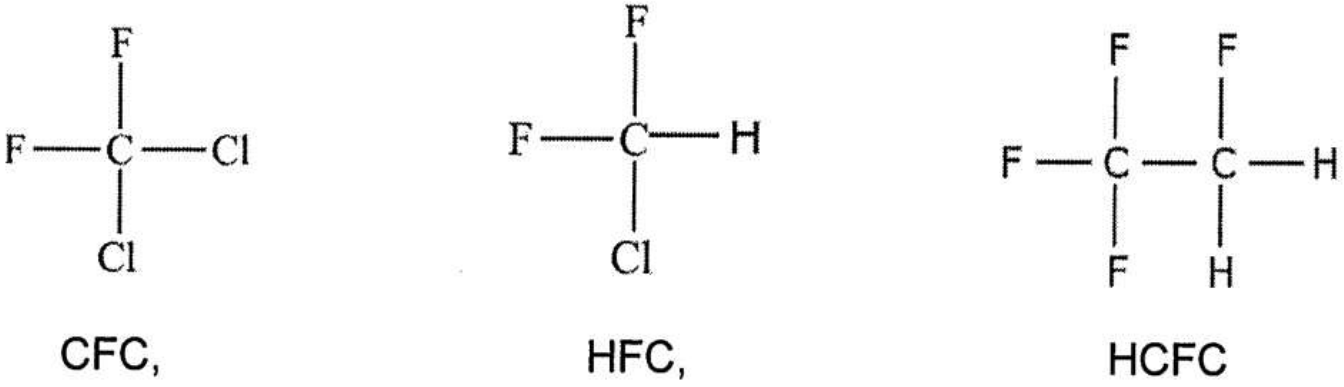
CO_2 – action of aerobic bacteria on organic substances / plant materials / animal materials
CH_4 – action of anaerobic bacteria on organic substances / materials
N_2O – action of denitrifying bacteria on ammonia / nitrogen fertilizers (urea) / nitrogen-containing substances
Any two (04 + 04) · 10(b)(iv): 08 marks

(v) In addition to the gases you stated in (iii), name two classes of synthetic volatile compounds that directly contribute to the global warming, and selecting one compound from each class, draw their structures.

Answer

Classes: CFC, HFC, HCFC (any two, each with one structure). The scheme draws CCl_2F_2 (labelled CFC), $CHClF_2$ (labelled HFC) and CF_3CH_2F (labelled HCFC). (03 for class + 03 for the structure) × 2 = 12 marks; no marks for the structure if the class is wrong
Note: in addition to these compounds, award marks for the following structures in each class. CFC – any saturated organic compound that contains one or two carbon atoms with only Cl and F atoms. HCFC – any saturated organic compound that contains one or two carbon atoms with only one hydrogen atom and others Cl and F atoms. HFC – any saturated organic compound that contains one or two carbon atoms with only one hydrogen atom and others F atoms. 10(b)(v): 12 marks

CFC, HFC, HCFC



CFC, HFC, HCFC

Structures of CFC, HFC and HCFC given in the scheme

(vi) Select one class of compounds from the two classes you stated in (v) that contributes to the catalytic degradation of ozone in the upper atmosphere.

Answer

CFC or HCFC (must be selected from (v) to get marks) (03)

(vii) The slow down of industrial activities due to the Covid-19 pandemic temporarily eased the global environmental issues in many countries. Justify this statement by using two main global environmental issues you have learnt.

Answer

Reduction of global warming

(01)

2

(01)

(02)

(01)

(01)

Reduction of acid rain

(01)

2

(01)

(01 + 01)

(01 + 01)

(01)

2

(01)

(01)

(01)

(02)

Reduction of photochemical smog

(01)

(01 + 01)

(01)

(02)

(06 × 2 = 12 marks) · 10(b)(vii): 12 marks · 10(b): 50 marks

Review.

Principle: the greenhouse effect, greenhouse gases and their sources, ozone depletion by CFCs/HCFCs, and the link between fossil-fuel burning and global warming, acid rain and photochemical smog. Method: link each gas to its source (aerobic decay gives CO_2, anaerobic decay gives CH_4, denitrification gives N_2O), pick one named class and draw a valid saturated structure with the right atoms (a CFC has only C, F and Cl; an HFC has C, H and F; an HCFC has C, H, F and Cl), and only CFCs/HCFCs (which carry Cl) take part in the

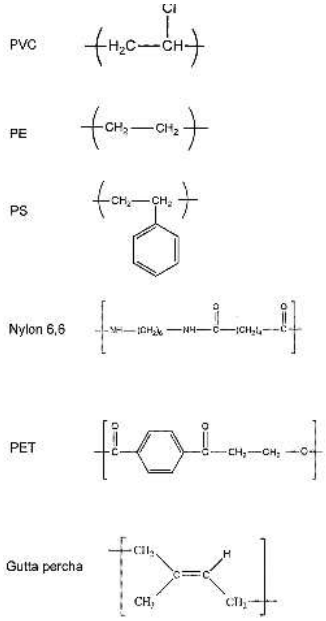
catalytic destruction of ozone. Issue in the scheme: the printed labels of the second and third structures look swapped ($CHClF_2$ contains Cl, so it is an HCFC, and CF_3CH_2F contains no Cl, so it is an HFC); the scheme's own note defines the classes by composition, so match the class to the atoms present. Common mistakes: drawing an HFC and then selecting it as the ozone-depleting class, naming ozone depletion as the cause of global warming, and giving only the effect (not the cause) in (vii).

(c) [50 marks]

The following questions are based on the polymers given below: Polyvinyl chloride (PVC), Polyethylene (PE), Polystyrene (PS), Bakelite, Nylon 6,6, Polyethylene terephthalate (PET), Gutta percha.
(i) Draw the repeating units of four of the above polymers.

Answer

PVC: –[CH_2–CHCl]–; PE: –[CH_2–CH_2]–; PS: –[CH_2–CH(C_6H_5)]–; Nylon 6,6: –[NH–$(CH_2)_6$–NH–CO–$(CH_2)_4$–CO]–; PET: –[CO–C_6H_4–CO–O–CH_2–CH_2–O]– (benzene-1,4-diyl); gutta percha: –[CH_2–C(CH_3)=CH–CH_2]– (trans-polyisoprene). Brackets are not required for award of marks. Any four (02 × 4 = 08) · 10(c)(i): 08 marks



Repeating units (scheme)

(ii) Categorize each of the above seven (7) polymers as either, I. natural or synthetic polymers; II. addition or condensation polymers.

Answer

Polymer	I – natural / synthetic	II – addition / condensation
PVC	synthetic	addition
PE	synthetic	addition
PS	synthetic	addition
Bakelite	synthetic	condensation
Nylon 6,6	synthetic	condensation
PET	synthetic	condensation
Gutta percha	natural	addition

(02 × 6 = 12)

(02 × 6 = 12) · 10(c)(ii): 24 marks

(iii) Name the two monomers used in the formation of bakelite.

Answer

Phenol and formaldehyde (methanal, HCHO) (02 × 2 = 04) · 10(c)(iii): 04 marks

(iv) Polymers can be grouped into two categories based on their thermal properties. State these two categories. Write to which of these categories PVC and bakelite belong.

Answer

Thermoset polymers (02); thermoplastic polymers (02); bakelite – thermoset polymer (02); PVC – thermoplastic polymer (02) · 10(c)(iv): 08 marks

(v) Give one use each for three of the polymers given in the above list.

Answer

PVC – pipes to supply water, seat covers, electric wire covers
PE – food wrapping, garbage bags
PS – styrofoam cups, rigiform, insulating materials, packing materials
Bakelite – heat-resistant parts of electric utensils, insulating materials
Nylon 6,6 – clothes, fishing nets and lines, tyre threads
PET – bottles
Gutta percha – insulation, permanent tooth fillings, golf balls
Any three (02 × 3 = 06) · 10(c)(v): 06 marks · 10(c): 50 marks

Review.

Principle: classification of polymers (natural/synthetic, addition/condensation, thermoplastic/thermoset), their monomers and uses. Method: addition polymers come from alkene monomers with no by-product (PVC, PE, PS, and natural gutta percha from isoprene); condensation polymers lose a small molecule (water) — nylon 6,6 from hexane-1,6-diamine and hexanedioic acid, PET from benzene-1,4-dicarboxylic acid and ethane-1,2-diol, bakelite from phenol and methanal; bakelite is cross-linked (thermoset, cannot be remelted) while PVC softens on heating (thermoplastic). Common mistakes: drawing the monomer rather than the repeating unit, calling gutta percha a condensation polymer, and classifying PET as an addition polymer.

Read: RB U14 §1.9 · p. 31 RB U14 §1.13 · p. 58 RB U14 §1.11 · p. 37 RB U14 §1.1 · p. 2

2019 · Chemistry Digital Paper

50 questions · 2 hours

MCQ · Paper I

Question 1 · Q1–30 · single answer

Consider the following statements, I and II.

I. The energy absorbed or released by atoms is quantized.

II. Small particles under appropriate conditions show wave properties.

The two scientists who proposed the theories as given by statements I and II respectively are,

- (1)Louis de Broglie and Albert Einstein
- (2)Max Planck and Louis de Broglie
- (3)Max Planck and Ernest Rutherford
- (4)Niels Bohr and Louis de Broglie
- (5)Louis de Broglie and Max Planck

Answer and review

Answer **(2/4)** Official marking scheme

The official scheme accepts (2) or (4). Statement I (energy is absorbed or emitted only in quanta, $E = h\nu$) is Planck's quantum theory, and Bohr applied the same quantisation to the energy levels of the atom, so either Planck or Bohr is accepted for I. Statement II (matter has wave character, $\lambda = h/mv$) is de Broglie's hypothesis. Options (1), (3) and (5) pair de Broglie with the wrong idea, or Rutherford (nuclear atom) with quantisation.

RB U1 §1.2 · p. 13 RB U1 §1.3 · p. 17

Question 2 · Q1–30 · single answer

The maximum number of **electron pairs** of an atom that are associated with principal quantum number n = 3 is,

- (1)3
- (2)4
- (3)5
- (4)8
- (5)9

Answer and review

Answer **(5)** Official marking scheme

For n = 3 the subshells are 3s (1 orbital), 3p (3 orbitals) and 3d (5 orbitals): $1 + 3 + 5 = 9 = n^2$ orbitals. Each orbital holds a pair of electrons (Pauli), so the maximum is 9 pairs (18 electrons). The trap is answering 18 (electrons) or counting only the s and p orbitals (4 pairs).

RB U1 §1.3 · p. 17 RB U1 §1.4 · p. 23

Question 3 · Q1–30 · single answer

The number of stable resonance structures that can be drawn for the oxalate ion [$C_2O_4^{2-}$ / $(O_2C{-}CO_2)^{2-}$] is,

- (1)2
- (2)3
- (3)4
- (4)5
- (5)6

Answer and review

Answer **(3)** Official marking scheme

Each CO_2^− end can place the double bond on either oxygen (O=C–O^- or ^−O–C=O). The two ends are independent, so the stable structures are 2 × 2 = 4, which is option (3). Structures with a charge-separated C–C double bond or unequal charge distribution are not stable, so 5 or 6 is too many.

RB U2 §2.3 · p. 52 RB U2 §2.1 · p. 44

Question 4 · Q1–30 · single answer

What is the IUPAC name of the following compound?

$HOCH_2CH_2CH_2C(=O)CH_2NH_2$

- (1)5-hydroxy-2-oxo-1-pentanamine
- (2)1-amino-5-hydroxy-2-oxopentane
- (3)1-amino-5-hydroxy-2-pentanone
- (4)5-hydroxy-1-amino-2-pentanone
- (5)5-amino-4-oxo-1-pentanol

Answer and review

Answer **(All)** Official marking scheme

The official scheme accepts every option (all candidates receive the mark). The compound is a five-carbon chain with C=O at C-2, NH_2 at C-1 and OH at C-5. Since the ketone has the highest priority among ketone, amine and alcohol, the strictly correct IUPAC name is 1-amino-5-hydroxypentan-2-one, the form in option (3). The other options use non-standard ordering or a substituent-style prefix, but because the question is ambiguous about the naming style, all were credited.

RB U7 §1.3 · p. 7

Question 5 · Q1–30 · single answer

Identify the pair of elements which has the **largest** difference in electronegativities.

- (1)B and Al
- (2)Be and Al
- (3)B and Si
- (4)B and C

- (5)Al and C

Answer and review

Answer **(5)** Official marking scheme

Electronegativity increases across a period and decreases down a group. Pauling values: B 2.0, Al 1.5, Be 1.5, Si 1.8, C 2.5. Differences: B–Al 0.5, Be–Al about 0, B–Si 0.2, B–C 0.5, Al–C 1.0. Al (lowest) and C (highest) give the largest difference, option (5).

RB U1 §1.6 · p. 32

Question 6 · Q1–30 · single answer

The electron pair geometry and shape around the two nitrogen atoms (labelled as N^1 and N^2) in the H_2NNO molecule (skeleton: $H_2N^1—N^2—O$, i.e. two H atoms on N^1) respectively are,

(For each nitrogen atom the options give the electron pair geometry first and then the shape.)

- (1)N^1: tetrahedral, pyramidal; N^2: trigonal planar, angular
- (2)N^1: pyramidal, trigonal planar; N^2: trigonal planar, angular
- (3)N^1: trigonal planar, pyramidal; N^2: trigonal planar, trigonal planar
- (4)N^1: tetrahedral, pyramidal; N^2: angular, trigonal planar
- (5)N^1: tetrahedral, angular; N^2: trigonal planar, trigonal planar

Answer and review

Answer **(1)** Official marking scheme

In $H_2N–N=O$, N^1 has three bond pairs (two N–H, one N–N) and one lone pair: four electron pairs, so the electron pair geometry is tetrahedral and the shape is pyramidal. N^2 has a double bond to O, a single bond to N^1 and one lone pair: three electron domains, so the geometry is trigonal planar and the shape (counting only atoms) is angular. Only option (1) matches both.

RB U2 §2.3 · p. 52

Question 7 · Q1–30 · single answer

Which of the following statements is **incorrect** regarding benzene?

(1) The resonance hybrid of benzene is depicted as follows:

- (1)The resonance hybrid of benzene is depicted as the pair of Kekulé structures joined by ⇌, as shown above.
- (2)All six carbon atoms of benzene are sp^2 hybridized.
- (3)The bond lengths between any two carbon atoms of benzene have the same value.
- (4)All the C—C—C and the C—C—H bond angles of benzene have the same value.

- (5)All the hydrogen atoms of benzene lie in the same plane.

Answer and review

Answer **(1)** Official marking scheme

Statement (1) is incorrect: resonance structures are linked by a double-headed arrow (↔) and the real molecule is a single hybrid, not an equilibrium between two forms, so the ⇌ sign is wrong. Statements (2)–(5) are true: benzene is a planar regular hexagon with six sp^2 carbons, all C–C bonds equal (about 140 pm) and all angles 120°.

RB U8 §2.4 · p. 44 RB U2 §2.3 · p. 52

Question 8 · Q1–30 · single answer

$TiCl_4(g)$ reacts with liquid magnesium metal (Mg(l)) to give Ti(s) metal and $MgCl_2(l)$ at high temperature. When 0.95 kg of $TiCl_4(g)$ is made to react with 97.2 g of Mg(l), the reactant that is completely consumed (this is commonly referred to as limiting reactant) and the amount of Ti(s) metal formed respectively are, (Molar mass: $TiCl_4$ = 190 g mol^{-1}; Mg = 24.3 g mol^{-1}; Ti = 48 g mol^{-1})

- (1)$TiCl_4$ and 96 g
- (2)Mg and 96 g
- (3)Mg and 48 g
- (4)$TiCl_4$ and 192 g
- (5)Mg and 192 g

Answer and review

Answer **(2)** Official marking scheme

$TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2$. $n(TiCl_4)$ = 950/190 = 5.0 mol; n(Mg) = 97.2/24.3 = 4.0 mol. 5.0 mol $TiCl_4$ would need 10 mol Mg, so Mg is limiting. n(Ti) = 4.0/2 = 2.0 mol, mass = 2.0 × 48 = 96 g. The trap is comparing the mole numbers directly (5 vs 4) without the 1 : 2 ratio, which gives $TiCl_4$ as limiting and 192 g.

RB U3 §3.8 · p. 115 RB U3 §3.4 · p. 99

Question 9 · Q1–30 · single answer

The ideal gas equation can be expressed in the form, P = ρRT/M where ρ is the density of the gas, M is the molar mass (g mol^{-1}) of the gas, P is the pressure (Pa) and T is the temperature (K). If the units of R are J mol^{-1} K^{-1}, units of ρ in this equation should be,

- (1)kg m^{-3}
- (2)g m^{-3}
- (3)g cm^{-3}
- (4)g dm^{-3}
- (5)kg cm^{-3}

Answer and review

Answer **(2)** Official marking scheme

From PV = nRT with n = m/M: P = (m/V)RT/M = ρRT/M. Pa = N m^{-2} = J m^{-3}. RT/M has units (J mol^{-1}) / (g mol^{-1}) = J g^{-1}, so ρ × J g^{-1} = J m^{-3} requires ρ in g m^{-3}. Using kg m^{-3} would need M in kg mol^{-1}.

RB U4 §1.2 · p. 5

Question 10 · Q1–30 · single answer

The **decreasing** order of conductivity of the following aqueous solutions including H_2O is, 0.01 M KCl, 0.1 M KCl, 0.1 M HAc; (HAc = acetic acid; M = mol dm^{-3})

- (1)H_2O > 0.1 M HAc > 0.1 M KCl > 0.01 M KCl
- (2)0.01 M KCl > 0.1 M HAc > 0.1 M KCl > H_2O
- (3)0.01 M KCl > 0.1 M KCl > 0.1 M HAc > H_2O
- (4)0.1 M KCl > 0.01 M KCl > 0.1 M HAc > H_2O
- (5)0.1 M HAc > H_2O > 0.01 M KCl > 0.1 M KCl

Answer and review

Answer **(4)** Official marking scheme

Conductivity depends on the concentration of ions. KCl is a strong electrolyte, fully ionised: 0.1 M gives 0.2 M ions and 0.01 M gives 0.02 M ions. 0.1 M acetic acid is only about 1% ionised (K_a about 1.8×10^{-5}, $[H^+]$ about 1.3×10^{-3} M), far fewer ions than 0.01 M KCl. Pure water has the least. The order is 0.1 M KCl > 0.01 M KCl > 0.1 M HAc > H_2O.

RB U13 §3.1 · p. 234 RB U12 §2.2 · p. 118

Question 11 · Q1–30 · single answer

The correct answer when the chemical species SO_2, SO_3, SO_3^{2-}, SO_4^{2-} and SCl_2 are arranged in the **increasing** order of the electronegativity of sulphur (S) atom is,

- (1)$SCl_2 < SO_3^{2-} < SO_2 < SO_3 < SO_4^{2-}$
- (2)$SO_3 < SO_4^{2-} < SO_2 < SO_3^{2-} < SCl_2$
- (3)$SO_3^{2-} < SO_4^{2-} < SCl_2 < SO_3 < SO_2$
- (4)$SCl_2 < SO_3^{2-} < SO_4^{2-} < SO_2 < SO_3$
- (5)$SCl_2 < SO_4^{2-} < SO_3^{2-} < SO_2 < SO_3$

Answer and review

Answer **(4)** Official marking scheme

The effective electronegativity of an atom rises with its oxidation state (more positive charge on S) and falls when the species carries a negative charge. Oxidation numbers of S: SCl_2 +2; SO_3^{2-} +4; SO_2 +4; SO_4^{2-} +6; SO_3 +6. SCl_2 (+2) is lowest; the two anions come next, SO_3^{2-} (+4) < SO_4^{2-} (+6); the neutral oxides are highest, SO_2 (+4) < SO_3 (+6). This gives $SCl_2 < SO_3^{2-} < SO_4^{2-} < SO_2 < SO_3$, option (4). Option (5) reverses the two anions.

RB U1 §1.6 · p. 32 RB U3 §3.1 · p. 88

Question 12 · Q1–30 · single answer

Which of the following answers gives the maximum hydroxide concentration that can exist in a 1.775 mol dm^{-3} aqueous solution of $MgCl_2$ at 25 °C? At this temperature, solubility product of $Mg(OH)_2$ is 7.1×10^{-12} mol^3 dm^{-9}.

- (1)4.0×10^{-6} mol dm^{-3}

- (2)2.0×10^{-6} mol dm^{-3}
- (3)1.775×10^{-12} mol dm^{-3}
- (4)$\sqrt{7.1 \times 10^{-6}}$ mol dm^{-3}
- (5)1.0×10^{-6} mol dm^{-3}

Answer and review

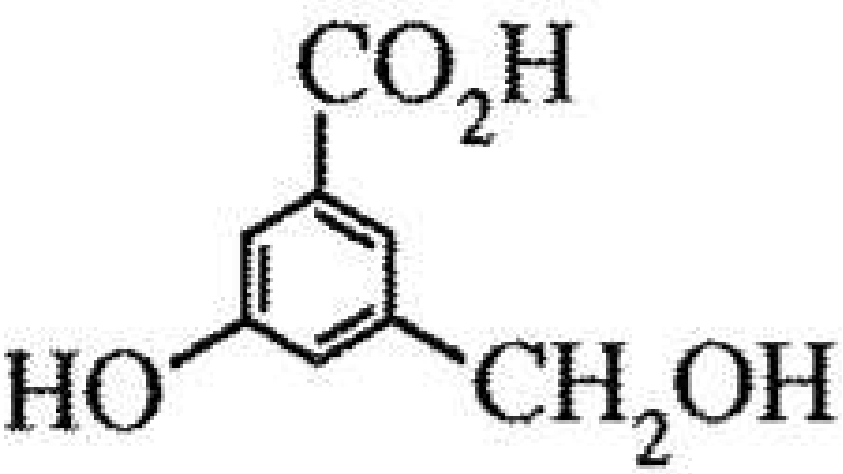
Answer **(2)** Official marking scheme

No precipitate forms while $[Mg^{2+}][OH^-]^2 \le K_{sp}$. $[OH^-]_{max} = \sqrt{(K_{sp}/[Mg^{2+}])} = \sqrt{(7.1 \times 10^{-12} / 1.775)} = \sqrt{(4.0 \times 10^{-12})} = 2.0 \times 10^{-6}$ mol dm^{-3}. The trap is stopping at 4.0×10^{-12}, which is $[OH^-]^2$ (option (1) is 4.0×10^{-6}, a slip of the exponent), or ignoring the common ion Mg^{2+} and taking the pure-water value.

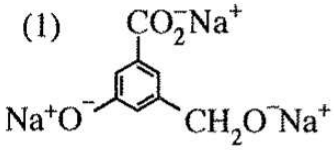
RB U12 §2.4 · p. 175

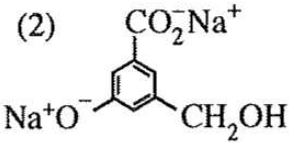
Question 13 · Q1–30 · single answer

What is the major product of the following reaction?



Reactant: 3-hydroxy-5-(hydroxymethyl)benzoic acid, treated with excess aq. NaOH

(1)


(2)


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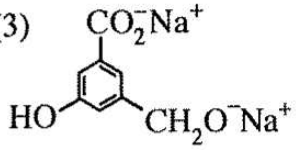
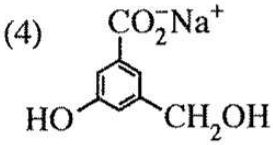


(4)


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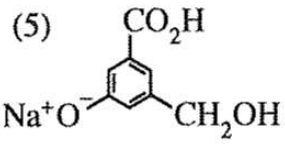


Answer and review

Answer **(2)** Official marking scheme

With excess aqueous NaOH only groups acidic enough to be deprotonated by hydroxide react: the carboxylic acid (pK_a about 4) gives $-CO_2{}^-Na^+$ and the phenol (pK_a about 10) gives $-O^-Na^+$. The benzylic alcohol $-CH_2OH$ (pK_a about 16) is a weaker acid than water and stays unchanged. This is option (2). Options (1) and (3) wrongly ionise the alcohol; (4) leaves the phenol and (5) leaves the carboxylic acid unionised.

RB U9 §3.3 · p. 59 RB U9 §3.2 · p. 58 RB U9 §3.5 · p. 66

Question 14 · Q1–30 · single answer

Identify the correct statement from the following.

- (1)The bond angle of NF_3 is larger than the bond angle of NH_3.
- (2)Elements in group 17 (or 7A) exhibit oxidation states from −1 to +7.
- (3)Monoclinic sulphur is the most stable allotrope of sulphur at room temperature.
- (4)The density of graphite is higher than the density of diamond.
- (5)Aluminium chloride satisfies the octet rule in the gaseous state.

Answer and review

Answer **(2/5)** Official marking scheme

The official scheme accepts (2) or (5). (2) is the textbook statement (the Resource Book says the halogens other than F show nearly all oxidation numbers from −1 to +7), although strictly F shows only −1. (5) is also acceptable because gaseous $AlCl_3$ exists largely as the dimer Al_2Cl_6, where dative Cl→Al bonds give every atom an octet. (1) is false (F pulls the bond pair away from N, so NF_3 about 102° < NH_3 about 107°); (3) is false (rhombic sulphur is the stable form at room temperature); (4) is false (diamond about 3.5 g cm^{-3}, graphite about 2.3 g cm^{-3}).

RB U6 §4.7 · p. 149 RB U2 §2.3 · p. 52 RB U6 §4.6 · p. 141 RB U2 §2.1 · p. 44

Question 15 · Q1–30 · single answer

The standard electromotive force of the electrochemical cell $Mn(s)|Mn^{2+}(aq)||Br^{-}(aq)|Br_2(g)|Pt(s)$ is 2.27 V. The standard reduction potential of $Br_2(g)|Br^{-}(aq)$ is 1.09 V. The standard reduction potential of $Mn^{2+}(aq)|Mn(s)$ is,

- (1)−3.36 V
- (2)−1.18 V
- (3)0.59 V
- (4)1.18 V
- (5)3.36 V

Answer and review

Answer **(2)** Official marking scheme

$E°_{cell} = E°_{reduction,\ cathode} - E°_{reduction,\ anode}$. In this cell Mn is oxidised (anode) and Br_2 is reduced (cathode): $2.27 = 1.09 - E°(Mn^{2+}/Mn)$, so $E°(Mn^{2+}/Mn) = 1.09 - 2.27 = -1.18$ V. The trap is adding the two values (3.36 V) or using the wrong sign (+1.18 V).

RB U13 §3.3 · p. 250 RB U13 §3.2 · p. 238

Question 16 · Q1–30 · single answer

The enthalpy change of vaporization and the entropy change of vaporization of a liquid are, 45.00 kJ mol^{-1} and 90.0 J K^{-1} mol^{-1} respectively. The boiling point of the liquid is,

- (1)45.0 °C
- (2)62.7 °C
- (3)100.0 °C

- (4)135.0 °C
- (5)227.0 °C

Answer and review

Answer **(5)** Official marking scheme

At the boiling point liquid and vapour are in equilibrium, so ΔG = 0 and $T_b = \Delta H_{vap}/\Delta S_{vap}$ = 45 000 J mol^{-1} / 90.0 J K^{-1} mol^{-1} = 500 K = 500 − 273 = 227 °C. Forgetting to convert kJ to J gives 0.5 K, and forgetting to convert K to °C leaves 500.

RB U5 §2.4 · p. 53

Question 17 · Q1–30 · single answer

What is the **incorrect** statement about $C_6H_5N^+{\equiv}NCl^-$?

- (1)$C_6H_5N^+{\equiv}NCl^-$ can be obtained by reacting aniline with HNO_2 ($NaNO_2$/HCl) at 0 – 5 °C.
- (2)$C_6H_5N^+{\equiv}NCl^-$ reacts with KI to give iodobenzene.
- (3)The $C_6H_5N^+{\equiv}N$ ion can act as an electrophile.
- (4)When an aqueous solution of $C_6H_5N^+{\equiv}NCl^-$ is heated, it decomposes to give benzene.
- (5)$C_6H_5N^+{\equiv}NCl^-$ reacts with phenols in a basic medium to give coloured compounds.

Answer and review

Answer **(4)** Official marking scheme

Benzenediazonium chloride is made by diazotisation of aniline at 0–5 °C (1), gives iodobenzene with KI (2), acts as an electrophile in azo coupling (3), and couples with phenoxide in basic medium to give coloured azo dyes (5). On warming in water it is hydrolysed to phenol, C_6H_5OH, with loss of N_2, not benzene; benzene would need a reducing agent such as H_3PO_2. So (4) is incorrect.

RB U10 §4.3 · p. 78

Question 18 · Q1–30 · single answer

$H_2S(g)$ reacts with $O_2(g)$ to give only water vapour ($H_2O(g)$) and $SO_2(g)$, as products. When 4 dm^3 of $H_2S(g)$ reacts with 10 dm^3 of $O_2(g)$ at a constant pressure and 250 °C, the final volume of the mixture is,

- (1)6 dm^3
- (2)8 dm^3
- (3)10 dm^3
- (4)12 dm^3
- (5)14 dm^3

Answer and review

Answer **(4)** Official marking scheme

$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$. At constant T and P gas volumes are proportional to moles. 4 dm^3 H_2S needs 6 dm^3 O_2, leaving 10 − 6 = 4 dm^3 O_2 unreacted; it forms 4 dm^3 $H_2O(g)$ and 4 dm^3 SO_2. Final volume = 4 (O_2) + 4 (H_2O) + 4 (SO_2) = 12 dm^3. At 250 °C water is a vapour and counts; leaving it out gives 8 dm^3.

RB U3 §3.8 · p. 115 RB U4 §1.2 · p. 5

Question 19 · Q1–30 · single answer

A mixture of A(g) and D(g) was introduced in to a rigid evacuated container at the temperature T. At this temperature, both A(g) and D(g) decompose according to the elementary reactions given below.

2A(g) → B(g) + 3C(g); rate constant k_1

D(g) → B(g) + 2C(g)

The initial pressure of the container P, changed to 2.7 P after the complete decomposition of both reactants. The initial rate of decomposition of A(g) at this temperature is, (R is the universal gas constant)

- (1)1.7 k_1 (P/RT)
- (2)2.7 k_1 (P/RT)
- (3)0.09 k_1 $(P/RT)^2$
- (4)2.89 k_1 $(P/RT)^2$
- (5)7.29 k_1 $(P/RT)^2$

Answer and review

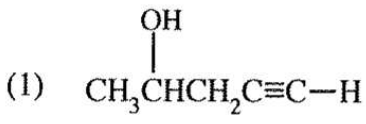
Answer **(3)** Official marking scheme

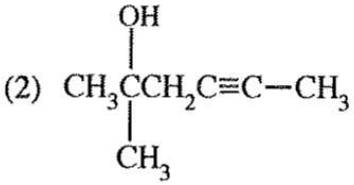
Let the initial partial pressures be p_A and p_D, so $p_A + p_D = P$. In a rigid container at constant T, pressure is proportional to moles of gas. 2A → B + 3C raises the moles from 2 to 4 (factor 2); D → B + 2C from 1 to 3 (factor 3). Final pressure: $2p_A + 3p_D = 2.7P$. Substituting $p_D = P - p_A$: $3P - p_A = 2.7P$, so $p_A = 0.3P$. $[A] = p_A/RT = 0.3P/RT$. The step is elementary and bimolecular in A, so rate $= k_1[A]^2 = k_1(0.3P/RT)^2 = 0.09\ k_1 (P/RT)^2$. Options (1) and (2) are first order, which cannot arise from an elementary 2A step; (4) and (5) are the squares of 1.7 and 2.7, from misreading the pressure change.

RB U11 §1.6 · p. 16 RB U11 §1.3 · p. 9 RB U4 §1.3 · p. 16

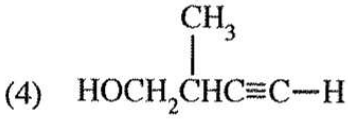
Question 20 · Q1–30 · single answer

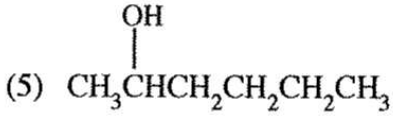
An organic compound (**X**) decolourizes bromine water (Br_2/H_2O). **X** does not give a precipitate with ammoniacal CuCl. When **X** is treated with an acidic $K_2Cr_2O_7$ solution, a green coloured solution is obtained. **X** could be:

(1) 

(2) 

(3)

(4) 

(5) 

Options (1)–(5)

Answer and review

Answer **(3)** Official marking scheme

The three observations mean: (i) unsaturation (C=C or C≡C) decolourises Br_2/H_2O; (ii) no precipitate with ammoniacal CuCl means there is no terminal alkyne (≡C–H); (iii) orange $Cr_2O_7^{2-}$ turning green Cr^{3+} means the compound is oxidised, so it is a primary or secondary alcohol (a tertiary alcohol is not oxidised). Option (3), $CH_3CH(OH)CH_2CH{=}CHCH_3$, is a secondary alcohol with an internal alkene. (1) and (4) are terminal

alkynes (CuCl precipitate); (2) is a tertiary alcohol; (5) is saturated and does not decolourise bromine water.

RB U9 §3.1 · p. 54 RB U8 §2.3 · p. 41 RB U8 §2.2 · p. 33

Question 21 · Q1–30 · single answer

A buffer solution of pH 5.0 was prepared by mixing equal volumes of a 0.10 mol dm^{-3} monobasic weak acid solution and a 0.10 mol dm^{-3} solution of the sodium salt of this acid. The pH of the resultant solution, when 20.00 cm^3 of this buffer solution was mixed with 90.00 cm^3 of 0.10 mol dm^{-3} weak acid solution, is,

- (1)3.0
- (2)4.0
- (3)4.5
- (4)5.5
- (5)6.0

Answer and review

Answer **(2)** Official marking scheme

Equal concentrations of acid and salt mean pH = pK_a = 5.0. Mixing equal volumes of the two 0.10 M solutions gives 0.050 M of each. 20.00 cm^3 of the buffer contains 1.0 mmol HA and 1.0 mmol A^-. Adding 90.00 cm^3 × 0.10 M = 9.0 mmol HA gives 10.0 mmol HA and 1.0 mmol A^-. pH = pK_a + log($[A^-]/[HA]$) = 5.0 + log(1/10) = 4.0. Because both species are in the same final volume, only the ratio of the amounts matters, not the dilution itself.

RB U12 §2.3 · p. 167

Question 22 · Q1–30 · single answer

Consider the following three aqueous solutions.

P

Q

R

When each solution is diluted by the same amount at constant temperature, the pH of **P**, **Q** and **R** respectively, will

- (1)decrease, increase, not change.
- (2)increase, not change, decrease.
- (3)increase, not change, not change.
- (4)increase, not change, increase.
- (5)increase, increase, increase.

Answer and review

Answer **(2)** Official marking scheme

P: dilution lowers $[H^+]$ (α rises but $[H^+] = \sqrt{(K_{aC})}$ falls), so pH increases. Q: a buffer, pH = pK_a + log($[A^-]/[HA]$); both concentrations fall by the same factor, so the ratio and the pH do not change. R: at the equivalence point the solution is the salt of a weak acid and a strong base, which is basic from A^- hydrolysis; dilution makes $[OH^-] = \sqrt{(K_{wC}/K_a)}$ smaller, so pH decreases towards 7. Hence increase, not change, decrease.

RB U12 §2.3 · p. 167 RB U12 §2.2 · p. 118

Question 23 · Q1–30 · single answer

The **incorrect** statement with regard to the oxoacids of chlorine HOCl, $HClO_2$, $HClO_3$ and $HClO_4$ is,

- (1)The shapes around chlorine in $HClO_2$, $HClO_3$ and $HClO_4$ respectively are angular, pyramidal and tetrahedral.
- (2)The oxidation states of chlorine in HOCl, $HClO_2$, $HClO_3$ and $HClO_4$ respectively are +1, +3, +5 and +7.
- (3)The acid strength of the oxoacids varies as HOCl < $HClO_2$ < $HClO_3$ < $HClO_4$.
- (4)All these oxoacids contain at least one double bond.
- (5)All these oxoacids contain at least one OH group.

Answer and review

Answer **(4)** Official marking scheme

HOCl is H–O–Cl and has no Cl=O bond, so "all contain at least one double bond" is incorrect. The others are true: Cl has 2, 3 and 4 bond pairs (plus 2, 1 and 0 lone pairs) in $HClO_2$, $HClO_3$ and $HClO_4$, giving angular, pyramidal and tetrahedral shapes; oxidation numbers are +1, +3, +5, +7; acid strength rises with the number of terminal oxygens; and each acid has an O–H group.

RB U6 §4.7 · p. 149 RB U2 §2.3 · p. 52

Question 24 · Q1–30 · single answer

The density of an aqueous acidic solution at 25 °C is 1.0 kg dm^{-3}. If the pH of this solution is 1.0, its H^+ concentration in ppm would be,

- (1)0.1
- (2)1
- (3)100
- (4)1000
- (5)10,000

Answer and review

Answer **(3)** Official marking scheme

pH = 1.0 gives $[H^+]$ = 0.10 mol dm^{-3} = 0.10 g dm^{-3} (M = 1 g mol^{-1}). One dm^3 of solution has mass 1.0 kg = 1000 g, so the mass ratio is 0.10 g / 1000 g = 1.0 × 10^{-4}. In ppm (parts per million by mass) this is 1.0 × 10^{-4} × 10^6 = 100 ppm. Equivalently 0.10 g dm^{-3} = 100 mg per kg of solution = 100 ppm.

RB U3 §3.5 · p. 102 RB U12 §2.2 · p. 118

Question 25 · Q1–30 · single answer

A 25.0 g sample of polluted air containing ozone (O_3) is treated with an acidic solution containing excess KI. Ozone is converted to O_2 and H_2O during this reaction. The iodine liberated is titrated with 0.002 mol dm^{-3} $Na_2S_2O_3$ solution. Volume of $Na_2S_2O_3$ required was 25.0 cm^3. The mass percent of O_3 in the air sample is, (O = 16)

- (1)4.8 × 10^{-3}

- (2)6.4×10^{-3}
- (3)9.6×10^{-3}
- (4)1.0×10^{-2}
- (5)3.2×10^{-2}

Answer and review

Answer **(1)** Official marking scheme

$O_3 + 2I^- + 2H^+ \rightarrow O_2 + I_2 + H_2O$ and $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$, so 1 mol $O_3 \equiv$ 1 mol $I_2 \equiv$ 2 mol $S_2O_3^{2-}$. $n(S_2O_3^{2-}) = 0.002 \times 25.0/1000 = 5.0 \times 10^{-5}$ mol; $n(O_3) = 2.5 \times 10^{-5}$ mol; mass $= 2.5 \times 10^{-5} \times 48 = 1.2 \times 10^{-3}$ g. Mass percent $= 1.2 \times 10^{-3}/25.0 \times 100 = 4.8 \times 10^{-3}$ %. Using 1 : 1 with thiosulfate gives 9.6×10^{-3}.

RB U3 §3.8 · p. 115 RB U6 §4.6 · p. 141

Question 26 · Q1–30 · single answer

Which of the following reaction steps is **not** present in the Born-Haber cycle of NaCl(s) formation?

- (1)$Na^+(aq) + Cl^-(aq) \rightarrow NaCl(aq)$
- (2)$Na(s) \rightarrow Na(g)$
- (3)$Cl_2(g) \rightarrow 2Cl(g)$
- (4)$Cl(g) + e \rightarrow Cl^-(g)$
- (5)$Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$

Answer and review

Answer **(1)** Official marking scheme

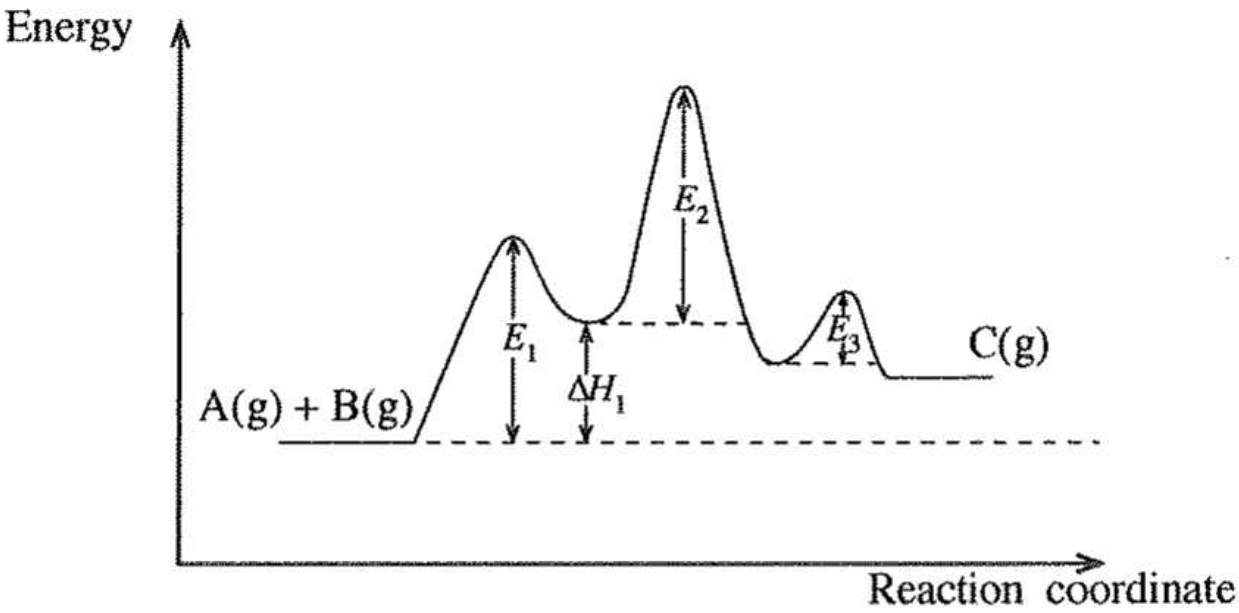
The Born-Haber cycle contains only steps starting from the elements and ending with the solid, through gaseous atoms and gaseous ions: sublimation of Na (2), dissociation of Cl_2 (3), ionisation of Na(g), electron gain of Cl(g) (4) and lattice formation from gaseous ions (5). The aqueous-ion step (1) belongs to a dissolution/hydration cycle, not to the Born-Haber cycle.

RB U5 §2.3 · p. 51

Question 27 · Q1–30 · single answer

Activation energy of the elementary reaction A(g) + B(g) → C(g) is Ea. This reaction is catalysed by the metal **M**. The energy diagram of the catalysed reaction is given below.

Which of the following is always correct with regard to this reaction?



E

1

E

E

- (1)Ea < E_1
- (2)Ea = E_1 + E_2 + E_3 − ΔH_1
- (3)Ea < E_1, Ea < E_2 and Ea < E_3
- (4)Ea > E_1 + E_2
- (5)Ea > ΔH_1 + E_2

Answer and review

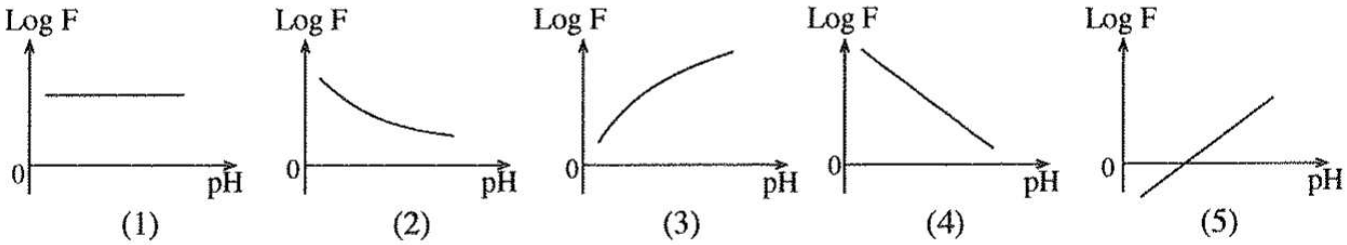
Answer **(5)** Official marking scheme

A catalyst gives an alternative pathway with a lower overall barrier. The overall barrier of the catalysed route is the height of its highest point above the reactants. Reading the diagram, the first intermediate lies ΔH_1 above A + B and the highest peak lies E_2 above that intermediate, so its height is ΔH_1 + E_2 (the intermediate is not at the height of the first peak, so E_1 + E_2 would overstate it). The uncatalysed barrier Ea must exceed this highest point, otherwise the catalyst would not speed up the reaction, so Ea > ΔH_1 + E_2. Statements comparing Ea with the single steps E_1 or E_3 need not hold.

RB U11 §1.9 · p. 54 RB U11 §1.10 · p. 57

Question 28 · Q1–30 · single answer

For a weak acid, it can be given that F = (Amount of the acid dissociated) / (Amount of the acid undissociated). Which of the following graphs shows the relationship between Log F and pH?



Graphs (1)–(5): Log F against pH

Answer and review

Answer **(5)** Official marking scheme

F = $[A^-]/[HA]$. From $K_a = [H^+][A^-]/[HA]$, $F = K_a/[H^+]$, so $\log F = \log K_a - \log[H^+] = pH - pK_a$. This is a straight line of slope +1 that cuts the pH axis ($\log F = 0$) at $pH = pK_a$, with a negative intercept at pH = 0. That is graph (5). Graph (4) has the wrong (negative) slope, and (2) and (3) are curves.

RB U12 §2.2 · p. 118 RB U12 §2.3 · p. 167

Question 29 · Q1–30 · single answer

Which of the following statements with regard to polymers is correct?

- (1)Nylon is an addition polymer.
- (2)Teflon is a condensation polymer.
- (3)Bakelite is a linear polymer.
- (4)The number of carbon atoms in the repeating unit of natural rubber is 4.
- (5)Small covalent molecules are eliminated when monomers combine to form condensation polymers.

Answer and review

Answer **(5)** Official marking scheme

In condensation polymerisation small molecules such as H_2O or HCl are lost as the monomers join, so (5) is correct. Nylon is a condensation polymer (polyamide), Teflon (PTFE) is an addition polymer of $CF_2{=}CF_2$, Bakelite is a cross-linked (network) thermosetting polymer, and natural rubber is poly(isoprene), whose repeating unit C_5H_8 has 5 carbons, not 4.

RB U14 §1.11 · p. 37

Question 30 · Q1–30 · single answer

Two ideal gases that do not react with each other are separated by a valve and kept in a rigid container. This system is maintained at constant temperature and pressure. Which of the following correctly describes the change in Gibbs energy, enthalpy and entropy of the system respectively when the valve is opened?

- (1)decreased, decreased, decreased
- (2)decreased, decreased, increased
- (3)decreased, unchanged, increased
- (4)decreased, increased, increased
- (5)increased, increased, increased

Answer and review

Answer **(3)** Official marking scheme

Ideal gases have no intermolecular forces, so mixing does not change the enthalpy: $\Delta H = 0$. Mixing is spontaneous because the disorder rises: $\Delta S > 0$. Then $\Delta G = \Delta H - T\Delta S = -T\Delta S < 0$, so G decreases. Result: decreased, unchanged, increased.

RB U5 §2.4 · p. 53

Questions 31–40: response code

(1)	(2)	(3)	(4)	(5)
Only (a) and (b) are correct	Only (b) and (c) are correct	Only (c) and (d) are correct	Only (d) and (a) are correct	Any other number or combination of responses is correct

Question 31 · Q31–40 · response code

Which of the following statement/statements is/are correct with regard to simple covalent molecules containing oxygen and sulphur atoms?

- H_2O shows amphoteric properties.
- The boiling point of H_2O_2 is higher than the boiling point of H_2O.
- H_2O_2 can act as an oxidizing agent only in an acidic medium.
- Both H_2S and SO_2 have the capacity to act only as reducing agents.

Answer and review

Answer **(1/5)** Official marking scheme

The official scheme accepts (1) or (5). (a) is true (H_2O accepts H^+ to form H_3O^+ and donates H^+ to form OH^-). (b) is true: H_2O_2 has stronger hydrogen bonding and a larger molar mass (b.p. about 150 °C against 100 °C). (c) is false: H_2O_2 is an oxidant in acidic and in basic medium. (d) is false: SO_2 (S at +4) can also act as an oxidant (e.g. with H_2S), and H_2S can oxidise active metals by taking up electrons as H^+. So (a) and (b) alone are correct, code (1); the scheme also accepts (5), the scheme does not give the reason (the wording of one statement was probably considered ambiguous).

RB U6 §4.6 · p. 141 RB U2 §2.6 · p. 79

Question 32 · Q31–40 · response code

Which of the following statement/statements is/are correct with regard to hydrocarbons?

- All hydrocarbons give CO_2 and H_2O when completely reacted with excess O_2.
- All alkynes react with Grignard reagents to give alkynylmagnesium halides.
- The boiling point of a branched alkane is higher than the boiling point of an unbranched alkane with the same relative molecular mass.
- None of the hydrocarbons react with aqueous NaOH.

Answer and review

Answer **(4)** Official marking scheme

(a) true: complete combustion of any hydrocarbon gives CO_2 and H_2O. (b) false: only terminal alkynes (R–C≡C–H) have the acidic hydrogen that the Grignard reagent removes. (c) false: branching reduces the surface area and the London forces, so the branched isomer boils lower. (d) true: hydrocarbons are non-polar and do not react with aqueous NaOH. Only (a) and (d), code (4).

RB U8 §2.1 · p. 26 RB U8 §2.3 · p. 41 RB U8 §2.7 · p. 50

Question 33 · Q31–40 · response code

If an endothermic reaction occurs spontaneously at constant temperature and pressure, then,

- enthalpy of the system decreases.
- entropy of the system increases.
- enthalpy of the system increases.
- entropy of the system does not change.

Answer and review

Answer **(2)** Official marking scheme

Endothermic means $\Delta H > 0$, so the enthalpy of the system increases, (c) is true and (a) is false. Spontaneity needs $\Delta G = \Delta H - T\Delta S < 0$ at constant T and P, which with $\Delta H > 0$ is only possible if $T\Delta S > \Delta H > 0$, i.e. the entropy of the system increases, (b) true and (d) false. Code (2).

RB U5 §2.4 · p. 53

Question 34 · Q31–40 · response code

Which of the following statement/statements is/are correct regarding the precipitation of metal ions by passing $H_2S(g)$ in to their aqueous solutions?

- When the pressure of $H_2S(g)$ is decreased, the sulphide ion concentration is increased.
- When the temperature is increased, the sulphide ion concentration is decreased.
- Addition of $Na_2S(s)$ to the solution, decreases the dissociation of dissolved $H_2S(aq)$.
- Increase in pH of the solution decreases sulphide ion concentration.

Answer and review

Answer **(2)** Official marking scheme

Overall $H_2S \rightleftharpoons 2H^+ + S^{2-}$ gives $[S^{2-}] = K_{a1}K_{a2}[H_2S]/[H^+]^2$, and $[H_2S]$ is proportional to the pressure of H_2S. (a) false: lower pressure gives lower $[H_2S]$ and lower $[S^{2-}]$. (b) true: the gas is less soluble at higher temperature, so $[H_2S]$ and $[S^{2-}]$ fall. (c) true: Na_2S adds S^{2-} (common ion), shifting the dissociation equilibria back. (d) false: higher pH means lower $[H^+]$, so $[S^{2-}]$ increases (this is how metal sulphides are selectively precipitated). Code (2).

RB U12 §2.4 · p. 175 RB U12 §2.2 · p. 118

Question 35 · Q31–40 · response code

Which of the following is/are nucleophilic substitution reaction/reactions?

- $CH_3C(=O)–H + HCN \rightarrow CH_3CH(OH)CN$
- $CH_3CH_2OH + PCl_3 \rightarrow CH_3CH_2Cl$

- $(CH_3)_2CHCl + NaOH \rightarrow (CH_3)_2CHOH$
- $(CH_3)_3CH + Cl_2 \xrightarrow{(h\nu)} (CH_3)_3CCl$

Answer and review

Answer **(2)** Official marking scheme

(a) is nucleophilic addition to the C=O of an aldehyde (CN^- adds to the carbonyl carbon). (b) replaces OH by Cl with attack of Cl^- on the activated alcohol, a nucleophilic substitution. (c) replaces Cl by OH^-, a nucleophilic substitution. (d) is free-radical substitution (chlorination with light). Only (b) and (c): code (2).

RB U8 §2.6 · p. 49 RB U9 §3.4 · p. 60 RB U9 §3.1 · p. 54 RB U8 §2.2 · p. 33

Question 36 · Q31–40 · response code

Which of the following statement/statements is/are correct regarding the elevation of carbon dioxide level in the atmosphere?

- It contributes to the increase in acidity of sea water.
- It reduces the hardness of water bodies.
- It strongly absorbs UV radiation coming from the sun.
- It does not contribute to acid rain.

Answer and review

Answer **(4)** Official marking scheme

(a) true: CO_2 dissolves in sea water to give carbonic acid ($CO_2 + H_2O \rightleftharpoons H^+ + HCO_3\text{^}-$), lowering the pH. (b) false: the extra acid dissolves carbonate rocks and shells, which would increase, not reduce, Ca^{2+}/Mg^{2+} hardness. (c) false: CO_2 absorbs infrared (heat) radiation re-emitted by the Earth, which is the greenhouse effect, not UV from the sun. (d) true as the scheme intends: acid rain is attributed to the strong acids from SO_2 and NO_x; CO_2 gives only the weak carbonic acid (rain pH about 5.6, natural). Hence (a) and (d): code (4).

RB U14 §1.13 · p. 58

Question 37 · Q31–40 · response code

Which of the following statement/statements is/are correct with regard to 3d-block elements?

- Zn has the highest first ionization energy among the 3d-block elements.
- In contrast to the ions of most main group elements (s and p-block), 3d-block metal ions rarely attain the noble gas configuration.
- Although the electronegativities of 3d-block elements are higher than the electronegativities of the corresponding s-block elements, their atomic radii are smaller than the atomic radii of the corresponding s-block elements.
- The 3d-block elements that form colourless compounds are Ti and Zn.

Answer and review

Answer **(5)** Official marking scheme

(a) true: Zn ($3d^{10}4s^2$, filled subshells) has the highest first ionisation energy of the 3d series (about 906 kJ mol^{-1}). (b) true: 3d ions such as Fe^{2+}, Cu^{2+} have partly filled d subshells, not [Ar]. (c) true: across a period the d-block atoms have higher nuclear charge, so they are smaller and more electronegative than the s-block metals of the same period. (d) false: the Resource Book names Sc^{3+} and Zn^{2+} (d^0 and d^{10}) as the colourless

ions, not Ti. So (a), (b), (c) are correct, which is not one of the pair codes (1)–(4); the answer is code (5).

RB U6 §4.10 · p. 160 RB U1 §1.6 · p. 32

Question 38 · Q31–40 · response code

Volatile liquids **A** and **B** having saturated vapour pressures P_A° and P_B° ($P_A^\circ \neq P_B^\circ$) form an ideal solution. A mixture of the liquids **A** and **B** is in equilibrium with their vapour phase, in a closed container. When the volume of the container is increased and the equilibrium is re-established at the same temperature, which of the following statement/statements is/are correct?

- While some amount of **A** and **B** go to the gas phase, the composition of the liquid phase remains unchanged.
- While some amount of **A** and **B** go to the gas phase, the composition of the gas phase remains unchanged.
- While some amount of **A** and **B** go to the gas phase, the composition of the liquid phase changes.
- While some amount of **A** and **B** go to the gas phase, the composition of the gas phase changes.

Answer and review

Answer **(3)** Official marking scheme

With $P_A^\circ \neq P_B^\circ$ the vapour is richer in the more volatile component than the liquid ($y_A = x_A P_A^\circ / P_{total}$). When more liquid evaporates, the more volatile component leaves preferentially, so the liquid becomes richer in the less volatile one: the liquid composition changes (c true, a false). Because the vapour composition is fixed by the liquid composition through Raoult's law, it changes too (d true, b false). Code (3).

RB U12 §2.6 · p. 216

Question 39 · Q31–40 · response code

Which of the following statement/statements is/are correct regarding an aqueous solution of a weak acid?

- Conductivity of the solution increases as the concentration of the weak acid decreases.
- Conductivity of the solution increases as the temperature increases.
- Conductivity of the solution decreases but the fraction dissociated of the weak acid increases as more water is added to the solution.
- When NaCl(s) is dissolved in the weak acid solution, conductivity decreases.

Answer and review

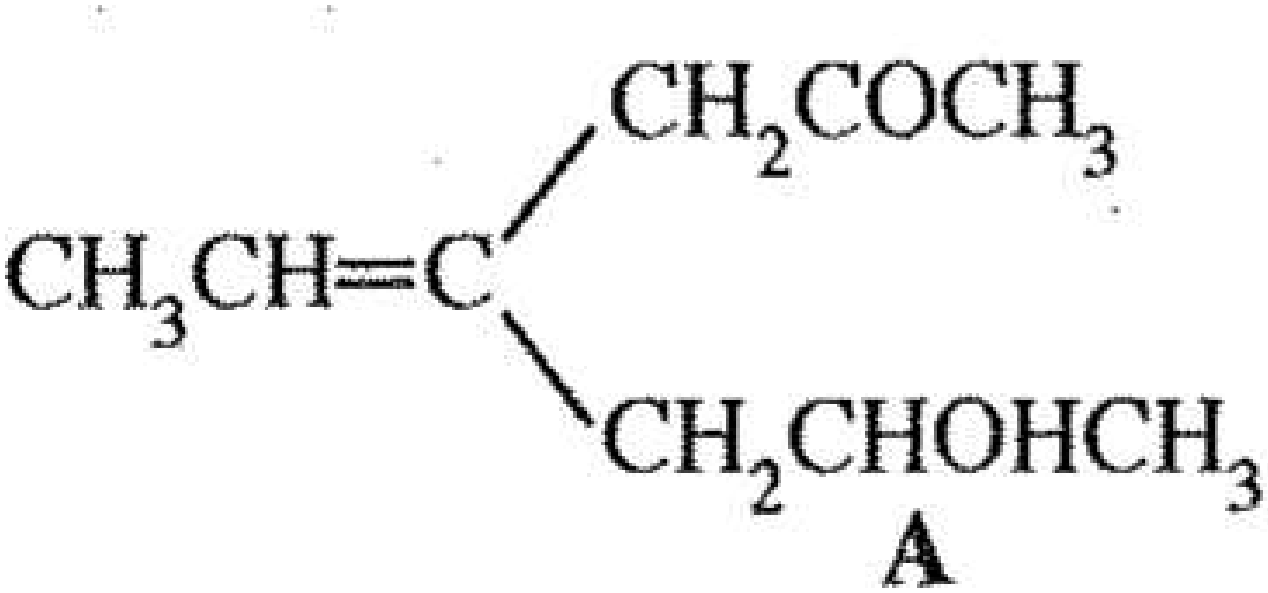
Answer **(2)** Official marking scheme

(a) false: the conductivity of the solution depends on the ion concentration, which falls as the acid is diluted (it is the molar conductivity that rises). (b) true: ions move faster, and ionisation of a weak acid increases, with temperature. (c) true: dilution lowers the ion concentration (conductivity falls) while Ostwald's dilution law shows the degree of dissociation α rises. (d) false: dissolved NaCl adds Na^+ and Cl^- ions, so conductivity increases. Code (2).

RB U13 §3.1 · p. 234 RB U12 §2.2 · p. 118

Question 40 · Q31–40 · response code

Which of the following statement/statements regarding compound **A** is/are correct?



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- **A** exhibits geometric isomerism.
- **A** does not exhibit optical isomerism.
- The product obtained when **A** is reacted with pyridinium chlorochromate (PCC) exhibits optical isomerism.
- The product obtained when **A** is reacted with pyridinium chlorochromate does not exhibit geometric isomerism.

Answer and review

Answer **(4)** Official marking scheme

(a) true: each carbon of C=C carries two different groups (CH_3 and H; CH_2COCH_3 and $CH_2CHOHCH_3$), so E/Z isomers exist. (b) false: the CH(OH) carbon in $–CH_2CH(OH)CH_3$ has four different groups (H, OH, CH_3, CH_2–), so A is chiral. PCC oxidises the secondary alcohol to a ketone, giving $CH_3CH=C(CH_2COCH_3)_2$. (c) false: it has no chiral centre. (d) true: the two groups on one C=C carbon are now identical, so there is no geometric isomerism. Only (a) and (d): code (4).

RB U7 §1.4 · p. 21 RB U9 §3.1 · p. 54

Questions 41–50: statement pairs

Response	First statement	Second statement
(1)	True	True, and correctly explains the first statement
(2)	True	True, but does not explain the first statement correctly
(3)	True	False
(4)	False	True
(5)	False	False

Question 41 · Q41–50 · statement pair

Statement 1

Among the halogens, I_2 is a solid whereas Br_2 is a liquid.

Statement 2

London forces become stronger with increase in molecular surface area.

Answer and review

Answer **(1)** Official marking scheme

Halogen molecules are non-polar and held only by London (dispersion) forces. I_2 is larger and more polarisable, with a larger surface area, so its London forces are stronger than those of Br_2 and it is a solid at room temperature while Br_2 is a liquid. Both true; the second explains the first.

RB U2 §2.6 · p. 79 RB U6 §4.7 · p. 149

Question 42 · Q41–50 · statement pair

Statement 1

At a given pressure, the spontaneity of the reaction between N_2 and H_2 to give NH_3 drops with increasing temperature.

Statement 2

Entropy change of the reaction between N_2 and H_2 to give NH_3 is negative.

Answer and review

Answer **(1)** Official marking scheme

$N_2 + 3H_2 \rightarrow 2NH_3$ is exothermic ($\Delta H < 0$) and 4 mol of gas become 2 mol, so $\Delta S < 0$. $\Delta G = \Delta H - T\Delta S = -|\Delta H| + T|\Delta S|$, which becomes less negative as T rises, so spontaneity drops. Both true, and the negative ΔS explains the temperature dependence.

RB U5 §2.4 · p. 53

Question 43 · Q41–50 · statement pair

Statement 1

Essential oils are generally extracted from plant materials by steam distillation.

Statement 2

Essential oils have a high solubility in water.

Answer and review

Answer **(3)** Official marking scheme

Essential oils are volatile, water-immiscible (sparingly soluble) liquids, and steam distillation separates them at a temperature below 100 °C so they are not decomposed: the first statement is true. The second is false; if the oils were highly soluble in water, the distillate would not separate into an oil layer and could not be collected as the oil.

RB U14 §1.12 · p. 48

Question 44 · Q41–50 · statement pair

Statement 1

A spontaneous reaction always has a negative Gibbs energy change no matter what the conditions are.

Statement 2

Gibbs energy change can be used to predict the direction of a reaction only under constant temperature and constant pressure conditions.

Answer and review

Answer **(4)** Official marking scheme

The criterion $\Delta G < 0$ for spontaneity is derived for constant temperature and pressure ($\Delta G = \Delta H - T\Delta S$), so the second statement is true. The first is false because "no matter what the conditions are" is not valid: under other conditions (e.g. constant V and T the Helmholtz energy applies) ΔG is not the criterion.

RB U5 §2.4 · p. 53

Question 45 · Q41–50 · statement pair

Statement 1

Solubility of 1-butanol in water is less than the solubility of methanol in water.

Statement 2

The solubility of alcohols in water decreases as the size of the non-polar alkyl group increases relative to the polar OH group.

Answer and review

Answer **(1)** Official marking scheme

Methanol is miscible with water, whereas 1-butanol dissolves only to about 8 g per 100 g. Both alcohols hydrogen-bond through OH, but the larger non-polar C_4H_9 group of butanol disrupts the water hydrogen-bond network and adds little attraction, which is exactly what the second statement says. Both true; the second explains the first.

RB U9 §3.1 · p. 54 RB U2 §2.6 · p. 79

Question 46 · Q41–50 · statement pair

Statement 1

The reaction $CH_3—CH=CH_2$ —(HBr)→ $CH_3—CH(Br)—CH_3$ is a nucleophilic addition reaction.

Statement 2

A secondary carbocation is formed as a reaction intermediate in the following reaction: $CH_3—CH=CH_2$ —(HBr)→ $CH_3—CH(Br)—CH_3$

Answer and review

Answer **(4)** Official marking scheme

The attack on the electron-rich C=C is first made by the electrophile H^+, so the reaction is electrophilic addition and the first statement is false. H^+ adds to the terminal carbon to give the more stable secondary carbocation $CH_3–CH^+–CH_3$ (Markovnikov), which then combines with Br^-, so the second statement is true.

RB U8 §2.2 · p. 33

Question 47 · Q41–50 · statement pair

Statement 1

Coke is used in several industrial processes.

Statement 2

Coke is only used industrially as a fuel.

Answer and review

Answer **(3)** Official marking scheme

Coke is used as the reducing agent and fuel in the blast furnace for iron, in the chlorination of rutile (TiO_2) to $TiCl_4$, and in producing industrial gases such as producer gas, so the first statement is true. "Only as a fuel" is therefore false.

RB U14 §1.10 · p. 33 RB U14 §1.9 · p. 31

Question 48 · Q41–50 · statement pair

Statement 1

The carbonyl carbon atom of a ketone and the other atoms bonded to it lie in the same plane.

Statement 2

The carbonyl carbon atom of a ketone is sp^2 hybridized.

Answer and review

Answer **(1)** Official marking scheme

The carbonyl carbon forms three σ bonds (to O and two carbons) using sp^2 hybrid orbitals, with one unhybridised p orbital forming the π bond. The sp^2 geometry is trigonal planar (about 120°), so the carbonyl C, O and the two attached carbons are coplanar. Both true; the second explains the first.

RB U9 §3.4 · p. 60 RB U2 §2.3 · p. 52

Question 49 · Q41–50 · statement pair

Statement 1

Any two ideal gases have the same average kinetic energies at the same temperature.

Statement 2

At a given temperature, the average speed of gas molecules adjust according to their masses.

Answer and review

Answer **(1)** Official marking scheme

The average kinetic energy $\frac{1}{2}mv^2 = (3/2)kT$ of an ideal gas depends only on temperature, so it is the same for any two gases at the same T. For this to hold for gases of different molecular mass, the lighter molecules must move faster ($v_{rms} = \sqrt{(3RT/M)}$), i.e. the average speed adjusts according to mass. Both true; the second explains the first.

RB U4 §1.4 · p. 19

Question 50 · Q41–50 · statement pair

Statement 1

Although CFC contribute to ozone layer depletion, the contribution from HFC is negligible.

Statement 2

HFC undergoes complete decomposition before reaching the upper atmosphere.

Answer and review

Answer **(All)** Official marking scheme

The official scheme accepts every response. The first statement is true: HFCs contain no chlorine, so they do not release Cl atoms in the stratosphere, whereas CFCs do. The second statement is open to dispute: the Resource Book explains HFCs are less stable because of their C–H bonds and so are largely broken down before the ozone layer, but "complete decomposition" is too strong, and the reason their effect is negligible is the absence of chlorine. Because of this ambiguity all answers were credited. HFCs are still powerful greenhouse gases.

RB U14 §1.13 · p. 58

Structured essay · answer all four

SEQ · Paper II Part A

Question 1 · Part A · structured essay

(a) [24 marks]

1. (a) The following questions are related to the elements of the second row in the Periodic Table. Write the **symbol** of the element in the space provided in answering parts (i) to (vi).

(i) Identify the element that has the highest electronegativity (disregard the noble gas).

Answer

F (04 marks)

(ii) Identify the element that has an allotrope which conducts electricity.

Answer

C (04 marks)

(iii) Identify the element that forms the monoatomic ion largest in size (this should be a stable ion).

Answer

N (04 marks)

(iv) Identify the element that has **no** p electrons but has a stable s configuration.

Answer

Be (04 marks)

(v) Identify the element that has the highest first ionization energy.

Answer

Ne (04 marks)

(vi) Identify the element that forms mostly electron deficient trigonal planar covalent compounds.

Answer

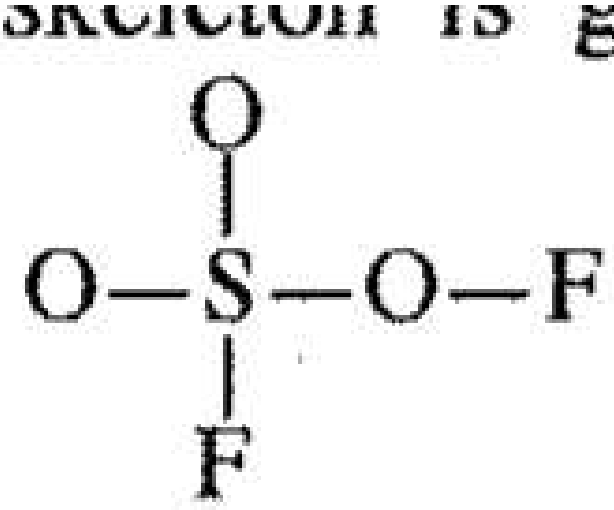
B (04 marks)
Note: if the name is given instead of the symbol, do not award marks. (04 marks × 6 = 24 marks) · 1(a): 24 marks

Review.

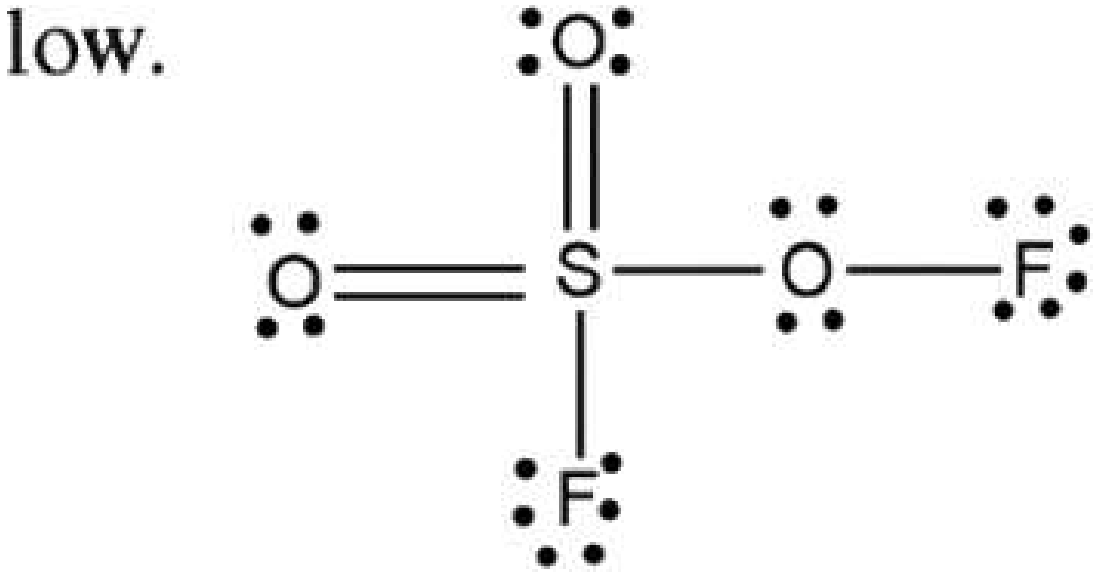
Second-row trends (Resource Book Unit 1, periodic trends). Electronegativity is highest for F. Graphite (an allotrope of C) conducts electricity through its delocalised π electrons. Among the stable monoatomic ions of period 2 (Li^+, Be^{2+}, N^{3-}, O^{2-}, F^-), N^{3-} is the largest because it has the lowest nuclear charge for the same 10 electrons. Be ($1s^2\ 2s^2$) has no p electrons but a filled s subshell. Ne, the noble gas, has the highest first ionization energy. Boron halides such as BF_3 are electron deficient (six electrons around B) and trigonal planar. Common mistake: writing names instead of symbols, which earns no marks.

(b) [52 marks]

(i) Draw the **most** acceptable Lewis dot-dash structure for the molecule SO_3F_2. Its skeleton is given below.



Answer



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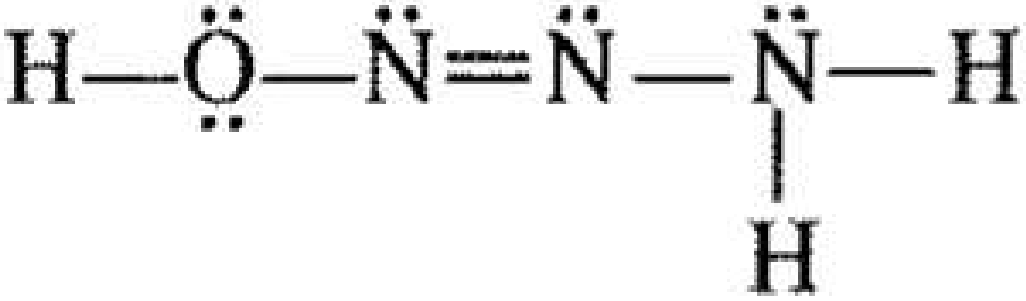
The structure drawn in the scheme (see figure) has S with a double bond to the terminal O at the top (O with two lone pairs), a double bond to the O on the left (two lone pairs), a single bond to F below (three lone pairs) and a single bond to the bridging O, which is bonded to the second F (bridging O with two lone pairs, F with three lone pairs). All formal charges are zero. (06 marks)

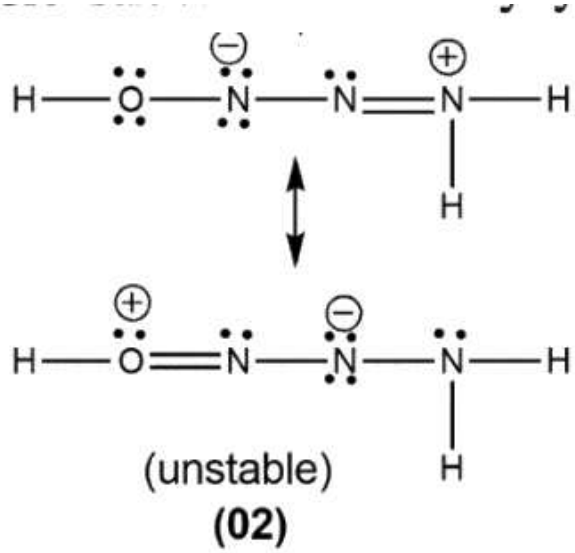
(ii) The most stable Lewis dot-dash structure for the molecule H_3N_3O is shown below. Draw **two** more Lewis dot-dash structures (resonance structures) for this molecule. Write 'unstable' under the more unstable structure drawn by you.

aw **two** more Lewis dot-dash

ite 'unstable' under the more



Answer



(02)

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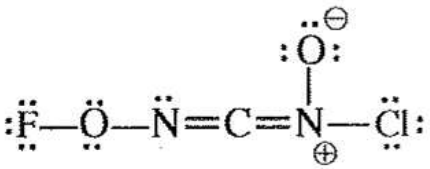
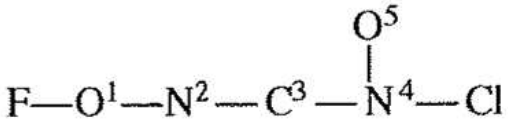
Structure 1: H–Ö–N̈^−–N=N^+H_2 (formal charge − on the middle N, + on the terminal N; O has two lone pairs) (04 marks)
Structure 2: H–O^+=N̈–N̈^−–NH_2 (+ charge on O, − on the middle N); this is the **unstable** structure because the positive charge is on the more electronegative O atom (04 marks)

'unstable' written under it (02 marks) (10 marks)

(iii) Based on the Lewis dot-dash structure given below, state the following regarding the C, N and O atoms given in the table. I. VSEPR pairs around the atom; II. electron pair geometry around the atom; III. shape around the atom; IV. hybridization of the atom. The atoms are numbered as follows: F–O^1–N^2–C^3–N^4(–O^5)–Cl.



The atoms are numbered as follows:



Answer

	O^1	N^2	C^3	N^4
I. VSEPR pairs	4	3	2	3
II. electron pair geometry	tetrahedral	trigonal planar	linear	trigonal planar
III. shape	angular / V / bent	angular / V / bent	linear	trigonal planar
IV. hybridization	sp^3	sp^2	sp	sp^2

(01 mark × 16 = 16 marks)

(iv) Identify the atomic/hybrid orbitals involved in the formation of the following σ bonds in the Lewis dot-dash structure given in part (iii) above. (Numbering of atoms is as in part (iii).)
I. F–O^1 II. O^1–N^2 III. N^2–C^3 IV. C^3–N^4 V. N^4–O^5 VI. N^4–Cl

Answer

I. F: 2p **or** sp^3; O^1: sp^3
II. O^1: sp^3; N^2: sp^2
III. N^2: sp^2; C^3: sp
IV. C^3: sp; N^4: sp^2
V. N^4: sp^2; O^5: 2p **or** sp^3
VI. N^4: sp^2; Cl: 3p **or** sp^3 (01 mark × 12 = 12 marks)

(v) Identify the atomic orbitals involved in the formation of the following π bonds in the Lewis dot-dash structure given in part (iii) above.
I. N^2–C^3 II. C^3–N^4

Answer

I. N^2: 2p; C^3: 2p
II. C^3: 2p; N^4: 2p (01 mark × 4 = 04 marks)

(vi) I. How are the two double bonds oriented in the Lewis dot-dash structure given in part (iii)?
II. Give an example of a molecule/ion that has a similar orientation of double bonds.
Note: Your example should not contain more than 3 atoms. The elements in your example should be restricted to the first and second periods of the Periodic Table.

Answer

I. The double bonds are perpendicular to each other (02 marks)
OR the σ bonds are linear and the π bonds are perpendicular (01 + 01 marks)
II. CO_2, NO_2^+, CN_2^{2-}, N_3^- (any one) (02 marks) · 1(b): 52 marks

Review.

Tests Lewis structures, formal charge, VSEPR, hybridization, σ/π bonding and resonance (Resource Book Unit 2). For SO_3F_2 the most acceptable structure expands the S octet and gives zero formal charges (S=O rather than S^+–O^-). Resonance structures keep the same atom positions and move only electrons; a structure that puts a positive charge on the more electronegative O is the less stable one. The shape is read from VSEPR pairs (lone pairs included): O^1 has 4 pairs (2 bond + 2 lone) so is angular, N^2 has 3 pairs (angular), C^3 has 2 and N^4 has 3 pairs and no lone pair (trigonal planar). In cumulated double bonds (C=N=C type, as in CO_2) the two π bonds use perpendicular 2p orbitals on the central atom. Common mistakes: giving shape equal to the electron pair geometry when lone pairs are present, and forgetting that the σ bond to a halogen may use 2p or 3p.

(c) [24 marks]

(i) An atomic orbital is described by three quantum numbers n, l and m_l. Write the appropriate quantum numbers and the name of the atomic orbital in the blanks.

	n	l	m_l	atomic orbital
I.	?	?	+1	3p
II.	3	2	−2	?
III.	?	?	?	2s

Answer

	n	l	m_l	atomic orbital
I.	3	1	+1	3p
II.	3	2	−2	3d
III.	2	0	0	2s

(01 mark × 6 = 06 marks)

(ii) Arrange the following in the **increasing** order of the property indicated in parenthesis. (Reasons are **not** required.)
I. LiF, LiI, KF (melting point)
II. NO_2^-, NO_4^{3-}, NF_5 (stability)
III. NOCl, $NOCl_3$, NO_2F (N–O bond distance)

Answer

I. LiI < LiF < KF
II. NF_5 < NO_4^{3-} < NO_2^-
III. NOCl < NO_2F < $NOCl_3$ (06 marks × 3 = 18 marks) · 1(c): 24 marks

Review.

Quantum numbers: n = shell, l = 0, 1, 2 for s, p, d, and m_l runs from −l to +l (Resource Book Unit 1.3). Melting points (Unit 2.4): LiI is the most covalent salt (small, strongly polarizing Li^+ with the large, easily polarized I^-), so it has the lowest melting point; LiF and KF are both highly ionic and the scheme places KF above LiF. NF_5 and NO_4^{3-} would need N to exceed its octet (no d orbitals in the second period), so they are

unstable and NO_2^− is the most stable. N–O bond distance: NOCl has N=O (shortest), NO_2F has a bond order of about 1.5, and $NOCl_3$ would have only a N–O single bond (longest).

Read: RB U1 §1.6 · p. 32 RB U2 §2.1 · p. 44 RB U2 §2.3 · p. 52 RB U1 §1.3 · p. 17 RB U2 §2.4 · p. 75 RB U1 §1.5 · p. 28

Question 2 · Part A · structured essay

(a) [50 marks]

2. (a) **X** is an s-block element in the Periodic Table. The first, second and third ionization energies of **X**, in kJ mol^{-1}, are 738, 1451 and 7733 respectively. **X** reacts slowly with hot water, liberating $H_2(g)$ and forming its hydroxide. The hydroxide is basic. **X** also liberates $H_2(g)$ on reaction with dilute acids. **X** burns in air with a bright white light. The cation of **X** contributes to hardness of water.

(i) Identify **X**.

Answer

Mg **OR** Magnesium (07 marks)

(ii) Write the ground state electronic configuration of **X**.

Answer

$1s^2\ 2s^2\ 2p^6\ 3s^2$ (04 marks)

(iii) Write the chemical formulae of the **two** compounds formed when **X** burns in air.

Answer

MgO and Mg_3N_2 (03 + 03 marks)
Note: if X has been identified correctly, marks can be awarded for XO and X_3N_2.

(iv) Consider the given compounds of the elements in the group in the Periodic Table to which **X** belongs. In the given boxes, write whether the indicated property **increases** or **decreases** down the group.
I. Solubility of sulphates in water
II. Solubility of hydroxides in water
III. Thermal stability of metal carbonates
Give reasons for your answer in III.

Answer

I. Decreases (03 marks)
II. Increases (03 marks)
III. Increases (03 marks)
Reasons for III: Cation size increases down the group. Charge same. (03 marks) **OR** Charge density decreases down the group. (03 marks)
Therefore, polarizing power decreases down the group. (02 marks)
Hence, decomposition of the carbonates becomes difficult on going down the group. (03 marks)

(v) Identify the element in the s-block of the Periodic Table, which reacts in a similar manner to **X** with $H_2(g)$, $O_2(g)$ and $N_2(g)$, but does **not** belong to the same group as **X**.

Answer

Lithium **OR** Li (04 marks)

(vi) Identify another **metal ion** that contributes to hardness of water.

Answer

Ca^{2+} (no marks for Ca or Calcium) (04 marks)

(vii) Identify the compound most commonly used to remove hardness of water.

Answer

Na_2CO_3 **OR** Soda Ash (04 marks)

(viii) **X** is a component of a well-known reagent used in organic chemistry. Give the **name** of this reagent.

Answer

Grignard reagent (04 marks)
Note: if X is incorrect, do not award marks for (a)(ii) – (iv). 2(a): 50 marks

Review.

The large jump between the second (1451) and third (7733) ionization energies shows two valence electrons (Group 2), and the values with the reactions described (slow reaction with hot water, bright white flame, hard water) identify Mg (Resource Book Unit 6, 4.2). Mg burns in air to give MgO and Mg_3N_2, as does Li (diagonal relationship, Li_2O and Li_3N). Down Group 2 sulphate solubility decreases ($BaSO_4$ is insoluble) while hydroxide solubility and carbonate thermal stability increase; the carbonate trend is explained by the falling polarizing power (charge density) of the larger cation, which distorts the CO_3^{2-} ion less. Common mistakes: writing Ca instead of Ca^{2+} and answering (iv) III without mentioning polarizing power. Hardness is removed with Na_2CO_3, which precipitates Ca^{2+} and Mg^{2+} as carbonates, and RMgX is the Grignard reagent.

(b) [50 marks]

(b) Test tubes labelled **A** to **E** contain aqueous solutions of $Na_2S_2O_3$, Na_2CO_3, KNO_2, KBr and Na_2S (not in order). The characteristics of the solutions obtained and gases evolved on addition of dil. HCl (warming if required) to each of the test-tubes **A** to **E** are given in the table below.

Test-tube	Appearance of solution	Gas
A	colourless	colourless and odourless
B	colourless	reddish-brown with a pungent odour
C	colourless	colourless with a rotten egg odour
D	turbid	colourless with a pungent odour
E	colourless	not evolved

A

E

Answer

A: Na_2CO_3 B: KNO_2 C: Na_2S D: $Na_2S_2O_3$ E: KBr (04 marks × 5 = 20 marks)

(ii) Write balanced chemical equations for the reactions that take place in test-tubes **A**, **B**, **C** and **D**.

Answer

In A: $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$
In B: $KNO_2 + HCl \rightarrow KCl + HNO_2$ **OR**
$2KNO_2 + 2HCl \rightarrow 2KCl + NO_2 + NO + H_2O$ **OR**
$3KNO_2 + 3HCl \rightarrow 3KCl + HNO_3 + 2NO + H_2O$ **OR**
$3KNO_2 + 3HCl + O_2 \rightarrow 3KCl + HNO_3 + H_2O + 2NO_2$ **OR**
$4KNO_2 + 4HCl + O_2 \rightarrow 4KCl + 4NO_2 + 2H_2O$
In C: $Na_2S + 2HCl \rightarrow 2NaCl + H_2S$
In D: $Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + SO_2 + S + H_2O$ (04 marks × 4 = 16 marks)

(iii) Write a chemical test to identify each of the gases evolved in **A**, **C** and **D**.
Note: Observations are also required.

Answer

2

2

(02)

(02)

2

(03)

(02)

OR

(03)

(02)

OR

4

(03)

(02)

OR

2

2

7

(03)

(02)

2

4

(03)

(02)

OR

2

2

7

2

2

7

(03)

(02)

OR

2

(03)

(02)

OR

(03)

(02)

2(b): 50 marks

Review.

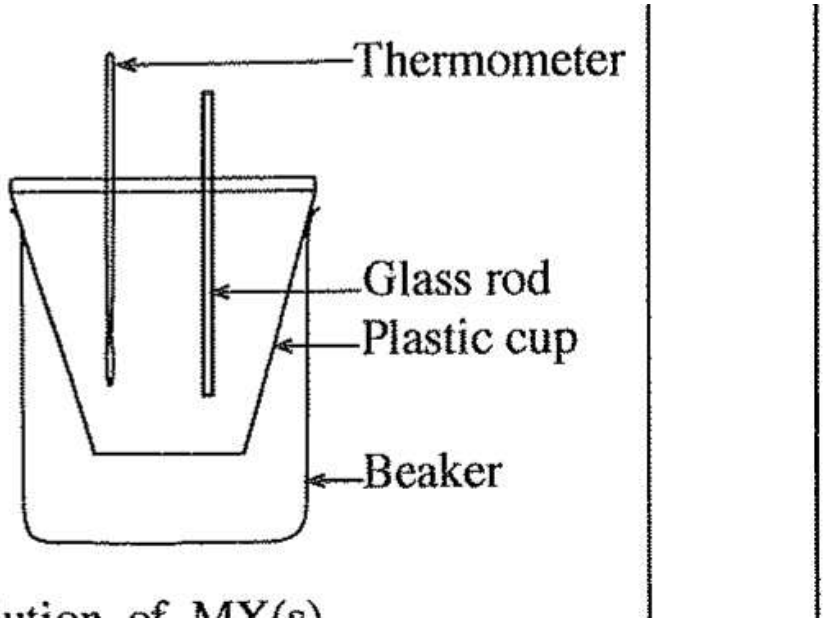
Each anion is identified from the product of its reaction with dil. HCl (Resource Book Unit 6, 4.4–4.6): carbonate gives odourless CO_2; nitrite gives HNO_2, which decomposes to brown NO_2 (with NO); sulphide gives H_2S (rotten egg); thiosulphate gives SO_2 (pungent) and a turbidity of sulphur; bromide gives no gas. CO_2 and SO_2 both turn lime water milky, so SO_2 is better identified with acidified $KMnO_4$ or $K_2Cr_2O_7$, which H_2S also decolourizes but with turbidity (sulphur). Common mistakes: writing the equation for thiosulphate without the sulphur, and giving a test without the observation.

Read: RB U6 §4.2 · p. 126 RB U1 §1.6 · p. 32 RB U14 §1.3 · p. 8 RB U6 §4.5 · p. 136 RB U6 §4.6 · p. 141 RB U6 §4.4 · p. 133

Question 3 · Part A · structured essay

(a) [100 marks]

3. The set up shown in the figure was used to calculate the heat change associated with the dissolution of MX(s) in water. 100.00 cm^3 of distilled water was added to the cup. The initial temperature of distilled water was measured to be 25.0 °C. Then 0.10 mol of MX(s) was added to the water and stirred continuously. It was observed that the temperature of the solution decreased gradually. The lowest temperature measured was 17.0 °C. The amount of water used was sufficient to completely dissolve MX(s). Density and specific heat capacity of water are 1.00 g cm^{-3} and 4.20 J g^{-1} °C^{-1} respectively. Assume that the density and the specific heat capacity of water are not changed due to the dissolution of MX(s).



Apparatus: thermometer, glass rod, plastic cup in a beaker

(i) Calculate the amount of heat that should be supplied to bring the system (solution) back to 25.0 °C.

Answer

q = m s ΔT (**OR** q = m c ΔT) (5)
= 100.00 cm^3 × 1.0 g cm^{-3} × 4.2 J $°C^{-1}$ g^{-1} × (25.0 − 17.0) °C (4+1)+(4+1)+(4+1)+(4+1)
= 3360 J (4+1)

(ii) Is the dissolution of MX(s) in water an endothermic or exothermic process? Explain your answer.

Answer

Dissolution of MX(s) has absorbed heat (**OR** temperature of water decreased) (2)
Process is endothermic (2)

(iii) Calculate the enthalpy change (in kJ mol^{-1}) associated with reaction MX(s) + H_2O(l) → M^+(aq) + X^-(aq).

Answer

ΔH = 3360 J / 0.10 mol (4+1)+(4+1)
= 33.6 kJ mol^{-1} (**OR** 33600 J mol^{-1}) (4+1)

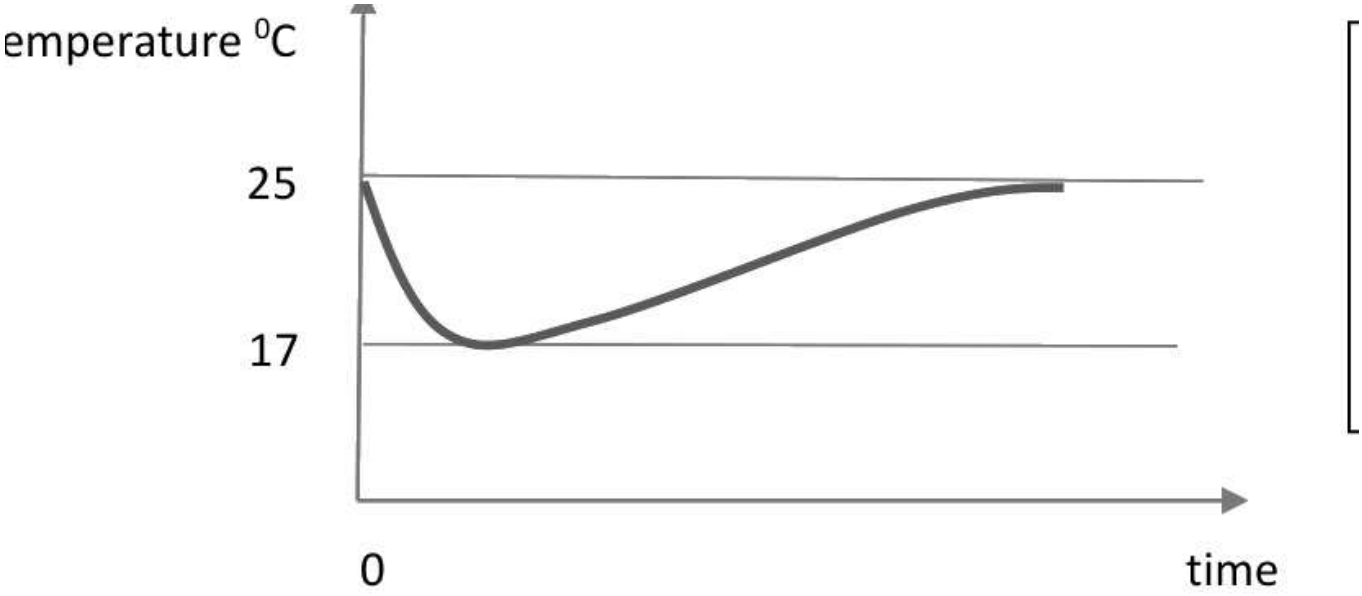
(iv) If this experiment was conducted using 200.00 cm^3 of water, would you expect the temperature change to be larger than the above value? Explain your answer.

Answer

No (**OR** the temperature change would be smaller) (2)
The amount of heat (q) is constant, the mass (m) has increased. Therefore, the temperature change (ΔT) would be smaller (**OR** more water is available to release heat). (2)

(v) Show the variation of temperature of the system (solution) by drawing the temperature – time curve.
Note: Eventually the system reaches the room temperature (25.0 °C).

Answer



Temperature–time curve

The curve starts from t = 0 (or the time of salt addition is marked) (2); starts from 25 °C (2); goes down to 17 °C (2); has the correct shape (falls to a minimum of 17 °C, then rises gradually back to 25 °C) (4)

(vi) In this experiment, explain why a plastic cup is used instead of a metal cup.

Answer

Metals are good thermal conductors (**OR** when the temperature is decreased, metal provides and conducts heat from the surroundings). (2)
Plastics are poor thermal conductors and have low heat capacity. (2)

(vii) Gibbs energy change (ΔG) for the dissolution of MX(s) in water at the temperature of 25.0 °C and pressure of 1.0 atm was calculated to be −26.0 kJ mol^{-1}. Calculate the entropy change (ΔS) of dissolution of MX(s) in water at 25.0 °C using the enthalpy change calculated above.

Answer

ΔG = ΔH − TΔS (no marks for ΔG° = ΔH° − TΔS°) (5)
ΔS = (ΔH − ΔG) / T
= (33.6 kJ mol^{-1} − (−26.0 kJ mol^{-1})) / 298 K (4+1)+(4+1)+(4+1)
= 200 J mol^{-1} K^{-1} (4+1)

(viii) Would you expect the solubility of MX(s) to increase or decrease with increasing temperature? Give reasons for your answer.

Answer

Solubility of MX(s) in water increases with increasing temperature (4) because ΔG becomes more negative (4) (**OR** because the dissolution of MX(s) is endothermic).

Review.

Calorimetry (Resource Book Unit 5, 2.2): the heat absorbed by the dissolving salt equals the heat the water would need to regain, q = mcΔT = 100 g × 4.20 × 8.0 = 3360 J, and ΔH = +q/n = +33.6 kJ mol^{-1} (positive, endothermic, because the temperature fell). ΔS = (ΔH − ΔG)/T = (33 600 + 26 000)/298 = 200 J mol^{-1} K^{-1}; the process is spontaneous despite being endothermic because ΔS is positive (T ΔS = 59.6 kJ mol^{-1} outweighs ΔH). Since ΔG = ΔH − TΔS and ΔS > 0, raising T makes ΔG more negative. Common mistakes: using the unit kJ with J in ΔS, writing ΔG° instead of ΔG, a metal cup (conducts heat from surroundings), and a

curve that does not return to 25 °C.

Read: RB U5 §2.2 · p. 36 RB U5 §2.1 · p. 31 RB U5 §2.4 · p. 53

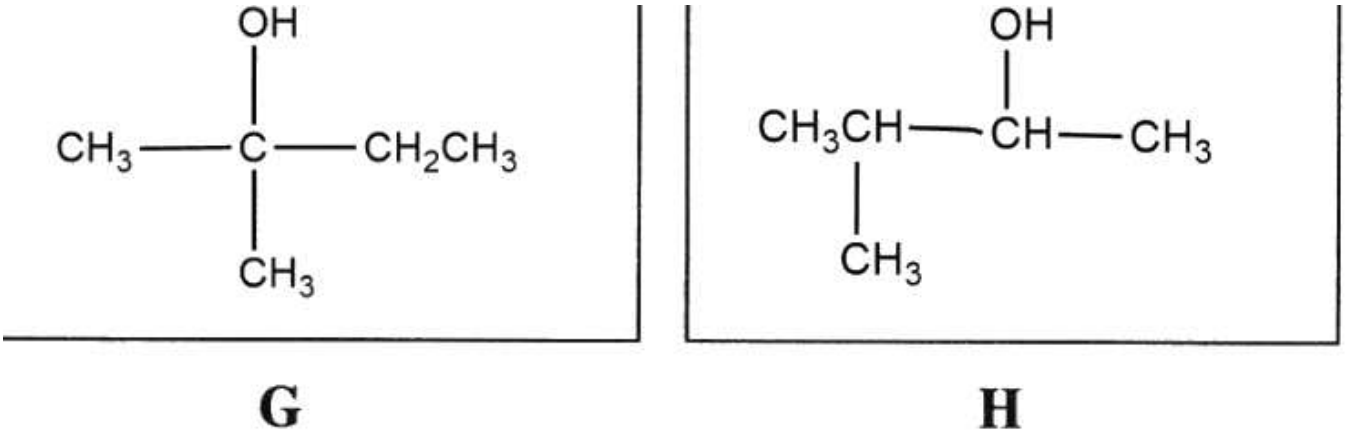
Question 4 · Part A · structured essay

(a) [50 marks]

4. (a) Compounds **A** and **B** both have the same molecular formula $C_5H_{10}O$. Both **A** and **B** give orange/red precipitates with 2,4-dinitrophenylhydrazine. When **A** and **B** are reacted separately with $NaBH_4$ in methanol, compound **A** gives **C** and compound **B** gives **D**. When **C** is heated with Al_2O_3, two alkenes **E** (C_5H_{10}) and **F** (C_5H_{10}) are formed. When **E** and **F** are reacted separately with conc. H_2SO_4 and the products obtained are hydrolysed, compound **E** gives **G**, while compound **F** gives **H**. **G** gives a turbidity immediately with the Lucas reagent. **H** also gives a turbidity with the Lucas reagent but not immediately.

(i) Draw the structures of **G** and **H**.

Answer

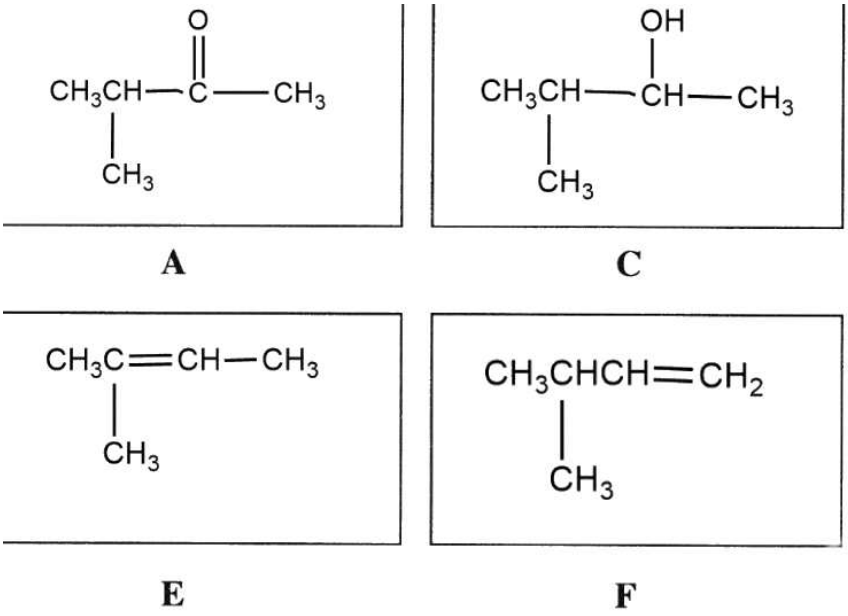


G and H

G: $(CH_3)_2C(OH)CH_2CH_3$ (2-methylbutan-2-ol); H: $(CH_3)_2CH–CH(OH)CH_3$ (3-methylbutan-2-ol) (05 × 2 = 10 marks)

(ii) Draw the structures of **A**, **C**, **E** and **F**.

Answer

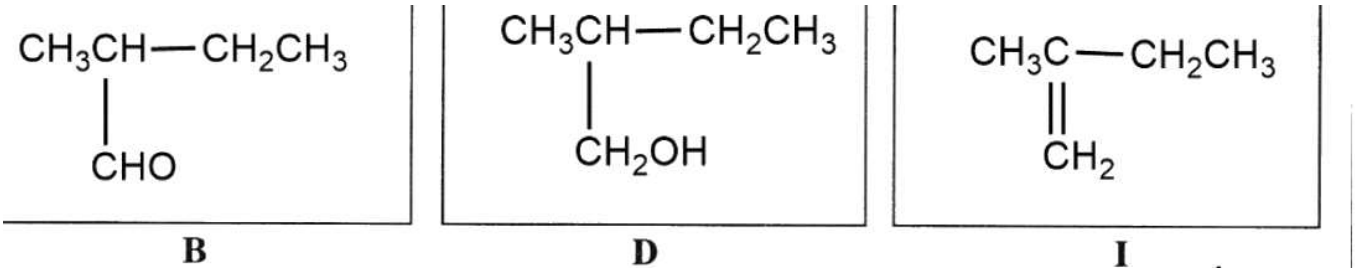


A, C, E and F

A: $(CH_3)_2CH–CO–CH_3$ (3-methylbutan-2-one); C: $(CH_3)_2CH–CH(OH)CH_3$ (3-methylbutan-2-ol); E: $(CH_3)_2C=CH–CH_3$ (2-methylbut-2-ene); F: $(CH_3)_2CH–CH=CH_2$ (3-methylbut-1-ene) (05 × 4 = 20 marks)

When heated with Al_2O_3, **D** gives alkene **I** (C_5H_{10}). When **I** is reacted with conc. H_2SO_4 and the product obtained hydrolysed, **G** is obtained.
(iii) Draw the structures of **B**, **D** and **I**.

Answer



B, D and I

B: $CH_3CH_2CH(CH_3)–CHO$ (2-methylbutanal); D: $CH_3CH_2CH(CH_3)–CH_2OH$ (2-methylbutan-1-ol); I: $CH_3CH_2C(CH_3)=CH_2$ (2-methylbut-1-ene) (05 × 3 = 15 marks)
Notes: 1. Mark A–I independently. 2. If the correct structure is given for either C or H, award full marks for both C and H (05 × 2 = 10).

(iv) Describe a test/reaction to distinguish between **A** and **B**.

Answer

B

2

2

7

4

(05 marks)

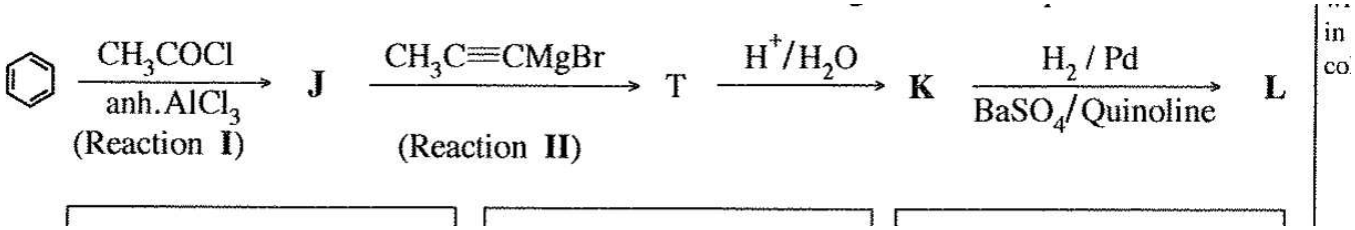
4(a): 50 marks

Review.

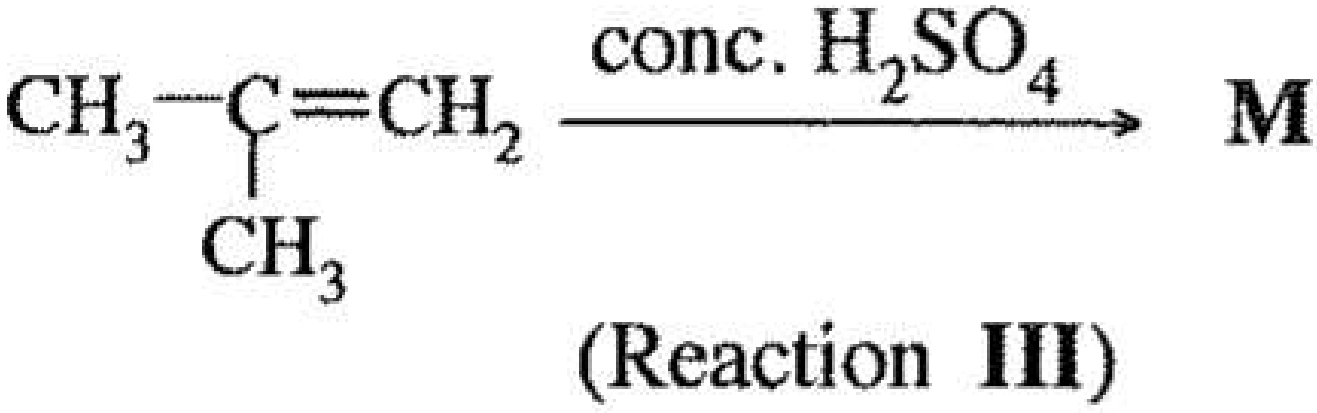
A and B are a ketone and an aldehyde (both give 2,4-DNP precipitates and are reduced by $NaBH_4$ to alcohols); Resource Book Unit 9, 3.4 and 3.1. Lucas reagent separates alcohols: tertiary (G) cloud immediately, secondary (H) cloud slowly, primary do not react at room temperature. Dehydration of the secondary alcohol C with Al_2O_3 gives two alkenes, and acid-catalysed hydration follows Markovnikov's rule: E (trisubstituted) gives the tertiary alcohol G and F gives the secondary alcohol H via the more stable carbocation, which fixes the carbon skeleton as 3-methylbutan-2-one (A). D is a primary alcohol whose dehydration product I also hydrates to G, so B is 2-methylbutanal. Aldehydes, but not ketones, are oxidised, so Tollens, Fehling's, acidified $K_2Cr_2O_7$ or $KMnO_4$ distinguish B from A. Common mistake: using 2,4-DNP, which does not distinguish them.

(b) [50 marks]

(b) (i) Give the structures of **J**, **K**, **L** and **M** in the following reaction sequences.
Benzene → (CH_3COCl, anh. $AlCl_3$; Reaction I) J → ($CH_3C{\equiv}CMgBr$; Reaction II) T → (H^+/H_2O) K → (H_2/Pd, $BaSO_4$/Quinoline) L
$(CH_3)_2C{=}CH_2$ → (conc. H_2SO_4; Reaction III) M



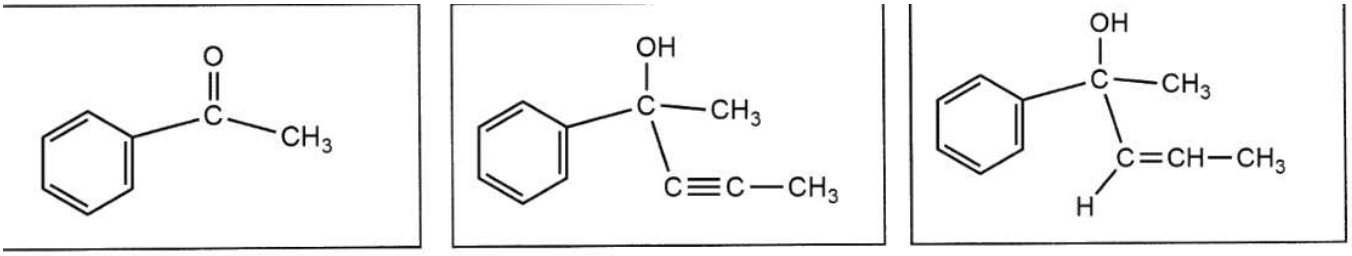
Reaction sequence (Reactions I and II)



Reaction III

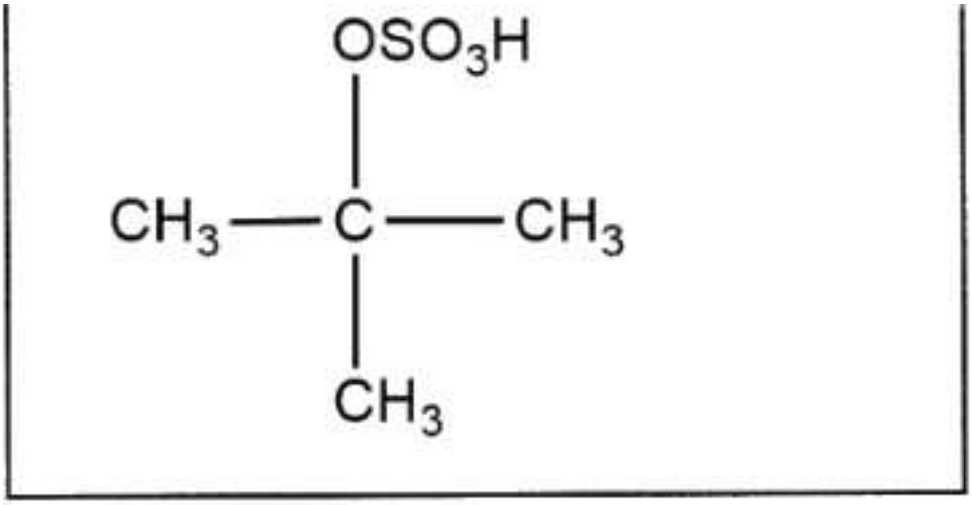
Answer

J: C_6H_5–CO–CH_3 (acetophenone); K: C_6H_5–C(OH)(CH_3)–C≡C–CH_3; L: C_6H_5–C(OH)(CH_3)–CH=CH–CH_3 (cis); M: $(CH_3)_3C$–OSO_3H (05 × 4 = 20 marks)



J K L

Structures of J, K and L



M

Structure of M

(ii) Selecting from the list given below, write the type of reaction taking place in reactions I, II and III.
Nucleophilic Addition, Nucleophilic Substitution, Electrophilic Addition, Electrophilic Substitution, Elimination

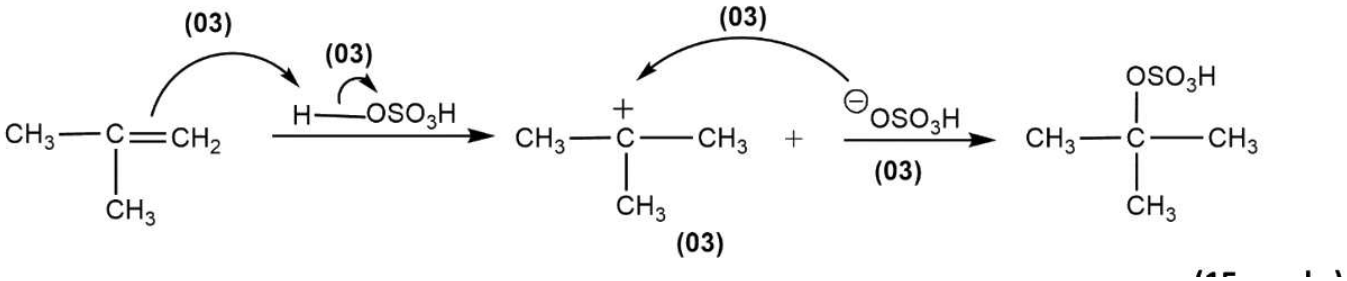
Answer

Reaction I: Electrophilic substitution
Reaction II: Nucleophilic addition
Reaction III: Electrophilic addition (05 × 3 = 15 marks)
Note: marks awarded only if each of the reactions I, II and III is correct as given in the marking scheme.

(iii) Using your knowledge of the mechanism of the reaction between alkenes and HBr, give the mechanism of reaction III.

Answer

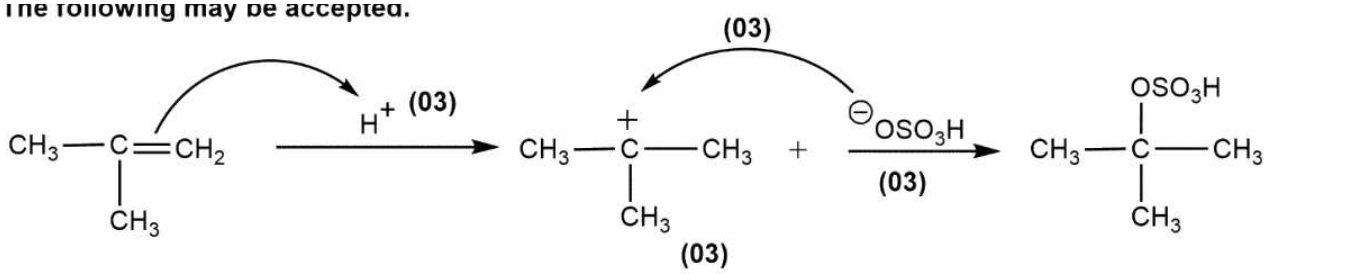
The π electrons of the alkene attack the H of H–OSO_3H (curved arrow from C=C to H, and from the H–O bond to O) (03 + 03), giving the tertiary carbocation $(CH_3)_3C^+$ (03) and the HSO_4^− ion; the HSO_4^− ion then attacks the carbocation (03) to give $(CH_3)_3C–OSO_3H$ (03). (15 marks)



Mechanism of reaction III

The following may also be accepted: the C=C attacks H^+ directly (03) to give the tertiary carbocation (03), which is attacked by ^−OSO_3H (03) to give the product (03). (12 marks)

The following may be accepted.



(12 marks)

Accepted alternative mechanism

4(b): 50 marks

Review.

Reaction I is Friedel–Crafts acylation, an electrophilic substitution of benzene (CH_3CO^+) (Resource Book Unit 8, 2.4). The Grignard-type reagent $CH_3C{\equiv}CMgBr$ adds to the carbonyl carbon (nucleophilic addition; Unit 9, 3.4), and acid hydrolysis converts the alkoxide T to the tertiary alcohol K. Pd on $BaSO_4$/quinoline (Lindlar catalyst) partially reduces the alkyne to the cis-alkene L. Reaction III is electrophilic addition of H_2SO_4 to isobutene following Markovnikov's rule, with the tertiary carbocation as intermediate (Unit 8, 2.2). Common mistakes: wrong curved-arrow direction, writing the product as the anti-Markovnikov primary sulphate, and labelling reaction II as substitution.

Read: RB U9 §3.4 · p. 60 RB U9 §3.1 · p. 54 RB U8 §2.2 · p. 33 RB U8 §2.4 · p. 44 RB U7 §1.4 · p. 21

Answer two from each part

Essay · Paper II Parts B and C

Part B

Question 5 · Part B · essay

Scheme note: physical states are necessary for the award of marks.

(a) [75 marks]

A titration between the mono acidic weak base B (0.15 mol dm^{-3}) and HCl (0.10 mol dm^{-3}) was carried out using a suitable indicator as described below.
The HCl solution (25.00 cm^3) was kept in the titration flask and the weak base B was added using a burette. The dissociation constant, K_b of the weak base at 25 °C is 1.00×10^{-5} mol dm^{-3}. All the experiments were conducted at 25 °C.
(i) Calculate the pH of the acid solution in the titration flask, before the addition of the base, B.

Answer

pH = $-\log[H^+]$ (2) = $-\log(0.1)$ = **1.0** (2 + 1)

(ii) Calculate the pH of the solution in the titration flask, after the addition of 10.00 cm^3 of the solution of B. Can the solution in the titration flask act as a buffer solution? Explain your answer.

Answer

$[H^+]$ = (0.1 mol dm^{-3} × 25.00 cm^3 − 0.15 mol dm^{-3} × 10.00 cm^3)/35.00 cm^3 (4 + 1) = 0.028 mol dm^{-3}
pH = **1.5 (or 1.6)** (4 + 1)
No, this solution cannot act as a buffer solution. (3) Only the protonated base (conjugate acid) is present (no unreacted or unprotonated base). (3)
Note: if correctly explained using the addition of H^+ and OH^-, award full marks.

(iii) Calculate the volume of the weak base solution required to reach the equivalence point.

Answer

V = (0.1 mol dm^{-3} × 25.00 cm^3)/0.15 mol dm^{-3} (4 + 1) = **16.66 cm^3** (4 + 1) (16.67 cm^3, or the answer reported to one decimal place, is also accepted)

(iv) Another 10.00 cm^3 volume of the weak base was added to the titration flask after reaching the equivalence point. Calculate the pH of the solution in the titration flask.

Answer

The weak base dissociates according to: B(aq) + H_2O(l) ⇌ BH^+(aq) + OH^-(aq) (2)
K_b = $[BH^+(aq)][OH^-(aq)]/[B(aq)]$ (4) OR pOH = pK_b + log($[BH^+(aq)]/[B(aq)]$)
Note: physical states are required for the award of marks.
Assuming that the amount dissociated is negligible (2):
[B(aq)] = (0.15 mol dm^{-3} × 10.00 cm^3)/(25.00 cm^3 + 16.66 cm^3 + 10.00 cm^3) (4 + 1)
$[BH^+(aq)]$ = (0.15 mol dm^{-3} × 16.66 cm^3)/(25.00 cm^3 + 16.66 cm^3 + 10.00 cm^3) (4 + 1)
pOH = $-\log(1 \times 10^{-5})$ + log[(0.15 mol dm^{-3} × 16.66 cm^3)/(0.15 mol dm^{-3} × 10.00 cm^3)] (4 + 1) = 5.0 + 0.221 = 5.221
pH = **8.78 (or 8.7 or 8.9 or 9)** (4 + 1)

(v) Can the solution obtained in (iv) above act as a buffer solution? Explain your answer.

Answer

Yes

(3)

(3)

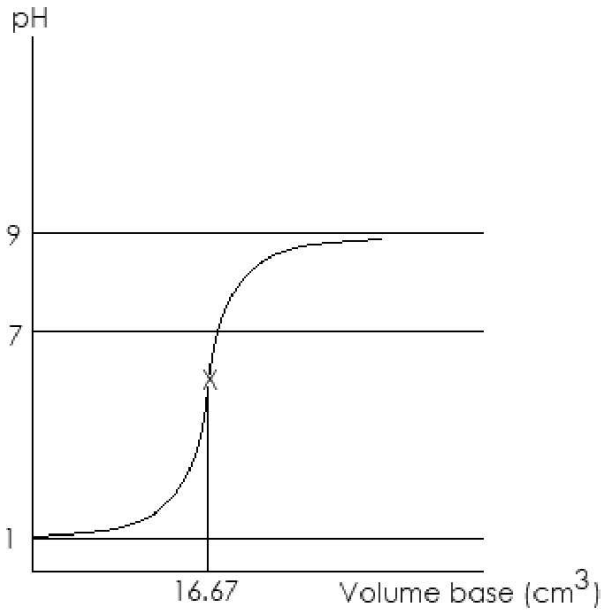
+

−

(vi) Sketch the variation in pH of the mixture in the titration flask with the volume of the weak base solution added (titration curve). Label the axes, indicate pH on the y-axis and the volume of weak base solution added on the x-axis. Mark the equivalence point approximately. [Calculation of pH at equivalence point is not expected.]

Answer

The curve starts at pH = 1, rises steeply around the equivalence volume (16.67 cm^3) and levels off near pH = 9. The equivalence point is marked at 16.67 cm^3 on the x-axis, with its pH between 5 and 7.
Marking: curve starts at pH = 1, reaches pH = 9 and has the correct shape (4); equivalence volume marked (2); equivalence pH (between pH = 5 and pH = 7) marked (2); axes labelled with units where applicable (1 + 1)



Titration curve: pH against volume of weak base B added (scheme)

Review.

This is a strong acid (HCl) titrated with a weak base, so the pH changes only gently while strong acid remains (pH from $[H^+]$ left after neutralisation), the equivalence solution contains only the weak acid BH^+ (pH below 7, hence the equivalence pH of 5–7), and after the equivalence point the excess B together with BH^+ forms a basic buffer, so the Henderson-type relation $pOH = pK_b + \log([BH^+]/[B])$ applies. In (ii) only BH^+ and leftover H^+ are present, so there is no buffer. Common mistakes: forgetting to use the total volume in each concentration, taking $[BH^+]$ as 0.15 mol dm^{-3} instead of the diluted value, treating the equivalence pH as 7, and drawing the curve ending at a strongly basic pH (the weak base cannot raise the pH above about 9).

(b) [75 marks]

The following two experiments were carried out at a constant temperature using the volatile liquids C and D which form an ideal solution.
Experiment I: The liquids C and D were introduced in to an evacuated rigid container and allowed to reach equilibrium. When the system was at equilibrium, it was observed that the mole fractions of C and D in the liquid phase (L_I) were 0.3 and 0.7 respectively. Total pressure in the container was 2.70×10^4 Pa.
Experiment II: This experiment was conducted using different amounts of C and D. When the equilibrium was established, it was observed that the mole fractions of C and D in the liquid phase (L_{II}) were 0.6 and 0.4 respectively. Total pressure of the container was 2.40×10^4 Pa.
(i) Give the relationship between the partial pressure of C in the vapour phase (P_C), its saturated vapour pressure ($P°_C$) and its mole fraction in the liquid phase (X_C) in the form of an equation. This equation states a commonly used law in physical chemistry. Write the name of the law.

Answer

$P_C = x_C P°_C$ (award marks only for these symbols) (5)
Raoult's law (4)

(ii) Calculate the saturated vapour pressures of C and D.

Answer

Experiment I: 2.7×10^4 Pa = 0.3 $P°_C$ + 0.7 $P°_D$ ... (1) (4 + 1)
Experiment II: 2.4×10^4 Pa = 0.6 $P°_C$ + 0.4 $P°_D$ ... (2) (4 + 1)
(1) × 2 − (2): $P°_D$ = **3.0×10^4 Pa** (4 + 1)
$P°_C$ = (2.4×10^4 Pa − $0.4 \times 3.0 \times 10^4$ Pa)/0.6 = **2.0×10^4 Pa** (4 + 1)

(iii) Calculate the mole fractions of C and D in the vapour phase (V_I) of experiment I.

Answer

$X^g_{C,I}$ = ($0.3 \times 2.0 \times 10^4$ Pa)/(2.7×10^4 Pa) (1 + 1) = **0.2** (or 0.22 or 2/9) (1 + 1)
$X^g_{D,I}$ = 1 − 0.2 (1 + 1) = **0.8** (or 0.78 or 7/9) (1 + 1)

(iv) Calculate the mole fractions of C and D in the vapour phase (V_{II}) of experiment II.

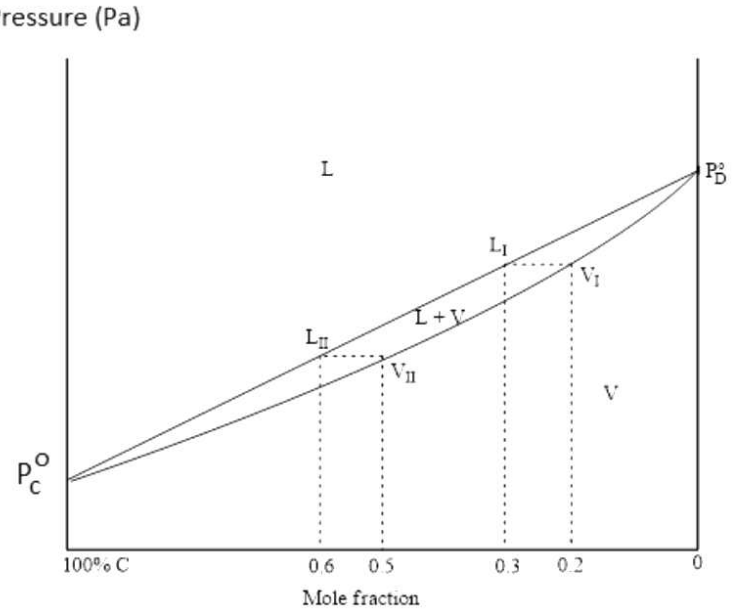
Answer

$X^g_{C,II}$ = ($0.6 \times 2.0 \times 10^4$ Pa)/(2.4×10^4 Pa) (1 + 1) = **0.5** (1 + 1)
$X^g_{D,II}$ = 1 − 0.5 (1 + 1) = **0.5** (1 + 1)

(v) Show the compositions of liquid and vapour phases (L_I, L_{II}, V_I and V_{II}) and relevant pressures in the above two experiments on a pressure-composition phase diagram drawn at constant temperature.

Answer

Pressure (Pa) on the y-axis and mole fraction on the x-axis (L = liquid, V = vapour). The straight line (liquid line) runs from $P°_C$ to $P°_D$ and the curve (vapour line) lies below it with the same end points; the region above the line is liquid (L), between the line and the curve is L + V, and below the curve is vapour (V). L_I (X_C = 0.3) and V_I (X_C = 0.2) lie at the same pressure (2.70×10^4 Pa); L_{II} (X_C = 0.6) and V_{II} (X_C = 0.5) lie at the same pressure (2.40×10^4 Pa).
Marking: axes labelled with appropriate units (2 + 2); $P°_C$ and $P°_D$ marked (2 + 2); line and curve start and end at the correct pressures (2 + 2); phases at equilibrium identified in each region (2 + 2 + 2); point L_I marked at X_C = 0.3 (2); point L_{II} at X_C = 0.6 (2); point V_I at X_C = 0.2 (2); point V_{II} at X_C = 0.5 (2); L_I and V_I at the same level (2); L_{II} and V_{II} at the same level (2)
Note: the graph could also be drawn with the direction of increasing mole fraction of C reversed. No marks for a temperature-composition phase diagram. 5(b): 75 marks



Pressure-composition phase diagram at constant temperature (scheme)

Review.

Raoult's law gives each partial pressure, so the total pressure of a liquid mixture is $P = x_C P°_C + x_D P°_D$, a straight line against liquid composition; two experiments give two simultaneous equations for $P°_C$ and $P°_D$ (check: $0.3 \times 2.0 + 0.7 \times 3.0 = 2.7$ and $0.6 \times 2.0 + 0.4 \times 3.0 = 2.4$, both $\times 10^4$ Pa). The vapour is richer in the more volatile component D, so the vapour mole fraction of C (0.2 and 0.5) is smaller than its liquid mole fraction (0.3 and 0.6), and each vapour point lies on the curve at the same pressure as its liquid point. Common mistakes: using the total pressure as P° of one component, and plotting the vapour composition on the straight line instead of the curve.

Read: RB U12 §2.2 · p. 118 RB U12 §2.3 · p. 167 RB U12 §2.6 · p. 216 RB U12 §2.5 · p. 199

Question 6 · Part B · essay

Scheme note: physical states are necessary for the award of marks.

(a) [20 marks]

An organic solvent (org-1) and water(aq) are immiscible and form a biphasic system. Partition coefficient for the distribution of X between org-1 and water at temperature T is, $K_D = [X]_{org\text{-}1}/[X]_{aq} = 4.0$.
An amount of 0.50 mol of X was added to a system containing 100.00 cm^3 of org-1 and 100.00 cm^3 of water. The system was allowed to reach equilibrium at temperature T.
(i) Calculate the concentration of X in org-1.
(ii) Calculate the concentration of X in water.

Answer

$K_D = [X]_{org\text{-}1}/[X]_{aq} = 4.0$. Let V = volume (of each phase) and x = amount (mol) of X in the aqueous phase.
$K_D = [(0.5 \text{ mol} - x)/V]/[x/V] = 4.0$ (4 + 1) (no marks for substitution in moles only, i.e. the volumes must appear)
$x = 0.1$ mol (4 + 1)
(i) $[X]_{org\text{-}1} = 0.4 \text{ mol}/(100 \times 10^{-3} \text{ dm}^3) =$ **4.0 mol dm^{-3}** (4 + 1)
(ii) $[X]_{aq} = 0.1 \text{ mol}/(100 \times 10^{-3} \text{ dm}^3) =$ **1.0 mol dm^{-3}** (4 + 1) · 6(a): 20 marks

Review.

The partition coefficient is the ratio of the equilibrium concentrations (not amounts) of the same molecular species in two immiscible solvents at a given temperature; here the volumes are equal so the amounts split 4 : 1 (0.4 mol and 0.1 mol). Common mistake: substituting moles instead of concentrations when the two volumes differ, or forgetting to convert cm^3 to dm^3.

(b) [105 marks]

The compound Y is soluble only in the aqueous phase. In the aqueous phase, X and Y react to form Z. The presence of Y and Z does not affect the distribution of X between org-1 and water.
A series of biphasic systems containing org-1 and water were prepared. Then different amounts of X were distributed in the biphasic systems and the systems were allowed to reach equilibrium. The initial rate of the reaction between X and Y in the aqueous phase was measured after adding Y into the aqueous phase of these biphasic systems. Results of these experiments conducted at temperature T are given in the table.

Experiment Number	Volume of water (cm^3)	Volume of org-1 (cm^3)	Total amount of X added (mol)	Total amount of Y added (mol)	Initial rate of the reaction (mol dm^{-3} s^{-1})
1	100.00	100.00	0.05	0.02	2.00×10^{-6}
2	100.00	100.00	0.10	0.04	1.60×10^{-5}
3	50.00	50.00	0.25	0.02	4.00×10^{-4}

aq

aq

aq

aq

Answer

Rate = $k[X]_{aq}^{m}[Y]_{aq}^{n}$ OR $-\Delta[X]_{aq}/\Delta t = k[X]_{aq}^{m}[Y]_{aq}^{n}$ OR $-\Delta[Y]_{aq}/\Delta t = k[X]_{aq}^{m}[Y]_{aq}^{n}$ (10)

(ii) Calculate the initial concentration of X in the aqueous phase in each experiment.

Answer

Let n_X be the total amount (mol) of X added. Equal volumes of org-1 and water are used in each experiment, and $K_D = 4.0$, so n_X is shared 1 : 4 between water and org-1 ($n_X = 5 \times$ amount in water):
$[X]_{aq} = n_X/(5 \times V_{aq})$

Experiment	$[X]_{aq}$ / mol dm^{-3}
1	0.1 (4)
2	0.2 (4)
3	1.0 (4)

(iii) Calculate the initial concentration of Y in the aqueous phase in each experiment.

Answer

Let n_Y be the total amount (mol) of Y added. Y is soluble only in the aqueous phase, so $[Y]_{aq} = n_Y/V_{aq}$

Experiment	$[Y]_{aq}$ / mol dm^{-3}
1	0.2 (4)
2	0.4 (4)
3	0.4 (4)

(iv) Calculate the orders m and n of the reaction with respect to X and Y respectively.

Answer

2.00×10^{-6} mol dm^{-3} s^{-1} = k (0.1 mol dm^{-3})^m (0.2 mol dm^{-3})^n ... (1) (10 + 2)
1.60×10^{-5} mol dm^{-3} s^{-1} = k (0.2 mol dm^{-3})^m (0.4 mol dm^{-3})^n ... (2) (10 + 2)
4.00×10^{-4} mol dm^{-3} s^{-1} = k (1.0 mol dm^{-3})^m (0.4 mol dm^{-3})^n ... (3) (10 + 2)
Order m: (2)/(3): $1.60 \times 10^{-5}/4.00 \times 10^{-4}$ = (0.2/1.0)^m (5); 0.04 = (0.2)^m, **m = 2** (4 + 1)
Order n: (3)/(1): $4.00 \times 10^{-4}/2.00 \times 10^{-6}$ = (1.0/0.1)^m (0.4/0.2)^n (5); 200 = 10^2 (2)^n, **n = 1** (4 + 1)

(v) Calculate the rate constant of the reaction.

Answer

From (1): k = 2.00×10^{-6} mol dm^{-3} $s^{-1}/[(0.1 \text{ mol } dm^{-3})^2 (0.2 \text{ mol } dm^{-3})^1]$ (4 + 1) = **1.0×10^{-3} mol^{-2} dm^6 s^{-1}** (4 + 1)

(vi) An experiment is designed to study the effect of temperature on the reaction rate using the partition coefficient given above. Is this a suitable experiment to study the effect of temperature on the rate of the reaction? Explain your answer.

Answer

Not suitable.

(2)

aq

(3) · 6(b): 105 marks

Review.

The reaction takes place only in the aqueous phase, so the rate law must be written with aqueous concentrations obtained from the partition equilibrium: $[X]_{aq} = n_X/(V_{aq} + K_D\ V_{org})$, which for equal volumes and $K_D = 4.0$ is $n_X/(5V_{aq})$. Orders are found by dividing pairs of rate equations (here m = 2 and n = 1, overall third order, k in $mol^{-2}\ dm^6\ s^{-1}$). Check: $k[X]^2[Y]$ gives $1.0 \times 10^{-3} \times 0.01 \times 0.2 = 2.0 \times 10^{-6}$, $1.0 \times 10^{-3} \times 0.04 \times 0.4 = 1.6 \times 10^{-5}$ and $1.0 \times 10^{-3} \times 1.0 \times 0.4 = 4.0 \times 10^{-4}$. Common mistakes: using the total amount of X as if it were all in water, and ignoring that K_D (and therefore $[X]_{aq}$) changes with temperature.

(c) [25 marks]

The organic solvent org-2 and water are also immiscible and form a biphasic system. X (0.20 mol) was added to a system containing 100.00 cm^3 of org-2 and 100.00 cm^3 of water and allowed to reach equilibrium at the temperature T. Then Y (0.01 mol) was added to the aqueous phase and the initial rate of the reaction was measured. Y does not dissolve in org-2. The initial rate of the reaction between X and Y in the aqueous phase was found to be 6.40×10^{-7} mol $dm^{-3}\ s^{-1}$.
Calculate the partition coefficient $[X]_{org\text{-}2}/[X]_{aq}$ for the distribution of X between org-2 and water. $[X]_{org\text{-}2}$ is the concentration of X in the org-2 phase.

Answer

The reaction takes place in the aqueous medium, therefore the rate constant is the same. (5)
$[Y]_{aq}$ = 0.01 mol/0.1 dm^3 = 0.1 mol dm^{-3}
Rate = $k[X]_{aq}^{2}[Y]_{aq}$
6.40×10^{-7} mol $dm^{-3}\ s^{-1} = 1.00 \times 10^{-3}\ mol^{-2}\ dm^6\ s^{-1}$ $[X]_{aq}$^2 (0.1 mol dm^{-3}) (4 + 1)
$[X]_{aq}$^2 = $6.4 \times 10^{-3}\ mol^2\ dm^{-6} = 64 \times 10^{-4}\ mol^2\ dm^{-6}$; $[X]_{aq} = 8.0 \times 10^{-2}$ mol dm^{-3} (4 + 1)
$K_D = [X]_{org\text{-}2}/[X]_{aq}$ = (0.2 mol/0.1 dm^3 − 0.08 mol dm^{-3})/0.08 mol dm^{-3} (4 + 1)
K_D = **24** (4 + 1)
Alternate answer: $K_D = [(0.2\ mol - x)/0.1\ dm^3]/[x/0.1\ dm^3]$ (4 + 1), so $x = 0.2\ mol/(K_D + 1)$; $[X]_{aq} = [0.2\ mol/(K_D + 1)]/0.1\ dm^3 = 2/(K_D + 1)$ mol dm^{-3} (4 + 1)
$6.4 \times 10^{-7} = 1 \times 10^{-3}\ (2/(K_D + 1))^2\ (0.1)$ (4 + 1); $64 \times 10^{-4} = (2/(K_D + 1))^2$ (4 + 1); K_D = 24 (4 + 1) · 6(c): 25 marks

Review.

The rate law found in (b) is used in reverse: the measured rate gives $[X]_{aq}$ (0.080 mol dm^{-3}), the rest of the 0.20 mol is in org-2 (1.92 mol dm^{-3}), and $K_D = 1.92/0.080 = 24$. Common mistakes: using the amount of Y as a concentration without dividing by the aqueous volume, and forgetting that the rate constant is unchanged because the reaction occurs only in the aqueous phase at the same temperature T.

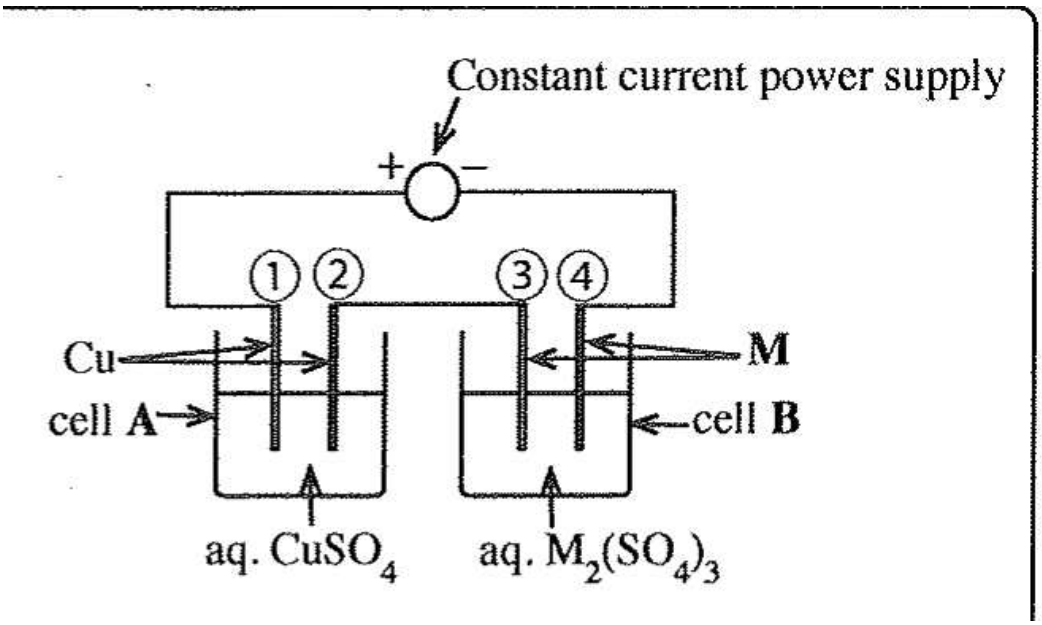
Read: RB U12 §2.7 · p. 229 RB U11 §1.6 · p. 16 RB U11 §1.7 · p. 26 RB U11 §1.8 · p. 53

Question 7 · Part B · essay

Scheme note: physical states are necessary for the award of marks.

(a) [75 marks]

The setup shown in the figure was used to find the relative atomic mass of the metal, M. The electrolysis was carried out for 10 minutes using a constant current. The mass of the cathode in cell A was increased by 31.75 mg whereas the mass of the cathode in cell B increased by 147.60 mg during this time period. (Assume that the electrolysis of water does not take place in cells A and B.) In the figure, cell A contains aq. $CuSO_4$ (Cu electrode) and cell B contains aq. $M_2(SO_4)_3$ (M electrode); the two cells are connected in series to a constant current power supply and the electrodes are numbered ①, ② (cell A) and ③, ④ (cell B).



(i) Identify the anode and cathode in each of the cells A and B (in terms of the numbers ①, ②, ③, and ④).

Answer

Cell A: anode = ① (5); cathode = ② (5)
Cell B: anode = ③ (5); cathode = ④ (5)

(ii) Write the half reaction taking place at each electrode in each cell.

Answer

Cell A, electrode ①: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e$ (6)
Cell A, electrode ②: $Cu^{2+}(aq) + 2e \rightarrow Cu(s)$ (6)
Cell B, electrode ③: $M(s) \rightarrow M^{3+}(aq) + 3e$ (6)
Cell B, electrode ④: $M^{3+}(aq) + 3e \rightarrow M(s)$ (6)
Note: physical states must be given.

(iii) Calculate the constant current used in electrolysis.

Answer

Amount of Cu(s) deposited = 31.75×10^{-3} g
Charge required for this: 2×96500 C $mol^{-1} \times (31.75 \times 10^{-3}$ g/63.5 g $mol^{-1}) = i \times 10 \times 60$ s (1 + 1) + (1 + 1) + (1 + 1) + (1 + 1)
Correct stoichiometry (5); the current used in the electrolysis = i = **0.16 A** (4 + 1)
Alternative answer: amount of Cu deposited = 31.75×10^{-3} g/63.5 g $mol^{-1} = 0.5 \times 10^{-3}$ mol (1 + 1) + (1 + 1); amount of electrons (charge) = $0.5 \times 10^{-3} \times 2$ mol = 10^{-3} mol (for using correct stoichiometry 5); charge = 10^{-3} mol × 96500 C $mol^{-1} = 96.5$ C (1 + 1); current = 96.5 C/(10 × 60 s) (1 + 1) = 0.16 A (4 + 1)

(iv) Calculate the relative atomic mass of metal, M.

Answer

The increase in mass of electrode ④ in cell B is due to deposition of M(s): increase in mass = 147.6 × 10^{-3} g. Let W = molar mass of M.
Charge needed: 3 × 96500 C mol^{-1} × (147.6 × 10^{-3} g/W) = 0.16 A × 600 s (1 + 1) + (1 + 1) + (1 + 1); correct stoichiometry (5); W = 445.1 g mol^{-1} (1 + 1) (using the rounded value 0.16 A)
Alternative answer (I): the same charge flows through both cells, so mol e^- for M = mol e^- for Cu: (147.6 × 10^{-3} g × 3/W) = (31.75 × 10^{-3} g × 2/63.5 g mol^{-1}) (1 + 1) + (1 + 1) + (1 + 1); correct stoichiometry (5); W = (147.6 × 3 × 63.5)/(31.75 × 2) = **442.8 g mol^{-1}** (1 + 1)
Alternative answer (II): amount of M deposited = (charge in mol)/3 = 10^{-3}/3 mol (1 + 1; correct stoichiometry 5); molar mass of M = 147.6 × 10^{-3} g/(10^{-3}/3 mol) = 147.6 × 3 = **442.8 g mol^{-1}** (1 + 1) + (1 + 1)
Note: if symbols (or any other values) are used for the atomic mass of Cu and the Faraday constant and the answers are provided with those symbols or using those values, award full marks. 7(a): 75 marks

Review.

Cells in series carry the same charge: Q = It, moles of electrons = Q/F, and moles of metal = moles of electrons/charge on the ion (2 for Cu^{2+}, 3 for M^{3+}); the anode is the electrode joined to the positive terminal, where oxidation occurs. Using 0.16 A exactly (0.1608 A) gives 445 g mol^{-1}, whereas the ratio method gives 442.8 g mol^{-1}; the scheme accepts both, and the ratio method avoids rounding error. Common mistakes: using 2 instead of 3 electrons for M^{3+}, forgetting to convert 10 min to seconds, and reversing anode and cathode.

(b) [75 marks]

(i) A, B and C are coordination compounds. They have an octahedral geometry. In each compound, two types of ligands are coordinated to the metal ion. The molecular formulae of the compounds are (not in order): $NiCl_2H_{12}N_4$, $NiI_2H_{16}N_4O_2$ and $NiCl_2H_{15}N_3O_3$. Given below are the observations when aqueous solutions of the compounds are treated with $Pb(CH_3COO)_2$(aq): A — a white precipitate that is soluble in hot water; B — no precipitate; C — a yellow precipitate that is soluble in hot water.
I. Give the structures of A, B and C.

Answer

A: $[Ni(NH_3)_3(H_2O)_3]Cl_2$ OR $[Ni(H_2O)_3(NH_3)_3]Cl_2$ (06)
B: $[Ni(NH_3)_4Cl_2]$ OR $[NiCl_2(NH_3)_4]$ (06)
C: $[Ni(NH_3)_4(H_2O)_2]I_2$ OR $[Ni(H_2O)_2(NH_3)_4]I_2$ (06)
Note: OH_2 may be used instead of H_2O.

II. Write the chemical formulae of the precipitates formed on treatment of the compounds with $Pb(CH_3COO)_2$(aq). (Note: Indicate compound and reagent)

Answer

A with $Pb(CH_3COO)_2$: $PbCl_2\downarrow$ (03)
C with $Pb(CH_3COO)_2$: $PbI_2\downarrow$ (03)

III. State a chemical test, together with the observation, to identify each of the anion/s if present, that is/are not coordinated to the metal ion in the compounds given above. (Note: The tests given by you should not be a test stated here.)

Answer

Cl^-: add a solution of $AgNO_3$ (03); a white precipitate is formed, which dissolves in dilute NH_4OH (03)
I^-: add a solution of $AgNO_3$ (03); a yellow precipitate is formed, which does not dissolve in conc. NH_4OH (03)
OR add a few drops of $CHCl_3$ and then a little Cl_2 water (03), shake the tube; the $CHCl_3$ layer turns violet (03)

(ii) A transition metal M forms a coloured complex ion P in aqueous medium. It has the general formula $[M(H_2O)_n]^{m+}$. It undergoes the reactions given below: P + aq. NH_3 → Q (green coloured precipitate), which on excess NH_3 gives S (deep blue coloured solution); P + conc. HCl → R (yellow coloured solution).
I. Identify the metal M. Give the oxidation state of M in complex ion P.
II. Give the electronic configuration of M in the complex ion P.
III. Give the values of n and m.
IV. Give the geometry of P.
V. Give the structures of Q, R and S.
VI. Give the IUPAC names of the complex ions, P, R and S.

Answer

I. M = Ni, oxidation state +2 (OR Ni^{2+}) (06 + 03)
II. $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8$ (03)
III. n = 6, m = 2 (03 + 03)
IV. Octahedral (03)
V. Q: $Ni(OH)_2$ (03); R: $[NiCl_4]^{2-}$ (03); S: $[Ni(NH_3)_6]^{2+}$ (03)
VI. P: hexaaquanickel(II) ion (03); R: tetrachloridonickelate(II) ion (03); S: hexaamminenickel(II) ion (03) · 7(b): 75 marks

Review.

Work out the ligands from the formulae: count NH_3 and H_2O from the H and N or O counts, put the Cl^- or I^- inside or outside the bracket from the Pb^{2+} result (a precipitate means the halide is a free counter-ion; B gives none, so its two Cl^- are coordinated). For (ii), green hexaaquanickel(II) gives green $Ni(OH)_2$ with ammonia, which dissolves in excess NH_3 to give deep blue $[Ni(NH_3)_6]^{2+}$, and gives yellow tetrahedral $[NiCl_4]^{2-}$ with conc. HCl; names list ligands alphabetically (ammine before aqua) with the anionic complex ending in −ate. Common mistakes: writing Cl^- outside the bracket for B, and naming $[NiCl_4]^{2-}$ as nickel(II) chloride or omitting −ate.

Read: RB U13 §3.4 · p. 261 RB U6 §4.10.6 · p. 169 RB U6 §4.10 · p. 160

Part C

Question 8 · Part C · essay

(a) [60 marks]

Using $C_6H_5CO_2CH_3$ as the only organic starting material and as reagents only those given in the list, show how you would synthesize the compound $C_6H_5C(CH_2C_6H_5)=CHC_6H_5$ in not more than seven (7) steps.
List of reagents: PCl_3, Mg/dry ether, H^+/H_2O, $LiAlH_4$, conc. H_2SO_4

Answer

Answer:

6

5

2

3

4

+

2

6

5

2

3

6

5

2

6

5

2

6

5

2

3

6

5

2

+

2

6

5

2

6

5

2

2

4

6

5

2

6

5

6

5

4

(06)

+

2

(03)

6

5

2

(06)

3

(06)

6

5

2

(06)

(06)

6

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2

(06)

6

5

2

(06)

+

2

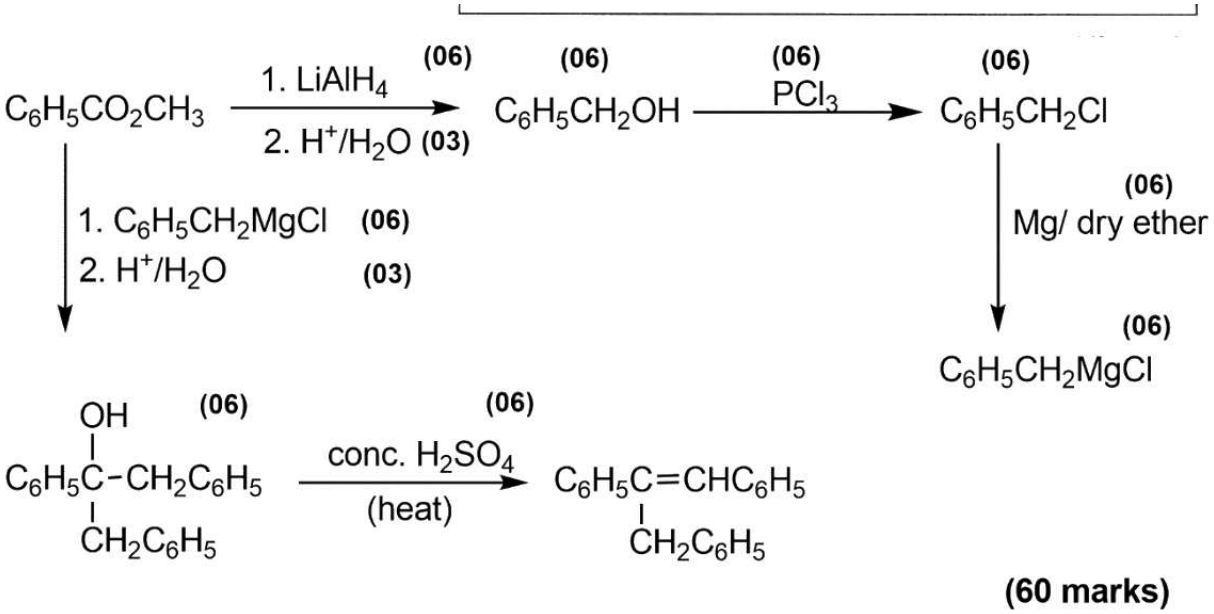
(03)

(06)

2

4

(06)



(60 marks)

Synthesis route (scheme)

Alternative answer (I):

6

5

2

3

+

2

6

5

2

(03 + 03)

4

+

2

6

5

2

(02 + 01 + 06)

3

6

5

2

(06 + 06)

6

5

2

(06 + 06)

6

5

2

+

2

(06 + 03)

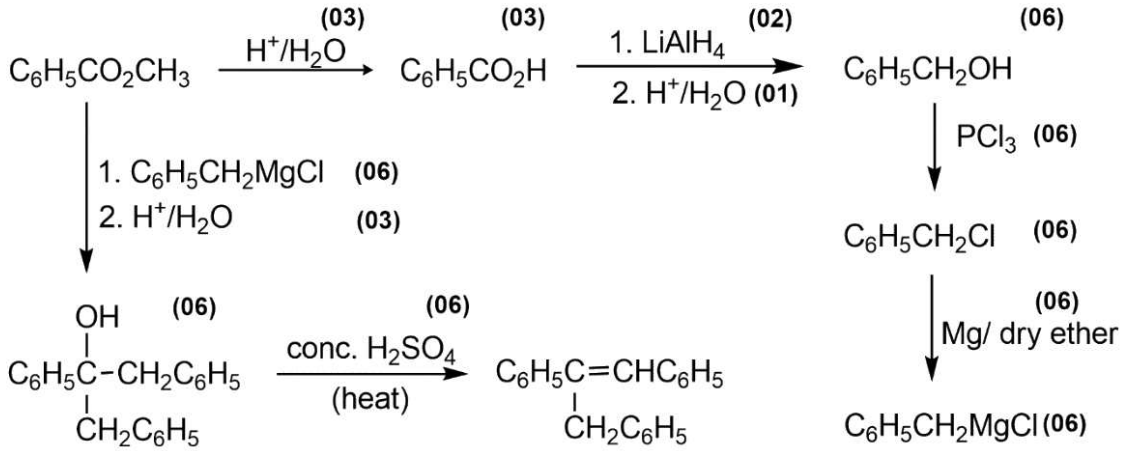
(06)

2

4

(06)

Alternative Answer (I) for 8(a)



(60 marks)

Alternative answer (I) (scheme)

Alternative answer (II):

6

5

2

3

+

2

6

5

2

(03 + 03)

3

(01)

6

5

(01)

6

5

2

(06)

+

2

(01)

6

5

2

6

5

2

(06)

2

4

(06)

6

5

2

4

+

2

(02 + 01)

6

5

2

(06)

3

(06)

6

5

2

(06)

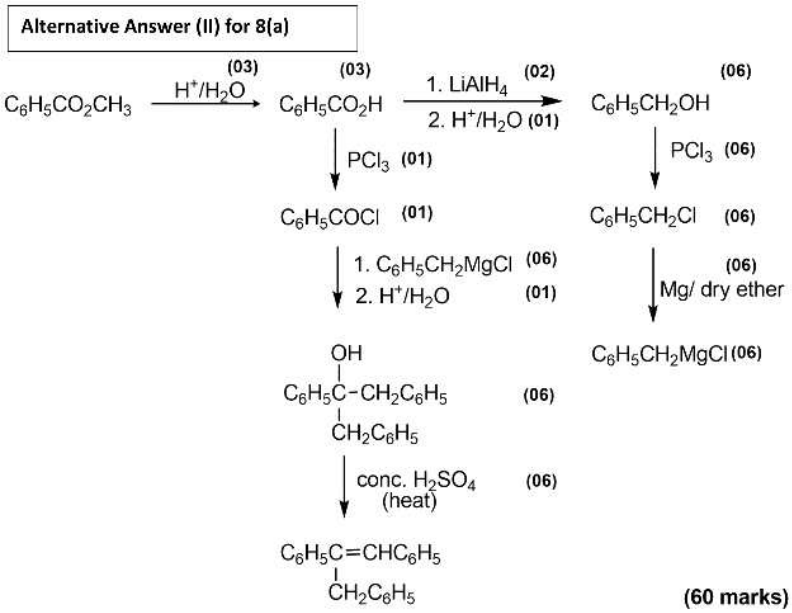
(06)

6

5

2

(06)



Alternative answer (II) (scheme)

Note: 1. Do not award any marks if there are more than 7 steps. 2. Do not count the hydrolysis steps subsequent to the reaction with Grignard reagent and with $LiAlH_4$ as separate steps. 8(a): 60 marks

Review.

The target has the $C_6H_5CH_2$– group attached to the carbon that carried the ester carbonyl, so the $C_6H_5CH_2MgCl$ Grignard reagent (made from the alcohol obtained by reducing the ester, then PCl_3, then Mg/dry ether) adds to the ester, and dehydration of the tertiary alcohol with conc. H_2SO_4 gives the alkene. Each organometallic or hydride step needs a separate aqueous acid work-up, which the scheme does not count as an extra step. Common mistakes: using H^+/H_2O (aqueous) when making the Grignard reagent (it must be dry ether), and exceeding seven steps.

(b) [60 marks]

Show how you would carry out each of the following conversions in not more than three (3) steps.
(i) aniline → 1-bromo-4-chlorobenzene ($C_6H_5NH_2$ to a benzene ring with Br and Cl para to each other)
(ii) benzene → 1-ethyl-3-methylbenzene (a benzene ring with CH_2CH_3 and CH_3 meta to each other)

Answer

(i)

2

6

5

2

–

(06 + 06)

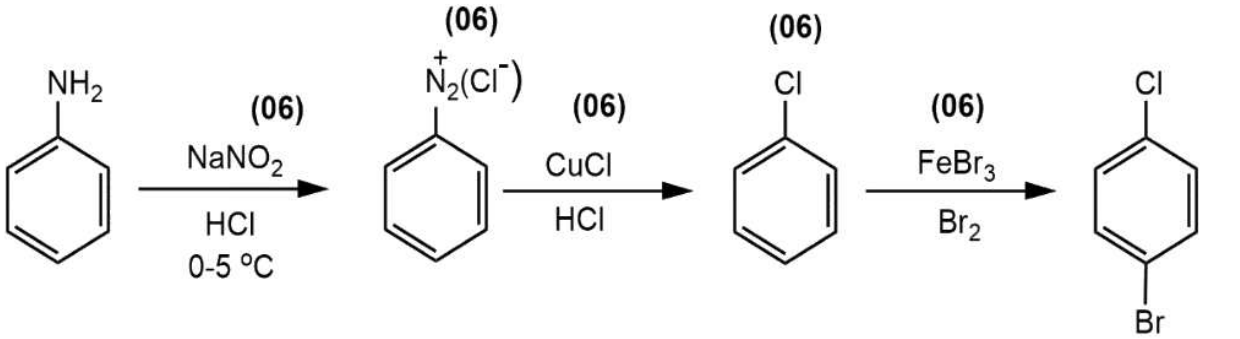
(06 + 06)

2

3

(06) · 30 marks

(b) (i)



(30 marks)

(i) Conversion of aniline (scheme)

Alternative answer for (i):

2

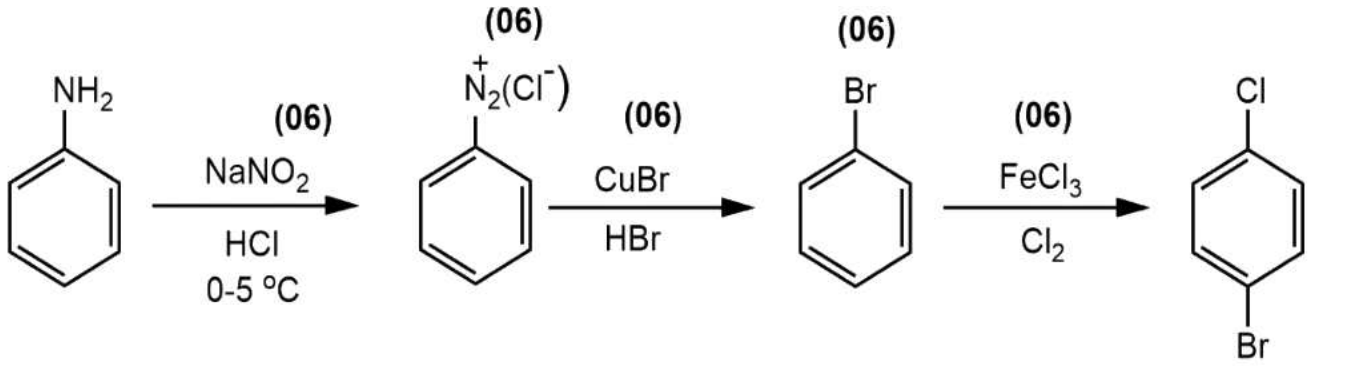
(06 + 06)

(06 + 06)

2

3

(06) · 30 marks



(30 marks)

Alternative answer for (i) (scheme)

(ii)

3

3

6

5

3

(06 + 06)

3

3

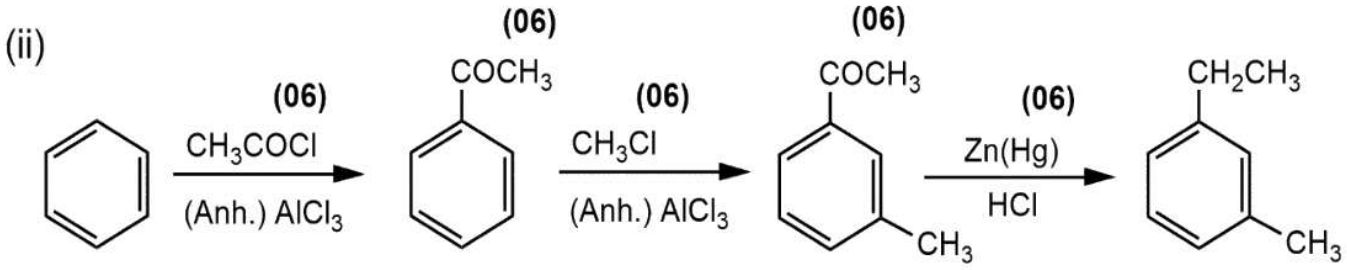
3

3

(06 + 06)

(06) · 30 marks

(ii)



(30 marks)

(ii) Conversion of benzene (scheme)

Alternative answer for (ii):

3

(06 + 06)

2

5

3

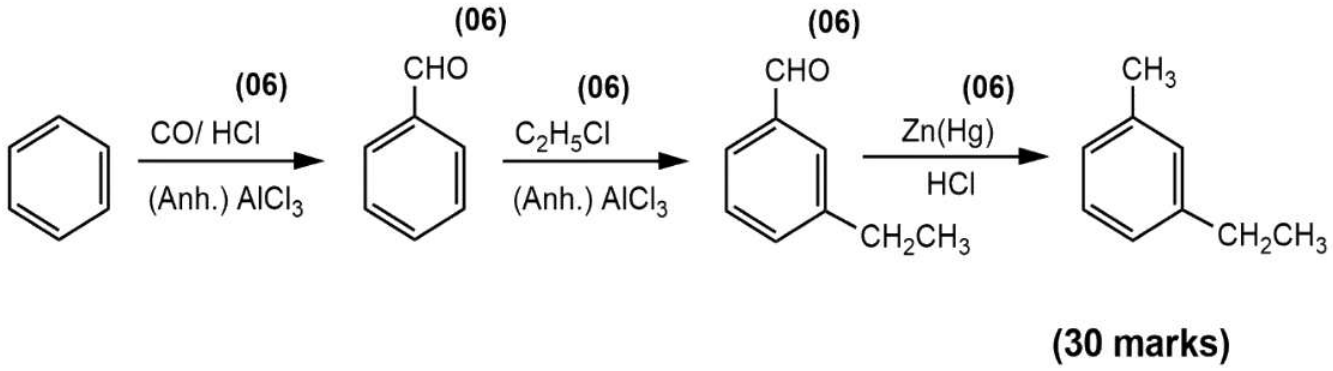
2

5

(06 + 06)

(06) · 30 marks · 8(b): 60 marks

Alternative Answer for 8(b) (ii)



(30 marks)

Alternative answer for (ii) (scheme)

Review.

In (i) the $-NH_2$ group is converted to a diazonium salt and replaced by Cl (Sandmeyer reaction, CuCl/HCl) before bromination, because chlorine then directs the incoming Br to the para position (ortho/para director, para favoured). In (ii) the meta relationship is obtained by first introducing a meta-directing C=O group (acylation or formylation), adding the second alkyl group meta to it, and finally reducing C=O to CH_2 (Clemmensen, Zn(Hg)/conc. HCl) (in the alternative route the meta-directing CHO group is reduced to CH_3). Common mistakes: brominating aniline directly (it gives the 2,4,6-tribromo product) and performing the reduction first, which would give an ortho/para-directing group.

(c) [30 marks]

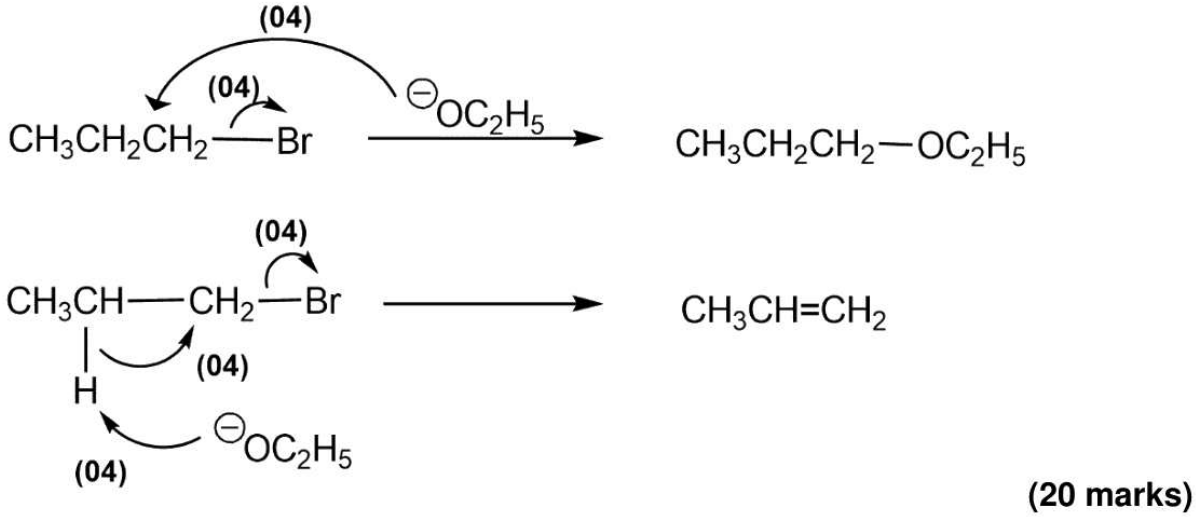
The following reaction gives two products: $CH_3CH_2CH_2Br + C_2H_5O^- \rightarrow$
(i) Write the structures of the two products.
(ii) Write the mechanisms for the formation of these two products.

Answer

(i) Products: $CH_3CH_2CH_2–OC_2H_5$ (05) and $CH_3CH=CH_2$ (05)
(ii) Substitution (S_{N2}): $C_2H_5O^-$ attacks the carbon bonded to Br from the back while Br^- leaves in one step (curved arrow from the oxygen lone pair to carbon, and from the C–Br bond to Br), giving $CH_3CH_2CH_2–OC_2H_5$. Elimination (E2): $C_2H_5O^-$ removes a hydrogen from the carbon next to the C–Br carbon, the C–H electrons form the C=C bond and Br^- leaves, giving $CH_3CH=CH_2$. Each mechanism carries four curly arrows/steps at (04) each (20 marks) · 8(c): 30 marks

(i). Products $CH_3CH_2CH_2\text{-}OC_2H_5$ $CH_3CH{=}CH_2$ **(05 + 05)**

(ii)



(20 marks)

Products and mechanisms (scheme)

Review.

A primary alkyl halide with a strong, basic nucleophile such as ethoxide undergoes both S_{N2} (substitution, ether product) and E2 (elimination of β-hydrogen, alkene product) at the same time; the two mechanisms differ in whether the ethoxide attacks carbon or abstracts a β-hydrogen. Common mistakes: drawing curly arrows from atoms rather than from the lone pair or bond, omitting the leaving group's electrons, and showing a carbocation intermediate (neither pathway forms one for a primary halide).

Read: RB U8 §2.7 · p. 50 RB U9 §3.1 · p. 54 RB U9 §3.6 · p. 70 RB U10 §4.3 · p. 78 RB U8 §2.5 · p. 49 RB U8 §2.6 · p. 49

Question 9 · Part C · essay

Scheme note: physical states are necessary for the award of marks.

(a) [75 marks]

Solution X contains four metal cations. The following tests were carried out to identify these cations.

	Test	Observation
①	Dilute HCl was added to a small portion of X.	No precipitate.
②	H_2S was bubbled through the solution from ① above.	A black precipitate (P_1)
③	P_1 was separated by filtration. The filtrate was boiled to remove the H_2S, cooled, and NH_4Cl/NH_4OH was added.	A green precipitate (P_2)
④	P_2 was separated by filtration and H_2S was bubbled through the filtrate.	A white precipitate (P_3)

	Test	Observation
⑤	P_3 was separated by filtration. The filtrate was boiled to remove the H_2S, cooled, and $(NH_4)_2CO_3$ was added.	A white precipitate (P_4)

1

2

3

4

Precipitate	Test	Observation
P_1	P_1 was dissolved in hot dil. HNO_3 and conc. NH_4OH was added in excess.	A deep blue coloured solution (solution 1)
P_2	* Excess dil. NaOH was added to P_2 followed by H_2O_2.	A yellow coloured solution (solution 2)
* Dilute H_2SO_4 was added to solution 2.	An orange coloured solution (solution 3)	
P_3	* P_3 was dissolved in dil. HCl and dil. NaOH was added gradually.	A white precipitate (P_5)
* Addition of dil. NaOH was continued.	P_5 dissolved to give a colourless solution (solution 4)	
P_4	P_4 was dissolved in conc. HCl and subjected to the flame test.	A brick-red flame

Answer

Cu^{2+}, Cr^{3+}, Zn^{2+}, Ca^{2+} (05 marks × 4 = 20)

(ii) Identify the precipitates P_1, P_2, P_3, P_4 and P_5 and the chemical species responsible for the colours of solutions 1, 2, 3 and 4. (Note: Write chemical formulae only.)

Answer

P_1: CuS; P_2: $Cr(OH)_3$; P_3: ZnS; P_4: $CaCO_3$; P_5: $Zn(OH)_2$ (06 marks × 5 = 30)
Solution 1: $[Cu(NH_3)_4]^{2+}$ (07)
Solution 2: Na_2CrO_4 OR CrO_4^{2-} (06)
Solution 3: $Na_2Cr_2O_7$ OR $Cr_2O_7^{2-}$ (06)
Solution 4: Na_2ZnO_2 OR ZnO_2^{2-} OR $Na_2Zn(OH)_4$ OR $[Zn(OH)_4]^{2-}$ (06) · 9(a): 75 marks

Review.

Work through the group scheme in order: no precipitate with dilute HCl (no Group I), black sulfide from acidified H_2S (CuS), hydroxide precipitated by NH_4Cl/NH_4OH after boiling off H_2S (green $Cr(OH)_3$), a white sulfide from the ammoniacal solution (ZnS), and a white carbonate with brick-red flame ($CaCO_3$, Ca^{2+}). $Cr(OH)_3$ dissolves in excess $NaOH/H_2O_2$ to give yellow chromate, which turns orange dichromate in acid; $Zn(OH)_2$ is amphoteric, so it dissolves in excess NaOH; Cu^{2+} gives the deep blue tetraamminecopper(II) ion with excess ammonia. Common mistakes: writing $Cr(OH)_3$ for solution 2 (it is the chromate ion), and giving

$Zn(OH)_2$ rather than the zincate for solution 4.

(b) [75 marks]

The water sample Y contains the anions SO_3^{2-}, SO_4^{2-} and NO_3^−. The following procedures were carried out for the quantitative analysis of the anions present in the water sample.

Procedure 1

To 25.00 cm^3 of sample Y, an excess of a dilute solution of $BaCl_2$ was added with stirring. Thereafter, excess dilute HCl was added with stirring to the precipitate formed until there was no further evolution of a gas with pungent odour. The solution was allowed to stand for 10 minutes and filtered. The precipitate was washed with distilled water and dried in an oven at 105 °C until a constant mass was obtained. The mass of the precipitate was 0.174 g. The filtrate obtained was kept for further analysis (see procedure 3).

Procedure 2

To 25.00 cm^3 of sample Y, an excess of dilute H_2SO_4 and acidified 5% KIO_3 solutions were added. The liberated I_2 was immediately titrated with 0.020 mol dm^{-3} $Na_2S_2O_3$ solution using starch as the indicator. The volume of $Na_2S_2O_3$ used was 20.00 cm^3. (Assume that in this procedure, SO_3^{2-} ions are oxidized to sulphate ions (SO_4^{2-}) without any loss to the atmosphere.)

Procedure 3

The filtrate from procedure 1 was neutralized with dilute NaOH and to it excess Al powder and dilute NaOH were added. The solution was heated and the gas evolved was transferred quantitatively to react with a 20.00 cm^3 volume of 0.11 mol dm^{-3} HCl solution. Completion of the reaction was tested with litmus. The HCl remaining after reacting with the gas evolved was titrated with 0.10 mol dm^{-3} NaOH solution using methyl orange as the indicator. The volume of NaOH required was 10.00 cm^3.

(i) Write balanced ionic/non-ionic equations for the reactions taking place in procedures 1, 2 and 3.

Answer

Procedure 1

3

2−

2

3

−

2+

3

2−

3

(02)

4

2−

2

4

−

2+

4

2−

4

(02)

3

2

2

2

(03)

4

Procedure 2

3

+

2

2

(02)

3

2−

2

4

2−

+

(02)

3

3

2−

+

2

4

2−

2

(03)

2

3

+

2

2

(02)

2

2

4

2−

+

(02)

3

2

2

2

4

2−

+

(03)

2

−

(02)

2

3

2−

4

6

2−

(02)

2

2

3

2−

4

6

2−

−

(03)

3

2−

2

3

2−

2

2

3

2−

2

3

2−

(02)

Procedure 3

3

−

2

2

3

(02)

3

4

(02)

2

(02)

(ii) Determine the concentrations (mol dm^{-3}) of SO_3^{2-}, SO_4^{2-} and NO_3^− in water sample Y. (Ba = 137; S = 32; O = 16)

Answer

4

2−

4

(02)

4

4

(02)

4

2−

−4

(02)

4

2−

−4

(02)

−3

(03 + 01)

3

2−

2

3

2−

(02)

3

2−

(02)

3

2−

(02)

−3

(03 + 01)

3

(02)

(02)

3

(02)

(02)

3

(02)

3

(02)

3

(02)

−3

(03 + 01)

(iii) Give colour changes that would be observed in the titrations in procedures 2 and 3. (Note: Assume that other ions that may interfere with the analysis are not present in sample Y.)

Answer

Procedure 2: blue → colourless (03)
Procedure 3: red → yellow (03) · 9(b): 75 marks

Review.

Procedure 1 separates sulphate ($BaSO_4$ is insoluble in acid, while $BaSO_3$ dissolves with evolution of SO_2); procedure 2 is an iodometric back-titration in which iodate oxidises sulphite and the iodine formed is titrated with thiosulphate ($5SO_3^{2-} \equiv 1I_2 \equiv 2S_2O_3^{2-}$); procedure 3 reduces nitrate to NH_3 with Al in alkali and finds it by back-titration of the excess HCl (the 1.2 mmol of HCl neutralised equals the mmol of NH_3, hence of NO_3^−, in 25.00 cm^3). Check: 7.47 × 10^{-4} mol/25.00 cm^3 = 0.0299, 1.0 × 10^{-3} mol/25.00 cm^3 = 0.040 and 1.2 × 10^{-3} mol/25.00 cm^3 = 0.048 mol dm^{-3}. Common mistakes: forgetting the 5 : 2 stoichiometry, using the 25.00 cm^3 sample volume in the wrong place, and forgetting that the HCl in procedure 3 is only partly consumed (the NaOH titre measures the excess).

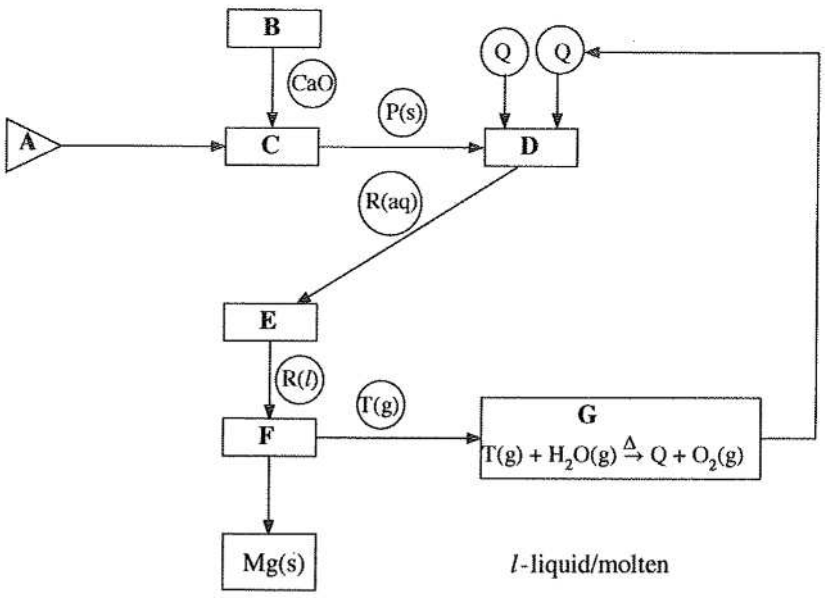
Read: RB U6 §4.10 · p. 160 RB U12 §2.4 · p. 175 RB U3 §3.8 · p. 115 RB U6 §4.6 · p. 141

Question 10 · Part C · essay

Scheme note: physical states are required for the award of marks for half reactions.

(a) [50 marks]

The flow chart given below indicates the production of metal magnesium (Mg) using the Dow Process (l = liquid/molten).



Answer the following questions based on the flow chart.
(i) Identify the starting material A.

Answer

Sea water / bittern solution (03)

(ii) Identify the processes employed at B, C, D, E, F and G from the list below: evaporation, dissolution, thermal decomposition, electrolysis, recycling of a reagent, precipitation.

Answer

B: thermal decomposition; C: precipitation; D: dissolution; E: evaporation; F: electrolysis; G: recycling of a reagent (02 × 6 = 12 marks)

(iii) Identify the chemical compound used in B.

Answer

$CaCO_3$ OR lime stone (03)

(iv) Identify the chemical species P, Q, R and T.

Answer

P: $Mg(OH)_2$; Q: HCl; R: $MgCl_2$; T: Cl_2 (02 × 4 = 8 marks)

(v) Give balanced chemical equations/half reactions for the processes taking place in B, C, D, and F. (Note: When writing half reactions, identify the anode and cathode where applicable.)

Answer

B: $CaCO_3 \rightarrow CaO + CO_2$ (02) (award marks even if heating is not shown)
C: $CaO + H_2O \rightarrow Ca(OH)_2$ (02); $Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$ (02); $Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2$ (02)
OR $CaO + H_2O \rightarrow Ca^{2+} + 2OH^-$ (04); $Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2$ (02)
OR $CaO + H_2O + Mg^{2+} \rightarrow Mg(OH)_2 + Ca^{2+}$ (06)
D: $Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$ (02)
F: Anode – (C): $2Cl^-(l)/(aq) \rightarrow Cl_2(g) + 2e$ (02 + 02); Cathode – (Fe): $Mg^{2+}(l)/(aq) + 2e \rightarrow Mg(l)$ (02 + 02)
Note: physical states are required for the award of marks for half reactions.

(vi) State the importance of the reaction occurring in G.

Answer

Here a product (HCl, Q) is recycled / reproduced. (03) It is very cost effective. (03) · 10(a): 50 marks

Review.

Sea water (or bittern) supplies Mg^{2+}, which is precipitated as $Mg(OH)_2$ with lime made from limestone ($CaCO_3 \rightarrow CaO + H_2O$), dissolved in HCl to give $MgCl_2$ solution, evaporated, and the molten $MgCl_2$ is electrolysed (Cl^- oxidised at the graphite anode, Mg^{2+} reduced at the iron cathode). The Cl_2 is burned with steam to regenerate HCl, so the process is economical. Common mistakes: electrolysing aqueous $MgCl_2$ (water is reduced instead of Mg^{2+}), omitting state symbols in the half reactions, and writing $Mg(OH)_2 \rightarrow MgCl_2$ without HCl.

(b) [50 marks]

(i) Consider the industries given below: coal power plants; refrigeration and air conditioning; transport; agriculture; animal farming.
I. All five industries given above contribute to global warming. Identify the gaseous chemical species associated with each of these industries that contribute to global warming.
II. State three adverse climate changes that could occur due to global warming.

Answer

I. Coal power plants – CO_2; refrigeration and air conditioning industry – CFC OR HFC OR HCFC; transportation – CO_2; agriculture – N_2O, CH_4; animal farming – CH_4 (03 × 5 = 15 marks)
II. Any three: rise in sea level; frequent strong cyclones and tornadoes; severe floods in certain areas; reduction in rainfall in certain areas (severe droughts)/desertification; sea water infusion to rivers; heavy rainfall in certain areas (03 × 3 = 9 marks)

(ii) Identify the main industry/industries given in (i) above that contribute to
I. photochemical smog,
II. acid rain,
III. eutrophication.

Answer

I. Transportation
II. Coal power plants and transportation
III. Agriculture and animal farming (02 × 5 = 10 marks)

(iii) Due to the reduction in rainfall in Sri Lanka, inducing artificial rain has been tested near catchment areas of reservoirs that are used for hydro-power generation. In this process, fine particles of hygroscopic salts (NaCl, $CaCl_2$, NaBr) are sprayed to induce cloud formation by condensation of water vapour.
From the list given below, select the water quality parameters that are directly I. affected, II. unaffected due to salts entering water around catchment areas. Give reasons for your choice briefly.
List of water quality parameters: pH, conductivity, turbidity, dissolved oxygen

Answer

I. Affected: conductivity (02) – the concentration of ions increases, therefore conductivity increases (02)
II. Unaffected: pH, turbidity and dissolved oxygen (02 + 02 + 02) – these salts do not undergo hydrolysis, therefore pH is unaffected; these salts are very soluble in water, hence the ions do not contribute to turbidity; these salts do not react with O_2 (02 × 3 = 6 marks) · 10(b): 50 marks

Review.

Each greenhouse gas is tied to its source: CO_2 from burning fossil fuels, CH_4 from livestock digestion and waterlogged paddy, N_2O from nitrogenous fertilisers, and CFC/HFC/HCFC as refrigerants. NO_x and hydrocarbons from vehicles give photochemical smog; SO_2 and NO_x give acid rain; fertiliser and manure run-off (nitrate and phosphate) cause eutrophication. NaCl, $CaCl_2$ and NaBr are neutral salts of strong acids and bases (or of a strong acid and the strong base $Ca(OH)_2$), so pH is unchanged; they only add ions and raise conductivity. Common mistakes: naming coal power plants for photochemical smog, and saying that pH or turbidity changes.

(c) [50 marks]

The following questions are based on biodiesel production.
(i) State the raw materials used in the manufacture of biodiesel.

Answer

Vegetable oil / plant oil (palm oil etc.) and CH_3OH / methanol / C_2H_5OH / ethanol / alcohol / ROH (05 + 05)

(ii) Name the main chemical compound present in each raw material where applicable.

Answer

Vegetable oil – triglycerides (05)

(iii) State the name of the chemical compound used as the catalyst in the manufacture of biodiesel in the school laboratory.

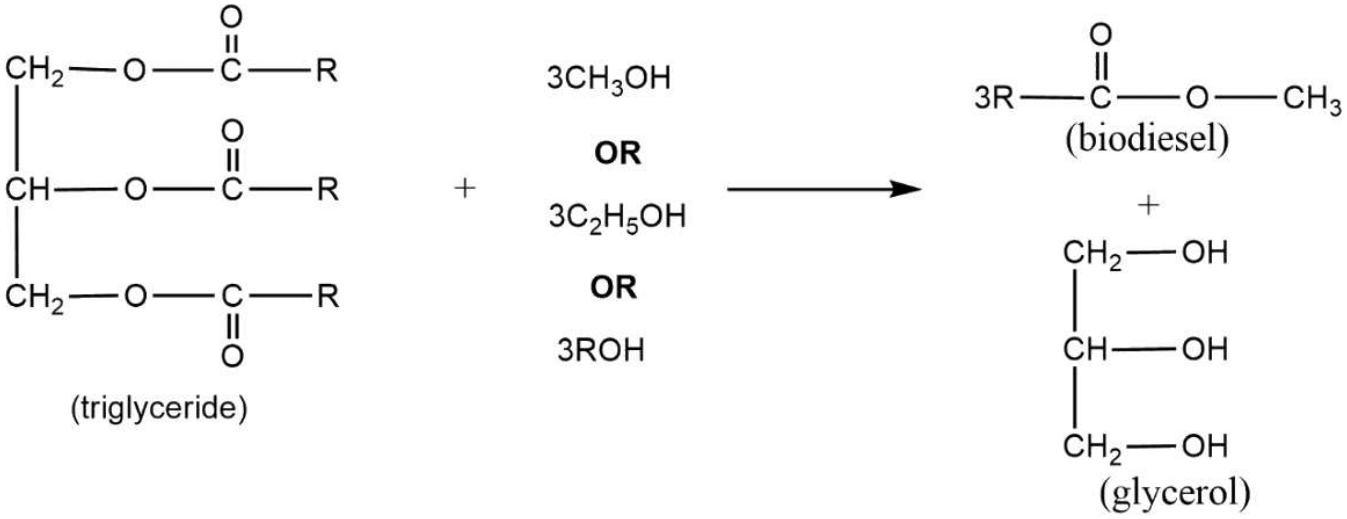
Answer

Sodium hydroxide (NaOH) / potassium hydroxide (KOH) (05)

(iv) Give a balanced chemical equation to show the synthesis of biodiesel using the chemical compounds stated in part (ii) above.

Answer

Triglyceride $CH_2(OCOR)–CH(OCOR)–CH_2(OCOR)$ + $3CH_3OH$ (OR $3C_2H_5OH$ OR 3ROH) → $3R–CO–O–CH_3$ (biodiesel) + glycerol $CH_2(OH)–CH(OH)–CH_2(OH)$ (20)
Notes: 1. R could be written as R_1, R_2 and R_3; the equation should be balanced accordingly. 2. For a correct balanced equation (20 marks); if the equation is not balanced, award (04) for each correct reactant and product. 3. C_2H_5OH and ROH may be accepted for this year ONLY.



Equation for the synthesis of biodiesel (scheme)

(v) Identify a side reaction that would take place, along with its products, if the catalyst is used in excess.

Answer

Saponification reaction OR its description (05); product – soap ($R–COO^-Na^+$) (05) · 10(c): 50 marks

Review.

Biodiesel is made by base-catalysed transesterification (alcoholysis) of the triglycerides in vegetable oil with methanol, giving fatty acid methyl esters and glycerol; the catalyst (NaOH or KOH) is needed in small amounts only, because excess hydroxide hydrolyses (saponifies) the ester to soap, which lowers the yield and makes separation difficult. Common mistakes: writing only one mole of alcohol per triglyceride in the equation, and naming the oil rather than the triglyceride as the main compound.

Read: RB U14 §1.2 · p. 6 RB U14 §1.13 · p. 58 RB U14 §1.14 · p. 80 RB U14 §1.12 · p. 48 RB U14 §1.4 · p. 14

2018 · Chemistry Digital Paper

50 questions · 2 hours

MCQ · Paper I

Question 1 · Q1–30 · single answer

The number of unpaired electrons present in a gaseous Co^{3+} ion in its ground state is,

- (1)1
- (2)2
- (3)3
- (4)4
- (5)5

Answer and review

Answer **(4)** Official marking scheme

Co is [Ar]$3d^7$ $4s^2$; Co^{3+} loses the two 4s electrons and one 3d electron to give [Ar]$3d^6$. By Hund's rule the six d electrons occupy the five d orbitals as one pair and four unpaired electrons. Trap: counting the neutral Co atom's 3 unpaired electrons, or removing 3d electrons before the 4s electrons.

RB U1 §1.4 · p. 23 RB U6 §4.10 · p. 160

Question 2 · Q1–30 · single answer

Which quantum number(s) (n, l, m_l, m_s) is/are associated with the shape of an atomic orbital of an atom?

- (1)l
- (2)m_l
- (3)n and l
- (4)n and m_l
- (5)l and m_l

Answer and review

Answer **(1/5)** Official marking scheme

The shape of an orbital (s, p, d, f) is fixed by the azimuthal (subsidiary) quantum number l, so (1) is right. The magnetic quantum number m_l only decides the orientation in space of orbitals of the same shape, but because the orientation is part of the full description of the orbital the official scheme accepts (1), (5) or both. n gives size/energy and m_s gives electron spin, so any option containing n or m_s alone is wrong.

RB U1 §1.3 · p. 17

Question 3 · Q1–30 · single answer

What is the IUPAC name of the compound shown below?

$CH_3CH_2CH(Br)–C(NO_2)=CHCO_2H$

- (1)4-bromo-3-nitro-2-hexenoicacid
- (2)4-bromo-3-nitro-2-hexenoic acid
- (3)3-nitro-4-bromo-2-hexenoicacid
- (4)3-nitro-4-bromo-2-hexenoic acid
- (5)3-bromo-4-nitro-4-hexenoic acid

Answer and review

Answer **(2)** Official marking scheme

The principal chain is the six-carbon chain that includes the –COOH carbon (C1): C1 COOH, C2 =CH, C3 $C(NO_2)$, C4 CH(Br), C5 CH_2, C6 CH_3. The C=C starts at C2 (2-hexenoic acid), substituents are 4-bromo and 3-nitro, listed alphabetically (bromo before nitro). Options (1) and (3) differ from (2) and (4) only by the missing space in "hexenoicacid" as printed; (3) and (4) are not in alphabetical order.

RB U7 §1.3 · p. 7

Question 4 · Q1–30 · single answer

The **correct** answer when the molecules O_2, H_2O, H_2O_2, OF_2 and O_2F_2 (structure similar to H_2O_2) are arranged in the **decreasing** order of the oxidation state of oxygen (O) is,

- (1)$O_2F_2 > OF_2 > O_2 > H_2O > H_2O_2$
- (2)$H_2O > H_2O_2 > O_2 > O_2F_2 > OF_2$
- (3)$H_2O_2 > O_2F_2 > O_2 > OF_2 > H_2O$
- (4)$OF_2 > O_2F_2 > O_2 > H_2O > H_2O_2$
- (5)$OF_2 > O_2F_2 > O_2 > H_2O_2 > H_2O$

Answer and review

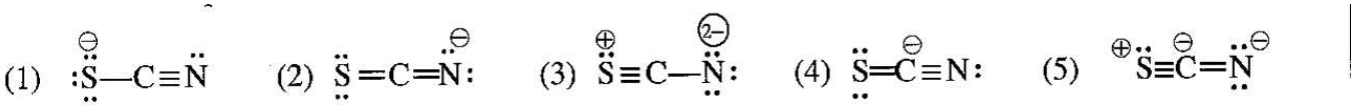
Answer **(5)** Official marking scheme

F is more electronegative than O, so F is −1 and O is positive in its fluorides: OF_2 (+2) and O_2F_2 (+1, with an O–O bond like H_2O_2). O_2 is 0, H_2O_2 is −1 (O–O bond, H is +1) and H_2O is −2. Order: OF_2 (+2) > O_2F_2 (+1) > O_2 (0) > H_2O_2 (−1) > H_2O (−2). Trap: putting H_2O above H_2O_2, or treating O_2F_2 as +2.

RB U3 §3.1 · p. 88

Question 5 · Q1–30 · single answer

The **most** acceptable Lewis structure for the thiocyanate ion SCN^- is,



Answer and review

Answer **(2)** Official marking scheme

Count 16 valence electrons (6 + 4 + 5 + 1 for the charge). In (2), $S=C=N^-$ with two lone pairs on S and two on N, every atom has an octet and the formal charges are S 0, C 0, N −1; the negative charge sits on the more electronegative atom N. (3), (4) and (5) put unfavourable charges on C, or a 2− on N, or three

separated formal charges, so they are less acceptable. Structure (1), S^{-}–C≡N, is also a valid resonance form (and the other main contributor), but the scheme chooses (2) because it places the formal charge on the more electronegative atom and has no charge separation beyond the ion's single charge.

RB U2 §2.1 · p. 44 RB U2 §2.3 · p. 52

Question 6 · Q1–30 · single answer

The molarity (mol dm^{-3}) of a NaI solution which has a density of 1.03 g cm^{-3} and is 3% NaI by mass is,

(Na = 23, I = 127)

- (1)0.21
- (2)0.23
- (3)0.25
- (4)0.28
- (5)0.30

Answer and review

Answer **(1)** Official marking scheme

Take 1 dm^3 of solution: mass = 1030 g, of which 3% is NaI = 30.9 g. M(NaI) = 150 g mol^{-1}, so n = 30.9/150 = 0.206 mol, i.e. 0.21 mol dm^{-3}. Trap: using 1000 g (ignoring the density) gives 30/150 = 0.20, which is not an option, and dividing by the wrong molar mass (e.g. 127) gives 0.24.

RB U3 §3.5 · p. 102

Question 7 · Q1–30 · single answer

Precipitates of AgI and AgBr were added to a small amount of distilled water. This mixture was allowed to reach equilibrium at 25 °C. It was observed that both the solids were present in the system at equilibrium. Which of the following relations is applicable to this solution?

($K_{sp(AgI)}$ = 8.0 × 10^{-17} mol^2 dm^{-6}, $K_{sp(AgBr)}$ = 5.0 × 10^{-13} mol^2 dm^{-6} at 25 °C)

- (1)$[Br^-]$ = √(5.0 × 10^{-13}) mol dm^{-3} and $[I^-]$ = √(8.0 × 10^{-17}) mol dm^{-3}
- (2)$[Br^-]$ $[I^-]$ = $[Ag^+]^2$
- (3)$[Ag^+]$ = (√(5.0 × 10^{-13}) + √(8.0 × 10^{-17})) mol dm^{-3}
- (4)$[Br^-]/[I^-]$ = (5.0/8.0) × 10^4
- (5)$[Ag^+]$ = $[Br^-]$ = $[I^-]$

Answer and review

Answer **(4)** Official marking scheme

With both solids present, both K_{sp} expressions hold with the same $[Ag^+]$. Dividing, $[Br^-]/[I^-]$ = $K_{sp(AgBr)}/K_{sp(AgI)}$ = 5.0 × 10^{-13}/8.0 × 10^{-17} = (5.0/8.0) × 10^4. Options (1) and (3) treat each salt as if it were alone in water, and (2) and (5) are not true because $[Ag^+]$ = $[Br^-]$ + $[I^-]$ (charge balance), so it is larger than either anion concentration.

RB U12 §2.4 · p. 175

Question 8 · Q1–30 · single answer

Which of the following statements is **false**?

- (1)Although the carbonates of all the group two metals in the Periodic Table are insoluble in water, their bicarbonates are soluble.
- (2)The hydroxides of all the group two metals in the Periodic Table are soluble in water.
- (3)The nitrates of all the group two metals in the Periodic Table are soluble in water.
- (4)The oxides and hydroxides of Na and Mg show basic properties whereas the oxide and hydroxide of Al show amphoteric properties.
- (5)The hydrides of Si and S show weakly acidic properties.

Answer and review

Answer **(2)** Official marking scheme

Group 2 hydroxide solubility increases down the group, but $Be(OH)_2$ and $Mg(OH)_2$ are practically insoluble ($Mg(OH)_2$ is only sparingly soluble), so "all are soluble" is false. The carbonates are insoluble, the nitrates all soluble, Na/Mg oxides are basic and Al_2O_3/$Al(OH)_3$ amphoteric. Statement (5) is loosely worded (H_2S is a weak acid, SiH_4 is barely acidic), but (2) is unambiguously false, so it is the key.

RB U6 §4.2 · p. 126 RB U6 §4.9 · p. 155

Question 9 · Q1–30 · single answer

In which list are the elements given in the order of **increasing** (left to right) atomic radii?

- (1)Li, Na, Mg, S
- (2)C, Si, S, Cl
- (3)B, C, N, P
- (4)Li, Na, K, Ca
- (5)B, Be, Na, K

Answer and review

Answer **(5)** Official marking scheme

Radius decreases across a period and increases down a group. B (≈88 pm) < Be (≈112 pm) < Na (≈186 pm) < K (≈227 pm) is increasing. (1) fails because Mg > S; (2) has S > Cl and Si > S; (3) has C > N; (4) fails because Ca is smaller than K.

RB U1 §1.6 · p. 32

Question 10 · Q1–30 · single answer

Liquids A and B form an ideal solution. Consider a mixture of liquids A and B in equilibrium with the vapour in a closed rigid container at constant temperature. $P_A^{\,o}$ and $P_B^{\,o}$ respectively are the saturated vapour pressures of A and B while P is the total pressure of the container and $X_A^{\,g}$ is the mole fraction of A in the vapour phase. Which of the following is correct about this system?

- (1)$P = (P_A^{\,o} - P_B^{\,o})\, X_A^{\,g} + P_B^{\,o}$
- (2)$1/P = (1/P_A^{\,o} - 1/P_B^{\,o})\, X_A^{\,g} + 1/P_B^{\,o}$
- (3)$P = (P_A^{\,o} + P_B^{\,o})\, X_A^{\,g} - P_B^{\,o}$

- (4)$1/P = (1/P_B^{o} - 1/P_A^{o}) \cdot 1/X_A^{g}$
- (5)$1/P = (1/P_A^{o} - 1/P_B^{o}) \cdot 1/X_A^{g}$

Answer and review

Answer **(2)** Official marking scheme

By Raoult's and Dalton's laws, the partial pressure of A is $p_A = X_A^{g} P = X_A^{l} P_A^{o}$, and similarly for B. So $X_A^{l} = X_A^{g}P/P_A^{o}$ and $X_B^{l} = X_B^{g}P/P_B^{o}$; since $X_A^{l} + X_B^{l} = 1$, $P(X_A^{g}/P_A^{o} + (1 - X_A^{g})/P_B^{o}) = 1$, i.e. $1/P = (1/P_A^{o} - 1/P_B^{o})\, X_A^{g} + 1/P_B^{o}$. Option (1) is the correct liquid-phase relation, $P = (P_A^{o} - P_B^{o})\, X_A^{l} + P_B^{o}$, but it is written here with the vapour mole fraction, which makes it wrong; (3) and (4)/(5) do not follow from the laws.

RB U12 §2.6 · p. 216

Question 11 · Q1–30 · single answer

The **increasing** order of boiling points of the following substances is,

He, CH_4, CCl_4, CBr_4, SiH_4

- (1)$CH_4 < He < SiH_4 < CCl_4 < CBr_4$
- (2)$He < SiH_4 < CH_4 < CCl_4 < CBr_4$
- (3)$He < CH_4 < SiH_4 < CCl_4 < CBr_4$
- (4)$CH_4 < He < SiH_4 < CBr_4 < CCl_4$
- (5)$He < CH_4 < CCl_4 < SiH_4 < CBr_4$

Answer and review

Answer **(3)** Official marking scheme

All are non-polar, so the only intermolecular force is the London dispersion force, which grows with the number of electrons (size). He (4 K) < CH_4 (112 K) < SiH_4 (161 K) < CCl_4 (350 K) < CBr_4 (463 K). Traps: He is the smallest, so it must come first; and CBr_4 (heavier, more polarizable) boils higher than CCl_4.

RB U2 §2.6 · p. 79

Question 12 · Q1–30 · single answer

Identify the **correct** statement from the following.

- (1)Among the electronic transitions n = 2 → n = 1, n = 3 → n = 2 and n = 4 → n = 3 in a hydrogen atom, most energy is released in n = 3 → n = 2.
- (2)Among the species OF_2, OF_4 and SF_4, the least stable is SF_4.
- (3)Among the elements Li, C, N, Na and P, the least electronegative element is Li.
- (4)In the following pairs (Li & F), (Li^+ & F^-), (Li^+ & O^{2-}) and (O^{2-} & F^-), the difference in radii is greatest between Li^+ and O^{2-}.
- (5)The only type of intermolecular force present in CH_2Cl_2 in the liquid phase is dipole-dipole forces.

Answer and review

Answer **(4)** Official marking scheme

(1) is false: the energy released is largest for n = 2 → 1 (the gaps shrink as n rises). (2) is false because O cannot expand its octet, so OF_4 is the species that does not exist or is least stable, not SF_4 (S can use 3d orbitals). (3) is false because Na is less electronegative than Li. (5) is false because London dispersion forces

are also present. The key therefore rests on (4) by elimination. Note: with common atomic radii the Li–F atom pair (about 150 pm versus 70 pm) shows a larger difference than Li^+ (76 pm) and O^{2-} (140 pm), so statement (4) is itself doubtful and the question is weaker than the others. The official key (4) is retained.

RB U1 §1.6 · p. 32 RB U1 §1.3 · p. 17 RB U2 §2.4 · p. 75

Question 13 · Q1–30 · single answer

Consider the reaction: $CH_4(g) \rightarrow CH_3(g) + H(g)$

The standard change in enthalpy of the above reaction is,

- (1)the standard enthalpy change for the dissociation of the first C–H bond in methane.
- (2)the standard atomisation enthalpy change of methane.
- (3)the standard first ionisation enthalpy change of methane.
- (4)the standard bond dissociation enthalpy change of methane.
- (5)the standard radical formation enthalpy change of methane.

Answer and review

Answer **(1)** Official marking scheme

Breaking one C–H bond of gaseous CH_4 into the CH_3 and H radicals is the dissociation of the first C–H bond. Atomisation of methane would break all four C–H bonds ($CH_4 \rightarrow C(g) + 4H(g)$), and no ions form, so it is not an ionisation. Option (4) is a trap: the "bond dissociation enthalpy" of methane normally means the mean C–H value, which is one quarter of the atomisation enthalpy and differs from the first-bond value. Option (5) is not a standard term.

RB U5 §2.2 · p. 36

Question 14 · Q1–30 · single answer

The elementary reaction $2A(g) \rightarrow B(g)$ occurs in a closed rigid container at a constant temperature. Initial pressure of the container is P_o and the pressure when the rate of reaction is 50% of the initial value is P_t. Which of the following gives the correct value for P_t/P_o?

- (1)$P_t/P_o = 1/2$
- (2)$P_t/P_o = 1/\sqrt{2}$
- (3)$P_t/P_o = (1 + \sqrt{2})/(2\sqrt{2})$
- (4)$P_t/P_o = \sqrt{2}/(1 + \sqrt{2})$
- (5)$P_t/P_o = (\sqrt{2} - 1)/(1 + \sqrt{2})$

Answer and review

Answer **(3)** Official marking scheme

An elementary step $2A \rightarrow B$ is second order, so rate = k P_A^2 (at constant T, V). Rate falling to 50% means P_A^2 = P_o^2/2, so $P_A = P_o/\sqrt{2}$. Each 2 mol of A gives 1 mol of B, so $P_B = (P_o - P_A)/2$ and $P_t = P_A + P_B = (P_o + P_A)/2 = P_o(1 + 1/\sqrt{2})/2 = P_o(\sqrt{2} + 1)/(2\sqrt{2})$. Traps: treating the reaction as first order ($P_A = P_o/2$) or forgetting that the total pressure includes B.

RB U11 §1.6 · p. 16 RB U11 §1.10 · p. 57

Question 15 · Q1–30 · single answer

An equimolar aqueous solution of the weak acids HA and HB (1.0 mol dm^{-3} in each acid) with pK_a values 4.7 and 5.0 respectively is at equilibrium. The value of $\log([A^-]/[B^-])$ is approximately equal to,

- (1)23.5
- (2)−0.3
- (3)0.3
- (4)0.94
- (5)1.06

Answer and review

Answer **(3)** Official marking scheme

In the mixture $[H^+]$ is common: $K_{a(HA)} = [H^+][A^-]/[HA]$ and $K_{a(HB)} = [H^+][B^-]/[HB]$. With $[HA] \approx [HB] \approx 1.0$ (the acids are weak), $[A^-]/[B^-] = K_{a(HA)}/K_{a(HB)} = 10^{-4.7}/10^{-5.0} = 10^{0.3}$, so the log is 0.3. The first option is printed as "23.5" in the paper. Trap: sign error (−0.3) from inverting the ratio.

RB U12 §2.2 · p. 118

Question 16 · Q1–30 · single answer

Which of the following statements about C_6H_5OH is **false**?

- (1)Reacts with CH_3COCl to form a phenyl ester.
- (2)Reacts with bromine water to give a white precipitate.
- (3)Evolves CO_2 gas when treated with $NaHCO_3$.
- (4)Gives a coloured compound when treated with $C_6H_5N_2$^+Cl^- in the presence of NaOH.
- (5)Gives a coloured (purplish) solution when treated with neutral $FeCl_3$.

Answer and review

Answer **(3)** Official marking scheme

Phenol ($pK_a \approx 10$) is a weaker acid than H_2CO_3 ($pK_{a1} \approx 6.4$), so it does not liberate CO_2 from $NaHCO_3$; (3) is false. The other statements are true: acylation gives phenyl ethanoate, bromine water gives white 2,4,6-tribromophenol, the phenoxide couples with the benzenediazonium ion in NaOH to give a coloured azo dye, and neutral $FeCl_3$ gives a violet complex.

RB U9 §3.2 · p. 58 RB U9 §3.3 · p. 59 RB U10 §4.3 · p. 78

Question 17 · Q1–30 · single answer

The half life of a reaction is,

- (1)always independent of the initial concentration of reactants.
- (2)always dependent on the rate constant.
- (3)always independent of the order of the reaction.
- (4)always independent of temperature.
- (5)equal to twice the total reaction time.

Answer and review

Answer **(2)** Official marking scheme

Every half-life expression contains k: $t_{1/2}$ = ln 2/k (first order), 1/(k[A]$_0$) (second order, one reactant) and [A]$_0$/2k (zero order), so it always depends on k. It is independent of [A]$_0$ only for first-order reactions, depends on the order, depends on temperature through k, and is not related to the total time in the way stated in (5).

RB U11 §1.7.2 · p. 28

Question 18 · Q1–30 · single answer

Electromotive force of an electrochemical cell does **not** depend on,

- (1)the nature of the electrolytes.
- (2)temperature.
- (3)the concentrations of the electrolytes.
- (4)the surface areas of the electrodes.
- (5)the types of metals that form the electrodes.

Answer and review

Answer **(4)** Official marking scheme

The cell emf is E° (set by the electrode materials and the species in solution) corrected for concentration and temperature (Nernst equation). The electrode surface area changes only the amount of current that can flow, not the potential, which is an intensive property.

RB U13 §3.3 · p. 250

Question 19 · Q1–30 · single answer

IO_3^− (iodate ion) oxidizes the SO_3^{2-} ion to SO_4^{2-} in acidic medium. The mass of KIO_3 required to totally oxidize the amount of Na_2SO_3 present in 25.0 cm^3 of a solution of Na_2SO_3 (0.50 mol dm^{-3}) to Na_2SO_4 is 1.07 g. (O = 16, K = 39, I = 127)

The final oxidation state of iodine after the completion of the reaction is,

- (1)−1
- (2)0
- (3)+1
- (4)+2
- (5)+3

Answer and review

Answer **(2)** Official marking scheme

n(SO_3^{2-}) = 0.0250 dm^3 × 0.50 mol dm^{-3} = 0.0125 mol; each SO_3^{2-} → SO_4^{2-} gives 2 electrons, so 0.0250 mol of electrons. n(KIO_3) = 1.07 g ÷ 214 g mol^{-1} = 0.005 mol, so each I accepts 0.0250/0.005 = 5 electrons and goes from +5 to 0 (I_2). Trap: assuming iodate is reduced all the way to I^- (6 electrons, −1).

RB U3 §3.6 · p. 105 RB U3 §3.8 · p. 115

Question 20 · Q1–30 · single answer

Which of the following statements is **false** with regard to the s-block elements in the Periodic Table?

- (1)All elements in group I react with water liberating H_2 gas.
- (2)All elements in group I except Li react with N_2 gas.
- (3)All elements in group II react with N_2 gas.
- (4)Na reacts with excess O_2 to give Na_2O_2 whereas K gives KO_2.
- (5)All elements in the s-block are good reducing agents.

Answer and review

Answer **(2)** Official marking scheme

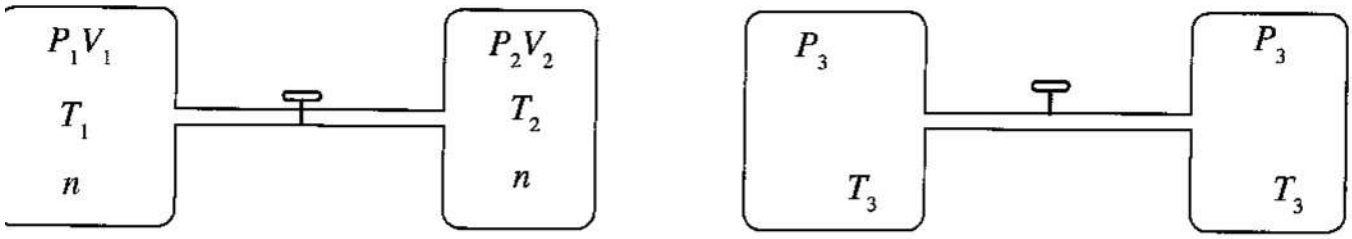
The reverse of (2) is true: lithium is the only Group 1 metal that reacts directly with N_2 (forming Li_3N), because the small Li^+ ion gives a high lattice enthalpy for the nitride. All Group 2 metals form nitrides M_3N_2 on heating in N_2, all Group 1 metals liberate H_2 from water, Na gives the peroxide and K the superoxide in excess O_2, and all s-block metals are good reducing agents.

RB U6 §4.1 · p. 122 RB U6 §4.2 · p. 126

Question 21 · Q1–30 · single answer

A system consisting of two rigid containers containing an ideal gas is shown in the diagram. The containers can be connected to each other by opening the tap. The system changes from configuration **A** to configuration **B** when the tap is opened. In general n, P, V and T represent number of moles, pressure, volume and temperature respectively.

Which of the following relations is **correct** about this system?



configuration **A** (tap closed) configuration **B** (tap opened)

1

1

1

2

2

2

3

3

- (1)$P_1V_1 = P_2V_2$
- (2)$P_3T_1/P_1 + P_3T_2/P_2 = 2T_3$

- (3)$T_1/P_1 = T_2/P_2$
- (4)$P_1T_1 = P_2T_2$
- (5)$P_1V_1 + P_2V_2 = P_3(V_1 + V_2)$

Answer and review

Answer **(2)** Official marking scheme

Each container holds n mol, so $V_1 = nRT_1/P_1$ and $V_2 = nRT_2/P_2$. After opening, 2n mol at P_3 and T_3 fill $V_1 + V_2$: $P_3(V_1 + V_2) = 2nRT_3$. Substituting gives $P_3(nRT_1/P_1 + nRT_2/P_2) = 2nRT_3$, i.e. $P_3T_1/P_1 + P_3T_2/P_2 = 2T_3$. The other relations hold only if the temperatures (and for (3), the volumes) happen to be equal; (5) ignores the temperature change.

RB U4 §1.2 · p. 5

Question 22 · Q1–30 · single answer

Which of the following statements is **false** with regard to 3d-elements of the Periodic Table?

- (1)Atomic radii are smaller than the atomic radii of the s-block elements in the same period.
- (2)Densities are higher than the densities of the s-block elements in the same period.
- (3)V_2O_5, CrO_3 and Mn_2O_7 are acidic oxides.
- (4)First ionization energies are less than the first ionization energies of the s-block elements in the same period.
- (5)The most common oxidation states of cobalt in cobalt compounds are +2 and +3.

Answer and review

Answer **(4)** Official marking scheme

The 3d elements have a higher nuclear charge and smaller atoms than K and Ca, so their first ionization energies are higher (e.g. Sc–Zn are all above K and Ca), making (4) false. Smaller radii and higher densities follow from the same trend, oxides in high oxidation states (V^{+5}, Cr^{+6}, Mn^{+7}) are acidic, and cobalt is common as Co(II) and Co(III).

RB U6 §4.10 · p. 160 RB U1 §1.6 · p. 32

Question 23 · Q1–30 · single answer

Standard Gibbs energy changes for the reaction, MO(s) → M(s) + ½O_2(g) at two different temperatures are given below.

T/K	ΔG°/kJ mol^{-1}
1000	−100.2
2000	−148.6

The standard entropy change of the reaction is,

- (1)248.8 J K^{-1} mol^{-1}
- (2)−248.8 J K^{-1} mol^{-1}
- (3)−48.4 J K^{-1} mol^{-1}
- (4)348.4 J K^{-1} mol^{-1}

- (5)48.4 J K^{-1} mol^{-1}

Answer and review

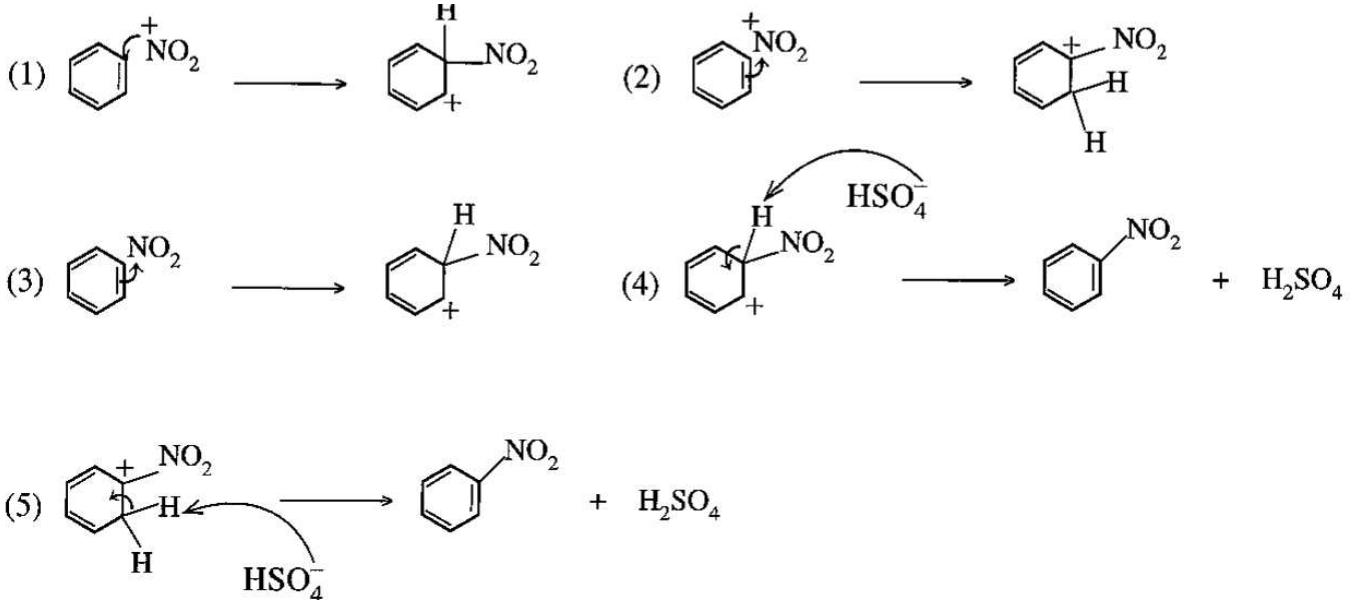
Answer **(5)** Official marking scheme

Taking ΔH° and ΔS° as constant, ΔG° = ΔH° − TΔS°, so ΔS° = −(ΔG°$_{2000}$ − ΔG°$_{1000}$)/(2000 − 1000) = −(−148.6 + 100.2) kJ mol^{-1}/1000 K = +0.0484 kJ K^{-1} mol^{-1} = 48.4 J K^{-1} mol^{-1}. A positive value is expected because a gas is formed. Trap: dropping the minus sign (−48.4) or forgetting to convert kJ to J.

RB U5 §2.4 · p. 53

Question 24 · Q1–30 · single answer

Which of the following represents a **correct** step in the mechanism of nitration of benzene with conc. HNO_3 / conc. H_2SO_4?



Answer and review

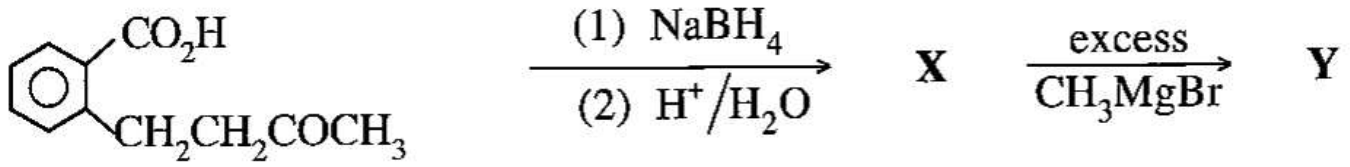
Answer **(4)** Official marking scheme

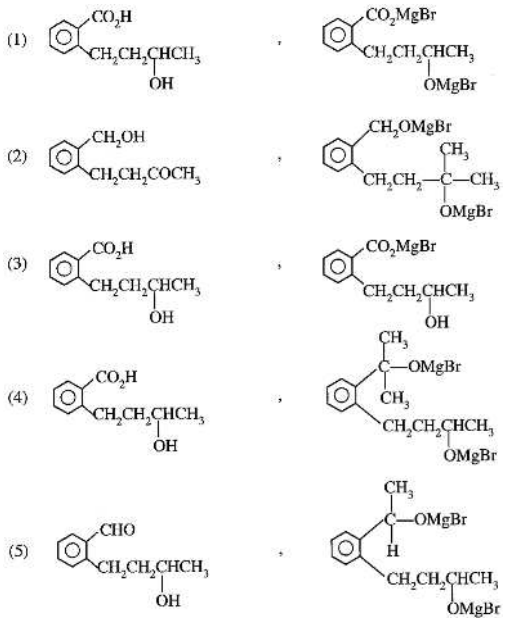
In (4) HSO_4^− removes H^+ from the sp^3 carbon of the arenium (σ-complex) ion that carries the NO_2 group, and the C–H bond electrons restore the aromatic ring, giving nitrobenzene and H_2SO_4. In (1) the curly arrow wrongly starts at NO_2^+ (it must start at the π electrons of the ring); in (3) the electrophile is shown as neutral NO_2, not NO_2^+; (2) and (5) show an extra H added to the ring, which does not occur.

RB U8 §2.4 · p. 44

Question 25 · Q1–30 · single answer

In the reaction sequence given above, the structures of **X** and **Y** respectively are,





Answer and review

Answer **(1)** Official marking scheme

$NaBH_4$ reduces the ketone C=O to a secondary alcohol but does not reduce $–CO_2H$, so X is 2-(3-hydroxybutyl)benzoic acid (options 1, 3, 4). With excess CH_3MgBr the Grignard reagent acts as a base towards both acidic hydrogens: $–CO_2H \rightarrow –CO_2MgBr$ and $–OH \rightarrow –OMgBr$ (with CH_4 evolved), giving the structure in (1). Trap: (4) assumes CH_3MgBr adds to $–CO_2H$, but the carboxylate formed first is not attacked; (2) and (5) assume $NaBH_4$ reduces the acid group.

RB U9 §3.4 · p. 60 RB U8 §2.7 · p. 50 RB U9 §3.5 · p. 66

Question 26 · Q1–30 · single answer

When $(NH_4)_2CO_3(s)$, $(NH_4)_2Cr_2O_7(s)$ and $NH_4NO_3(s)$ are heated, the nitrogen containing compounds obtained are respectively,

- (1)NH_3, N_2 and NO_2
- (2)N_2O, N_2 and NH_3
- (3)NH_3, N_2 and N_2O
- (4)N_2, N_2O and NH_3
- (5)N_2, NH_3 and N_2O

Answer and review

Answer **(3)** Official marking scheme

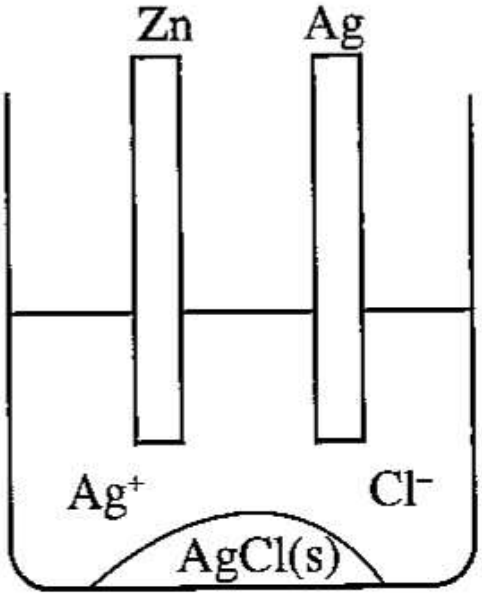
$(NH_4)_2CO_3 \rightarrow 2NH_3 + CO_2 + H_2O$ (a non-oxidising anion, so NH_3 is released). $(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3 + 4H_2O$ (the dichromate oxidises $NH_4\hat{}+$ to N_2). $NH_4NO_3 \rightarrow N_2O + 2H_2O$ (internal redox between $NH_4\hat{}+$ and $NO_3\hat{}-$). Trap: NO_2 comes from heating metal nitrates, not ammonium nitrate.

RB U6 §4.5 · p. 136 RB U6 §4.10 · p. 160

Question 27 · Q1–30 · single answer

Which of the following would occur soon after connecting a rod of Zn and a rod of Ag immersed in a saturated solution of AgCl and AgCl(s) kept in a beaker as shown in the diagram, by a conductor?

$Zn^{2+}(aq) + e \rightarrow Zn(s)$ $E° = -0.76$ V
$Ag^{+}(aq) + e \rightarrow Ag(s)$ $E° = 0.80$ V



- (1)Zn dissolves, Ag deposits, AgCl(s) dissolves.
- (2)Zn dissolves, Ag dissolves, AgCl(s) dissolves.
- (3)Zn dissolves, Ag dissolves, AgCl(s) deposits.
- (4)Zn deposits, Ag dissolves, AgCl(s) dissolves.
- (5)Chloride concentration in the solution decreases.

Answer and review

Answer **(1)** Official marking scheme

Zn has the much lower electrode potential, so it is the anode and dissolves ($Zn \rightarrow Zn^{2+} + 2e$); the electrons reduce Ag^{+} on the Ag rod ($Ag^{+} + e \rightarrow Ag$), so Ag deposits. Removal of Ag^{+} makes the ionic product less than K_{sp}, so more AgCl(s) dissolves and $[Cl^{-}]$ in solution rises, which rules out (5). (The printed half-equation for zinc omits the 2 before e.)

RB U13 §3.3 · p. 250 RB U12 §2.4 · p. 175

Question 28 · Q1–30 · single answer

In the reaction sequence given below, the structures of **P** and **Q** respectively are,

$C_6H_5C{\equiv}CH$ —(Hg^{2+}/dil. H_2SO_4)→ **P** —(Zn/Hg, conc. HCl)→ **Q**

- (1)$C_6H_5C(OH){=}CH_2$, $C_6H_5CH{=}CH_2$
- (2)$C_6H_5CH{=}CH(OH)$, $C_6H_5CH{=}CH_2$
- (3)C_6H_5–CO–CH_3 , C_6H_5–CH(OH)–CH_3
- (4)C_6H_5–CO–CH_3 , $C_6H_5CH_2CH_3$
- (5)$C_6H_5C(OH){=}CH_2$, $C_6H_5CH(OH)CH_3$

Answer and review

Answer **(4)** Official marking scheme

Hg^{2+}-catalysed hydration of the terminal alkyne follows Markovnikov's rule; the enol $C_6H_5C(OH)=CH_2$ tautomerises at once to the ketone, so P is $C_6H_5COCH_3$ (acetophenone), not an enol. Clemmensen reduction (Zn(Hg)/conc. HCl) converts C=O into CH_2, so Q is ethylbenzene. Trap: (3) gives the alcohol, which is the product of $NaBH_4$/$LiAlH_4$ reduction, not Zn(Hg)/HCl.

RB U8 §2.3 · p. 41 RB U9 §3.4 · p. 60

Question 29 · Q1–30 · single answer

Which of the following statements is **incorrect** regarding polymers?

- (1)Bakelite is a thermosetting polymer.
- (2)Teflon is a thermoplastic polymer.
- (3)Nylon 6,6 is formed by addition polymerisation between 1,6-diaminohexane and hexanedioic acid.
- (4)Terelene is formed by condensation polymerisation between ethylene glycol and terephthalic acid.
- (5)Natural rubber consists of cis-polyisoprene chains.

Answer and review

Answer **(3)** Official marking scheme

Nylon 6,6 forms by condensation polymerisation: each amide link formed between $–NH_2$ and –COOH releases a molecule of H_2O, so (3) is incorrect. Bakelite (cross-linked) is thermosetting, Teflon is a thermoplastic addition polymer, Terylene is a condensation polyester and natural rubber is cis-polyisoprene.

RB U14 §1.11 · p. 37

Question 30 · Q1–30 · single answer

An experiment was carried out to find the order (m) with respect to $S_2O_3^{2-}$ of the reaction $S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow H_2O(l) + SO_2(g) + S(s)$. Initial rate of the reaction (R) was measured by adding different volumes (v) of 0.01 mol dm^{-3} $S_2O_3^{2-}$ into a solution of an acid. The H^+ concentration of the reaction mixture was kept constant, but the total volume (V) was allowed to vary. Which of the following relations regarding the initial rate of the reaction is correct?

- (1)R ∝ (v/V)^m
- (2)R ∝ v^m
- (3)R ∝ $v^{1/m}$
- (4)R ∝ $(v/V)^{1/m}$
- (5)R ∝ V^m

Answer and review

Answer **(1)** Official marking scheme

With $[H^+]$ constant, $R = k'[S_2O_3^{2-}]$^m. The thiosulfate concentration in the mixture is 0.01 × v/V, so R ∝ (v/V)^m. Trap: (2) is correct only when the total volume V is kept constant (by adding water), which is how the experiment is usually designed; here V varies, so the dilution must be included.

RB U11 §1.7 · p. 26 RB U11 §1.6 · p. 16

Questions 31–40: response code

(1)	(2)	(3)	(4)	(5)
Only (a) and (b) are correct	Only (b) and (c) are correct	Only (c) and (d) are correct	Only (d) and (a) are correct	Any other number or combination of responses is correct

Question 31 · Q31–40 · response code

Consider a titration between a weak acid (fixed volume) and a strong base. Which of the following is/are independent of the weak acid concentration?

- pH at the equivalence point.
- Volume of the strong base required to reach the end point.
- Dissociation constant of the weak acid.
- Value of $[H^+] \times [OH^-]$ of the solution in the titration flask.

Answer and review

Answer **(3)** Official marking scheme

K_a and $K_w = [H^+][OH^-]$ are equilibrium constants that depend only on temperature, so (c) and (d) are independent of concentration. The volume of base needed is proportional to the moles of acid, and the pH at the equivalence point depends on the concentration of the salt A^- formed (its hydrolysis), so (a) and (b) change. Code (3).

RB U12 §2.2 · p. 118

Question 32 · Q31–40 · response code

Which of the following statements is/are **true** regarding the molecule given below?

CH_3–C≡C–CHO (carbon atoms labelled **a**, **b**, **c**, **d** from left to right)

- All four carbon atoms lie in the same plane.
- The angle between C_d–H and the C_d–C_c bonds is approximately 120°.
- Between C_b and C_c, there are two σ-bonds and one π-bond.
- Between C_b and C_c, there is one σ-bond and two π-bonds.

Answer and review

Answer **(5)** Official marking scheme

C_b and C_c are sp hybridised, so C_a–C_b≡C_c–C_d is a straight line and the four carbons certainly lie in one plane (a). C_d (the –CHO carbon) is sp^2, so its bond angles are about 120° (b). A triple bond is one σ and two π bonds (d), so (c) is false. (a), (b) and (d) are true, which is code (5).

RB U2 §2.3 · p. 52

Question 33 · Q31–40 · response code

Which of the following statement/s is/are **true** with regard to the manufacture of Na_2CO_3?

- CO_2 is one of the raw materials used.
- The reaction between CO_2 and aqueous NaCl saturated with NH_3 is endothermic.

- The manufacturing process involves five stages.
- Most of the NH_3 used in the process can be recovered.

Answer and review

Answer **(3)** Official marking scheme

In the Solvay (ammonia-soda) process, the raw materials supplied are NaCl (brine) and $CaCO_3$ (limestone); CO_2 is generated inside the plant from limestone and from heating $NaHCO_3$, so the scheme treats (a) as false. Carbonation of ammoniated brine is exothermic and the tower must be cooled, so (b) is false. The old-syllabus description had five stages and NH_3 is recovered from NH_4Cl with CaO, so (c) and (d) are true. Note that the current Resource Book lists NH_3, CO_2, NaCl and H_2O as the theoretical raw materials for $NaHCO_3$ and describes the process in four numbered steps plus NH_3 recovery, so (a) and (c) depend on the description used; the official key is (3).

RB U14 §1.5 · p. 18

Question 34 · Q31–40 · response code

Temperature must be maintained at a constant value during the experimental determination of the order of an elementary reaction, because,

- the order of the reaction depends on temperature.
- the activation energy changes with temperature.
- the mechanism of the reaction changes with temperature.
- the rate constant changes with temperature.

Answer and review

Answer **(5)** Official marking scheme

Rate = k[A]^m, and only k depends strongly on temperature (Arrhenius). If T drifted between runs, rate changes would reflect k as well as concentration, and the order would be wrong. For an elementary reaction the order and mechanism are fixed, and E_a is treated as constant. Only (d) is true, so the code is (5).

RB U11 §1.8 · p. 53 RB U11 §1.6 · p. 16

Question 35 · Q31–40 · response code

Which of the following statement/s is/are **true** regarding ethene and ethyne?

- CaC_2 reacts with water to form ethyne.
- CaC_2 reacts with water to form ethene.
- Ethene reacts with ammoniacal $AgNO_3$ to give a precipitate.
- Ethyne reacts with ammoniacal Cu_2Cl_2 to give a precipitate.

Answer and review

Answer **(4)** Official marking scheme

$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + HC{\equiv}CH$, so (a) is true and (b) false. Only terminal alkynes, with their weakly acidic ≡C–H, form precipitates with ammoniacal $AgNO_3$ (white Ag_2C_2) and ammoniacal Cu_2Cl_2 (red Cu_2C_2); ethene has no such hydrogen. (d) and (a) are true: code (4).

RB U8 §2.3 · p. 41 RB U8 §2.2 · p. 33

Question 36 · Q31–40 · response code

Which of the following statement/s is/are **true** with regard to halogens?

- The boiling points of halogens increase down the group.
- Unlike other halogens, fluorine always has an oxidation state of (−1) except in F_2.
- All halogens are good reducing agents.
- Although fluorine is the most reactive of all the elements in the Periodic Table, it does not react with inert gases.

Answer and review

Answer **(1/5)** Official marking scheme

The official scheme accepts (1), (5) or both. (a) is true: London forces grow with molecular size, so boiling points rise from F_2 to I_2. (b) is true because fluorine, the most electronegative element, cannot have a positive oxidation state; the scheme also accepts code (5) presumably because the wording "always … except in F_2" was open to objection, leaving only (a) clearly true. (c) is false (halogens are oxidizing agents) and (d) is false: F_2 reacts with Xe and Kr (e.g. XeF_2, XeF_4, XeF_6).

RB U6 §4.7 · p. 149 RB U6 §4.8 · p. 152

Question 37 · Q31–40 · response code

For the reaction C(s) + CO_2(g) ⇌ 2CO(g) occurring in a closed rigid container, percentage yields of CO(g) at 700 °C and 800 °C are 60% and 80% respectively. Which of the following statement/s is/are **correct** regarding the above reaction?

- The reaction is endothermic.
- The reaction is exothermic.
- Reverse reaction is favoured by decreasing the temperature.
- Equilibrium can be shifted towards the reactants by removing C(s).

Answer and review

Answer **(5)** Official marking scheme

The yield of CO rises with temperature, so K increases with T and the forward reaction is endothermic (a); by Le Chatelier's principle lowering the temperature favours the exothermic reverse reaction (c). C(s) is a pure solid and does not appear in K, so removing some of it (while some remains) does not shift the equilibrium. (a) and (c) are true, a pair not in codes (1)–(4), so the answer is (5).

RB U12 §2.1 · p. 76

Question 38 · Q31–40 · response code

Cyclopropane → propene is an elementary reaction.

Which of the following statement/s is/are **correct** regarding the above reaction?

- Half life of the reaction depends on cyclopropane concentration.
- Rate of the reaction does not depend on propene concentration.
- The fraction of cyclopropane molecules having energy greater than the activation energy increases with increasing temperature.

- Reaction occurs via a bimolecular collision (molecularity = 2).

Answer and review

Answer **(2)** Official marking scheme

As an elementary step with one reactant molecule, the isomerisation is unimolecular (molecularity 1) and first order: rate = k[cyclopropane]. The first-order half-life (ln 2/k) is independent of concentration, and the product does not appear in the rate law. A higher temperature shifts the Maxwell–Boltzmann distribution so a larger fraction of molecules exceeds E_a. (b) and (c) are true: code (2).

RB U11 §1.10 · p. 57 RB U11 §1.7.2 · p. 28 RB U11 §1.8 · p. 53

Question 39 · Q31–40 · response code

Which of the following statement/s is/are **true** regarding 3-hexene?

- Does not show geometric isomerism.
- Shows optical isomerism.
- The compound obtained when reacted with H_2/Pd does not show optical isomerism.
- The compound obtained when reacted with HBr shows optical isomerism.

Answer and review

Answer **(3)** Official marking scheme

$CH_3CH_2CH{=}CHCH_2CH_3$ has two different groups on each double-bond carbon, so it has cis/trans isomers, and it has no chiral carbon; (a) and (b) are false. H_2/Pd gives hexane, which is achiral (c true). HBr gives 3-bromohexane, $CH_3CH_2CHBrCH_2CH_2CH_3$, whose C-3 carries H, Br, ethyl and propyl, so it is chiral (d true). Code (3).

RB U7 §1.4 · p. 21 RB U8 §2.2 · p. 33

Question 40 · Q31–40 · response code

Which of the following statements is/are **correct** with regard to the nitrogen cycle?

- N_2 in the atmosphere is fixed only by atmospheric and industrial fixation.
- N_2 is reduced during atmospheric fixation.
- N_2 is oxidized during industrial fixation.
- Nitrates and nitrites formed during atmospheric fixation are utilized by plants to make proteins when the rainfall deposit them on the ground.

Answer and review

Answer **(5)** Official marking scheme

(a) is false because biological fixation (e.g. Rhizobium in legume root nodules) also fixes N_2. In atmospheric (lightning) fixation N_2 is oxidized to NO (N: 0 → +2), and in industrial fixation (Haber process) N_2 is reduced to NH_3 (0 → −3), so (b) and (c) are both reversed. Only (d) is true, so the code is (5). The nitrogen cycle as such is not treated in the current Resource Book; the Haber process is.

RB U14 §1.6 · p. 21 RB U6 §4.5 · p. 136

Questions 41–50: statement pairs

Response	First statement	Second statement
(1)	True	True, and correctly explains the first statement
(2)	True	True, but does not explain the first statement correctly
(3)	True	False
(4)	False	True
(5)	False	False

Question 41 · Q41–50 · statement pair

Statement 1

$BaCO_3$ is more thermally stable than $MgCO_3$.

Statement 2

Polarizing power of group two cations decreases down the group.

Answer and review

Answer **(1)** Official marking scheme

Down Group 2 the cations become larger, so their polarizing power falls and they distort the CO_3^{2-} ion less; the carbonate therefore needs a higher temperature to decompose to MO + CO_2. Both statements are true and the second explains the first.

RB U6 §4.2 · p. 126 RB U2 §2.4 · p. 75

Question 42 · Q41–50 · statement pair

Statement 1

The lone pair of electrons on nitrogen in an amine has a lower tendency to form a bond with H^+, than the lone pair of electrons on oxygen in an alcohol.

Statement 2

Nitrogen is less electronegative than oxygen.

Answer and review

Answer **(4)** Official marking scheme

Because nitrogen is less electronegative than oxygen, it holds its lone pair less tightly and donates it to H^+ more readily; amines are much stronger bases than alcohols. The first statement is false and the second is true.

RB U10 §4.2 · p. 77 RB U9 §3.1 · p. 54

Question 43 · Q41–50 · statement pair

Statement 1

A reaction at equilibrium can be driven forward (i.e. shift of equilibrium point to the right) by adding a catalyst.

Statement 2

The catalyst provides a pathway with a low activation energy only to the forward reaction.

Answer and review

Answer **(5)** Official marking scheme

A catalyst lowers the activation energy of the forward and reverse reactions by the same amount, so both rates increase equally: equilibrium is reached faster but its position (and K) is unchanged. Both statements are false.

RB U11 §1.9 · p. 54 RB U12 §2.1 · p. 76

Question 44 · Q41–50 · statement pair

Statement 1

CO_3^{2-} and SO_3^{2-} ions have similar shapes.

Statement 2

Central atoms of both CO_3^{2-} and SO_3^{2-} have lone pairs of electrons.

Answer and review

Answer **(5)** Official marking scheme

In CO_3^{2-} carbon has three VSEPR pairs and no lone pair, giving a trigonal planar ion; in SO_3^{2-} sulfur has three bonding pairs and one lone pair, giving a trigonal pyramidal ion. The shapes differ and only S carries a lone pair, so both statements are false.

RB U2 §2.3 · p. 52

Question 45 · Q41–50 · statement pair

Statement 1

The boiling point of $CH_3CH_2CH_2OH$ is higher than the boiling points of CH_3CH_2CHO and CH_3COCH_3.

Statement 2

The carbon oxygen double bond is stronger than the carbon oxygen single bond.

Answer and review

Answer **(2)** Official marking scheme

Propan-1-ol has an O–H group and forms hydrogen bonds between molecules, while propanal and propanone have only dipole–dipole and London forces, so the alcohol boils higher. C=O is indeed stronger than C–O, but boiling involves breaking intermolecular forces, not covalent bonds, so the second statement does not explain the first.

RB U2 §2.6 · p. 79 RB U9 §3.4 · p. 60

Question 46 · Q41–50 · statement pair

Statement 1

A reaction occurring spontaneously in an **isolated** system **always** has a negative Gibbs energy change.

Statement 2

A process in an **isolated** system cannot be changed from outside.

Answer and review

Answer **(4)** Official marking scheme

$\Delta G < 0$ is the criterion of spontaneity only at constant temperature and pressure; for an isolated system the criterion is an increase in entropy ($\Delta S > 0$), and the temperature of an isolated system can change during the process. So the first statement is false. The second is true: an isolated system exchanges neither energy nor matter with its surroundings.

RB U5 §2.4 · p. 53

Question 47 · Q41–50 · statement pair

Statement 1

Commonly used soap contain the sodium or potassium salts of fatty acids formed by the reaction of NaOH or KOH with oils and fats.

Statement 2

The reaction of an ester with aqueous NaOH or KOH gives the sodium or potassium salt of the carboxylic acid and the alcohol.

Answer and review

Answer **(1)** Official marking scheme

Oils and fats are triesters of glycerol with fatty acids. Their alkaline hydrolysis (saponification) gives glycerol and the sodium or potassium carboxylates, which are soap. Both statements are true and the second (the general ester reaction) explains the first.

RB U14 §1.4 · p. 14 RB U9 §3.6 · p. 70

Question 48 · Q41–50 · statement pair

Statement 1

C_6H_5Br does not react easily with NaOH to form C_6H_5OH.

Statement 2

The phenyl carbocation is very stable.

Answer and review

Answer **(3)** Official marking scheme

The C–Br bond in bromobenzene has partial double-bond character (the halogen lone pair overlaps with the ring π system), and the ring blocks backside attack, so neither S_{N2} nor S_{N1} occurs easily. The phenyl cation would be very unstable (the positive charge is in an sp^2 orbital that is not conjugated with the ring), so the second statement is false.

RB U8 §2.6 · p. 49

Question 49 · Q41–50 · statement pair

Statement 1

When an aqueous solution of a weak acid is diluted, both the fraction of dissociated acid molecules and pH of the medium are increased.

Statement 2

Dissociation of weak acid molecules occur in such a way that the acid dissociation constant K_a remains constant.

Answer and review

Answer **(1)** Official marking scheme

For HA, $K_a = c\alpha^2/(1 - \alpha) \approx c\alpha^2$. When c decreases, α must increase to keep K_a constant, but $[H^+] = c\alpha \approx \sqrt{(K_a\ c)}$ still falls, so the pH rises. Both statements are true and the constancy of K_a explains the change.

RB U12 §2.2 · p. 118

Question 50 · Q41–50 · statement pair

Statement 1

In the presence of sunlight CO_2 is fixed in green plants.

Statement 2

Increase of CO_2 level in the atmosphere cannot be controlled by green plants.

Answer and review

Answer **(3)** Official marking scheme

Photosynthesis fixes CO_2 into carbohydrates using light energy, so the first statement is true. Because plants remove CO_2 from the air, protecting forests and planting trees is one of the ways to control the rise in atmospheric CO_2, so the second statement is false.

RB U14 §1.13 · p. 58

Structured essay · answer all four

SEQ · Paper II Part A

Question 1 · Part A · structured essay

Source note: the collected paper does not include the pages for Question 1, so the question text is retyped from the official marking scheme. A tick (✓) for True and a cross (✗) for False can be accepted.

(a) [24 marks]

State whether the following statements are **true** or **false**. (Reasons are **not** required.)
(i) The polarizability of halide ions increases with increasing size.
(ii) The O–N–O bond angle of NO_2 is greater than that of NO_2^-.
(iii) London dispersion forces among CCl_4 molecules are smaller than the London dispersion forces among SO_3 molecules.
(iv) The shape of the HSO_4^- ion is trigonal bipyramidal.
(v) All 3d atomic orbitals of an atom are represented by quantum numbers (n, l, m_l) 3, 2, 1.
(vi) The addition of an electron to a gaseous phosphorus atom is an exothermic process whereas for a gaseous nitrogen atom it is endothermic.

Answer

(i) True (ii) True (iii) False (iv) False (v) False (vi) True (04 marks × 6 = 24 marks) · 1(a): 24 marks

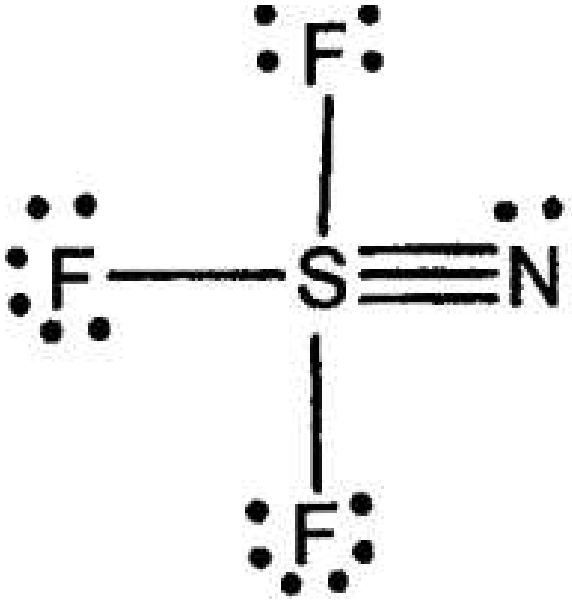
Review.

(i) Larger, more diffuse electron clouds are easier to distort. (ii) NO_2 has only one unpaired electron on N, which repels the bonding pairs less than the lone pair of NO_2^-, so its angle (about 134°) is larger than that of NO_2^- (about 115°). (iii) CCl_4 has far more electrons than SO_3 and so stronger London forces. (iv) HSO_4^- has four electron pairs around S: tetrahedral. (v) The five 3d orbitals have $m_l = -2, -1, 0, +1, +2$, so only one of them is (3, 2, 1). (vi) Electron gain by P is exothermic, whereas for N, whose half-filled 2p subshell is stable, it is endothermic.

(b) [52 marks]

(i) Draw the **most** acceptable Lewis structure for the molecule SF_3N.

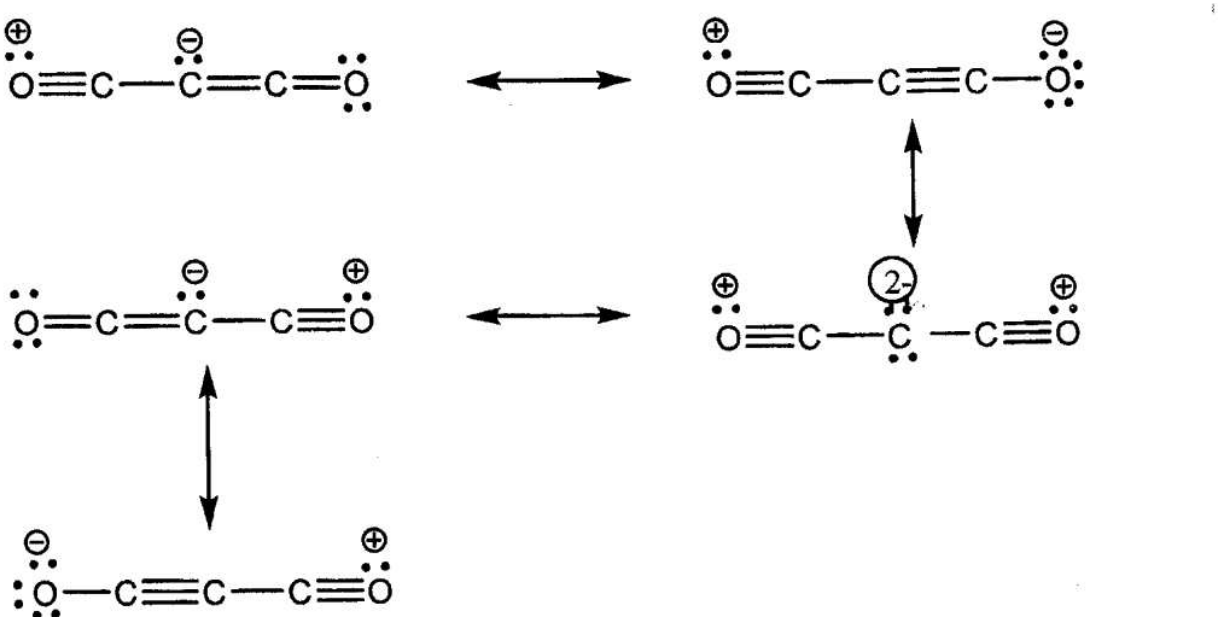
Answer



Three S–F single bonds and an S≡N triple bond; every F carries three lone pairs, N carries one lone pair, and S has no lone pair (six bonding pairs, zero formal charges). (08 marks)

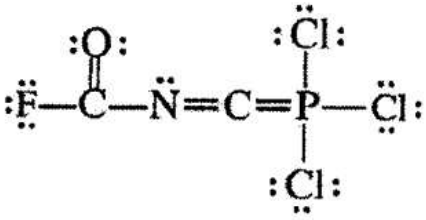
(ii) The most stable Lewis structure for the molecule C_3O_2 (carbon suboxide) is shown below. Draw another **two** Lewis structures (resonance structures) for this molecule.
(Note: Marks will not be awarded for Lewis structures drawn with octet rule violated.)
O=C=C=C=O

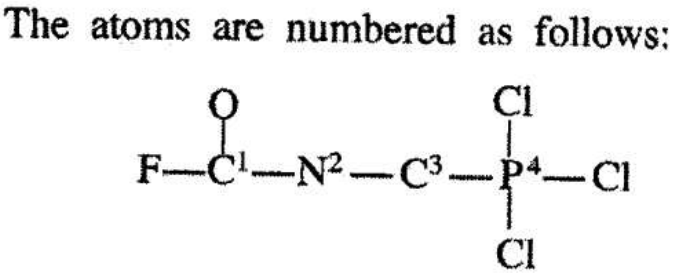
Answer



Any two of the following resonance structures (lone pairs on O and C as needed): $O^{+}\equiv C–C^{-}=C=O$; $O^{+}\equiv C–C\equiv C–O^{-}$; $O=C=C^{-}–C\equiv O^{+}$; $O^{+}\equiv C–C^{2-}–C\equiv O^{+}$ (C^{2-} with two lone pairs); ^−O–C≡C–C≡O^{+}. (07 marks × 2 = 14 marks)
Resonance arrows are not required for award of marks.

(iii) Based on the Lewis structure given below, state the following regarding the C, N and P atoms given in the table below.
I. VSEPR pairs around the atom
II. electron pair geometry around the atom
III. shape around the atom
IV. hybridization of the atom
The atoms are numbered as follows: F–C^{1}(O)–N^{2}–C^{3}–P^{4}(Cl)(Cl)–Cl (the structure is given in the figure).





Lewis structure (left) and numbering of the atoms (right)

Answer

	C^{1}	N^{2}	C^{3}	P^{4}
I. VSEPR pairs	3	3	2	4
II. electron pair geometry	trigonal planar	trigonal planar	linear	tetrahedral
III. shape	trigonal planar	angular / V	linear	tetrahedral
IV. hybridization	sp^{2}	sp^{2}	sp	sp^{3}

(01 mark × 16 = 16 marks)

(iv) Identify the atomic/hybrid orbitals involved in the formation of the following σ bonds in the Lewis structure given in part (iii) above. (Numbering of atoms is as in part (iii).)
I. F–C^1 II. C^1–N^2 III. N^2–C^3 IV. C^3–P^4 V. P^4–Cl

Answer

I. F: 2p or sp^3; C^1: sp^2
II. C^1: sp^2; N^2: sp^2
III. N^2: sp^2; C^3: sp
IV. C^3: sp; P^4: sp^3
V. P^4: sp^3; Cl: 3p or sp^3 (01 mark × 10 = 10 marks)

(v) Identify the atomic orbitals involved in the formation of the following π bonds in the Lewis structure given in part (iii) above. (Numbering of atoms is as in part (iii).)
I. N^2–C^3 II. C^3–P^4

Answer

I. N^2: 2p; C^3: 2p
II. C^3: 2p; P^4: 3d (01 mark × 4 = 04 marks) (Award 01 mark for any answer OR no answer for P^4.) · 1(b): 52 marks

Review.

The octet rule is not obeyed by S in SF_3N or P in the P-compound: the third-period atoms expand their octets, so S≡N with zero formal charges is preferred, and a P=C π bond has to use a P 3d (or antibonding) orbital. Count electron pairs (a double or triple bond counts as one pair) to get the geometry, then match the hybridization (2 pairs sp, 3 sp^2, 4 sp^3); an angular N^2 is the shape because one of its three pairs is a lone pair. The use of 3d orbitals for π bonding is a simplified old-syllabus treatment, so the P^4 part is not examined in this form in the current syllabus.

(c) [24 marks]

Arrange the following in the **increasing** order of the property indicated in parenthesis. (Reasons are **not** required.)
(i) B, Na, P, Be, N (first ionization energy)
(ii) NH_3, NOCl, NO_2Cl, NH_4^+, F_3C–NC (electronegativity of nitrogen)
(iii) Quantum numbers of electrons in an atom (n, l, m_l, m_s): (3, 1, 0, −½), (3, 0, 0, +½), (2, 0, 0, +½), (2, 1, +1, +½), (3, 2, −1, +½) (energy of electron)

Answer

(i) Na < B < Be < P < N (08 marks)
(ii) NH_3 < NH_4^+ < NOCl < NO_2Cl < CF_3NC (08 marks)
Note: NH_3 < NOCl < NH_4^+ < NO_2Cl < CF_3NC (only for this year)
(iii) (2, 0, 0, +½) < (2, 1, +1, +½) < (3, 0, 0, +½) < (3, 1, 0, −½) < (3, 2, −1, +½) (08 marks) · (08 marks × 3 = 24 marks) · 1(c): 24 marks

Review.

(i) Be and N are above B and P respectively because of the filled 2s and half-filled 2p subshells. (ii) Electronegativity of an atom rises with its oxidation state/positive character: N bonded to more electron-withdrawing atoms (O, Cl, F) is more electronegative. (iii) Subshell energy follows (n + l): 2s < 2p < 3s < 3p < 3d in a many-electron atom; the spin quantum number does not change the energy. Deducing the electronegativity of N in different molecules is beyond the current syllabus. The scheme also accepts a second order for (ii) ("only for this year").

Read: RB U1 §1.6 · p. 32 RB U2 §2.1 · p. 44 RB U2 §2.3 · p. 52 RB U1 §1.3 · p. 17

Question 2 · Part A · structured essay

Source note: the collected paper has Question 2 from part (a)(v) onwards (pages 4 and 5 of the paper); the earlier parts are retyped from the official marking scheme.

(a) [60 marks]

X

p

X

Y

X

Y

Y

X

Y

X

Y

Answer

X

2

(05)

Y

3

(05)

(ii) The diatomic gas of **X** is generally considered as inert. Briefly explain.

Answer

N_2 contains a triple bond. (03) Therefore it has a high bond dissociation enthalpy. (03)

(iii) Write the chemical formulae of **three** oxides of **X**, and indicate the oxidation state of **X** in each compound.

Answer

N_2O +1; NO +2; N_2O_3 +3; NO_2 / N_2O_4 +4; N_2O_5 +5 (any three) (03 + 03 + 03)
Note: award the mark for the oxidation state only if the formula is correct. Mark distribution: formula (02), oxidation state (01).

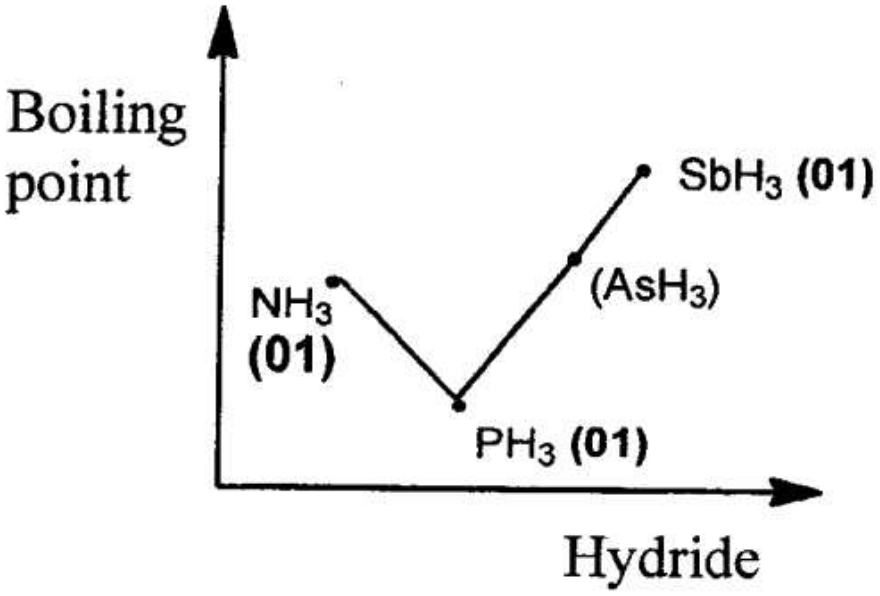
(iv) In each of the following instances, give a balanced chemical equation to indicate the action of **Y**.
I. **Y** as an oxidizing agent
II. **Y** as a reducing agent

Answer

I. Any one: $2Na(s) + 2NH_3(l) \rightarrow 2NaNH_2(s) + H_2(g)$; or $3Mg(s) + 2NH_3(l) \rightarrow Mg_3N_2(s) + 3H_2(g)$; or $6Li(s) + 2NH_3(l) \rightarrow 2Li_3N(s) + 3H_2(g)$ (03)
II. Any one: $3Cl_2(g) + 2NH_3(g) \rightarrow N_2(g) + 6HCl(g)$; or $3Cl_2(g) + 8NH_3(g) \rightarrow N_2(g) + 6NH_4Cl(s)$; or $3Cl_2(g) + NH_3(g) \rightarrow NCl_3(l) + 3HCl(g)$; or $3CuO(s) + 2NH_3(g) \rightarrow N_2(g) + 3Cu(s) + 3H_2O(g)$; or $3O_2(g) + 4NH_3(g) \rightarrow 2N_2(g) + 6H_2O(l)$; or $5O_2(g) + 4NH_3(g) \rightarrow 4NO(g) + 6H_2O(l)$ (03)
Note: physical states are not required for award of marks.

(v) Consider the hydrides of the elements in the group to which **X** belongs, which are analogous to **Y**. Sketch the variation in boiling points of these hydrides (including **Y**) in the graph below. In your sketch indicate the hydrides using their chemical formulae. (**Note**: Values of boiling points are **not** required.)
(axes: boiling point against hydride)

Answer



NH_3 is relatively high, the boiling point falls to a minimum at PH_3, then rises through AsH_3 to a maximum at SbH_3 (NH_3 lies between PH_3 and SbH_3). (05)
Note: shape (02); labelling (01 each for NH_3, PH_3, SbH_3). The shape needs to be correct for award of marks for labelling (i.e. maximum SbH_3; minimum PH_3; in between NH_3).

(vi) Give reasons for the variation in boiling points in part (v) above.

Answer

As molecular mass / size increases, boiling point increases. (03) But with NH_3 the boiling point is higher than expected because of H-bonding between NH_3 molecules. (03)

(vii) I. Write what you would observe when an excess of an aqueous solution of **Y** is added to a solution of $Al_2(SO_4)_3$.
II. Write the chemical formula of the species that gives rise to your observation in part I above.

Answer

I. White precipitate / white gelatinous precipitate (03)
II. $Al(OH)_3$ (03)

(viii) Give **one chemical** test to identify **Y**.

Answer

Any one: test with Nessler's reagent, observation brown precipitate / brown coloration; OR test with HCl vapour, white fumes; OR test with red litmus, red litmus turns blue; OR add to a solution of Cu(II) ions, deep blue solution. (03 for the test + 03 for the observation)

(ix) **Z** is an oxo-acid of **X** and a strong oxidizing agent.
I. Identify **Z**.
II. State the products obtained when hot concentrated **Z** reacts with sulphur.

Answer

I. HNO_3 or nitric acid (03)
II. H_2SO_4(l), NO_2(g), H_2O(l) (01 + 01 + 01) (physical states are not required) · 2(a): 60 marks

Review.

NH_3 is the Group 15 hydride: N_2 is inert because of its strong N≡N bond; NH_3 is reduced by Na or Mg (H^+ is reduced, so NH_3 acts as an oxidizing agent) and oxidized by Cl_2, CuO or O_2. In the boiling-point trend, London forces rise down the group (PH_3 < AsH_3 < SbH_3) but NH_3 is anomalously high because of hydrogen bonding. Excess NH_3(aq) does not dissolve $Al(OH)_3$ (unlike $Zn(OH)_2$), a typical mistake. Hot conc. HNO_3 oxidizes S to H_2SO_4: $S + 6HNO_3 \rightarrow H_2SO_4 + 6NO_2 + 2H_2O$. The Nessler's reagent test is not in the current Resource Book; the HCl vapour and litmus tests are the usual current-syllabus tests.

(b) [40 marks]

A

B

p

A

A

A

B

B

A

B

Answer

A

2

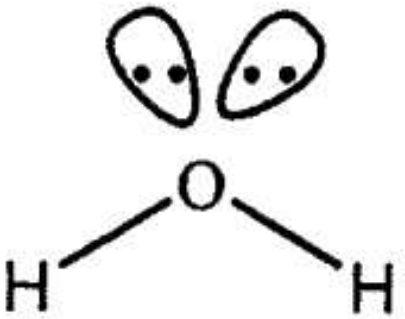
B

2

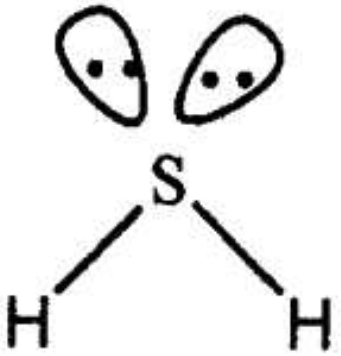
(04 + 04)

(ii) Sketch the shapes of **A** and **B** showing lone pairs of electrons where necessary.

Answer



A



B

Both are angular (V-shaped) with two lone pairs on the central atom (O or S). (03 + 03)

(iii) Giving reasons, state whether **A** or **B** has the larger bond angle.

Answer

Oxygen is more electronegative than sulphur. (01) Therefore the bonding pairs of electrons are located closer to the oxygen atom in H_2O than to the sulphur atom in H_2S. (01) Therefore the repulsion between the bonding electron pairs is greater in H_2O than in H_2S. (01) The bond angle of **A** (H_2O) is greater than the bond angle of **B** (H_2S). (02)

(iv) In each of the following instances, give a balanced chemical equation to indicate the action of **A**.
I. **A** as an acid
II. **A** as a base

Answer

I. $H_2O(l) + NH_3(aq) \rightleftharpoons NH_4\text{^}+(aq) + OH^-(aq)$ (or $NH_4OH(aq)$); OR $2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$ (or any other metal that reacts with water liberating H_2) (03) (→ accepted)
II. $H_2O(l) + HCl(aq) \rightarrow H_3O^+(aq) + Cl^-(aq)$; OR $H_2O(l) + CH_3COOH(aq) \rightarrow H_3O^+(aq) + CH_3COO^-(aq)$ (03)

(v) Write the balanced chemical equation for the reaction of **B** with aqueous lead acetate.

Answer

$Pb(CH_3COO)_2(aq) + H_2S(g) \rightarrow PbS(s) + 2CH_3COOH(aq)$ (OR $2CH_3COO^- + 2H^+$) (03)

(vi) I. Write what you would observe when **A** and **B** are added **separately** to an acidified solution of $BiCl_3$.
with **A** (excess): ..... with **B**: .....
II. Write balanced chemical equations for your observations in part I above.

Answer

I. With **A** (excess): white precipitate / white solid / white turbidity (03); with **B**: black precipitate (03)
II. $BiCl_3(aq) + H_2O(l) \rightleftharpoons BiOCl(s) + 2HCl(aq)$ (03) (→ can be accepted); $2BiCl_3(aq) + 3H_2S(g) \rightarrow Bi_2S_3(s) + 6HCl(aq)$ (03)
Note: physical states are not required for parts (iv), (v), (vi). · 2(b): 40 marks

Review.

Both H_2O and H_2S have 4 electron pairs (2 bonding + 2 lone) and are bent; the angle is larger in H_2O (104.5° versus about 92°) because O is more electronegative, so the bonding pairs are held nearer to the central atom and repel one another more strongly. Water is amphiprotic: it is an acid towards NH_3 or metals and a base towards HCl. Hydrolysis of $BiCl_3$ gives white BiOCl (reversed by adding acid), while H_2S gives black Bi_2S_3 (as it does with Pb^{2+}). The hydrolysis of $BiCl_3$ to BiOCl is covered in the current Resource Book (Unit 6, p. 152).

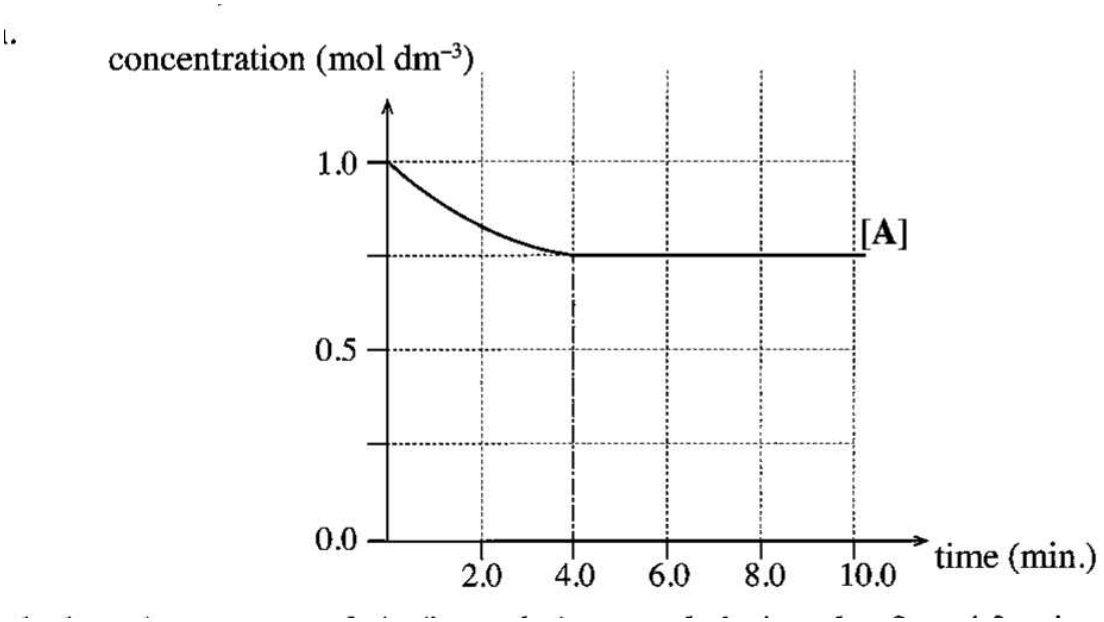
Read: RB U6 §4.5 · p. 136 RB U6 §4.6 · p. 141 RB U2 §2.6 · p. 79 RB U14 §1.6 · p. 21

Question 3 · Part A · structured essay

Source note: the stem, the graph and parts (i) and (ii) are from the collected paper (page 5); parts (iii) to (viii) are retyped from the official marking scheme. Part marks: (i) 10, (ii) 10, (iii) 15, (iv) 20, (v) 15, (vi) 10, (vii) 15, (viii) 5.

(a) [100 marks]

The reaction A + B ⇌ 2C + D (elementary in both directions) was carried out at 25 °C. Initially, the reaction mixture was made by dissolving 0.10 mol of A and 0.10 mol of B in distilled water (total volume 100.00 cm^3). Variation in the concentration of A in this solution with time is shown in the graph.



−3

(i) Calculate the amount of A (in moles) reacted during the first 4.0 minutes of the reaction.

Answer

Initial amount of A = 0.1 mol
Concentration of A after 4.0 min = 0.75 mol dm^{-3}
Amount of A reacted = (1.0 − 0.75) × 100 × 10^{-3} mol = (0.1 − 0.075) mol (04 + 01)
= **0.025 mol** (04 + 01)

(ii) Would the rate of the forward reaction be less than the rate of the reverse reaction after 4.0 minutes? Explain your answer.

Answer

No. (05) The forward and reverse rates will be equal after 4.0 min. OR the reaction has reached equilibrium. (05)

(iii) Given that the rate constant of the forward reaction ($k_{forward}$) is 18.57 mol^{-1} dm^3 min^{-1}, calculate the initial rate of the forward reaction.

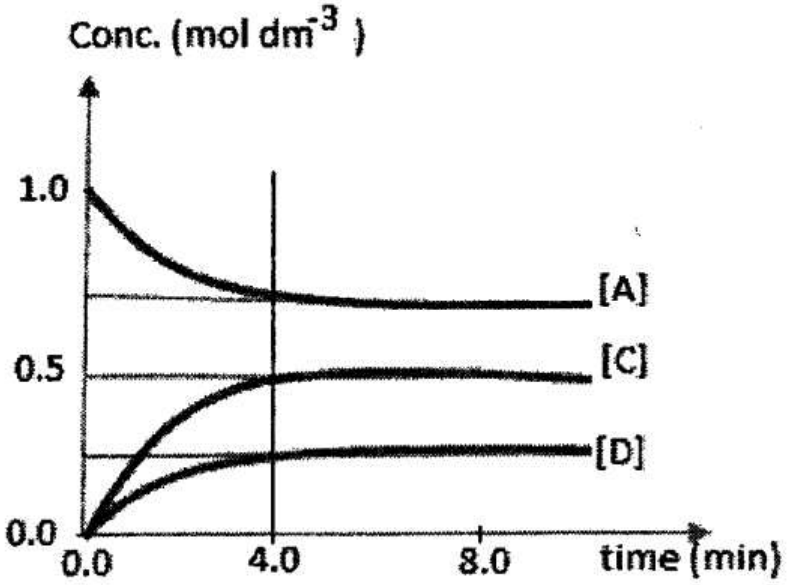
Answer

Rate of the forward reaction, $R_f = k[A][B]$ (05)
Initial rate of the forward reaction = 18.57 mol^{-1} dm^3 min^{-1} × 1.0 mol dm^{-3} × 1.0 mol dm^{-3} (04 + 01)
= **18.57 mol dm^{-3} min^{-1}** (04 + 01)

(iv) Calculate the concentrations of C and D at equilibrium. **Draw** the relevant curves showing the variation of the concentrations of C and D with time in the above graph and **label** them.

Answer

[C] at equilibrium = 2 × 0.025 mol / (100.00 × 10^{-3} dm^3) = **0.50 mol dm^{-3}** (02 + 01)(02 + 01)
[D] at equilibrium = 0.025 mol / (100.00 × 10^{-3} dm^3) = **0.25 mol dm^{-3}** (02 + 01)(02 + 01)
Curve C (04); curve D (04): both start from zero and rise, becoming flat at 4.0 min at 0.50 and 0.25 mol dm^{-3} respectively.



Concentration curves of A, C and D

Note: do not award marks if the curves do not become flat after 4.0 min, if the curves do not reach the respective concentrations at 4.0 min, if the curves for C and D are not labelled and if the curves do not start from zero.

(v) Write the expression for the equilibrium constant K_c of the above reaction and calculate its value.

Answer

$K_c = [C]^2[D] / ([A][B])$ (05)
K_c = (0.5 mol dm^{-3})^2 (0.25 mol dm^{-3}) / ((0.75 mol dm^{-3})(0.75 mol dm^{-3})) (04 + 01)
K_c = **1.11 × 10^{-1} mol dm^{-3}** (04 + 01)

(vi) Calculate the value of the rate constant ($k_{reverse}$) of the reverse reaction.

Answer

Using $K_c = k_f / k_r$, k_r = 18.57 mol^{-1} dm^3 min^{-1} / (1.11 × 10^{-1} mol dm^{-3}) (04 + 01)
k_r = **1.67 × 10^2 mol^{-2} dm^6 min^{-1}** (04 + 01)

(vii) After reaching equilibrium, the volume of the solution was doubled by adding 100.00 cm^3 of distilled water. Predict the direction of the net reaction soon after doubling the volume of the solution, by means of a

suitable calculation.

Answer

New concentrations: [A] = 0.75/2, [B] = 0.75/2, [C] = 0.5/2, [D] = 0.25/2 mol dm^{-3}
Rate of forward reaction, R_f = 18.57 mol^{-1} dm^3 min^{-1} × (0.75/2 mol dm^{-3})^2 = 2.61 mol dm^{-3} min^{-1} (05 + 01)
Rate of reverse reaction, R_r = 1.67 × 10^2 mol^{-2} dm^6 min^{-1} × (0.5/2 mol dm^{-3})^2 (0.25/2 mol dm^{-3}) = 1.30 mol dm^{-3} min^{-1} (05 + 01)
$R_f > R_r$: the net reaction occurs in the forward direction. (03)
Alternate answer: Q = (0.5/2 mol dm^{-3})^2 (0.25/2 mol dm^{-3}) / (0.75/2 mol dm^{-3})^2 (05 + 01); Q = 0.056 mol dm^{-3} (05 + 01); Q < K, therefore the net reaction occurs in the forward direction. (03)

(viii) Consider that the above experiment was conducted at a temperature lower than 25 °C. How would this affect the rate of the reverse reaction? Explain your answer giving reasons.

Answer

The rate of the reverse reaction will decrease. (01) Because the fraction of molecules having sufficient energy to overcome the activation energy barrier decreases (02) and the collision rate decreases. (02) · Q3: 100 marks

Review.

For an elementary reaction the rate law follows the stoichiometry ($R_f = k_f[A][B]$, $R_r = k_r[C]^2[D]$) and at equilibrium $R_f = R_r$, so $K_c = k_f/k_r$. Work in concentrations (mol dm^{-3}), not moles: the volume is 0.100 dm^3, so 0.025 mol of A reacted, giving 0.050 mol C and 0.025 mol D. Checking: $K_c = 0.5^2 \times 0.25 / 0.75^2 = 0.111$ mol dm^{-3}; $k_r = 18.57/0.111 = 167$. On dilution the concentrations of products (higher order in the numerator) fall faster, so Q = 0.056 < K_c and the reaction shifts forward. Common mistakes: forgetting the factor 2 for C, using moles instead of concentrations, and wrong units for k_r.

Read: RB U12 §2.1 · p. 76 RB U11 §1.6 · p. 16 RB U11 §1.8 · p. 53 RB U11 §1.5 · p. 15

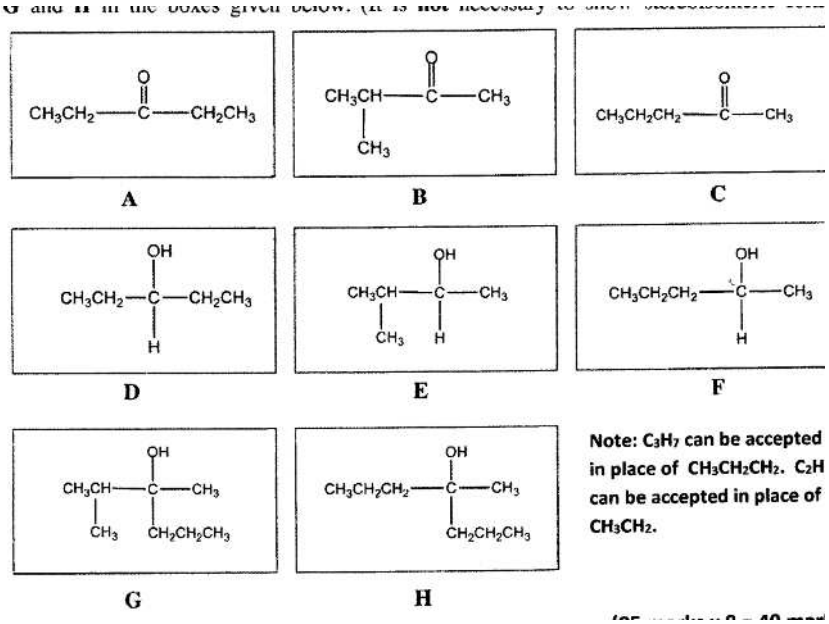
Question 4 · Part A · structured essay

Source note: the collected paper has no page of Question 4, so the question text is retyped from the official marking scheme. The scheme does not reprint the wording of part (c); it is reconstructed from the answer (marks and steps as in the scheme) and is marked as such below.

(a) [45 marks]

(i) Compounds **A**, **B** and **C** are structural isomers of each other having the molecular formula $C_5H_{10}O$. All three compounds give yellow-orange precipitates with 2,4-DNP. None of them give a silver mirror in the silver mirror test. When **A**, **B** and **C** were separately reacted with $NaBH_4$, compounds **D**, **E** and **F** respectively were obtained. Only **E** and **F** showed optical isomerism. When **B** and **C** were separately reacted with $CH_3CH_2CH_2MgBr$ followed by hydrolysis, compounds **G** and **H** respectively were obtained. Only **G** showed optical isomerism. Draw the structures of **A**, **B**, **C**, **D**, **E**, **F**, **G** and **H** in the boxes given below. (It is **not** necessary to show stereoisomeric forms.)

Answer



A

3

2

2

3

B

3

2

3

C

3

2

2

3

D

3

2

2

3

E

3

2

3

F

3

2

2

3

G

3

2

3

2

2

3

H

3

2

2

3

2

2

3

(05 marks × 8 = 40 marks)

3

7

3

2

2

2

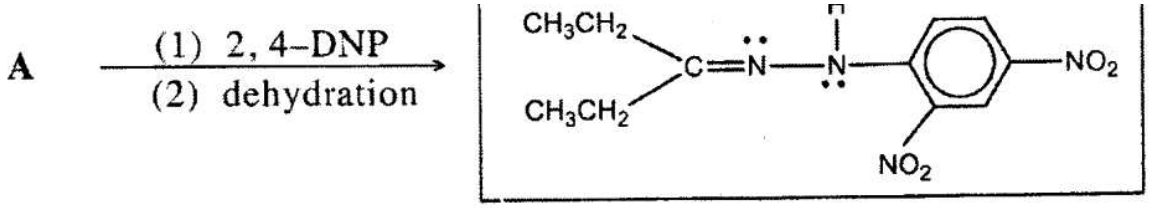
5

3

2

(ii) Draw the structure of the product of the following reaction: **A** → (1) 2,4-DNP; (2) dehydration

Answer



one pairs are not necessary. Award mark if B or C is used instead of A with the corresponding product. 4.(a):

$(CH_3CH_2)_2C{=}N{-}NH{-}C_6H_3(NO_2)_2$ (the 2,4-dinitrophenylhydrazone of pentan-3-one) (05 marks)
Note: lone pairs are not necessary. Award the mark if **B** or **C** is used instead of **A** with the correct corresponding product. · 4(a): 45 marks

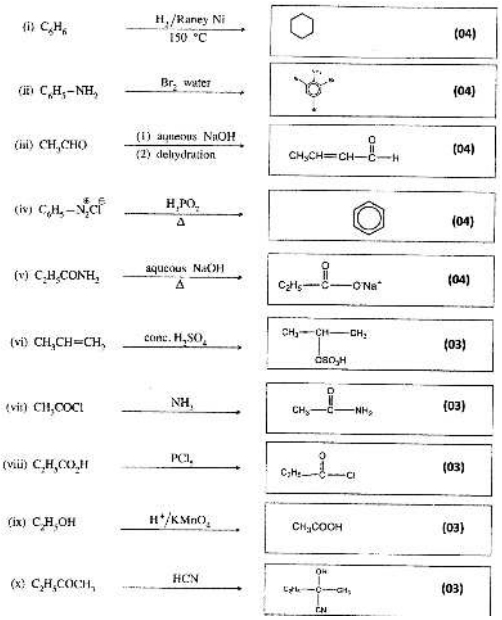
Review.

All three isomers are ketones (2,4-DNP positive, Tollens negative); $NaBH_4$ reduces them to secondary alcohols, and a secondary alcohol is chiral only if its two alkyl groups differ (D, from the symmetrical pentan-3-one, is not). Grignard addition to a ketone gives a tertiary alcohol; G (three different groups besides OH: CH_3, isopropyl, propyl) is chiral, whereas H has two identical propyl groups and is not. 2,4-DNP condensation (addition–elimination) gives a coloured hydrazone.

(b) [35 marks]

Draw the structure of the **major** organic **product** in each of the following reactions.
(i) $C_6H_6 \rightarrow H_2$/Raney Ni, 150 °C (ii) $C_6H_5{-}NH_2 \rightarrow Br_2$, water (iii) $CH_3CHO \rightarrow$ (1) aqueous NaOH, (2) dehydration (iv) $C_6H_5{-}N_2{\hat{}}{+}Cl^- \rightarrow H_3PO_2$, Δ (v) $C_2H_5CONH_2 \rightarrow$ aqueous NaOH, Δ (vi) $CH_3CH{=}CH_2 \rightarrow$ conc. H_2SO_4 (vii) $CH_3COCl \rightarrow NH_3$ (viii) $C_2H_5CO_2H \rightarrow PCl_5$ (ix) $C_2H_5OH \rightarrow H^+/KMnO_4$ (x) $C_2H_5COCH_3 \rightarrow HCN$

Answer



(i) cyclohexane (04) · (ii) 2,4,6-tribromoaniline (04) · (iii) $CH_3CH{=}CHCHO$ (but-2-enal) (04) · (iv) benzene (04) · (v) $C_2H_5COO{\hat{}}{-}Na^+$ (04) · (vi) $(CH_3)_2CHOSO_3H$ (03) · (vii) CH_3CONH_2 (03) · (viii) C_2H_5COCl (03) · (ix) CH_3COOH (03) · (x) $C_2H_5C(OH)(CN)CH_3$ (03)
Notes: (i) the structure showing hydrogens on the ring can be accepted. (iii) $CH_3CH{=}CHCHO$ can be accepted; no marks for $CH_3CH{=}CHCOH$. (iv) benzene ring structure can be accepted. (v) Charges on O and Na are not required for award of marks; no marks if given as O–Na. (vi) OSO_2OH can be accepted. (vii) CH_3CONH_2 can be accepted. (viii) C_2H_5COCl can be accepted. (ix) CH_3CO_2H can be accepted. · 4(b): 35 marks

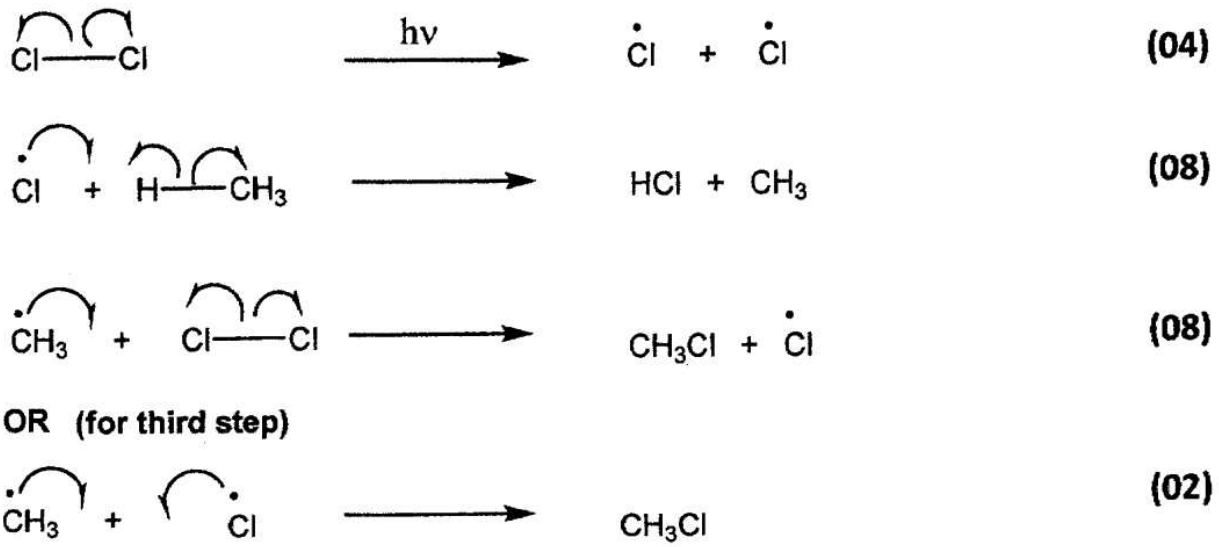
Review.

Typical reactions of the main functional groups: Br_2 water substitutes all three activated ring positions of aniline; H_3PO_2 replaces the diazonium group by H; alkaline hydrolysis of the amide gives the sodium carboxylate (and NH_3); electrophilic addition of conc. H_2SO_4 to propene follows Markovnikov's rule, giving the isopropyl hydrogensulphate; PCl_5 converts –COOH into –COCl; acidified $KMnO_4$ oxidizes ethanol fully to ethanoic acid; HCN gives a cyanohydrin. A common error in (iii) is to stop at the aldol (3-hydroxybutanal); the dehydration step gives the conjugated enal.

(c) [20 marks]

Give the free radical mechanism for the monochlorination of methane, $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$, in the presence of light (hν): the initiation step and the two propagation steps, using curved half arrows. (Wording reconstructed; the scheme reprints only the answer.)

Answer



Initiation: Cl–Cl → Cl· + Cl· (hν) (04)
Propagation 1: Cl· + H–CH_3 → HCl + ·CH_3 (08)
Propagation 2: ·CH_3 + Cl–Cl → CH_3Cl + Cl· (08)
OR (for the third step): ·CH_3 + ·Cl → CH_3Cl (02) · 4(c): 20 marks
Note: if no half arrows are drawn, deduct (01) mark once in each line. The radical needs to be shown for award of marks. Mark each step as an independent step.

Review.

Free-radical substitution of alkanes by Cl_2 proceeds by initiation (homolysis of Cl–Cl by light) and two propagation steps that regenerate Cl·. Use half-headed (fish-hook) arrows for single-electron movement. Common mistakes: full-headed arrows, omitting the radical dots, and treating the radical combination ·CH_3 + ·Cl (a termination step) as the third step, for which the scheme gives only 02 marks.

Read: RB U9 §3.4 · p. 60 RB U8 §2.2 · p. 33 RB U8 §2.4 · p. 44 RB U10 §4.3 · p. 78

Answer two from each part

Essay · Paper II Parts B and C

Part B

Question 5 · Part B · essay

Scheme note:

(a) [20 marks]

Consider the following reactions.
$M(CO_3)_2 \cdot nH_2O(s) \rightarrow M(CO_3)_2(s) + nH_2O(g)$
$M(CO_3)_2(s) \rightleftharpoons MO_2(s) + 2CO_2(g)$
A small amount (0.10 mol) of $M(CO_3)_2 \cdot nH_2O(s)$ is present in an evacuated rigid container of volume 0.08314 m^3. The temperature of the container was raised to 400 K. The metal carbonate, $M(CO_3)_2$ does not decompose at this temperature but the crystalline water evaporates completely. The pressure of the container was measured to be 1.60×10^4 Pa. Volume occupied by the solids is negligible.
Determine the value of 'n' in the formula $M(CO_3)_2 \cdot nH_2O(s)$.

Answer

$M(CO_3)_2 \cdot nH_2O(s) \rightarrow M(CO_3)_2(s) + nH_2O(g)$; the amount of $M(CO_3)_2 \cdot nH_2O$ used = 0.10 mol; the water is completely evaporated.
Using PV = nRT (05): $n_{H2O} = (1.60 \times 10^4 \text{ Pa} \times 0.08314 \text{ m}^3)/(8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 400 \text{ K})$ (04 + 01) = 0.40 mol (04 + 01)
0.10 mol of $M(CO_3)_2 \cdot nH_2O(s)$ has generated 0.40 mol of H_2O. Therefore **n = 4** (04 + 01) · 5(a): 20 marks

Review.

Principle: the ideal gas equation applied to a rigid container in which the only gas is the water vapour.
Method: $n(H_2O) = PV/RT$, then divide by the 0.10 mol of hydrate. Common mistakes: using the volume in dm^3 or the pressure in kPa with R = 8.314 J mol^{-1} K^{-1} (use m^3 and Pa together), or forgetting that the solids occupy no volume and exert no pressure. Topic is in the current syllabus (Resource Book, gaseous state).

(b) [65 marks]

The temperature of the above system was then increased to 800 K. It was observed that some amount of the solid metal carbonate is decomposed and is in equilibrium with the gas phase. The pressure of the container was measured to be 4.20×10^4 Pa.
(i) Calculate the partial pressure of water vapour in the container at 800 K.

Answer

$P_{H2O} = n_{H2O}RT/V = (0.4 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 800 \text{ K})/0.08314 \text{ m}^3$ (04 + 01) $= 3.20 \times 10^4$ Pa (04 + 01)
Alternate answer 01: total pressure at 800 K, $P_T = 4.20 \times 10^4$ Pa; total number of moles $n_T = (4.20 \times 10^4 \text{ Pa} \times 0.08314 \text{ m}^3)/(8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 800 \text{ K}) = 0.525$ mol (04 + 01); partial pressure of water $= P_T \times (n_{H2O}/n_T) = 3.20 \times 10^4$ Pa (04 + 01)
Alternate answer 02: because V and n_{H2O} are constant, at 800 K the partial pressure of water $= 2 \times 1.60 \times 10^4$ Pa (04 + 01) $= 3.20 \times 10^4$ Pa (04 + 01)

(ii) Calculate the partial pressure of CO_2 in the container at 800 K.

Answer

$P_{CO2} = P_{total} - P_{H2O} = 4.2 \times 10^4 \text{ Pa} - 3.2 \times 10^4 \text{ Pa}$ (04 + 01) $= 1.00 \times 10^4$ Pa (04 + 01)

(iii) Write an expression for the pressure equilibrium constant, K_p for the decomposition of $M(CO_3)_2(s)$. Calculate K_p at 800 K.

Answer

$K_p = P^2_{CO2}$ (05)
$K_p = (1.0 \times 10^4\ Pa)^2 = 1.00 \times 10^8\ Pa^2$ (04 + 01)

(iv) Calculate the molar percentage of the metal carbonate decomposed at 800 K.

Answer

Initial amount = 0.10 mol. Amount of CO_2 generated = $n_{CO2} = P_{CO2}V/RT = (1.0 \times 10^4\ Pa \times 0.08314\ m^3)/(8.314\ J\ mol^{-1}\ K^{-1} \times 800\ K)$ (04 + 01), or $(3.2 \times 10^4\ Pa)/(1.0 \times 10^4\ Pa) = 0.4/n_{CO2}$; $n_{CO2} = 0.125$ mol
Amount of $M(CO_3)_2$ decomposed = ½ × amount of CO_2 generated = 0.0625 mol
mol % of $M(CO_3)_2$ decomposed = (0.0625 mol/0.10 mol) × 100 (03) = **62.5 %** (02)

(v) Enthalpy change (ΔH) for the decomposition of the metal carbonate under the above conditions is 40.0 kJ mol^{-1}. Calculate the corresponding entropy change (ΔS).

Answer

System is at equilibrium, therefore ΔG = 0 (05). $\Delta S = \Delta H/T = (40.0 \times 10^3\ J\ mol^{-1})/(800\ K)$ (04 + 01) = **50.0 J mol^{-1} K^{-1}** (or 0.05 kJ mol^{-1} K^{-1}) (04 + 01)
Note: ΔS°, ΔH° cannot be accepted.

(vi) Suggest two ways to drive the decomposition reaction of $M(CO_3)_2(s)$ in the forward direction.

Answer

Increase temperature (05)
Remove CO_2 (05) · 5(b): 65 marks

Review.

Principle: Dalton's law and the heterogeneous equilibrium constant, where solids are left out of K_p, so $K_p = P_{CO2}$^2. Method: the water vapour is unchanged in amount, so its pressure only scales with T (1.60 → 3.20 × 10^4 Pa); the remainder of the total pressure is CO_2; each mole of CO_2 comes from ½ mol of carbonate. At equilibrium ΔG = 0, so ΔS = ΔH/T. Common mistakes: writing K_p with the solids or with P_{H2O}, forgetting the unit Pa^2, taking 0.125 mol as the amount of carbonate decomposed (stoichiometry is 1 : 2), and quoting ΔS° (the standard value) instead of ΔS under the given conditions. Fully within the current syllabus.

(c) [65 marks]

With the aid of thermochemical cycles and the data given in the table, answer the following questions.

Species	Standard enthalpy of formation ($\Delta H_f°$) (kJ mol^{-1})
M(s)	0.0
M(g)	800.0
$O_2(g)$	0.0
O(g)	249.2
$MO_2(g)$	−400.0

2

2

−1

Answer

Cycle: $M(s) + O_2(g) \rightarrow MO(g) + \frac{1}{2}O_2(g)$ with ΔH_f°; the alternative route goes $M(s) + O_2(g) \rightarrow MO_2(g)$, $\Delta H_1^\circ = -400.0$ kJ mol^{-1}, then $MO_2(g) \rightarrow MO(g) + \frac{1}{2}O_2(g)$, $\Delta H_2^\circ = +50.0$ kJ mol^{-1} (02 + 02 + 02 = 06)
Note: to award marks for the cycle, reactions must be balanced and physical states must be given.
Standard formation enthalpy of MO(g), $\Delta H_f^\circ = (-400.0 + 50.0)$ kJ mol^{-1} (04 + 01) = **−350.0 kJ mol^{-1}** (04 + 01)

(ii) Calculate M–O bond dissociation enthalpy in MO(g).

Answer

Cycle: $\frac{1}{2}O_2(g) + MO(g) \rightarrow M(g) + O(g) + \frac{1}{2}O_2(g)$ with ΔH_x°. Alternative route: $\frac{1}{2}O_2(g) + MO(g) \rightarrow M(s) + O_2(g)$, $\Delta H_1^\circ = 350.0$ kJ mol^{-1}; $M(s) + O_2(g) \rightarrow M(g) + O_2(g)$, $\Delta H_2^\circ = 800.0$ kJ mol^{-1}; $M(g) + O_2(g) \rightarrow M(g) + O(g) + \frac{1}{2}O_2(g)$, $\Delta H_3^\circ = 249.2$ kJ mol^{-1} (02 + 02 + 02 + 02 = 08)
Note: to award marks for the cycle, reactions must be balanced and physical states must be given.
M–O bond dissociation enthalpy change = $\Delta H_x^\circ = (350.0 + 800.0 + 249.2)$ kJ mol^{-1} (04 + 01) = **1399.2 kJ mol^{-1}** (02 + 01)

(iii) Calculate M–O bond dissociation enthalpy in $MO_2(g)$.

Answer

Cycle: $MO_2(g) \rightarrow M(g) + 2O(g)$ with ΔH_y°. Alternative route: $MO_2(g) \rightarrow M(s) + O_2(g)$, $\Delta H_1^\circ = 400.0$ kJ mol^{-1}; $M(s) + O_2(g) \rightarrow M(g) + O_2(g)$, $\Delta H_2^\circ = 800.0$ kJ mol^{-1}; $M(g) + O_2(g) \rightarrow M(g) + 2O(g)$, $\Delta H_3^\circ = 2 \times 249.2$ kJ mol^{-1} (02 + 02 + 02 + 02 = 08)
Note: to award marks for the cycle, reactions must be balanced and physical states must be given.
$\Delta H_y^\circ = (400.0 + 800.0 + 2 \times 249.2)$ kJ mol^{-1} (04 + 01) = 1698.4 kJ mol^{-1}
M–O bond dissociation energy in $MO_2 = \frac{1}{2}\Delta H_y^\circ$ = **849.2 kJ mol^{-1}** (04 + 01)

(iv) By means of a suitable calculation, predict whether the reaction $MO_2(g) \rightarrow MO(g) + \frac{1}{2}O_2(g)$ is spontaneous under standard conditions and 2000 K. Standard entropy change of this reaction is 30.0 J K^{-1} mol^{-1}.

Answer

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (03)
For the reaction $MO_2(g) \rightarrow MO(g) + \frac{1}{2}O_2(g)$ at 2000 K: $\Delta G^\circ = 50.0 \times 10^3$ J mol^{-1} − 2000 K × 30.0 J K^{-1} mol^{-1} (04 + 01) = −10000.0 J mol^{-1} = −10.0 kJ mol^{-1} (04 + 01)
The given reaction is **spontaneous** at 2000 K. (02)
Note: standard states are required for award of marks. 5(c): 65 marks

Review.

Principle: Hess's law (formation, atomisation and bond-dissociation enthalpies from a closed cycle) and the Gibbs criterion $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (negative means spontaneous). Method: write the cycle with balanced equations and states, then add the legs around it; the bond dissociation enthalpy in MO_2 is per M–O bond, hence the ½ (two equivalent bonds). Common mistakes: sign errors on reversed legs (the reversed $MO_2 \rightarrow M(s) + O_2(g)$ leg is +400.0), forgetting the factor of 2 for O(g) in part (iii) or the ½ at the end, omitting physical states, mixing J and kJ in ΔG°. Fully within the current syllabus (Resource Book, energetics).

Read: RB U4 §1.2 · p. 5 RB U4 §1.3 · p. 16 RB U12 §2.1 · p. 76 RB U5 §2.2 · p. 36 RB U5 §2.4 · p. 53

Question 6 · Part B · essay

(a) [45 marks]

An experiment was carried out to determine the partition coefficient of iodine (I_2) between water (**A**) and an organic solvent (**B**) which form an immiscible liquid system.
20.00 cm^3 of **B** containing 'n' moles of I_2 is mixed with 20.00 cm^3 of **A** and allowed to reach equilibrium at room temperature.
The concentration of I_2 in phase **A** is determined by titrating a 5.00 cm^3 sample drawn from phase **A** with a 0.005 mol dm^{-3} solution of $Na_2S_2O_3$. The volume of $Na_2S_2O_3$ required to reach the end point was 22.00 cm^3.
The concentration of I_2 in phase **B** was determined to be 0.040 mol dm^{-3}.
(i) Write the balanced chemical equation for the reaction between $Na_2S_2O_3$ and I_2.

Answer

$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$ (10)
OR $2S_2O_3^{2-} + I_2 \rightarrow 2I^- + S_4O_6^{2-}$

(ii) Calculate the concentration of I_2 in phase **A**.

Answer

Concentration of I_2 in phase A = (22.00 cm^3 × 0.005 mol dm^{-3})/(2 × 5.0 cm^3) (04 + 01) = **0.011 mol dm^{-3}** (04 + 01)

(iii) Calculate the value of the partition coefficient, K_D where $K_D = [I_2]_B/[I_2]_A$.

Answer

Partition coefficient, $K_D = [I_2]_B/[I_2]_A$ = 0.04 mol dm^{-3}/0.011 mol dm^{-3} (04 + 01) = **3.64** (K_D = 3.64 is used in the later parts)

(iv) Calculate the total number of moles of I_2 in the two phases **A** and **B**.

Answer

n_{I2} = 0.04 mol dm^{-3} × 20.0 × 10^{-3} dm^3 + 0.011 mol dm^{-3} × 20.0 × 10^{-3} dm^3 2 × (04 + 01) = **1.02 × 10^{-3} mol** (04 + 01) · 6(a): 45 marks

Review.

Principle: the Nernst distribution law, $K_D = [I_2]_B/[I_2]_A$ for a solute that exists in one molecular form in both immiscible solvents; thiosulfate titration of iodine (2 mol $S_2O_3^{2-}$: 1 mol I_2). Method: moles of I_2 titrated = ½ × 22.00 × 0.005 mmol, divided by the 5.00 cm^3 sample volume. Common mistakes: omitting the factor of ½ for the 2 : 1 stoichiometry, inverting K_D, and not multiplying each concentration by the 20.00 cm^3 volume of its own phase when finding the total. Within the current syllabus (partition coefficient, Resource Book Unit 12; thiosulfate titrations, Unit 3).

(b) [35 marks]

The above experiment was repeated under the same conditions, that is, at the same temperature, using the same amount of I_2 and the same volumes, but with the addition of I^- ions to phase **A**. The system was then thoroughly shaken and allowed to reach equilibrium. The volume of 0.005 mol dm^{-3} $Na_2S_2O_3$ solution required to titrate the I_2 in a 5.00 cm^3 sample of phase **A** was 41.00 cm^3. The concentration of I_2 in phase **B** was then determined to be 0.030 mol dm^{-3}.
(i) Calculate the amount of I_2 (moles) expected in 5.00 cm^3 of phase **A**, based on the partition coefficient for the distribution of I_2 between the phases **A** and **B**.

Answer

Concentration of I_2 in phase A (when excess I^- is added): $[I_2]_A = [I_2]_B/K_D$ (05) = (0.030 mol dm^{-3})/3.64 (02 + 01) = 8.242×10^{-3} mol dm^{-3} (01 + 01)
The amount of I_2 in 5.00 cm^3 of phase A = n = 8.242×10^{-3} mol $dm^{-3} \times 5.00 \times 10^{-3}$ dm^3 (02 + 01) = **4.121×10^{-5} mol** (01 + 01)

(ii) Calculate the amount (moles) of I_2 reacted with $Na_2S_2O_3$ in the above titration.

Answer

The amount of I_2 in 5.00 cm^3 of phase A, after the addition of iodide = n′ = 0.005 mol $dm^{-3} \times 41.00 \times 10^{-3}$ $dm^3 \times 0.5$ (04 + 01) = **1.025×10^{-4} mol** (or 1.03×10^{-4} mol) (04 + 01)

(iii) Considering the different iodine species present in phase **A**, explain why the answers obtained in parts (b)(i) and (b)(ii) above are different.

Answer

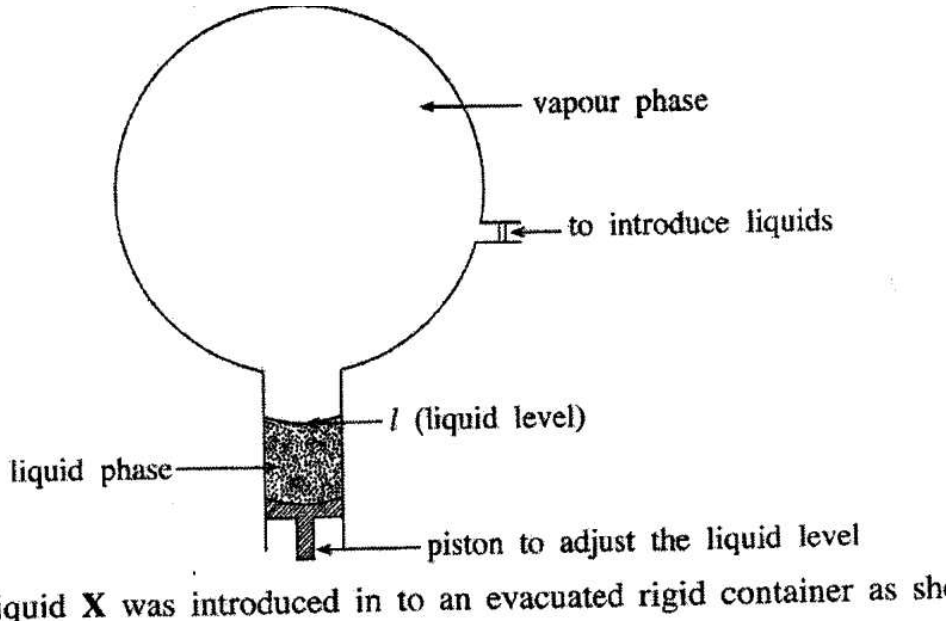
When I^- ions are added to the phase A, I_2 and I^- combine to form I_3^−. (05)
When phase A is titrated with $Na_2S_2O_3$, I_2 released from I_3^− is also reacted with $Na_2S_2O_3$. Therefore, n′ > n. (05) · 6(b): 35 marks

Review.

Principle: only free I_2 distributes between the two solvents, so $[I_2]_A$ calculated from K_D and $[I_2]_B$ gives free I_2 only. Iodide converts part of the aqueous iodine into I_3^− ($I_2 + I^- \rightleftharpoons I_3$^−) which stays in water; thiosulfate titrates all the iodine (free I_2 plus that released from I_3^−), so the titre is larger than the free I_2 predicted by K_D (1.025×10^{-4} against 4.121×10^{-5} mol). Method: compute $[I_2]_A = [I_2]_B/K_D$, scale by 5.00 cm^3, and compare with ½ × titre. Common mistakes: forgetting the ½ for the 2 : 1 stoichiometry, and explaining the difference as an experimental error. Within the current syllabus (Resource Book, partition coefficient).

(c) [70 marks]

Liquids **X** and **Y** form an ideal solution obeying Raoult's law.



, liquid **X** was introduced in to an evacuated rigid container as sh

Apparatus: rigid container with a vapour phase, an inlet to introduce liquids, and a liquid phase whose level l is adjusted by a piston

Initially only liquid **X** was introduced in to an evacuated rigid container as shown in the figure. Maintaining the liquid level at l, the system was allowed to reach equilibrium at 400 K. The pressure of the container was

measured to be 3.00×10^4 Pa. The volume of the vapour phase when the liquid level is at l was 4.157 dm^3. Then liquid **Y** was introduced in to the container mixed with liquid **X** and the system was allowed to reach equilibrium at 400 K. The liquid level was maintained at l. The molar ratio of **X** : **Y** in the liquid phase was found to be 1 : 3. The pressure of the container was measured to be 5.00×10^4 Pa.
(i) What is the saturated vapour pressure of **X** at 400 K?

Answer

Saturated vapour pressure of X at 400 K = 3.00×10^4 Pa. (04 + 01)

(ii) Calculate the mole fractions of **X** and **Y** in the liquid phase at equilibrium.

Answer

Mole fraction of X in the liquid phase = 1/(1 + 3) = ¼ or 0.25 (04 + 01)
Mole fraction of Y in the liquid phase = 3/(1 + 3) = ¾ or 0.75 (04 + 01)

(iii) Calculate the partial pressure of **X** at equilibrium after the addition of **Y**.

Answer

At equilibrium $P_X = P_X^\circ X_X$ (05) = $0.25 \times 3.0 \times 10^4$ Pa (02 + 01) = 7.5×10^3 Pa (01 + 01)

(iv) Calculate the partial pressure of **Y** at equilibrium.

Answer

$P_Y = P_{total} - P_X = 5.0 \times 10^4$ Pa − 7.5×10^3 Pa (02 + 01) = 4.25×10^4 Pa (01 + 01)

(v) Calculate the saturated vapour pressure of **Y**.

Answer

Saturated vapour pressure of Y, $P_Y^\circ = P_Y/X_Y$ = (4.25×10^4 Pa)/0.75 (04 + 01) = **5.67×10^4 Pa** (04 + 01)

(vi) Calculate the amounts (in moles) of **X** and **Y** in the vapour phase.

Answer

The amount of X in the gas phase, $n_X = P_{XV}/RT$ = (7.5×10^3 Pa × 4.157×10^{-3} m^3)/(8.314 J mol^{-1} K^{-1} × 400 K) (04 + 01); n_X = **9.38×10^{-3} mol** (04 + 01)
Similarly, n_Y = (4.25×10^4 Pa × 4.157×10^{-3} m^3)/(8.314 J mol^{-1} K^{-1} × 400 K) (04 + 01); n_Y = **5.31×10^{-2} mol** (04 + 01)

(vii) When a mixture of the liquids **X** and **Y** is subjected to fractional distillation, state which compound would distill out first from the fractional distillation column. Give reason/s for your answer.

Answer

Compound Y can be obtained first. (05)
Y is the more volatile compound, or the saturated vapour pressure of Y (P_Y°) is high. Therefore, its vapour comes out first from the fractional distillation column. (05)
Note: to award marks for (vii), answers for P_X° and P_Y° must have been calculated. The prediction must be according to the calculated P_X° and P_Y° values. 6(c): 70 marks

Review.

Principle: Raoult's law for an ideal binary mixture, $P_i = x_i P_i^\circ$, with Dalton's law $P_{total} = P_X + P_Y$; the more volatile component (higher P°) is richer in the vapour and distils first. Method: P_X° is the pressure with X alone; then $P_X = x_X P_X^\circ$, $P_Y = P_{total} - P_X$, and $P_Y^\circ = P_Y/x_Y$ (5.67×10^4 against 3.00×10^4 Pa). Amounts in the vapour come from n = PV/RT with the same 4.157 dm^3 (= 4.157×10^{-3} m^3). Common mistakes: using the mole ratio 1 : 3 directly instead of the mole fractions ¼ and ¾, using total pressure instead of P_Y in P_Y°, and a

volume left in dm^3 with pressure in Pa. Within the current syllabus (Resource Book, liquid–liquid mixtures).

Read: RB U12 §2.7 · p. 229 RB U3 §3.8 · p. 115 RB U12 §2.6 · p. 216 RB U4 §1.3 · p. 16

Question 7 · Part B · essay

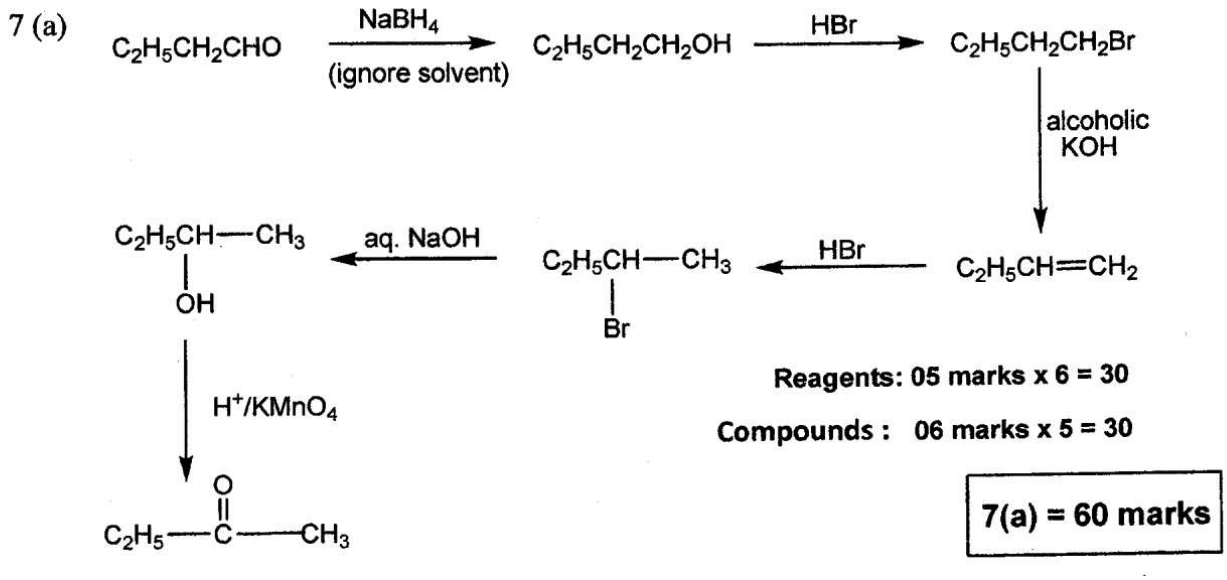
Marking note (7(a), 7(b)):

(a) [60 marks]

Using only the chemicals given in the list, show how you would carry out the following conversion
$C_2H_5CH_2CHO \rightarrow C_2H_5COCH_3$
List of chemicals: aqueous NaOH, HBr, alcoholic KOH, $NaBH_4$, $H^+/KMnO_4$
Your conversion should not exceed 7 steps.

Answer

$C_2H_5CH_2CHO \rightarrow$(NaBH$_4$; ignore solvent)$\rightarrow C_2H_5CH_2CH_2OH \rightarrow$(HBr)$\rightarrow C_2H_5CH_2CH_2Br \rightarrow$(alcoholic KOH)$\rightarrow$
$C_2H_5CH{=}CH_2 \rightarrow$(HBr)$\rightarrow C_2H_5CH(Br)CH_3 \rightarrow$(aq. NaOH)$\rightarrow C_2H_5CH(OH)CH_3 \rightarrow$($H^+/KMnO_4$)$\rightarrow C_2H_5COCH_3$
Reagents: 05 marks × 6 = 30; Compounds: 06 marks × 5 = 30 · 7(a) = 60 marks



Scheme answer for 7(a)

Note:

2

5

2

2

5

3

Marking of partially correct answer:

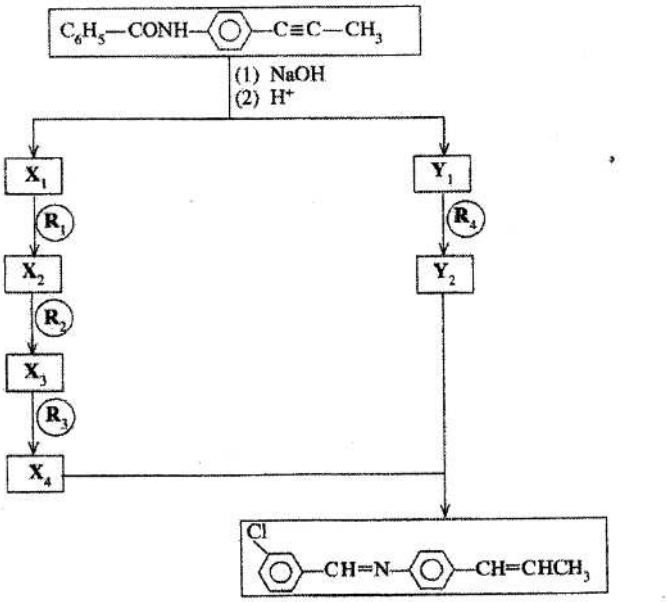
Review.

Principle: functional-group interconversion planning with a fixed reagent list. Route: reduce the aldehyde to the primary alcohol ($NaBH_4$), convert to the bromide (HBr), eliminate to the terminal alkene (alcoholic KOH), add HBr by Markovnikov's rule to put Br on the secondary carbon, hydrolyse to the secondary alcohol (aq.

NaOH), then oxidise to the ketone ($H^+/KMnO_4$). The alkene step is needed because a secondary halide cannot be made directly from the primary alcohol. Common mistakes: oxidising with $KMnO_4$ before the carbon skeleton is converted (it would give butanoic acid), using aq. NaOH where alcoholic KOH is needed for elimination, and ignoring Markovnikov orientation. Topic is within the current syllabus (reactions of alcohols, alkenes and halohydrocarbons).

(b) [60 marks]

Identify R_1–R_4 and X_1–X_4 and Y_1, Y_2 in order to complete the following reaction scheme.



6

5

6

4

3

+

1

1

1

2

3

4

1

2

3

1

2

4

4

2

Answer

Main pathway:

1

6

5

2

(06)

2

6

5

2

(06)

3

6

5

(06)

4

(06)

1

2

6

4

3

3

(06)

2

2

6

4

3

3

(06)

1

4

2

2

+

(06)

2

(06)

3

3

2

2

2

(06)

4

2

4

2

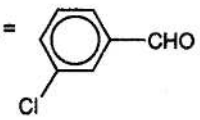
(06)

(06 marks × 10 = 60)

$X_1 =$ $C_6H_5CO_2H$ **(06)**

$X_2 =$ $C_6H_5CH_2OH$ **(06)**

$X_3 =$ C_6H_5CHO **(06)**

$X_4 =$  **(06)**

$Y_1 =$ **(06)**

$Y_2 =$ **(06)**

4

1

2

Alternative pathway:

1

6

5

2

(06)

2

(06)

3

6

4

2

(06)

4

(06)

1

2

(06 + 06)

1

3

2

2

2

(06)

2

4

2

2

+

(06)

3

(06)

4

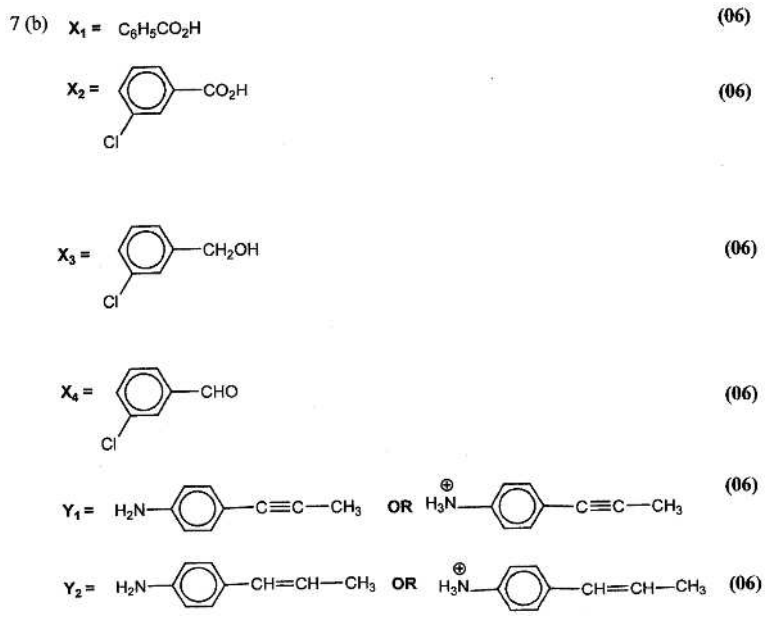
2

4

2

(06)

(06 marks × 10 = 60) · 7(b) = 60 marks



2

3

4

1

2

Review.

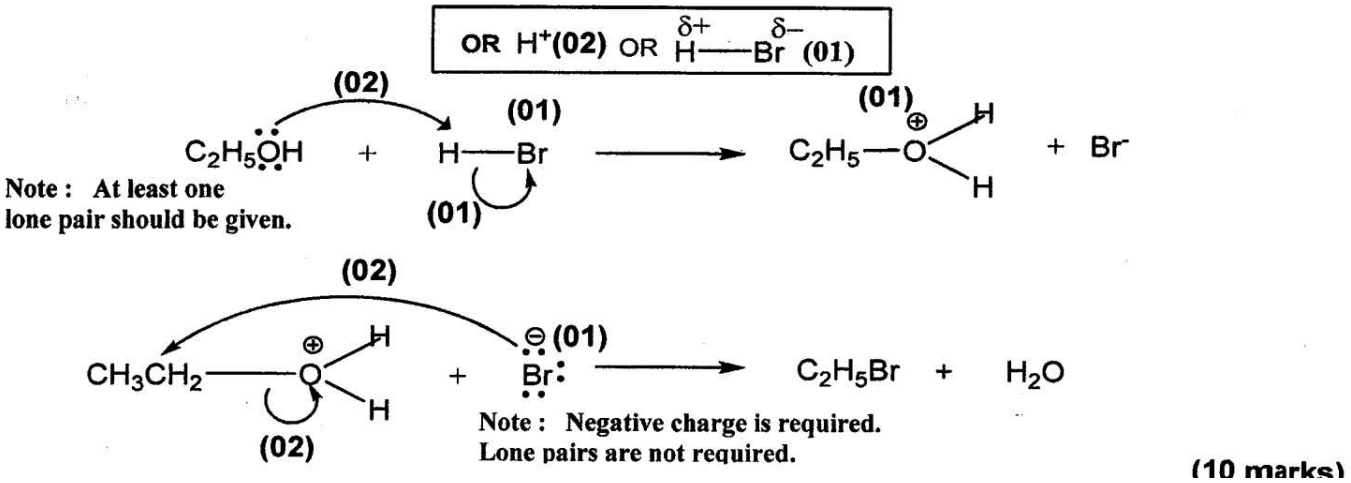
Principle: base hydrolysis of the amide (then acidification) gives benzoic acid and the aromatic amine Y_1; the imine in the final product is formed from the aldehyde X_4 and the amine Y_2. The alkyne in Y_1 must be reduced to a (Z)-alkene (poisoned Pd catalyst, partial hydrogenation) to make Y_2. The chlorine must go meta, so it is introduced on a ring that carries an electron-withdrawing meta-directing group (CO_2H or CHO) – hence chlorination of benzoic acid (alternative route) or of benzaldehyde; chlorinating benzyl alcohol would give o/p products. Common mistakes: chlorinating before oxidation/reduction in a way that puts Cl in the wrong position, and choosing H_2/Pd (no poison) which would reduce the alkyne fully to the alkane. Syllabus note: partial hydrogenation of alkynes with Lindlar/poisoned Pd and the formation of imines from aldehydes and aromatic amines are not in the current Resource Book in this form; the rest ($LiAlH_4$, PCC, electrophilic substitution and directing effects) is.

(c) [30 marks]

(i) Give the mechanism of the following reaction.
$C_2H_5OH + HBr \rightarrow C_2H_5Br + H_2O$

Answer

Step 1: the lone pair on oxygen of C_2H_5OH takes H^+ from H–Br (curved arrow from the lone pair to H and from the H–Br bond to Br; $H^{\delta+}$–$Br^{\delta-}$ or H^+ accepted) to give C_2H_5–O^+H_2 and Br^- (02 + 01 + 01) (at least one lone pair should be shown)
Step 2: Br^- attacks the carbon bearing the –O^+H_2 group and the C–O bond breaks (curved arrows from the Br^- lone pair to C and from the C–O bond to O), giving $C_2H_5Br + H_2O$ (02 + 02 + 01) (negative charge on Br is required; lone pairs not required) (10 marks)



(10 marks)

Mechanism from the scheme

(ii) State whether the above reaction is a nucleophilic substitution reaction or an electrophilic substitution reaction. Identify the nucleophile or electrophile as appropriate.

Answer

Nucleophilic substitution, Br^- (02 + 02)

(iii) State giving reasons which of the two compounds, phenol (C_6H_5OH) or ethanol (C_2H_5OH) is more acidic.

Answer

$C_2H_5OH + H_2O \rightleftharpoons C_2H_5O^- + H_3O^+$ (02)
$C_6H_5OH + H_2O \rightleftharpoons C_6H_5O^- + H_3O^+$ (02) (if H_2O is not included in the equations, only (01) per equation)
• In the above equilibria the equilibrium point for phenol is more toward the right than ethanol. (02)
• This is because the stability of the phenate ion relative to phenol is greater than the stability of the alkoxide relative to the alcohol. (02)
• The phenate ion is more stable because its negative charge gets delocalized by resonance. (02)
• Resonance structures drawn (02)
• In the alkoxide ion there is no such charge dispersion / no resonance (02)
• Phenol is more acidic than ethanol. (02) · 7(c) = 30 marks

Review.

Principle: a primary alcohol reacts with HBr by protonation of the –OH (a poor leaving group) followed by S_{N2} attack of Br^- on the carbon, so the reaction is nucleophilic substitution with Br^- as nucleophile. Acidity is judged by the stability of the conjugate base: phenoxide is resonance-stabilised by delocalisation into the ring, ethoxide is destabilised by the electron-donating ethyl group. Common mistakes: showing OH^- as the leaving group (it leaves only after protonation, as H_2O), omitting charges or curved arrows, and explaining phenol's acidity only by "benzene is electron withdrawing" without resonance structures. Within the current syllabus (Resource Book, alcohols and phenols; alkyl halides).

Read: RB U8 §2.2 · p. 33 RB U9 §3.1 · p. 54 RB U9 §3.4 · p. 60 RB U8 §2.4 · p. 44 RB U10 §4.1 · p. 75 RB U9 §3.3 · p. 59

Part C

Question 8 · Part C · essay

(a) [75 marks]

An aqueous solution **P** contains **two** cations and **two** anions. The following experiments were carried out to identify these cations and anions.

Cations

	Experiment	Observation
①	**P** was acidified with dilute HCl and H_2S was bubbled through the solution.	A clear solution was obtained.
②	The above solution was boiled till all the H_2S was removed. A few drops of conc. HNO_3 were added and the solution was heated further. The resulting solution was cooled and NH_4Cl/NH_4OH was added.	A brown precipitate (**Q**) was formed.
③	**Q** was removed by filtration and H_2S was bubbled through the filtrate.	A pale pink precipitate (**R**) was formed.
④	**R** was removed by filtration and the filtrate was boiled till all the H_2S was removed. $(NH_4)_2CO_3$ was added to the solution.	A clear solution was obtained.
⑤	Dilute NaOH was added to a **fresh portion** of **P**.	A dirty-green precipitate and a while [sic, white] precipitate were formed.

Experiments for precipitates Q and R:

	Experiment	Observation
⑥	**Q** was dissolved in dil. HNO_3 and a salicylic acid solution was added.	A light purple solution was obtained.
⑦	**R** was dissolved in dilute acid and dil. NaOH was added to the solution.	A white precipitate was formed. It turned brown on standing.

Anions

	Test	Observation
⑧ I.	$BaCl_2$ solution was added to **P**.	A white precipitate was formed.
⑧ II.	The white precipitate was separated by filtration and dil. HCl was added to the precipitate.	The white precipitate was not dissolved.
⑨	Cl_2 water and chloroform were added to a portion of the filtrate from ⑧ II, and the mixture was throughly shaken.	Chloroform layer turned yellowish-brown.

(i) Identify the **two** cations and the **two** anions in solution **P**. (Reasons are **not** required.)

Answer

Cations: **Fe^{2+}** and **Mn^{2+}** (10 + 10)
Anions: **SO_4^{2-}** and **Br^-** (08 + 07)
Note: first correct anion (08), second anion (07).

(ii) Write the chemical formulae of the precipitates **Q** and **R**.

Answer

Q

3

(10)

R

(10)

(iii) Give reasons for the following:
I. Removal of H_2S in experiment ② for cations.

Answer

• If H_2S is not removed, MnS/FeS/cations of group IV will also precipitate when NH_4OH/NH_4Cl solution is added. (10)
OR
• H_2S can be oxidized to sulphur by conc. HNO_3. (05)
• A fine precipitate of sulphur would be formed in solution if H_2S is not removed. (05)

II. Heating with conc. HNO_3 in experiment ② for cations.

Answer

• K_{sp} of $Fe(OH)_2$ > K_{sp} of $Fe(OH)_3$ (05)
• Therefore, Fe^{2+} needs to be converted to Fe^{3+} to be completely precipitated. (05)
OR
• Conc. HNO_3 must be added to oxidize iron, if present, to the ferric state. (04)
• If originally present, it would have been reduced by the H_2S to the ferrous ion. (02)
• Ferrous ion is not completely precipitated by NH_4OH/NH_4Cl solution (will get a mixture of Fe^{2+} and Fe^{3+}). (04) 8(a): 75 marks

Review.

Principle: systematic cation group separation based on solubility products (acidified H_2S → group II sulfides; NH_4Cl/NH_4OH → group III hydroxides; H_2S in ammoniacal solution → group IV sulfides; $(NH_4)_2CO_3$ → group V carbonates) plus confirmatory tests. Method: no precipitate in ① rules out group II; the brown group III precipitate Q that gives a violet colour with salicylic acid is $Fe(OH)_3$ (Fe^{3+}); the pale pink group IV sulfide R whose ion gives a white hydroxide turning brown in air is MnS (Mn^{2+}); nothing in group V. The dirty-green $Fe(OH)_2$ in ⑤ shows iron was originally Fe^{2+} (the white precipitate is $Mn(OH)_2$). $BaSO_4$ is insoluble in dil. HCl (SO_4^{2-}, not SO_3^{2-} or CO_3^{2-}); Cl_2 water liberates Br_2, giving a yellowish-brown $CHCl_3$ layer (I^- would give violet). Common mistakes: reporting Fe^{3+} because Q is $Fe(OH)_3$ (the HNO_3 oxidised it), and calling R a manganese hydroxide. Within the current syllabus (Resource Book Unit 12, application of K_{sp} in qualitative cation analysis; Unit 6, 3d elements).

(b) [75 marks]

The sample **X** contains lead, copper and an inert material. The following procedure was carried out to analyse lead and copper in **X**.

Procedure:

A mass of 0.285 g of **X** was dissolved in a slight excess of dil. HNO_3. A clear solution was obtained. A NaCl solution was added to the resulting clear solution. A white precipitate (**Y**) was formed. The precipitate was separated by filtration and the precipitate (**Y**) and filtrate (**Z**) were analysed separately.

Precipitate (Y)

The precipitate was dissolved in hot water. A solution of K_2CrO_4 was added in excess. A yellow precipitate was formed. The precipitate was separated by filtration and dissolved in dil. HNO_3. An orange coloured solution was obtained. Excess KI was added to this solution and the liberated I_2 was titrated with 0.100 mol dm^{-3} $Na_2S_2O_3$, with starch as the indicator. The volume of $Na_2S_2O_3$ required to reach the end point was 27.00 cm^3. (Assume that the NO_3^− ions do **not** interfere with the titration.)

Filtrate (Z)

The filtrate was neutralized and excess KI was added to it. The liberated I_2 was titrated with 0.100 mol dm^{-3} $Na_2S_2O_3$, with starch as the indicator. The volume of $Na_2S_2O_3$ required to reach the end point was 15.00 cm^3. (**Note:** Assume that the inert material was soluble in dil. HNO_3 and did **not** interfere with the experiment.)

(i) Calculate the mass percentages of lead and copper in **X**. Write balanced chemical equations where relevant.

Answer

Determination of Cu

2+

−

2

(05)

OR

2+

−

+

2

(05)

2

2

3

2−

−

4

6

2−

(05)

2+

2

3

2−

OR

(02)

2

3

2−

(03)

2+

(03)

(03)

(03)

(03)

33.4%

(03)

(30 marks)

Determination of Pb

2

7

2−

−

+

3+

2

2

(07)

2

2

3

2−

−

4

6

2−

2

7

2−

2

3

2−

OR

(03)

2

3

2−

(03)

2

7

2−

(03)

4

2−

+

2

7

2−

2

(03)

(03)

4

(03)

(03)

(03)

(03)

(03)

65.3%

(03)

(40 marks)

Alternate method – Determination of Pb

4

2−

−

+

3+

2

2

2

2

3

2−

−

4

6

2−

OR

4

2−

+

3+

2

−

2

4

2−

2

3

2−

OR

(03)

2

3

2−

(03)

2

(03)

3+

(03)

−4

4

−4

(03)

−4

(03)

−4

(03)

(03)

(03)

65.3%

(03)

(30 marks)

(ii) What is the colour change at the end point in the titration carried out in the analysis of precipitate **Y**? (Cu = 63.5, Pb = 207)

Answer

Blue → Green (05) 8(b): 75 marks

Review.

Principle: iodometric titrations. Pb^{2+} is separated as $PbCl_2$ (Y), redissolved in hot water and precipitated as yellow $PbCrO_4$; in acid the chromate becomes orange $Cr_2O_7^{2-}$, which oxidises I^- to I_2; Cu^{2+} in the filtrate (Z) oxidises I^- to I_2 (giving CuI). Key mole ratios: 1 Cu^{2+} ≡ ½ I_2 ≡ 1 $S_2O_3^{2-}$; 1 Pb ≡ 1 CrO_4^{2-} ≡ 3/2 I_2 ≡ 3 $S_2O_3^{2-}$. Working: n($S_2O_3^{2-}$) = 2.70×10^{-3} mol, so n(Pb) = 9.0×10^{-4} mol, m(Pb) = 0.1863 g; n(Cu) = 1.50×10^{-3} mol, m(Cu) = 0.0953 g, 33.4%. At the end point the blue starch–iodine colour disappears, leaving the green colour of Cr^{3+}. Scheme notes: (1) the scheme rounds the lead mass to 0.186 g and gives 65.3%; unrounded, 0.1863/0.285 = 65.4%, so either should be accepted. (2) The main lead method carries 40 marks, but the alternate method is labelled 30 marks (its listed steps add to 30 and omit the 07 marks for the equations); the 8(b) total of 75 requires 40, so the equation marks presumably apply to the alternate method as well. Common mistakes: using a 1:1 Pb : $S_2O_3^{2-}$ ratio, forgetting that two CrO_4^{2-} give one $Cr_2O_7^{2-}$, and giving the end point as "blue → colourless" (true only for the copper titration). Within the current syllabus (Resource Book Unit 3, titration calculations and redox equations).

Read: RB U12 §2.4 · p. 175 RB U6 §4.10 · p. 160 RB U3 §3.8 · p. 115 RB U3 §3.6 · p. 105

Question 9 · Part C · essay

(a) [75 marks]

The following questions are based on the environment and related issues.

(i) Identify **three** greenhouse gases that contribute to global warming. State **two** consequences of global warming.

Answer

Greenhouse gases that contribute to global warming:

2

x

2

3

(03 + 03 + 03)

Consequences:

(03 + 03)

(ii) Global environmental issues caused by coal power plants are well known. Identify **one** such issue that contributes **significantly** to change in certain water quality parameters in rivers and lakes.

Answer

Acid rain (03)

(iii) Name the chemical species responsible for the environmental issue identified in (ii) above and state **three** water quality parameters that are likely to be affected by this issue.

Answer

SO_2 / SO_3 / H_2SO_3 / H_2SO_4 (03)
Water parameters affected:
• pH (decreases) / acidity (increases)
• Salinity (increases)
• Concentration of heavy metals (increases)
• Hardness (increases)
• Conductivity (increases)
(Any three) (03 + 03 + 03)

(iv) Identify **two** environmental issues that change (increase **or** decrease) the ozone level in the atmosphere and explain briefly how these changes take place with the aid of balanced chemical equations.

Answer

Photochemical smog (ozone increases)

(03)

x

(03)

2

(03)

2

3

(03)

Ozone layer depletion (ozone decreases)

(03)

(03)

3

2

(03)

2

(03)

2

(03)

3

2

(03)

(v) I. "Most of the harmful gases in vehicle exhausts are converted to relatively harmless gases by catalytic converters." Briefly explain this statement.

Answer

Catalytic converters convert
• NO(g) formed to N_2(g) (03)
• CO(g) formed to CO_2(g) (03)
• Unburnt or partially burnt hydrocarbons to CO_2(g) + H_2O(g) (03)

II. Name the harmful gas (except CO_2) that is not converted to a less harmful gas by the catalytic converter. State briefly how this harmful gas is formed in the vehicle engine.

Answer

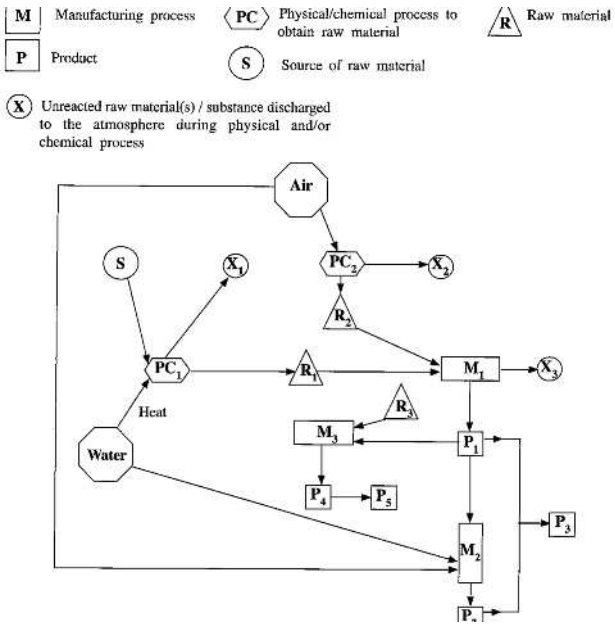
SO_2 (03)
Certain fossil fuels contain sulphur. (02)
Burning of sulphur produces SO_2. (01) 9(a): 75 marks

Review.

Principle: sources, chemistry and effects of the main air-pollution issues. Greenhouse gases absorb outgoing infrared radiation; SO_2 from sulfur in coal (and fuels) is oxidised and dissolves to give H_2SO_3/H_2SO_4 (acid rain), lowering pH and leaching metal ions, so hardness, conductivity and heavy-metal levels rise. Ozone rises near the ground in photochemical smog (NO_2 photolysis, then O + O_2 with a third body) but falls in the stratosphere through radical chain reactions in which the radical is regenerated, so one radical destroys many O_3 molecules. In the scheme's combination (1) × 2 + (2) + (3) × 2, the radicals X^• and XO^• and the O atoms cancel and one O_2 cancels from each side, leaving $2O_3 \rightarrow 3O_2$ (in the stratosphere the O atoms come from photolysis of O_2 or O_3 by UV light). Common mistakes: calling SO_2 or CO a greenhouse gas in place of CO_2/CH_4/N_2O, writing "ozone depletion" for smog, and leaving out the third body M. Catalytic converters are not described in the current Resource Book; the rest is in Unit 14 (air and water pollution).

(b) [75 marks]

The flow chart given below shows the production of two important compounds $\mathbf{P_1}$ and $\mathbf{P_2}$ and three other important compounds $\mathbf{P_3}$, $\mathbf{P_4}$ and $\mathbf{P_5}$ derived from them. $\mathbf{P_1}$ is used as a raw material in the manufacture of Na_2CO_3. $\mathbf{P_3}$ can be manufactured by the reaction between $\mathbf{P_1}$ and $\mathbf{P_2}$. $\mathbf{P_3}$ is used as a fertilizer and as an explosive. $\mathbf{P_1}$ is also used in the manufacture of $\mathbf{P_4}$ which is a widely used fertilizer. $\mathbf{P_4}$ is used to synthesize an important thermosetting polymer $\mathbf{P_5}$.



Key (M manufacturing process, PC physical/chemical process to obtain raw material, R raw material, P product, S source of raw material, X unreacted raw material(s)/substance discharged to the atmosphere) and flow chart

Answer the following questions based on the above flow chart.
(i) Identify $\mathbf{P_1}$, $\mathbf{P_2}$, $\mathbf{P_3}$, $\mathbf{P_4}$ and $\mathbf{P_5}$.

Answer

$P_1 = NH_3$ (03)
$P_2 = HNO_3$ (03)
$P_3 = NH_4NO_3$ (03)
P_4 = urea / $CO(NH_2)_2$ (03)
P_5 = urea-formaldehyde (03)

(ii) Identify $\mathbf{R_1}$, $\mathbf{R_2}$ and $\mathbf{R_3}$.

Answer

$R_1 = H_2$ (03)
$R_2 = N_2$ (03)
$R_3 = CO_2$ (03)

(iii) Identify $\mathbf{X_1}$, $\mathbf{X_2}$ and $\mathbf{X_3}$.

Answer

X_1 = CO / CO_2 (03)
$X_2 = O_2$ (03)
$X_3 = N_2 + H_2$ (both N_2 and H_2 must be present for the award of marks) (03)

(iv) Identify **S**.

Answer

S = natural gas / CH_4 **OR** naptha / (C_6H_{14}) **OR** coal / (carbon) (02)

(v) Briefly state the processes taking place in **PC_1** and **PC_2** giving balanced chemical equations where applicable.

Answer

PC_1: $C_6H_{14}(s) + 6H_2O(g) \rightarrow 6CO(g) + 13H_2(g)$ (02)
OR $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$ (02)
PC_2: fractional distillation of liquid air (02)

(vi) Identify manufacturing processes **M_1**, **M_2** and **M_3**. (e.g. contact process or manufacture of H_2SO_4.)

Answer

M_1 = Haber process **OR** manufacture of NH_3 (02)
M_2 = Ostwald process **OR** manufacture of HNO_3 (02)
M_3 = manufacture of urea (02)

(vii) Give balanced chemical equations with appropriate conditions, for reactions taking place in **M_1**, **M_2** and **M_3**.

Answer

1

2

2

3

(02)

(01)

(01)

(01)

2

2

3

(01)

2

3

2

2

(02)

(01)

(01)

2

2

(02)

(01)

2

2

2

3

(02)

3

3

2

2

4

(02)

(01)

(01)

2

4

2

2

2

(02)

(01)

2

2

(02)

Note:

(viii) I. Give one use of each compound $\mathbf{P_1}$ and $\mathbf{P_2}$ other than those mentioned above.

Answer

1

(02)

2

OR

3

OR

3

(02)

II. Give one use of **R_1** in the manufacturing process **P_1** other than being used as a raw material.

Answer

As a fuel **OR** to heat the system (to 450 °C) (02) 9(b): 75 marks

Review.

Principle: reading an industrial flow chart for the nitrogen-fertilizer chain. Clues: P_1 is the ammonia used in the Solvay process; H_2 (R_1) comes from steam reforming of natural gas or naphtha (S, PC_1, releasing CO/CO_2 as X_1) and N_2 (R_2) from fractional distillation of liquid air (PC_2, releasing O_2 as X_2); unreacted N_2 + H_2 (X_3) leave the Haber reactor M_1. Air and water feed the Ostwald process M_2 that gives HNO_3 (P_2); NH_3 + HNO_3 give NH_4NO_3 (P_3, fertilizer and explosive); NH_3 + CO_2 (R_3) give urea (P_4) via ammonium carbamate, and urea with methanal gives the thermosetting urea-formaldehyde resin (P_5). Scheme notes: the naphtha equation shows C_6H_{14} as (s), but hexane is a liquid (the Resource Book writes it as a gas at reforming temperature); also "naptha" is the scheme's spelling of naphtha. Common mistakes: confusing R_1 and R_2, giving NO for X_2, and quoting the Haber conditions without the catalyst/promoters. Syllabus note: the Haber and Ostwald processes and steam reforming are in the current Resource Book (Unit 14); the manufacture of urea and ammonium nitrate and urea-formaldehyde resins are not covered in detail there.

Read: RB U14 §1.13 · p. 58 RB U14 §1.14 · p. 80 RB U14 §1.6 · p. 21 RB U14 §1.11 · p. 37

Question 10 · Part C · essay

(a) [75 marks]

A

B

complex ions

5

3

6

two

A

coordination compound C

C

B

coordination compound D

D

C

D

Note:

A

B

(i) Identify the ligands coordinated to manganese in **A** and **B**.

Answer

CN^- and NH_3 (05 + 05)

(ii) Give the structures of **A**, **B**, **C** and **D**.

Answer

A

5

3

3−

OR

3

5

3−

(10)

B

5

3

2−

OR

3

5

2−

(10)

C

3

5

3

OR

3

3

5

(15)

D

2

5

3

OR

2

3

5

(15)

(iii) Write the electronic configurations of the manganese ions in **A** and **B**.

Answer

A

A

2

2

6

2

6

5

(03)

B

B

2

2

6

2

6

4

(02)

(iv) Write the IUPAC names of **C** and **D**.

Answer

C

(05)

D

(05)

Note:

10(a): 75 marks

Review.

Principle: deducing a complex ion's formula from its composition and the number of ions its salt gives. $MnC_5H_3N_6$ = Mn + 5 CN + 1 NH_3 (5 C, 3 H, 6 N), so the six octahedral positions hold five CN^- and one NH_3, giving a charge of (x − 5). C (K_3[...], 4 ions) needs a 3− complex, so Mn is +2 (d^5); D (K_2[...], 3 ions) needs a 2− complex, so Mn is +3 (d^4). Naming: ligands in alphabetical order (ammine before cyanido), anionic complex ends in "-ate" (manganate), oxidation state in Roman numerals, cation named first. Common mistakes: writing the 4s electrons in the configuration of the ion, using "cyano" or "amine" (the scheme penalises spelling), and "manganese" instead of "manganate" for an anionic complex. Within the current syllabus (Resource Book Unit 6, complex ions and their IUPAC names).

(b) [75 marks]

(i) I. Write the reduction half reaction corresponding to the electrode, Ag(s) | AgCl(s) | Cl^-(aq).

Answer

AgCl(s) + e → Ag(s) + Cl^-(aq) (05) (⇌ accepted). Physical states are required.

II. State whether the electrode potential of Ag(s) | AgCl(s) | Cl^-(aq) depends on the Ag^+ concentration in the solution. Explain your answer.

Answer

No. (05)
Ag^+(aq) does not appear in the electrode reaction (half reaction). (05)

(ii) Consider the following reaction.
Fe(s) + 2H^+(aq) + ½O_2(g) → Fe^{2+}(aq) + H_2O(l)
I. Write the oxidation and reduction half reactions relevant to the above reaction.

Answer

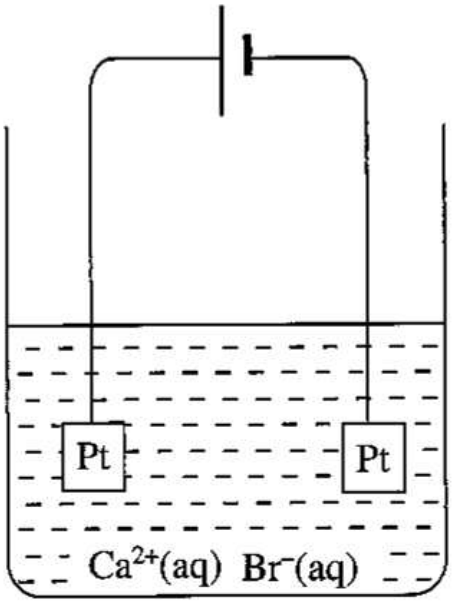
Fe(s) → Fe^{2+}(aq) + 2e (oxidation half reaction) (08)
½O_2(g) + 2H^+(aq) + 2e → H_2O(l) (reduction half reaction) (08)
(⇌ accepted). Physical states are required.

II. Given that the above reaction is the cell reaction of an electrochemical cell, determine the standard electromotive force of the cell.
$E°_{Fe^{2+}(aq)/Fe(s)}$ = −0.44 V $E°_{H^+(aq)/O_2(g)/H_2O(l)}$ = 1.23 V

Answer

Standard cell potential = 1.23 V − (−0.44 V) **OR** (1.23 − (−0.44)) V (01 + 01) + (01 + 01) = **1.67 V** (04 + 01)

(iii) A constant current of 100 mA was passed through 100.00 cm^3 of a 0.10 mol dm^{-3} aqueous $CaBr_2$ solution as shown in the diagram. The temperature of the system was maintained at 25 °C.



2+

−

I. Write the oxidation and reduction reactions that take place at the electrodes.

Answer

Oxidation half reaction: $2Br^-(aq) \rightarrow Br_2(g) + 2e$ **OR** $2Br^-(aq) \rightarrow Br_2(l) + 2e$ (05)
Reduction half reaction: $2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$ (05)
(⇌ accepted). Physical states are required.

II. Calculate the time taken for the commencement of precipitation of $Ca(OH)_2(s)$. Solubility product of $Ca(OH)_2$ at 25 °C is 1.0×10^{-5} mol^3 dm^{-9}. Neglect the ionization of water. Assume that the volume of the aqueous phase remains constant.

Answer

$K_{sp} = [Ca^{2+}(aq)][OH^-(aq)]^2$ (05)
Required concentration of OH^- to start precipitation of $Ca(OH)_2 = [OH^-]$
$[OH^-] = \sqrt{(1.0 \times 10^{-5}\ mol^3\ dm^{-9}/0.1\ mol\ dm^{-3})}$ **OR** 1.0×10^{-2} mol dm^{-3} (04 + 01)
The amount of OH^- required to provide the above concentration = n_{OH-}
$n_{OH-} = 1.0 \times 10^{-2}$ mol $dm^{-3} \times 100 \times 10^{-3}$ dm^3 **OR** 1.0×10^{-3} mol (04 + 01)
Amount of charge that must be passed through the solution, $Q = 1.0 \times 10^{-3}$ mol $\times$ 96500 C mol^{-1} **OR** 96.5 C (04 + 01)
Time required to pass the charge Q when the current flow is 100 mA = t
$t = 96.5\ C/(100 \times 10^{-3}\ C\ s^{-1})$ **OR** 965 s **OR** 16.08 min (04 + 01)
(For the Faraday constant, a value between 96500 ± 100 C mol^{-1} is accepted. If the symbol F is used for the Faraday constant, and t is calculated using F, full marks can be awarded. t = 16.08 min **OR** t = 16 min accepted.) 10(b) = 75 marks

Review.

Principle: electrode potentials and Faraday's laws combined with K_{sp}. The Ag/AgCl electrode is a metal–insoluble salt electrode: its half reaction involves Cl^-, not free Ag^+, so its potential depends on $[Cl^-]$ only. $E°_{cell} = E°_{cathode} - E°_{anode} = 1.23 - (-0.44) = 1.67$ V (do not multiply E° by stoichiometric coefficients). In the electrolysis, Br^- is oxidised at the anode and water (not Ca^{2+}) is reduced at the cathode, producing OH^-; Ca^{2+} is not consumed, so $[Ca^{2+}]$ stays 0.10 mol dm^{-3}. Precipitation starts when $[OH^-] = \sqrt{(K_{sp}/[Ca^{2+}])} = 1.0 \times 10^{-2}$ mol dm^{-3}, i.e. 1.0×10^{-3} mol OH^- in 100 cm^3; one electron gives one OH^-, so Q = 96.5 C and t = 965 s (16.1 min). Common mistakes: reducing Ca^{2+} to Ca, using 2 F per mole of OH^-, using

0.20 mol dm^{-3} (the Br^- concentration) for $[Ca^{2+}]$, and forgetting to convert mA to A. Within the current syllabus (Resource Book Unit 13, electrodes and electrolysis; Unit 12, solubility product).

Read: RB U6 §4.10.6 · p. 169 RB U13 §3.2 · p. 238 RB U13 §3.4 · p. 261 RB U12 §2.4 · p. 175

2017 · Chemistry Digital Paper

50 questions · 2 hours

MCQ · Paper I

Question 1 · Q1–30 · single answer

The scientist who disproved Thomson's 'plum pudding' model of the atomic structure is,

- (1)Ernest Rutherford.
- (2)Robert Millikan.
- (3)Niels Bohr.
- (4)Eugen Goldstein.
- (5)Henry Moseley.

Answer and review

Answer **(1)** Prepared from the Sinhala-medium official scheme

Rutherford's gold-foil (α-scattering) experiment, interpreted as a small, dense, positive nucleus, disproved the plum-pudding model. Millikan measured the electron charge, Goldstein discovered canal (positive) rays, Bohr proposed the quantised model that followed, and Moseley related X-ray frequencies to atomic number.

RB U1 §1.1 · p. 2

Question 2 · Q1–30 · single answer

Which of the following statements is **false** with regard to the following molecules?

CO_2, BF_3, PF_3, CF_4, XeF_4, SF_6

- (1)All molecules have polar covalent bonds.
- (2)All molecules have different shapes.
- (3)All molecules do not obey the octet rule.
- (4)All molecules are nonpolar.
- (5)Only two molecules possess lone pairs of electrons on their central atoms.

Answer and review

Answer **(3/4)** Prepared from the Sinhala-medium official scheme

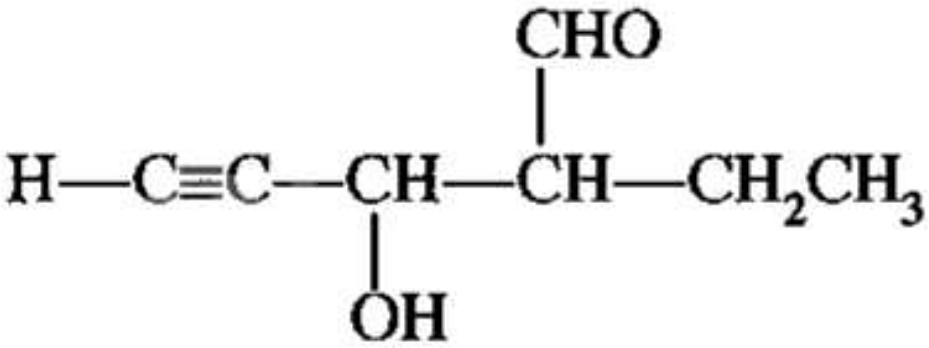
The official scheme accepts (3) or (4). (4) is clearly false: PF_3 is trigonal pyramidal with a lone pair and is polar. (3) is ambiguously worded: if read as "none obeys the octet rule" it is false (CO_2, PF_3 and CF_4 obey it; BF_3, XeF_4 and SF_6 do not), so both were accepted. (1), (2) (linear, trigonal planar, pyramidal, tetrahedral, square planar, octahedral) and (5) (lone pairs only on P in PF_3 and Xe in XeF_4) are true.

RB U2 §2.3 · p. 52

Question 3 · Q1–30 · single answer

What is the IUPAC name of the following compound?

IUPAC name of the following compound?



- (1)4-formylhex-1-yn-3-ol
- (2)4-formyl-3-hydroxyhex-1-yne
- (3)2-ethyl-3-hydroxy-4-ynepentanal
- (4)3-hydroxy-4-ethyl-1-ynepentanal
- (5)2-ethyl-3-hydroxypent-4-ynal

Answer and review

Answer **(5)** Prepared from the Sinhala-medium official scheme

The aldehyde (–CHO) is the principal group, so the chain is numbered from the CHO carbon: C1 (CHO), C2 (bears the ethyl), C3 (OH), C4≡C5. The longest chain through C1 has five carbons, giving 2-ethyl-3-hydroxypent-4-ynal. Naming it as an alcohol or alkyne ignores the priority order, and (3)/(4) have wrong "yne" endings and locants.

RB U7 §1.3 · p. 7

Question 4 · Q1–30 · single answer

The oxidation state of nitrogen is −1 in,

- (1)N_2O_4
- (2)N_2O
- (3)NO_2F
- (4)NH_3
- (5)NH_2OH

Answer and review

Answer **(5)** Prepared from the Sinhala-medium official scheme

In NH_2OH: N + 2(+1) + (−2) + (+1) = 0, so N = −1. The others are +4 (N_2O_4), +1 (N_2O), +5 (NO_2F) and −3 (NH_3).

RB U3 §3.1 · p. 88

Question 5 · Q1–30 · single answer

Several shapes of molecules originate based on the trigonal bipyramidal electron pair geometry around the central atom. They are,

- (1)linear, angular, see-saw.
- (2)linear, T-shape, see-saw.
- (3)linear, trigonal pyramidal, T-shape.
- (4)trigonal planar, angular, T-shape.
- (5)linear, trigonal planar, see-saw.

Answer and review

Answer **(2)** Prepared from the Sinhala-medium official scheme

Replacing equatorial positions of a trigonal bipyramid with lone pairs gives see-saw (1 lone pair, e.g. SF_4), T-shape (2, e.g. ClF_3) and linear (3, e.g. XeF_2). Lone pairs prefer the equatorial positions, so trigonal pyramidal, trigonal planar and angular shapes do not arise from this geometry.

RB U2 §2.3 · p. 52

Question 6 · Q1–30 · single answer

Ammonium nitrate decomposes explosively at high temperature to form nitrogen gas, oxygen gas and water vapour. The total number of litres of gases formed at standard temperature and pressure when 240 g of ammonium nitrate is decomposed is,

(H = 1, N = 14, O = 16, At standard temperature and pressure one mole of gas occupies 22.4 litres)

- (1)33.6
- (2)67.2
- (3)100.8
- (4)134.4
- (5)235.2

Answer and review

Answer **(2/3/5)** Prepared from the Sinhala-medium official scheme

The official scheme accepts (2), (3) or (5) because the question is ambiguous about the state of the water. $NH_4NO_3 \rightarrow N_2 + ½O_2 + 2H_2O$; 240 g = 3 mol. Counting $N_2 + O_2$ only (water liquid at STP): 3 × 1.5 = 4.5 mol = 100.8 L, (3). Counting water vapour too: 3 × 3.5 = 10.5 mol = 235.2 L, (5). 3 mol N_2 alone gives 67.2 L, (2).

RB U3 §3.8 · p. 115 RB U4 §1.2 · p. 5

Question 7 · Q1–30 · single answer

AX and BX_2 are two sparingly soluble salts in water. At room temperature, their solubility products are K_{sp1} and K_{sp2} respectively. Solubility of AX is p while that of BX_2 is q. When each salt is in equilibrium with its saturated solution, if $K_{sp1}/[A^+(aq)] = K_{sp2}/[B^{2+}(aq)]$, which of the following is correct?

- (1)$p = q^2$
- (2)$p^2 = q$
- (3)$4p = q^2$
- (4)$p = 4q^2$
- (5)$p = 2q^2$

Answer and review

Answer **(4)** Prepared from the Sinhala-medium official scheme

For AX: $K_{sp1} = p^2$ and $[A^+] = p$, so the left side = p. For BX_2: $K_{sp2} = [B^{2+}][X^-]^2 = q(2q)^2 = 4q^3$ and $[B^{2+}] = q$, so the right side = $4q^2$. Hence $p = 4q^2$. The trap is forgetting the factor 2 in $[X^-]$ for BX_2.

RB U12 §2.4 · p. 175

Question 8 · Q1–30 · single answer

Which of the following statements is **false** with regard to alkali and alkaline earth metals?

- (1)All alkaline earth metals react with N_2 gas at high temperature.
- (2)The melting points of alkaline earth metals are higher than the melting points of alkali metals in the same period.
- (3)Second ionization energies of alkali metals are much higher than those of alkaline earth metals in the same period.
- (4)All hydroxides formed by alkaline earth metals are strong bases.
- (5)The solubility of alkali metal hydroxides increases down the group.

Answer and review

Answer **(4)** Prepared from the Sinhala-medium official scheme

$Be(OH)_2$ is amphoteric and $Mg(OH)_2$ is only weakly basic (sparingly soluble), so (4) is false. The other statements are true: all Group 2 metals form nitrides (M_3N_2) when heated in N_2, two electrons in the metallic bond give higher melting points, removing a second electron from an alkali metal breaks a noble-gas core, and alkali hydroxide solubility increases down the group.

RB U6 §4.2 · p. 126 RB U6 §4.1 · p. 122

Question 9 · Q1–30 · single answer

The effective nuclear charge felt by the valence electron in lithium (Li) is,

(Li, Z = 3 and relative atomic mass = 7)

- (1)equal to +3
- (2)less than +3
- (3)greater than +3
- (4)equal to +7
- (5)less than +7

Answer and review

Answer **(2)** Prepared from the Sinhala-medium official scheme

The 2s electron is shielded by the two 1s electrons, so $Z_{eff} = Z -$ shielding is less than +3 (about +1.3). It cannot exceed Z, and the mass number (7) is irrelevant to nuclear charge.

RB U1 §1.6 · p. 32

Question 10 · Q1–30 · single answer

The following equilibrium exists in a closed-rigid container at a given temperature.

$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$

An extra amount of $O_2(g)$ is added into the container at the same temperature. After the equilibrium is re-established, which of the following has a lower value compared to its value at the initial equilibrium?

- (1)Equilibrium constant of the reaction.
- (2)The total pressure of the system.
- (3)The amount of $SO_2(g)$ in the system.
- (4)The amount of $SO_3(g)$ in the system.
- (5)The amount of $O_2(g)$ in the system.

Answer and review

Answer **(3)** Prepared from the Sinhala-medium official scheme

Added O_2 shifts the equilibrium to the left, consuming SO_2 and forming SO_3, so the amount of SO_2 falls and SO_3 rises. K depends only on temperature and is unchanged. Only part of the added O_2 is consumed, so O_2 and the total pressure are higher than before.

RB U12 §2.1 · p. 76

Question 11 · Q1–30 · single answer

Which of the following is true regarding the O—N—O angle of the nitrogen species?

- (1)$NO_2\hat{}+ > NO_2\hat{}- > NO_2 > NO_4^{3-}$
- (2)$NO_4^{3-} > NO_2\hat{}+ > NO_2 > NO_2\hat{}-$
- (3)$NO_2\hat{}+ > NO_2 > NO_2\hat{}- > NO_4^{3-}$
- (4)$NO_4^{3-} > NO_2 > NO_2\hat{}- > NO_2\hat{}+$
- (5)$NO_2\hat{}+ > NO_2\hat{}- > NO_4^{3-} > NO_2$

Answer and review

Answer **(3)** Prepared from the Sinhala-medium official scheme

$NO_2\hat{}+$ is linear (180°); NO_2 has one unpaired electron on N that repels less than a lone pair (about 134°); $NO_2\hat{}-$ has a lone pair (about 115°); NO_4^{3-} is tetrahedral (109.5°). Order: $NO_2\hat{}+ > NO_2 > NO_2\hat{}- > NO_4^{3-}$.

RB U2 §2.3 · p. 52

Question 12 · Q1–30 · single answer

A lamp produces 6.0 J of energy per second in the blue region (470 nm) of the visible light. For how long should the lamp be lit to generate 1.0×10^{20} photons?

- (1)2.4 s
- (2)7.1 s
- (3)8.5 s
- (4)9.2 s

- (5)10.5 s

Answer and review

Answer **(2)** Prepared from the Sinhala-medium official scheme

Energy per photon = hc/λ = $(6.626\times10^{-34} \times 3\times10^{8})/(470\times10^{-9}) = 4.23\times10^{-19}$ J. For 10^{20} photons: 42.3 J. Time = 42.3 / 6.0 = 7.05 ≈ 7.1 s.

RB U1 §1.2 · p. 13

Question 13 · Q1–30 · single answer

A reaction is spontaneous at 298 K and 100 kPa pressure, while it is non-spontaneous at high temperature and the same pressure. Which of the following is **true** for this reaction at 298 K and 100 kPa pressure?

	ΔG	ΔH	ΔS
(1)	positive	positive	positive
(2)	negative	negative	negative
(3)	negative	negative	positive
(4)	negative	positive	negative
(5)	positive	positive	negative

Answer and review

Answer **(2)** Prepared from the Sinhala-medium official scheme

Spontaneous at 298 K means ΔG < 0. ΔG = ΔH − TΔS becomes positive at high T only if −TΔS is positive and large, so ΔS < 0; for ΔG to be negative at low T, ΔH must be negative. So ΔG, ΔH and ΔS are all negative.

RB U5 §2.4 · p. 53

Question 14 · Q1–30 · single answer

The following procedure was used to determine the molar mass of an unknown gas X. First, the mass of a rigid container of volume V containing dry air was measured as m_1. Then the dry air was removed and the container was filled with an unknown gas X and the mass was measured as m_2. Both the dry air and unknown gas were at the same temperature (T) and pressure (P). Density of dry air is d. Which of the following expressions gives the molar mass of the unknown gas?

- (1)dRT/P
- (2)$[m_2 - (m_1 - dV)]RT/(PV)$
- (3)$(m_1 - m_2)RT/(PV)$
- (4)$(m_2 - m_1)RT/(PV)$
- (5)$[m_1 - (m_2 - dV)]RT/(PV)$

Answer and review

Answer **(2)** Prepared from the Sinhala-medium official scheme

The air in the container has mass dV, so the empty container has mass $m_1 - dV$. The mass of gas X is $m_2 - (m_1 - dV)$. From PV = (m/M)RT, M = mRT/(PV) = $[m_2 - (m_1 - dV)]RT/(PV)$. Forgetting to subtract the mass of the air gives option (4).

RB U4 §1.2 · p. 5

Question 15 · Q1–30 · single answer

A buffer solution is prepared by mixing a volume V_1 of a monobasic weak acid with a volume V_2 of a monoacidic strong base. The initial concentrations of the weak acid and the strong base are C_1 and C_2, respectively. The acid dissociation constant of the weak acid is K_a. If the pH of the buffer solution is to be maintained between $pK_a - 1$ and $pK_a + 1$, which of the following expressions gives the correct relationship for C_1, C_2, V_1 and V_2?

- (1)$1/10 < C_2V_2/(C_1V_1 - C_2V_2) < 10$
- (2)$1/10 < C_1V_1/(C_1V_1 - C_2V_2) < 10$
- (3)$1/10 < C_2V_2/(C_1V_1) < 10$
- (4)$1/10 < (C_1V_1 - C_2V_2)/(C_2V_2) < 10$
- (5)$1 < C_1V_1/(C_2V_2) < 10$

Answer and review

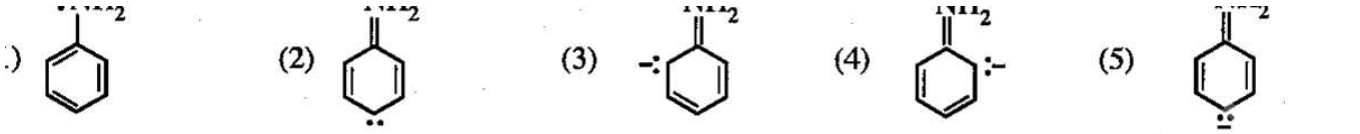
Answer **(1/4)** Prepared from the Sinhala-medium official scheme

The base converts C_2V_2 mol of acid to salt, leaving $C_1V_1 - C_2V_2$ mol of acid. pH = $pK_a + \log([A^-]/[HA])$ lies within $pK_a \pm 1$ when $1/10 < [A^-]/[HA] < 10$, i.e. $1/10 < C_2V_2/(C_1V_1 - C_2V_2) < 10$, option (1). Because the range 1/10 to 10 is symmetrical, the inverted ratio in (4) gives the same limits, so the scheme accepts both.

RB U12 §2.3 · p. 167

Question 16 · Q1–30 · single answer

Which of the following is **not** a resonance structure of aniline?



ıe initial rate of a zero-order reaction is R_n and its rate constant is k. The rate of the reaction when

Answer and review

Answer **(2)** Prepared from the Sinhala-medium official scheme

In aniline the N lone pair delocalises to the ortho and para ring carbons, putting a negative charge there and a positive charge on N. Structure (2) shows the lone pair at the para carbon but without the negative charge, so its overall charge is +1 and it cannot be a resonance form of the neutral molecule. (1) is the Kekulé structure; (3), (4) (ortho) and (5) (para) carry both charges.

RB U2 §2.3 · p. 52 RB U10 §4.2 · p. 77

Question 17 · Q1–30 · single answer

The initial rate of a zero-order reaction is R_0 and its rate constant is k. The rate of the reaction when the initial concentration is reduced by 50% is,

- (1)k
- (2)1/k
- (3)k/2
- (4)$R_0/2$
- (5)$R_0/4$

Answer and review

Answer **(1)** Prepared from the Sinhala-medium official scheme

For a zero-order reaction rate = $k[A]^0 = k$, independent of concentration, so $R_0 = k$ and halving the concentration leaves the rate at k. Options (4) and (5) wrongly treat it as first or second order.

RB U11 §1.6 · p. 16

Question 18 · Q1–30 · single answer

An electrochemical cell was constructed by connecting half-cells of Ni^{2+}(aq, 1.0 M)/Ni(s) and Cu^{2+}(aq, 1.0 M)/Cu(s) with a voltmeter and a salt bridge. The overall cell reaction and the initial reading of the voltmeter when the half-cells are connected are,

($E°_{Ni^{2+}/Ni} = -0.24$ V and $E°_{Cu^{2+}/Cu} = +0.34$ V)

- (1)$Ni^{2+}(aq) + Cu(s) \rightarrow Ni(s) + Cu^{2+}(aq)$; 0.00 V
- (2)$Cu^{2+}(aq) + Ni(s) \rightarrow Cu(s) + Ni^{2+}(aq)$; +0.58 V
- (3)$Cu^{2+}(aq) + Ni(s) \rightarrow Cu(s) + Ni^{2+}(aq)$; −0.58 V
- (4)$Cu^{2+}(aq) + Ni(s) \rightarrow Cu(s) + Ni^{2+}(aq)$; 0.00 V
- (5)$Cu(s) + Ni(s) \rightarrow Cu^{2+}(aq) + Ni^{2+}(aq) + 4e$; +0.58 V

Answer and review

Answer **(2)** Prepared from the Sinhala-medium official scheme

The more positive Cu^{2+}/Cu electrode is the cathode and Ni the anode: $Cu^{2+} + Ni \rightarrow Cu + Ni^{2+}$. $E°_{cell} = 0.34 - (-0.24) = +0.58$ V. A spontaneous cell reaction has a positive emf; (3) has the right equation but the wrong sign, and (5) is not a balanced reaction.

RB U13 §3.3 · p. 250

Question 19 · Q1–30 · single answer

Solid diiodine pentoxide (I_2O_5) reacts with carbon monoxide at room temperature to give carbon dioxide and iodine. This can be used to measure the amount of carbon monoxide in a sample of air. An air sample of 5.0 dm^3 was passed through a tube containing I_2O_5 and the liberated iodine was collected in an aqueous KI solution (KI in excess). The resulting solution was titrated with 0.005 mol dm^{-3} $Na_2S_2O_3$ solution using starch as the indicator. The volume of $Na_2S_2O_3$ required was 10.00 cm^3. The concentration (in ppm) of carbon monoxide in the air sample is, (C = 12, O = 16, density of the air sample = 1.40×10^{-3} g cm^{-3})

- (1)100
- (2)250
- (3)500
- (4)700

- (5)1000

Answer and review

Answer **(3)** Prepared from the Sinhala-medium official scheme

$I_2O_5 + 5CO \rightarrow I_2 + 5CO_2$; $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$. $n(S_2O_3^{2-}) = 0.005 \times 0.0100 = 5.0\times10^{-5}$ mol, so $n(I_2) = 2.5\times10^{-5}$ mol and $n(CO) = 1.25\times10^{-4}$ mol = 3.5×10^{-3} g. Mass of air = 5000 cm^3 × 1.40×10^{-3} = 7.0 g. ppm = $(3.5\times10^{-3}/7.0) \times 10^6$ = 500.

RB U3 §3.8 · p. 115 RB U3 §3.5 · p. 102

Question 20 · Q1–30 · single answer

Which of the following statements is **false** with regard to sulfur and its compounds?

- (1)S is a non metal with oxidation states in the range −2 to +6.
- (2)S reacts with conc. H_2SO_4 giving SO_3 as one of the products.
- (3)SO_2 can act both as an oxidizing agent and as a reducing agent.
- (4)Burning large quantities of S contributes to acid rain.
- (5)Concentrated H_2SO_4 can act as a strong acid, an oxidizing agent and a dehydrating agent.

Answer and review

Answer **(2)** Prepared from the Sinhala-medium official scheme

Hot concentrated H_2SO_4 oxidises sulfur to SO_2 ($S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$); SO_3 is not a product, as sulfuric acid is itself reduced to SO_2. The other statements are true (S is +4 in SO_2, which can go up to +6 or down to 0).

RB U6 §4.6 · p. 141

Question 21 · Q1–30 · single answer

At 298 K, for the reaction $N_2(g) + 3F_2(g) \rightarrow 2NF_3(g)$, $\Delta H° = -263$ kJ mol^{-1}. Bond dissociation enthalpies of N≡N and N—F are 946 kJ mol^{-1} and 272 kJ mol^{-1}, respectively. The value (in kJ mol^{-1}) of the bond dissociation enthalpy of the F—F bond is,

- (1)−423
- (2)−393
- (3)−141
- (4)141
- (5)423

Answer and review

Answer **(4)** Prepared from the Sinhala-medium official scheme

ΔH = Σ(bonds broken) − Σ(bonds formed): $-263 = 946 + 3x - 6(272)$. So $3x = -263 - 946 + 1632 = 423$ and $x = 141$ kJ mol^{-1}. Bond dissociation enthalpies are positive, ruling out (1)–(3); 423 (5) is 3x.

RB U5 §2.2 · p. 36

Question 22 · Q1–30 · single answer

Which of the following statements is **false** with regard to 3d-block elements?

- (1)Sc, Ti and Zn do not exhibit variable valency.
- (2)3d-block elements are good industrial catalysts.
- (3)Mn forms acidic, amphoteric and basic oxides.
- (4)Zn has the lowest melting point among all 3d-block elements.
- (5)Positive oxidation states of V range from +2 to +5.

Answer and review

Answer **(1)** Prepared from the Sinhala-medium official scheme

Ti shows +2, +3 and +4 (only Sc and Zn are essentially fixed at +3 and +2), so (1) is false. Mn oxides range from basic MnO to amphoteric Mn_2O_3/MnO_2 and acidic Mn_2O_7; V shows +2 to +5; Zn has the lowest melting point (420 °C) of the 3d metals.

RB U6 §4.10 · p. 160

Question 23 · Q1–30 · single answer

The following thermochemical data are given for the reaction.

$3NO(g) \rightleftharpoons NO_2(g) + N_2O(g)$

$\Delta H°_{f\ NO_2(g)} = 35\ kJ\ mol^{-1}$, $\Delta H°_{f\ N_2O(g)} = 80\ kJ\ mol^{-1}$, $\Delta H°_{f\ NO(g)} = 90\ kJ\ mol^{-1}$

Which of the following statements is **true** for the reaction above?

- (1)$\Delta H° = -155\ kJ\ mol^{-1}$ while the value of the equilibrium constant of the reaction decreases with increasing temperature.
- (2)$\Delta H° = 155\ kJ\ mol^{-1}$ while the value of the equilibrium constant of the reaction decreases with increasing temperature.
- (3)$\Delta H° = -25\ kJ\ mol^{-1}$ while the value of the equilibrium constant of the reaction decreases with increasing temperature.
- (4)$\Delta H° = 25\ kJ\ mol^{-1}$ while the value of the equilibrium constant of the reaction decreases with increasing temperature.
- (5)$\Delta H° = -155\ kJ\ mol^{-1}$ while the value of the equilibrium constant of the reaction increases with increasing temperature.

Answer and review

Answer **(1)** Prepared from the Sinhala-medium official scheme

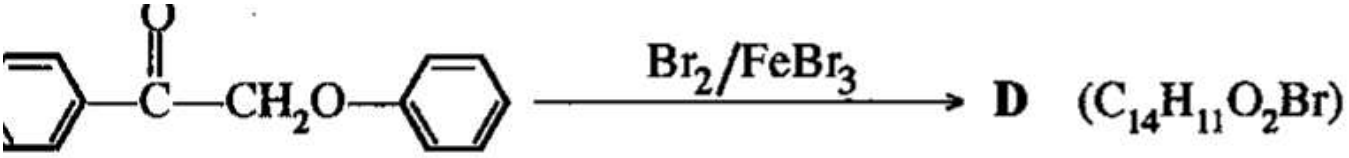
$\Delta H° = \Sigma\ \Delta H_f(\text{products}) - \Sigma\ \Delta H_f(\text{reactants}) = (35 + 80) - 3(90) = -155\ kJ\ mol^{-1}$. The reaction is exothermic, so raising the temperature shifts it to the left and K decreases (van 't Hoff / Le Chatelier). (5) has the right ΔH but the wrong temperature effect.

RB U5 §2.2 · p. 36 RB U12 §2.1 · p. 76

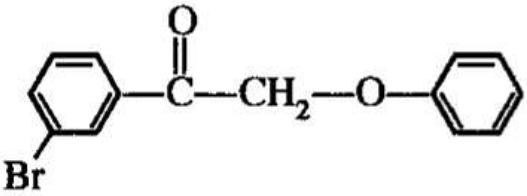
Question 24 · Q1–30 · single answer

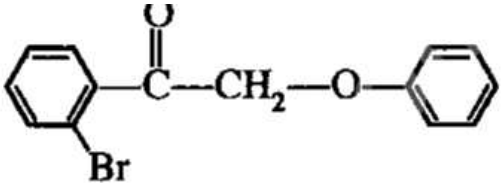
Consider the following reaction.

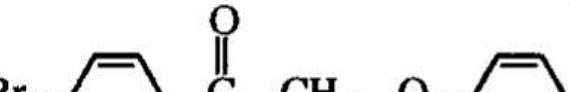
The most likely structure of D is,

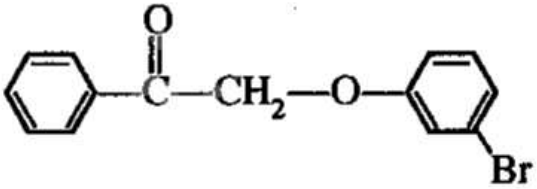


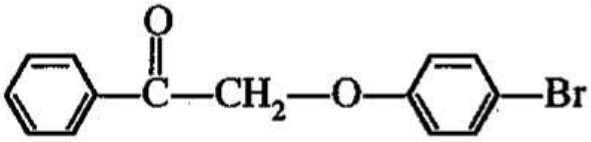
most likely structure of **D** is

(1) 

(2) 

(3) 

(4) 

(5) 

Answer and review

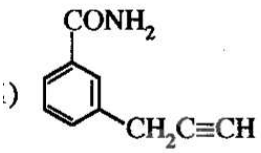
Answer **(5)** Prepared from the Sinhala-medium official scheme

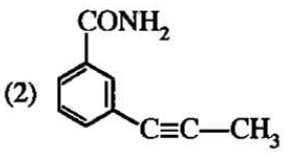
The ring bonded to C=O is deactivated and directs meta, whereas the ring bonded to the ether oxygen is activated (+M effect of O) and directs ortho/para. Bromination therefore occurs on the phenoxy ring, mainly at the less hindered para position, giving the para-bromo compound (5), $C_{14}H_{11}O_2Br$. (1)–(3) brominate the deactivated ring.

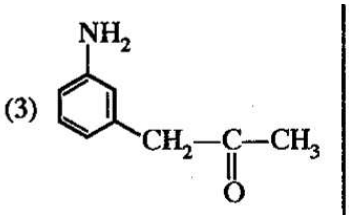
RB U8 §2.5 · p. 49 RB U8 §2.4 · p. 44

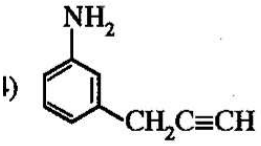
Question 25 · Q1–30 · single answer

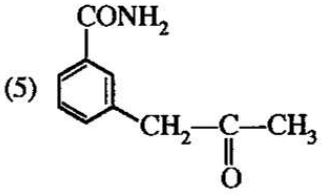
Compound A reacts with $LiAlH_4$ to give B. B is more basic than A. B liberates N_2 when treated with $NaNO_2$/HCl at 0–5 °C. Both A and B react with ammoniacal $AgNO_3$ to give precipitates. The structure of A could be,

(1) 

(2) 

(3) 

(4) 

(5) 

Answer and review

Answer **(1)** Prepared from the Sinhala-medium official scheme

$LiAlH_4$ reduces an amide (–$CONH_2$) to a primary amine (–CH_2NH_2), which is more basic. An aliphatic primary amine gives N_2 with HNO_2 at 0–5 °C (an aromatic –NH_2 would give a stable diazonium salt). A precipitate with ammoniacal $AgNO_3$ shows a terminal alkyne (–C≡C–H) in both A and B: this is (1), the amide with a $CH_2C{\equiv}CH$ side chain. (2) has an internal alkyne, (3) and (4) are not amides, and (5) has a ketone and no alkyne.

RB U10 §4.1 · p. 75 RB U9 §3.6 · p. 70 RB U8 §2.3 · p. 41

Question 26 · Q1–30 · single answer

Which of the following statements is **true** with regard to ozone layer depletion?

- (1)Chlorofluorocarbons (CFCs) react directly with ozone and deplete the ozone layer.
- (2)Falling of IR radiation on the earth surface is encouraged by the depletion of the ozone layer.
- (3)Hydrofluorocarbons (HFCs) contribute to ozone layer depletion.
- (4)Ozone in the ozone layer undergoes natural decomposition in the presence of ultraviolet radiation.
- (5)Ozone layer depletion takes place only by ClO^• free radicals.

Answer and review

Answer **(4)** Prepared from the Sinhala-medium official scheme

Ozone is continually formed and photolysed by UV in the stratosphere. CFCs do not attack ozone directly: UV releases Cl^•, which catalyses ozone destruction. Depletion increases UV (not IR) reaching Earth. HFCs contain no Cl and do not deplete ozone, and other radicals (e.g. NO^•, Br^•) also deplete it, so (5) is false.

RB U14 §1.13 · p. 58

Question 27 · Q1–30 · single answer

Which of the following is **true** about the half-reaction, $AlF_6^{3-}(aq) + 3e \rightarrow Al(s) + 6F^-(aq)$, that occurs in an electrolytic cell?

- (1)Al is oxidized.
- (2)AlF_6^{3-} is reduced.
- (3)Oxidation state of Al is changed from −3 to 0.
- (4)F^- acts as a reducing agent.
- (5)F^- is reduced.

Answer and review

Answer **(2)** Prepared from the Sinhala-medium official scheme

The half-reaction gains electrons, so it is a reduction; AlF_6^{3-} is reduced and Al changes from +3 to 0 (not −3). F^- is only a spectator in this half-reaction (its oxidation state stays −1).

RB U13 §3.4 · p. 261 RB U3 §3.1 · p. 88

Question 28 · Q1–30 · single answer

$CH_3CHO \xrightarrow{(OH^-)} P \xrightarrow{(H^+)} Q \xrightarrow{((1)\ CH_3MgBr,\ (2)\ H^+)} R$

In the reaction scheme given above, the structures of P, Q and R respectively are,

- (1)$CH_3CH_2CH(OH)CHO$, $CH_3CH{=}CHCHO$, $CH_3CH{=}CH{-}C(CH_3)_2{-}OH$

- (2)$CH_3CH(OH)CH_2CHO$, $CH_3CH{=}CHCHO$, $CH_3CH{=}CH{-}C(CH_3)_2{-}OH$
- (3)$CH_3CH(OH)CH_2CHO$, $CH_2{=}CHCH_2CHO$, $CH_2{=}CH{-}CH_2{-}CH(CH_3)OH$
- (4)$CH_3CH(OH)CH_2CHO$, $CH_3CH{=}CHCHO$, $CH_3CH{=}CH{-}CH(CH_3)OH$
- (5)$CH_3CH_2CH(OH)CHO$, $CH_3CH{=}CHCHO$, $CH_3CH{=}CH{-}CH(CH_3)OH$

Answer and review

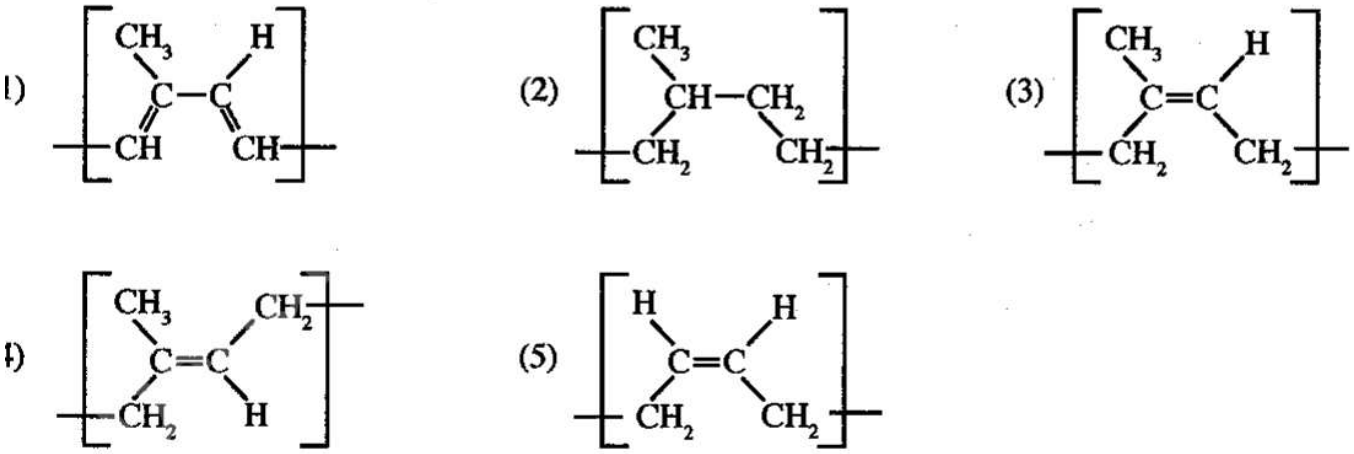
Answer **(4)** Prepared from the Sinhala-medium official scheme

Base-catalysed aldol addition of ethanal gives P, 3-hydroxybutanal; acid dehydrates it to the conjugated crotonaldehyde Q (but-2-enal). CH_3MgBr adds to the aldehyde C=O (1,2-addition), and hydrolysis gives the secondary alcohol R, pent-3-en-2-ol. (1) and (2) would need a ketone for a tertiary alcohol; (1) and (5) show a wrong aldol product.

RB U9 §3.4 · p. 60

Question 29 · Q1–30 · single answer

The repeating unit of natural rubber is,



Answer and review

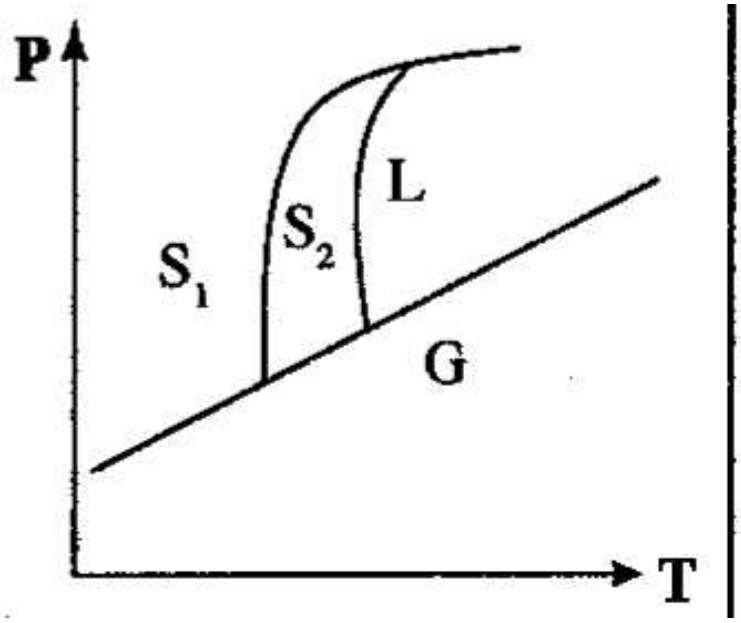
Answer **(3)** Prepared from the Sinhala-medium official scheme

Natural rubber is cis-1,4-polyisoprene, $-[CH_2{-}C(CH_3){=}CH{-}CH_2]-_n$, with the two chain CH_2 groups on the same side of the C=C. Structure (3) is this unit; (5) lacks the methyl group, (2) has no double bond, and (1) and (4) have a different arrangement of the carbon skeleton.

RB U14 §1.12 · p. 48

Question 30 · Q1–30 · single answer

The phase diagram of an element is shown in the figure. Which of the following statements is **false** with regard to the phase diagram of this element?



- (1)There is one T, P condition at which the phases S_1, S_2 and G are in equilibrium.
- (2)There is one T, P condition at which the phases S_1, S_2 and L are in equilibrium.
- (3)There is one T, P condition at which the phases S_2, L and G are in equilibrium.
- (4)There is one T, P condition at which the phases S_1, L and G are in equilibrium.
- (5)Three T, P conditions at which more than two phases are in equilibrium are shown in the phase diagram.

Answer and review

Answer **(4)** Prepared from the Sinhala-medium official scheme

Triple points occur where three phase regions meet: $S_1/S_2/G$ (low P, on the sublimation line), $S_2/L/G$ (where S_2 meets liquid on the sublimation line), and $S_1/S_2/L$ (top, where the S_1–S_2 boundary meets the liquid). S_1, L and G never meet at one point, since S_2 lies between S_1 and L along the gas line, so (4) is false and (5) is true.

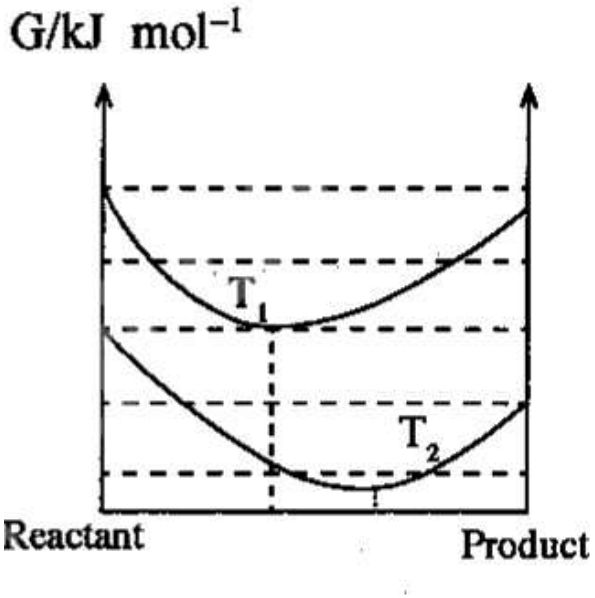
RB U12 §2.5 · p. 199

Questions 31–40: response code

(1)	(2)	(3)	(4)	(5)
Only (a) and (b) are correct	Only (b) and (c) are correct	Only (c) and (d) are correct	Only (d) and (a) are correct	Any other number or combination of responses is correct

Question 31 · Q31–40 · response code

The variation of standard Gibbs energy of A(g) ⇌ B(g) with the extent of reaction at two temperatures T_1, T_2 ($T_2 > T_1$) and constant pressure is shown in the figure. Which of the following statements is/are **correct** for this reaction?



- Equilibrium constant at T_2 is greater than that at T_1.
- The reaction is endothermic.
- The reaction has a positive ΔS° value.
- The reaction is exothermic.

Answer and review

Answer **(5)** Prepared from the Sinhala-medium official scheme

The G-minimum (the equilibrium position) lies further toward the product side at the higher temperature T_2, so K is larger at T_2; K increasing with T means the reaction is endothermic. The T_2 curve also lies lower overall, i.e. ΔG° falls with temperature, so ΔS° (= −dΔG°/dT) is positive. (a), (b) and (c) are true and (d) is false, which is none of the listed pairs, so code (5).

RB U5 §2.4 · p. 53 RB U12 §2.1 · p. 76

Question 32 · Q31–40 · response code

$CH_3CH_2CH{=}CH_2$ —HBr→ $CH_3CH_2CHBrCH_3$ (P) + $CH_3CH_2CH_2CH_2Br$ (Q)

Which of the following statements is/are **correct** regarding the above reaction?

- This reaction is a nucleophilic addition reaction.
- P is the major product.
- A carbocation is formed in the first step of the reaction.
- Q is the major product.

Answer and review

Answer **(2)** Prepared from the Sinhala-medium official scheme

HBr adds to an alkene by electrophilic addition: H^+ attacks the C=C to form the more stable secondary carbocation, which Br^- then attacks (Markovnikov), giving P as the major product. (b) and (c) are correct.

RB U8 §2.2 · p. 33

Question 33 · Q31–40 · response code

The following statements refer to certain industrial processes. Which of the following statements is/are **correct**?

- Baby soap is manufactured using KOH.
- Reaction of SO_2 with O_2 to give SO_3 in the contact process is favoured under low pressures.
- K_2CO_3 can be synthesised using the Solvay process.
- Cathode and anode compartments are separated by a diaphragm to prevent the reaction between Na and chlorine gas in the manufacture of Na using the Down's cell.

Answer and review

Answer **(4)** Prepared from the Sinhala-medium official scheme

Potassium soaps (from KOH) are soft and used in baby/toilet soaps; (a) is true. $2SO_2 + O_2 \rightleftharpoons 2SO_3$ reduces the number of moles, so high pressure favours SO_3 (b is false). K_2CO_3 cannot be made by the Solvay process because $KHCO_3$ is too soluble to precipitate (c false). In the Down's cell a gauze/diaphragm keeps Na and Cl_2 apart (d true). So (a) and (d): code (4).

RB U14 §1.4 · p. 14 RB U14 §1.5 · p. 18 RB U14 §1.8 · p. 27 RB U14 §1.2 · p. 6

Question 34 · Q31–40 · response code

Which of the following is/are always **correct** for the slowest step of a multi-step reaction?

- Its molecularity is an integer.
- Its molecularity is higher than the overall order of the reaction.
- Overall rate of the reaction depends on its rate.
- Its molecularity is equal to the number of steps in the reaction.

Answer and review

Answer **(5)** Prepared from the Sinhala-medium official scheme

Molecularity of an elementary step is always a whole number (a) and the overall rate is controlled by the rate of the slowest step (c). The molecularity need not exceed the overall order (b) nor equal the number of steps (d). The correct pair (a, c) is not one of the listed pairs, so the answer is (5).

RB U11 §1.10 · p. 57

Question 35 · Q31–40 · response code

Which of the following reaction steps is/are most **unlikely** to take place, when Cl_2 reacts with CH_4 in the presence of light?

- $^{\wedge}\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + Cl^{\wedge}\bullet$
- $^{\wedge}\bullet CH_3 + Cl^{\wedge}\bullet \rightarrow CH_3Cl$
- $CH_4 + Cl^{\wedge}\bullet \rightarrow CH_3Cl + H^{\wedge}\bullet$
- $Cl^{\wedge}\bullet + H^{\wedge}\bullet \rightarrow HCl$

Answer and review

Answer **(3)** Prepared from the Sinhala-medium official scheme

(a) is the normal propagation step. (c) is strongly endothermic (the C–H bond is broken but no stable HCl forms; the real step is $CH_4 + Cl^{\wedge}\bullet \rightarrow {}^{\wedge}\bullet CH_3 + HCl$), and $H^{\wedge}\bullet$ atoms are not present, so (d) cannot occur either. (b) is a genuine, if infrequent, termination step. So (c) and (d) are the most unlikely: code (3).

RB U8 §2.2 · p. 33

Question 36 · Q31–40 · response code

Which of the following statements is/are **correct** with regard to NH_3 and NF_3?

- Bonded pair repulsions are weaker in NF_3 than in NH_3.
- NF_3 has a higher dipole moment than NH_3.
- NF_3 is a stronger Lewis base than NH_3.
- The electronegativity difference between N and H in NH_3 and that between N and F in NF_3 are nearly equal.

Answer and review

Answer **(4)** Prepared from the Sinhala-medium official scheme

In NF_3 the bonding electrons are pulled to the very electronegative F, away from N, so bonded-pair repulsions are weaker (smaller bond angle, 102° versus 107°): (a) true. The N–F bond dipoles oppose the lone-pair dipole, so NF_3 has the smaller dipole moment (b false) and its lone pair is much less available, making it a weaker Lewis base (c false). The N–H (≈0.9) and N–F (≈1.0) electronegativity differences are nearly equal, so (d) is true. (d) and (a): code (4).

RB U2 §2.3 · p. 52 RB U6 §4.5 · p. 136

Question 37 · Q31–40 · response code

The equilibrium constant for the reaction $2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$ at 1000 K is 1.25×10^{-2} mol^{-1} dm^3. At this temperature, which of the following statements is/are **correct**?

- Equilibrium mixture consists mainly of NO(g) and $Br_2(g)$ and the equilibrium constant for the reverse reaction is 80 mol dm^{-3}.
- Equilibrium mixture consists mainly of NOBr(g) and the equilibrium constant for the reverse reaction is 80 mol dm^{-3}.
- Equilibrium mixture consists mainly of NO(g) and $Br_2(g)$ and the equilibrium constant for the reverse reaction is 1.25×10^{-2} mol^{-1} dm^3.
- Equilibrium mixture consists mainly of NOBr(g) and the equilibrium constant for the reverse reaction is 1.25×10^{-2} mol^{-1} dm^3.

Answer and review

Answer **(5)** Prepared from the Sinhala-medium official scheme

K_c is small, so the mixture is mainly reactants (NO and Br_2); the reverse reaction has $K = 1/(1.25\times10^{-2}) = 80$ mol dm^{-3}. Only (a) is correct. A single correct statement matches none of the paired codes, so the answer is (5). The trap is picking (1) because (a) is true.

RB U12 §2.1 · p. 76

Question 38 · Q31–40 · response code

Which of the following statements is/are **correct** regarding an elementary bimolecular reaction in the gas phase?

- The experimentally determined order of the reaction is two only when the concentrations of reactants are equal.
- The experimentally determined order of the reaction becomes three when the concentrations of reactants are in the 1:3 ratio.
- When the concentration of one of the reactants is in large excess compared to the other, the rate of the reaction becomes independent of the concentration of that reactant.
- When the volume of the container containing reactants is reduced at a constant temperature, the rate of collision between reactant molecules increases.

Answer and review

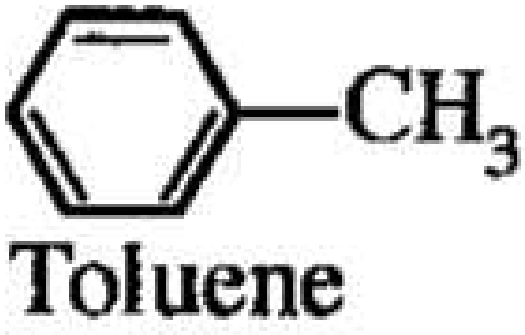
Answer **(5)** Prepared from the Sinhala-medium official scheme

For an elementary bimolecular step, rate = k[A][B] and the order is 2 whatever the ratio (a and b false). (d) is true: smaller volume means higher concentration and more collisions. Under a large excess of one reactant the rate appears pseudo-first-order, but it still depends on that reactant's concentration (its concentration is merely nearly constant), so the scheme treats (c) as incorrect. With only (d) true, the answer is (5). Statement (c) is arguable, which is the likely source of dispute.

RB U11 §1.6 · p. 16 RB U11 §1.5 · p. 15

Question 39 · Q31–40 · response code

Which of the following statements regarding methyl benzene (toluene) is/are **correct**?



- All carbon atoms lie in the same plane.
- Lengths of all carbon carbon bonds are equal to each other.
- Lengths of all carbon hydrogen bonds are equal to each other.
- Any C—C—C bond angle is 120°.

Answer and review

Answer **(4)** Prepared from the Sinhala-medium official scheme

The methyl carbon is attached to the sp^2 ipso carbon and lies in the ring plane, so (a) is true. The ring C–C bonds (about 140 pm) are shorter than the ring–CH_3 bond (about 151 pm) (b false), and sp^2 C–H bonds are shorter than the sp^3 C–H bonds of the methyl group (c false). Every C–C–C angle is centred on an sp^2 ring carbon, so all are 120° (d true). (d) and (a): code (4).

RB U8 §2.4 · p. 44

Question 40 · Q31–40 · response code

Which of the following statements is/are **correct** regarding air pollution?

- Sulphates in water bodies is a source of atmospheric H_2S.
- Conversion of $SO_2(g)$ to $SO_3(g)$ is accelerated by NO(g).
- NO(g) emitted during fossil fuel combustion is not considered as an air pollutant.
- $SO_2(g)$ in the atmosphere is removed by lightning.

Answer and review

Answer **(1/5)** Prepared from the Sinhala-medium official scheme

The official scheme accepts (1) or (5). Anaerobic bacteria reduce sulfate in water bodies to H_2S (a true), and nitrogen oxides catalyse the oxidation of SO_2 to SO_3 (b true). NO is a primary air pollutant (c false), and lightning produces NO rather than removing SO_2 (d false). So (a) and (b) give (1); (5) is also accepted, presumably because of ambiguity in (b) or (d).

RB U14 §1.13 · p. 58

Questions 41–50: statement pairs

Response	First statement	Second statement
(1)	True	True, and correctly explains the first statement
(2)	True	True, but does not explain the first statement correctly
(3)	True	False
(4)	False	True
(5)	False	False

Question 41 · Q41–50 · statement pair

Statement 1

C—O bonds in the bicarbonate ion are identical.

Statement 2

Bicarbonate ion is a resonance hybrid of three stable resonance structures.

Answer and review

Answer **(5)** Prepared from the Sinhala-medium official scheme

In HCO_3^- one oxygen carries the H (C–OH), so the three C–O bonds are not identical: one is C–OH and the other two share the C=O/C–O^- resonance. Only two equivalent resonance structures exist, not three. Both statements are false.

RB U2 §2.3 · p. 52

Question 42 · Q41–50 · statement pair

Statement 1

It is not possible to prepare a Grignard reagent by reacting $HOCH_2CH_2Br$ with Mg in dry ether.

Statement 2

Grignard reagent does not react with compounds having a hydroxyl group.

Answer and review

Answer **(3)** Prepared from the Sinhala-medium official scheme

The –OH group is acidic enough to protonate the Grignard reagent as soon as it forms (RMgX + R'OH → RH + R'OMgX), so it cannot be prepared from $HOCH_2CH_2Br$: statement 1 is true. Statement 2 is false: Grignard reagents do react with –OH compounds, which is exactly the reason for statement 1.

RB U8 §2.7 · p. 50

Question 43 · Q41–50 · statement pair

Statement 1

Increasing the pressure of the equilibrium mixture $2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$ at constant temperature shifts the position of equilibrium to the right.

Statement 2

When the pressure of a gas mixture at chemical equilibrium is increased at constant temperature, the reaction occurs in such a way as to decrease the number of moles.

Answer and review

Answer **(1)** Prepared from the Sinhala-medium official scheme

The forward reaction reduces the moles of gas from 3 to 1, so higher pressure favours the right-hand side. Statement 2 is Le Chatelier's principle applied to pressure and explains statement 1.

RB U12 §2.1 · p. 76

Question 44 · Q41–50 · statement pair

Statement 1

Solubility of group II sulphates and carbonates decreases down the group whereas the opposite is observed for hydroxides.

Statement 2

Solubility of an ionic compound depends only on its hydration energy.

Answer and review

Answer **(3)** Prepared from the Sinhala-medium official scheme

Statement 1 is true: sulphates and carbonates of Group 2 become less soluble down the group, hydroxides more soluble. Statement 2 is false: solubility depends on the balance between lattice energy and hydration energy (and entropy), not hydration energy alone.

RB U6 §4.2 · p. 126 RB U5 §2.3 · p. 51

Question 45 · Q41–50 · statement pair

Statement 1

The reactivity of alkanes with electrophiles is less than that of alkenes.

Statement 2

The C—H bonds in hydrocarbons have a low polarity due to the small difference in electronegativity between carbon and hydrogen atoms.

Answer and review

Answer **(2/3)** Prepared from the Sinhala-medium official scheme

The official scheme accepts (2) or (3). Statement 1 is true: alkenes have an electron-rich π bond that attacks electrophiles, but alkanes have only strong, nearly non-polar σ bonds. Statement 2 is also true, but low C–H polarity is only part of the reason (the key reason is the absence of a π bond), so it does not fully explain statement 1, giving (2); (3) is accepted as the statement could be judged inexact.

RB U8 §2.2 · p. 33 RB U8 §2.1 · p. 26

Question 46 · Q41–50 · statement pair

Statement 1

The entropy of the surroundings increases when water vapour in a closed container undergoes condensation.

Statement 2

Heat absorbed by a closed system increases the thermal motion of surroundings.

Answer and review

Answer **(3)** Prepared from the Sinhala-medium official scheme

Condensation is exothermic: the heat released to the surroundings increases their entropy ($\Delta S_{surr} = -\Delta H/T > 0$), so statement 1 is true. Statement 2 is false: heat absorbed by the system comes from the surroundings and reduces their thermal motion.

RB U5 §2.4 · p. 53

Question 47 · Q41–50 · statement pair

Statement 1

The cathode compartment and anode compartment of the membrane cell used in the manufacture of NaOH are separated by an ion selective membrane.

Statement 2

The ion selective membrane used in the membrane cell does not allow the transfer of cations.

Answer and review

Answer **(3)** Prepared from the Sinhala-medium official scheme

The cation-exchange membrane separates the compartments (statement 1 true) and allows Na^+ to pass from anode to cathode compartment while blocking Cl^- and OH^- (statement 2 is false: it passes cations, not anions).

RB U14 §1.2 · p. 6

Question 48 · Q41–50 · statement pair

Statement 1

2–butene shows diastereoisomerism.

Statement 2

There are two possible structures for 2-butene, which are not mirror images of each other.

Answer and review

Answer **(1)** Prepared from the Sinhala-medium official scheme

$CH_3CH=CHCH_3$ has two different groups (H and CH_3) on each double-bond carbon, so it exists as cis and trans (geometric) isomers, which are diastereoisomers. Both statements are true, and the existence of two non-mirror-image stereoisomers is exactly the definition of diastereoisomerism, so the second explains the first.

RB U7 §1.4 · p. 21

Question 49 · Q41–50 · statement pair

Statement 1

Solubility of MnS(s) in water at room temperature does not depend on pH.

Statement 2

S^{2-}(aq) is the conjugate base of a weak acid.

Answer and review

Answer **(4)** Prepared from the Sinhala-medium official scheme

S^{2-} is the conjugate base of the weak acid HS^- (H_2S is a weak diprotic acid), so statement 2 is true. In acidic solution H^+ removes S^{2-} ($S^{2-} + H^+ \rightarrow HS^-$, $\rightarrow H_2S$), shifting MnS(s) $\rightleftharpoons Mn^{2+} + S^{2-}$ to the right, so the solubility of MnS increases as pH falls; statement 1 is false. This pH dependence is the basis of separating metal sulfides in qualitative analysis.

RB U12 §2.4 · p. 175 RB U12 §2.2 · p. 118

Question 50 · Q41–50 · statement pair

Statement 1

The melting points of d-block elements are higher than the melting points of s-block elements.

Statement 2

d and s electrons are available to take part in delocalization in forming metallic bonds in d-bolck elements.

Answer and review

Answer **(All)** Prepared from the Sinhala-medium official scheme

The official scheme accepts all responses. The expected answer is (1): most d-block metals have more electrons (3d and 4s) in the delocalised sea and stronger metallic bonding than s-block metals, so they have higher melting points. However, statement 1 is not true for every element (e.g. Zn, Cd and Hg have low melting points, Hg being a liquid, and Be melts higher than some d-block metals), so the statement is ambiguous and all responses were accepted.

RB U6 §4.10 · p. 160 RB U2 §2.5 · p. 78

Structured essay · answer all four

SEQ · Paper II Part A

Question 1 · Part A · structured essay

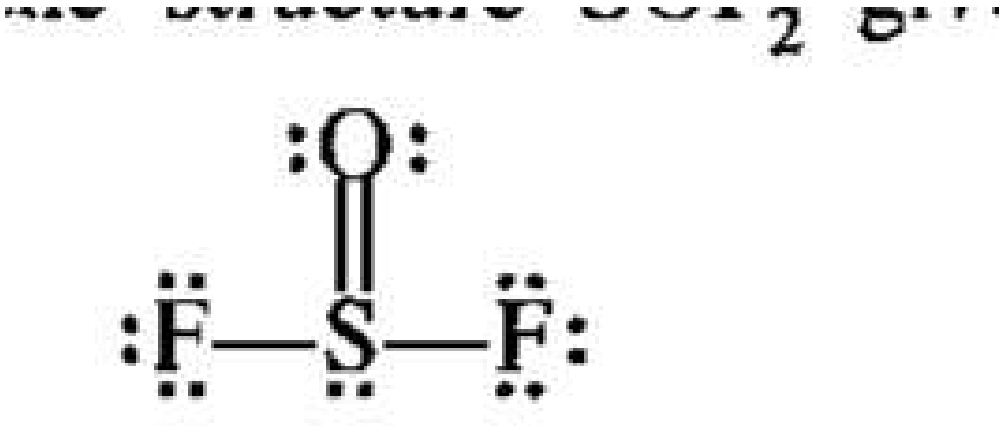
(a) [55 marks]

(i) I. Complete the expression given below to determine the charge (Q) of an atom in a Lewis structure by inserting the terms N_A, N_{LP} and N_{BP} in the appropriate boxes, where,
N_A = number of valence electrons in the atom
N_{LP} = number of electrons in lone pairs
N_{BP} = number of electrons in bonding pairs around the atom
Q = □ − □ − ½ □

Answer

Q = N_A − N_{LP} − ½ N_{BP} (01) + (01) + (01) = 03 marks

II. Fill in the values for N_A, N_{LP} and N_{BP} in the appropriate boxes and calculate the charge on S, Q(sulfur), in the structure SOF_2 given below.



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Q(sulfur) = □ − □ − ½ □ = ...

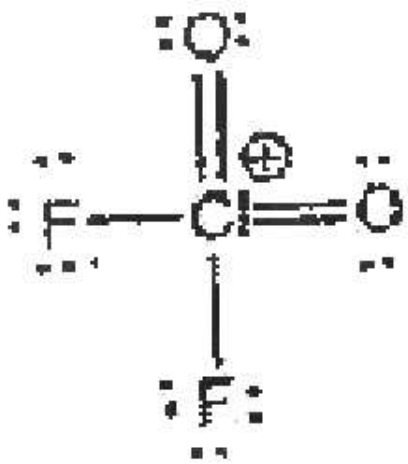
Answer

Q(sulfur) = 6 − 2 − ½(8) = 0 (01) + (01) + (01) + (04) = 07 marks (the marking scheme totals 10 marks for 1(a)(i), marks for the answer 0 being awarded automatically if the substitution is correct).

(ii) Draw the **most** acceptable Lewis structure for the ion, ClO_2F_2^+.

Answer

The structure has Cl as the central atom bonded to two F atoms by single bonds and to two O atoms by double bonds, with no lone pair on Cl and a positive formal charge (+1) on Cl; each F carries three lone pairs and each O two lone pairs. (07 marks)



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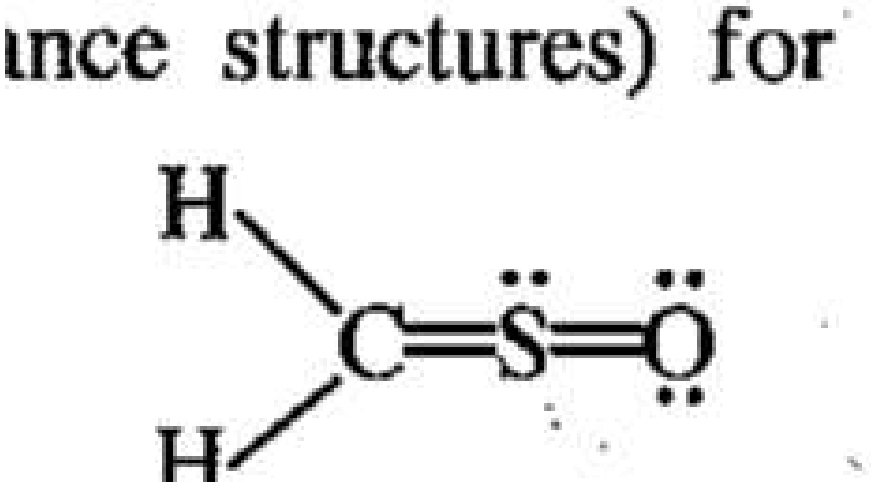
(iii) The most stable Lewis structure for the molecule CH_2SO (sulfine) is shown below. Draw another **two** Lewis structures (resonance structures) for this molecule.



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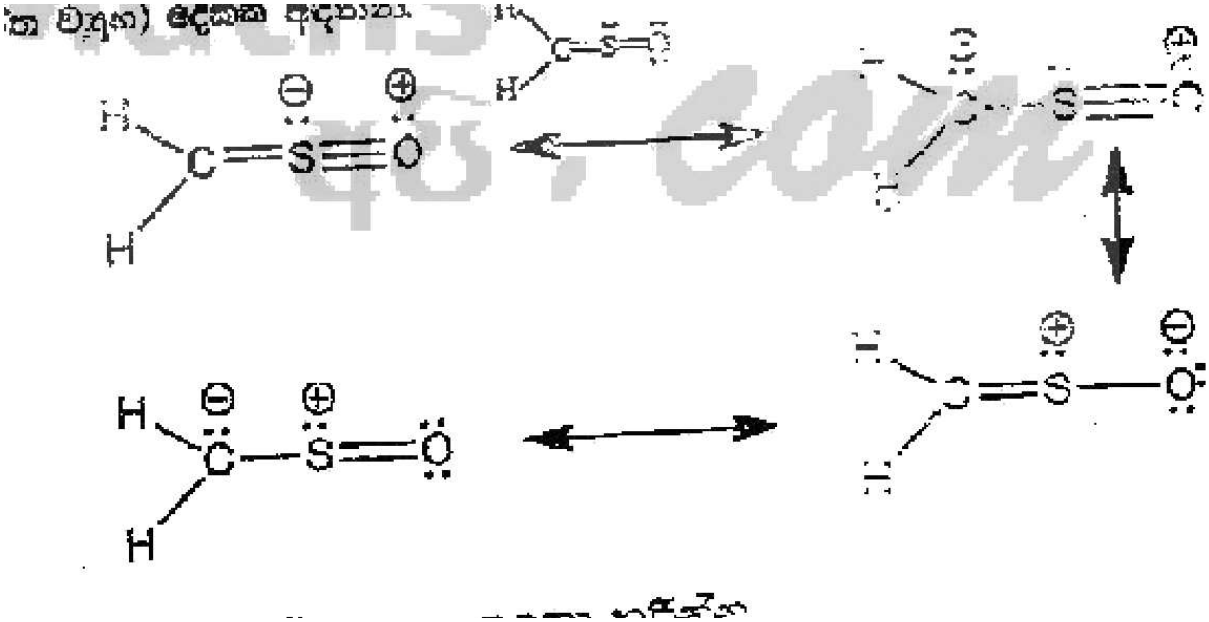
Answer

Any two of the resonance structures shown: (a) H_2C^{-}–S^{+}≡O (carbon with a negative charge, S≡O triple bond with positive charge on S); (b) H_2C=S^{+}–O^{-} (S^{+} and O^{-} with a S–O single bond); (c) H_2C^{-}–S^{+}=O (S=O double bond with a lone pair on S). The double-headed arrow (↔) must be ignored when marking. (07 × 2 = 14 marks) (any two)



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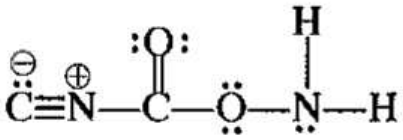
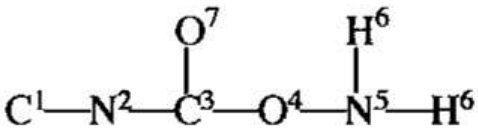
(iv) Based on the hypothetical Lewis structure given below, state the following regarding the N, C and O atoms given in the table below. I. VSEPR pairs around the atom II. electron pair geometry around the atom III. shape around the atom IV. hybridization of the atom. The atoms are numbered as shown.

III. shape around the atom

IV. hybridization of the atom



The atoms are numbered as follows:



Hypothetical Lewis structure and numbering of atoms

Answer

	N^2	C^3	O^4	N^5
I. VSEPR pairs	2	3	4	4
II. electron pair geometry	linear	trigonal planar	tetrahedral	tetrahedral
III. shape	linear	trigonal planar	angular (V-shape, bent)	trigonal pyramidal
IV. hybridization	sp	sp^2	sp^3	sp^3

(01 mark × 16 = 16 marks)

(v) Identify the atomic/hybrid orbitals involved in the formation of the following σ bonds in the Lewis structure given in part (iv) above. (Numbering of atoms is as in part (iv).)

I. N^2–C^3: N^2 ..... , C^3 .....

II. O^4–N^5: O^4 ..... , N^5 .....

III. N^5–H^6: N^5 ..... , H^6 .....

IV. C^3–O^7: C^3 ..... , O^7 .....

Answer

I. N^2: sp; C^3: sp^2
II. O^4: sp^3; N^5: sp^3
III. N^5: sp^3; H^6: 1s
IV. C^3: sp^2; O^7: sp^2 or 2p (01 mark × 8 = 08 marks) 1(a): 55 marks

Review.

Formal charge = valence electrons − lone-pair electrons − ½ bonding electrons (Resource Book Unit 2, Lewis structures); the structure with the lowest formal charges (here all zero in SOF_2, with the expanded octave on S) is preferred. Hybridization follows from the number of VSEPR pairs (steric number): 2 → sp, 3 → sp^2, 4 → sp^3; lone pairs count as pairs but not in the molecular shape, so O^4 (2 bond pairs + 2 lone pairs) is angular and N^5 (3 + 1) is pyramidal. A σ bond between a hybrid orbital and H uses the H 1s orbital. Common errors: counting only bond pairs for the VSEPR number, giving the electron-pair geometry in place of the shape, and writing sp^2 for the oxygen carrying two lone pairs. Hypervalent (expanded octet) Lewis structures such as ClO_2F_2^+ and SOF_2 are discussed in the current syllabus, but the formal-charge formula in this exact "N_A, N_{LP}, N_{BP}" form is a 2017 old-syllabus presentation; the underlying concepts remain in the current syllabus.

(b) [45 marks]

(i) Identify the sub-shells (atomic orbitals) along with their azimuthal quantum number (l), and magnetic quantum number/s (m_l) for the energy level with principal quantum number n = 3 in an atom. What is the maximum number of electrons present in each sub-shell? Write your answers in the table given below.

Answer

Sub-shell	Azimuthal quantum number (l)	Magnetic quantum number/s (m_l)	Maximum number of electrons in each sub-shell
3s	0	0	2
3p	1	−1, 0, +1	6
3d	2	−2, −1, 0, +1, +2	10

(01 mark × 12 = 12 marks)

(ii) Identify the type/s of intermolecular forces present in I, II and III given below.
I. Ar gas
II. NO gas
III. water sample containing a small amount of dissolved KCl

Answer

I. London (induced dipole–induced dipole) forces (01)
II. dipole–dipole forces + London forces (02)
III. ion–dipole forces + hydrogen bonds (02) (01 × 5 = 05 marks)

(iii) "The boiling point of n-butane (C_4H_{10}) is higher than the boiling point of propane (C_3H_8)." Giving reasons, state whether this statement is **true** or **false**.

Answer

True

(05)

(02)

(02)

(02)

(02)

4

10

3

8

(13 marks in total for (iii))

(iv) Arrange the following in the **decreasing** order of the property indicated in parentheses. (Reasons are **not** required.)
I. Li_2CO_3, Na_2CO_3, K_2CO_3 (solubility in water)
II. NF_3, NH_3, NOCl, NO_2^+ (bond angle)
III. $COCl_2$, CO_2, HCN, CH_3Cl (electronegativity of carbon)

Answer

I. $K_2CO_3 > Na_2CO_3 > Li_2CO_3$ (05)
II. NO_2^+ > NOCl > NH_3 > NF_3 (05)
III. CO_2 > HCN > $COCl_2$ > CH_3Cl (05) 1(b): 45 marks

Review.

Quantum numbers: for n = 3, l = 0, 1, 2 (s, p, d) and m_l runs from −l to +l, giving 1, 3 and 5 orbitals holding 2, 6 and 10 electrons. Intermolecular forces are decided by polarity and charge: Ar has only London forces, NO is polar, and ions dissolved in water give ion–dipole attractions in addition to hydrogen bonding. For hydrocarbons of the same type, boiling point rises with the size of the electron cloud (London forces). Group 1 carbonate solubility increases down the group, because the large cations have a low polarizing power and the lattice energy falls faster than the hydration energy (Li_2CO_3 is sparingly soluble). Bond angles: NO_2^+ is linear (180°), NOCl is angular (about 113°), NH_3 107° and NF_3 about 102° (the electronegative F draws the bond pairs away from N, reducing repulsion). The electronegativity of C increases with s character (sp in CO_2 and HCN) and falls when it is bonded to less electronegative atoms, so CH_3Cl (sp^3, with an attached electron-donating alkyl group on C) is lowest. Common errors: writing only "London forces" for NO, and ordering the bond angles of NF_3 and NH_3 the wrong way. The comparison of the electronegativity of an atom in different hybrid states is not examined in this form in the current syllabus.

Read: RB U2 §2.1 · p. 44 RB U2 §2.3 · p. 52 RB U1 §1.3 · p. 17 RB U5 §2.2 · p. 36

Question 2 · Part A · structured essay

(a) [50 marks]

X, Y and Z are elements that belong to the same group in the Periodic Table. They are in three successive periods respectively on descending the group. Y exists as a non-metallic coloured liquid at room temperature.
(i) Identify X, Y and Z. (Give atomic symbols.)

Answer

X = Cl, Y = Br, Z = I (04 marks × 3 = 12 marks)
Note: marks are given also if X: Cl_2, Y: Br_2, Z: I_2 are written.

(ii) Indicate the relative magnitudes of the following with regard to X, Y and Z.
I. Atomic size
II. Electron affinity
III. First ionization energy

Answer

I. Atomic size: I > Br > Cl (Z > Y > X)
II. Electron affinity: Cl > Br > I (X > Y > Z)
III. First ionization energy: Cl > Br > I (X > Y > Z) (03 marks × 3 = 09 marks)
Note: for 2(a)(ii), marks are awarded only if X, Y and Z are **all** correctly identified in (i). If X, Y and Z were correctly identified, X, Y and Z may be used in the answer to (ii).

(iii) You are provided with aqueous solutions of the anions of X, Y and Z, each in a separate test-tube. Suggest a **single** reagent that could be used to identify these anions. [Note: You are required to state the observation for each anion.]

Answer

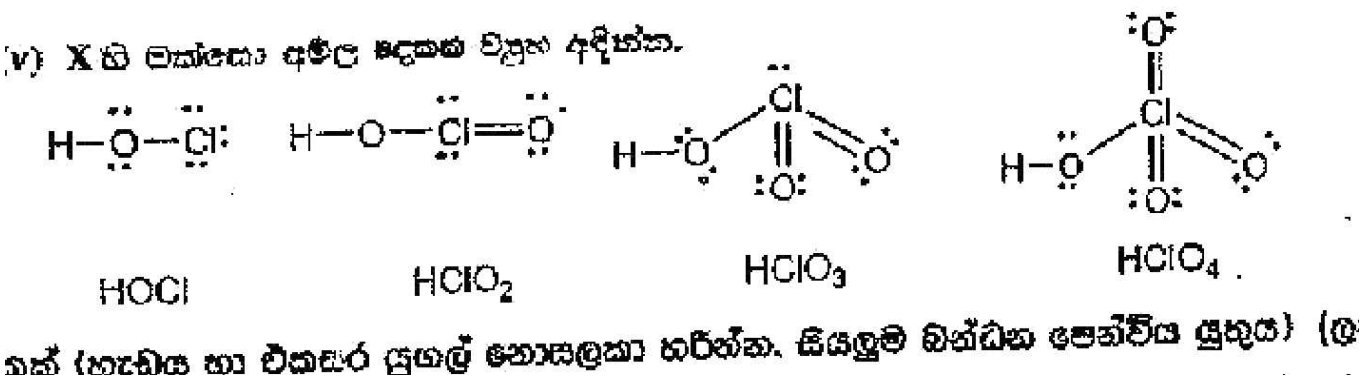
Reagent: $AgNO_3$ solution (04)
X: white precipitate (02)
Y: pale yellow precipitate (02)
Z: (deep) yellow precipitate (02)
or
Reagent: Cl_2/CCl_4 (04)
X: colourless organic (CCl_4) layer (02)
Y: reddish-brown organic layer (02)
Z: violet organic layer (02)
Note: marks for 2(a)(iii) are awarded only if X, Y and Z are all correctly identified; if Cl_2, Br_2 and I_2 were written for X, Y and Z, marks may be awarded.

(iv) Give balanced chemical equations for the reactions of $X_2(g)$ with the following.
I. $NH_3(g)$
II. dil. NaOH

Answer

I. $3Cl_2(g) + 2NH_3(g) \rightarrow N_2(g) + 6HCl(g)$ (03)
or $3Cl_2(g) + NH_3(g) \rightarrow NCl_3(g) + 3HCl(g)$
or $3Cl_2(g) + 8NH_3(g) \rightarrow N_2(g) + 6NH_4Cl(s)$
II. $Cl_2(g) + 2NaOH(aq) \rightarrow NaOCl(aq) + NaCl(aq) + H_2O(l)$ (03)
Note: physical states are not required for the award of marks.

(v) Draw the structures of **two** oxoacids of X.



Oxoacids of chlorine (marking scheme)

Answer

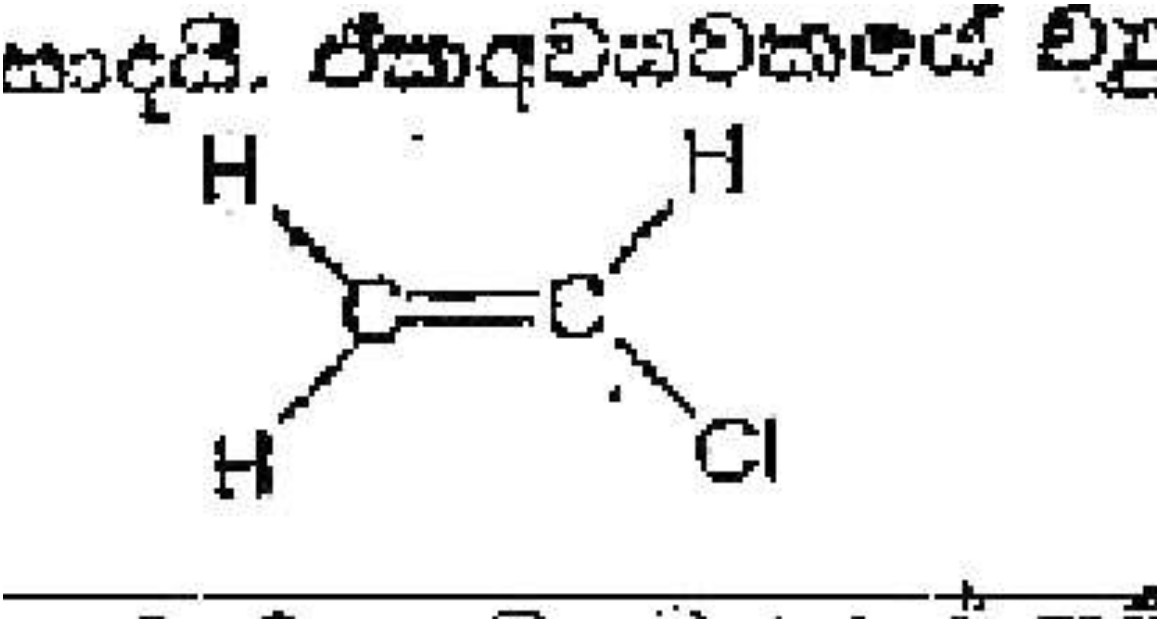
Any two of HOCl, HOClO ($HClO_2$), $HOClO_2$ ($HClO_3$) and $HOClO_3$ ($HClO_4$), drawn as H–O–Cl, H–O–Cl=O, H–O–Cl$(=O)_2$ and H–O–Cl$(=O)_3$. All bonds must be shown; the shape and the lone pairs are ignored. (03 × 2 = 06 marks)

(vi) Name **one** natural source of X.

Answer

Sea water / rock salt (NaCl) / sylvine (KCl) / carnallite ($KCl{\cdot}MgCl_2{\cdot}6H_2O$) (02 marks)

(vii) I. A monomer that contains X forms an addition polymer that is widely used in the manufacture of water pipes. Draw the structure of the monomer.
II. Write the full name of the polymer.



Monomer: vinyl chloride (marking scheme)

Answer

I. CH_2=CHCl (vinyl chloride, chloroethene) (03)
II. Polyvinyl chloride (poly(chloroethene)) (02) 2(a): 50 marks

Review.

The halogens form the group 17 series Cl, Br, I (Br is the only non-metallic liquid). Down the group atomic size increases while electron affinity (Cl has the highest value, F being anomalous) and first ionization energy decrease. $AgNO_3$ gives AgCl (white), AgBr (pale yellow) and AgI (yellow); a halogen–CCl_4 test relies on displacement (Cl_2 oxidizes Br^- and I^-, giving Br_2 reddish-brown and I_2 violet in CCl_4). Cl_2 oxidizes NH_3 to N_2 (excess Cl_2 gives NCl_3) and disproportionates in cold dilute NaOH to give hypochlorite and chloride. Common errors: giving the oxoacids without showing the double bonds or the correct number of O atoms, and stating colours of the precipitates inaccurately (AgBr pale yellow versus AgI deep yellow). The reactions of PVC production and uses are in Resource Book Unit 14.

(b) [50 marks]

An aqueous solution Q contains **three** anions. The following tests were carried out to identify these anions. (Fresh portions of solution Q were used for each test ① to ⑤.)

		Test	Observation
①	I	Dilute HCl was added.	A colourless gas was evolved. A clear solution was obtained.
II	The gas evolved was tested with filter paper moistened with lead acetate.	No colour change	
②	I	A $BaCl_2$ solution was added.	A white precipitate was obtained.
II	The white precipitate was separated by filtration, and dil. HCl was added to it.	The white precipitate dissolved with the evolution of a gas.	
III	The gas evolved was tested with a filter paper moistened with acidified potassium dichromate.	The colour changed from orange to green.	
③	Conc. HNO_3 and an excess of ammonium molybdate solution were added and the mixture was warmed.	A yellow precipitate did not form.	
④	Devarda's alloy and NaOH solution were added and the mixture was heated.	A gas that turned Nessler's reagent brown was evolved.	
⑤	A $FeCl_3$ solution was added.	A blood red coloured solution was obtained.	

three

Answer

NO_3^−, SCN^-, SO_3^{2-} (12 marks × 3 = 36 marks)

(ii) Write the balanced chemical equation for the reaction taking place in test number ② III.

Answer

$3SO_2 + Cr_2O_7^{2-} + 2H^+ \rightarrow 3SO_4^{2-} + 2Cr^{3+} + H_2O$ (14 marks)
or by half-reactions: $3(SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e)$ (03); $Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$ (03); adding: $3SO_2 + 6H_2O + Cr_2O_7^{2-} + 14H^+ \rightarrow 3SO_4^{2-} + 12H^+ + 2Cr^{3+} + 7H_2O$ (02); simplified: $3SO_2 + Cr_2O_7^{2-} + 2H^+ \rightarrow 3SO_4^{2-} + 2Cr^{3+} + H_2O$ (06) 2(b): 50 marks

Review.

Reasoning: ① no S^{2-} (lead acetate paper unchanged) and no $S_2O_3^{2-}$ (solution stays clear, no sulfur); ② $BaCl_2$ precipitate that dissolves in HCl giving SO_2 (turns acidified dichromate green) indicates SO_3^{2-} (CO_3^{2-} is excluded because the gas reduced dichromate); ③ no PO_4^{3-}; ④ NO_3^− is reduced to NH_3 by Devarda's alloy in alkali (Nessler's reagent turns brown); ⑤ blood-red $[Fe(SCN)(H_2O)_5]^{2+}$ shows SCN^-. For the equation, balance the electrons first (Cr from +6 to +3: 6 e^- per $Cr_2O_7^{2-}$; S from +4 to +6: 2 e^- per SO_2). A common mistake is naming Cl^- or CO_3^{2-} or listing $S_2O_3^{2-}$. Topic note: systematic anion tests (Devarda's alloy,

ammonium molybdate, Nessler's reagent) belong to the old syllabus and are not part of the current syllabus; the Fe^{3+}–SCN^{-} complex and redox balancing (Resource Book Unit 3 and Unit 6) are.

Read: RB U6 §4.7 · p. 149 RB U1 §1.6 · p. 32 RB U14 §1.11 · p. 37 RB U6 §4.7 · p. 149

Question 3 · Part A · structured essay

(a) [50 marks]

(a) Methylamine, CH_3NH_2 is a weak base. The following equilibrium exists in an aqueous solution of methylamine.
$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3\hat{}+(aq) + OH^{-}(aq)$

(i) Write the expression for K_b of methylamine.

Answer

$K_b = [CH_3NH_3\hat{}+(aq)][OH^{-}(aq)] / [CH_3NH_2(aq)]$ (05)
Note: correct physical states are required.

(ii) At 25 °C, the pH value of a 0.20 mol dm^{-3} aqueous solution of methylamine is 11.00. Calculate K_b.

Answer

$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3\hat{}+(aq) + OH^{-}(aq)$
When pH = 11, pOH = 3 (02)
$\therefore [OH^{-}(aq)] = [CH_3NH_3\hat{}+(aq)] = 1.0 \times 10^{-3}$ mol dm^{-3} (02)
$\therefore K_b = (1.0 \times 10^{-3}$ mol $dm^{-3} \times 1.0 \times 10^{-3}$ mol $dm^{-3}) / 0.2$ mol dm^{-3} (02 + 01)
$= 5.0 \times 10^{-6}$ mol dm^{-3} (02 + 01)

(iii) A volume of 25.00 cm^3 of the solution in (ii) above was titrated with 0.20 mol dm^{-3} HCl at 25 °C. Calculate the pH value of the solution at the equivalence point. ($K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6} at 25 °C.)

Answer

The reaction between $CH_3NH_2(aq)$ and HCl is
$CH_3NH_2(aq) + HCl(aq) \rightarrow CH_3NH_3Cl(aq)$ (or $CH_3NH_3\hat{}+(aq)$) (03)
Stoichiometry of the reaction: $CH_3NH_2(aq) : HCl(aq) : CH_3NH_3Cl(aq) = 1 : 1 : 1$
Volume of HCl at the equivalence point = 25.00 cm^3 (02)
$\therefore$ at the equivalence point, $[CH_3NH_3\hat{}+(aq)] = (0.2$ mol $dm^{-3} \times 25 \times 10^{-3}$ $dm^3) / (50 \times 10^{-3}$ $dm^3) = 0.10$ mol dm^{-3} (04 + 01)
The reaction that determines the pH at the equivalence point is
$CH_3NH_3\hat{}+(aq) + H_2O(l) \rightleftharpoons CH_3NH_2(aq) + H_3O^{+}(aq)$ ——— (A) (03)
Initial concentration: 0.10, 0, 0
Equilibrium concentration: 0.10 − x, x, x mol dm^{-3} (02)
For reaction (A): $K_a = [CH_3NH_2(aq)][H_3O^{+}(aq)] / [CH_3NH_3\hat{}+(aq)] = K_w / K_b$ (02)
$= 1.0 \times 10^{-14}$ mol^2 $dm^{-6} / 5.0 \times 10^{-6}$ mol $dm^{-3} = 2.0 \times 10^{-9}$ mol dm^{-3} (03)
$\therefore 2.0 \times 10^{-9} = x^2 / (0.10 - x) \approx x^2 / 0.10$ (02 + 03)
$2.0 \times 10^{-10} = x^2$
$x = 1.41 \times 10^{-5}$ mol dm^{-3} (04 + 01)
$\therefore$ pH $= -\log(1.41 \times 10^{-5}) = 4.85$ (05) 3(a): 50 marks

Review.

Principle: a weak base partly ionizes, and at the equivalence point of a weak base–strong acid titration the solution contains only the conjugate acid, which hydrolyses to give an acidic solution. Method: from pH get pOH and $[OH^{-}] = [CH_3NH_3\hat{}+]$, then $K_b = (1.0 \times 10^{-3})^2/0.20$; at equivalence the 25.00 cm^3 of base needs 25.00 cm^3 of acid, so the total volume doubles to 50.00 cm^3 and $[CH_3NH_3\hat{}+] = 0.10$ mol dm^{-3}; use $K_a =$

$K_w/K_b = 2.0 \times 10^{-9}$ and the approximation $x \ll 0.10$ to get $[H_3O^+] = 1.41 \times 10^{-5}$ mol dm^{-3}, pH 4.85. Common mistakes: forgetting the dilution (using 0.20 instead of 0.10 mol dm^{-3}), using K_b instead of K_a for the hydrolysis, giving pH 7 at the equivalence point, and omitting physical states in the K_b expression (they are required by the scheme).

(b) [50 marks]

(b) In an experiment, a limited volume of 1.00 mol dm^{-3} HNO_3 was added to a precipitate MX(s) and the system was allowed to reach equilibrium at 25 °C. This resulted in partial dissolution of the precipitate giving rise to a clear solution. The HX(aq) formed behaves as a weak acid.

(i) Write chemical reactions for the equilibria existing in the above solution.

Answer

$HX(aq) \rightleftharpoons H^+(aq) + X^-(aq)$ (04)
$MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$ (04)
$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$ (02)

(ii) Calculate $[X^-(aq)]$ in the solution assuming that the dissociation of HX(aq) is negligible. (Solubility product of MX at 25 °C, $K_{sp(MX)} = 3.6 \times 10^{-7}$ mol^2 dm^{-6}.)

Answer

$MX(s) + HNO_3 \rightarrow M^+(aq) + NO_3\hat{}-(aq) + HX(aq)$ (05)
Concentration of $M^+(aq) = 1.0$ mol dm^{-3} (04 + 01)
$K_{sp(MX)} = [M^+(aq)][X^-(aq)]$ (05)
$\therefore [X^-(aq)] = 3.6 \times 10^{-7}$ mol^2 dm^{-6} / 1.0 mol dm^{-3} $= 3.6 \times 10^{-7}$ mol dm^{-3} (04 + 01)

(iii) Giving reasons explain whether $[X^-(aq)]$ in a saturated aqueous solution of MX at 25 °C is equal to, smaller than or greater than the value obtained in (b)(ii) above.

Answer

In the aqueous solution, $[X^-(aq)]$ is determined only by K_{sp}. (05)
$K_{sp(MX)} = [M^+(aq)][X^-(aq)] = 3.6 \times 10^{-7}$ mol^2 dm^{-6}
$[X^-(aq)]^2 = 3.6 \times 10^{-7}$ mol^2 dm^{-6} (05)
$[X^-(aq)] = 6.0 \times 10^{-4}$ mol dm^{-3} (05)
This value is greater than the value in (ii). (05)
or
$[X^-(aq)]$ is determined only by K_{sp} (05); there is no common-ion effect (05); the solution is saturated (05); this value is greater than the value in (ii) (05) 3(b): 50 marks

Review.

Principle: the solubility product $K_{sp} = [M^+][X^-]$ holds in any solution in equilibrium with solid MX. Method: the strong acid converts X^- into the weak acid HX, so the limited HNO_3 (1.00 mol dm^{-3}) dissolves MX until all H^+ is used, giving $[M^+] = 1.0$ mol dm^{-3}; then $[X^-] = K_{sp}/[M^+] = 3.6 \times 10^{-7}$ mol dm^{-3}. In pure water $[M^+] = [X^-] = \sqrt{K_{sp}} = 6.0 \times 10^{-4}$ mol dm^{-3}, which is larger because there is no high concentration of M^+ to suppress $[X^-]$ (common-ion effect). Common mistakes: assuming $[X^-] = [M^+]$ in the acid solution, taking $[M^+]$ as unknown instead of equal to the acid concentration, and forgetting the water equilibrium in (i).

Read: RB U12 §2.2 · p. 118 RB U12 §2.4 · p. 175 RB U12 §2.1 · p. 76

Question 4 · Part A · structured essay

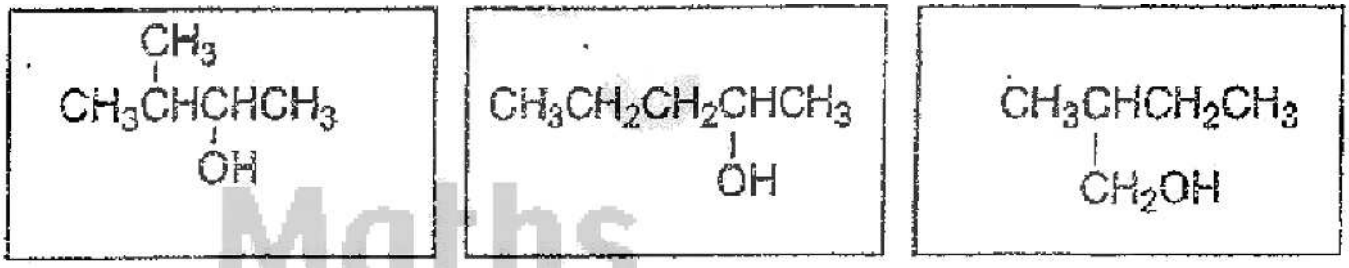
(a) [48 marks]

(a) The alcohols **A**, **B**, **C** and **D** are structural isomers of each other having the molecular formula $C_5H_{12}O$. **A**, **B** and **C** show optical isomerism.

(i) Draw possible structures for **A**, **B** and **C**.

Answer

$CH_3CH(CH_3)CH(OH)CH_3$ (3-methylbutan-2-ol), $CH_3CH_2CH_2CH(OH)CH_3$ (pentan-2-ol) and $CH_3CH_2CH(CH_3)CH_2OH$ (2-methylbutan-1-ol). The structures may be drawn in any order.



Possible structures for A, B and C (marking scheme)

When **B**, **C** and **D** are reacted with acidic $K_2Cr_2O_7$, **X**, **Y** and **Z** are formed respectively. The products **X**, **Y** and **Z** can be converted back to **B**, **C** and **D** respectively by reacting with $NaBH_4$.
(ii) What is the structure of **A**?

Answer

A

3

2

3

2

3

2

3

2

On heating with conc. H_2SO_4 **A** and **B** gave **E** and **F**, respectively, while **C** and **D** gave the same product **G**. **G** shows diastereoisomerism. All three compounds **E**, **F** and **G** have the molecular formula C_5H_{10}. When **E** and **F** are reacted with HBr the same product **H** was formed.
(iii) Draw the structures of **B**, **C**, **D**, **E**, **F** and **H**.

Answer

B

3

3

3

C

3

2

2

3

D

3

2

2

3

E

3

2

2

3

F

3

2

3

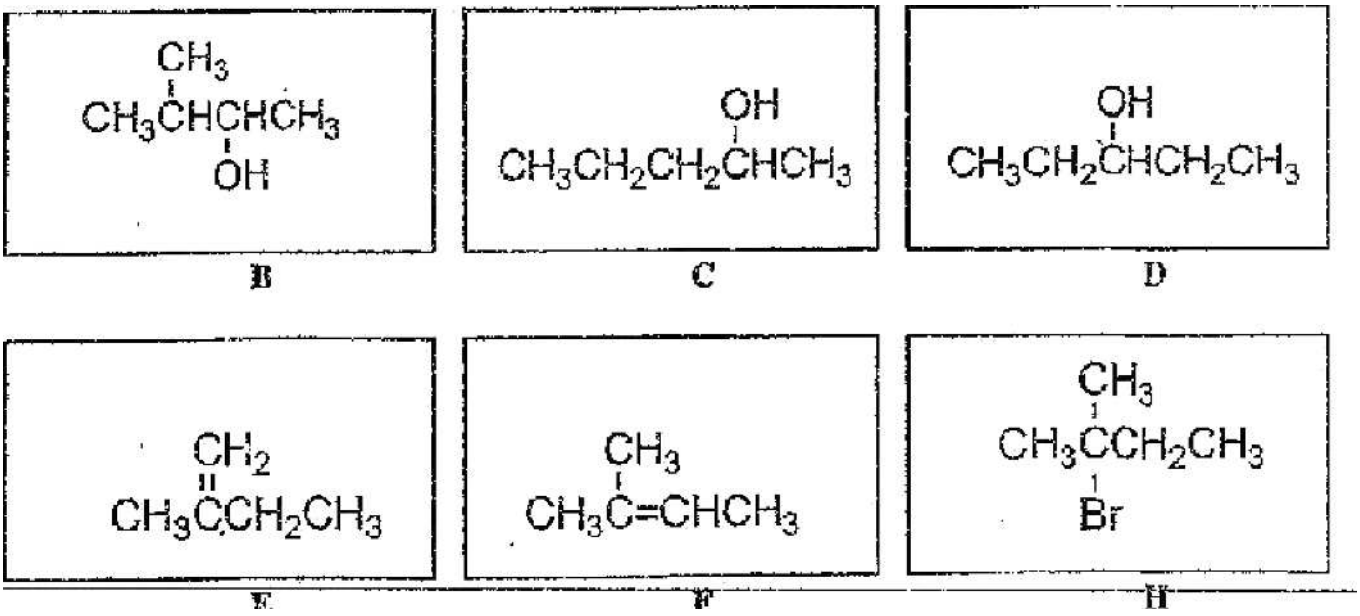
H

3

3

2

3



Structures of B, C, D, E, F and H (marking scheme)

(iv) Draw the structures of the diastereoisomers of **G**.

Answer

G

3

2

3

cis

3

2

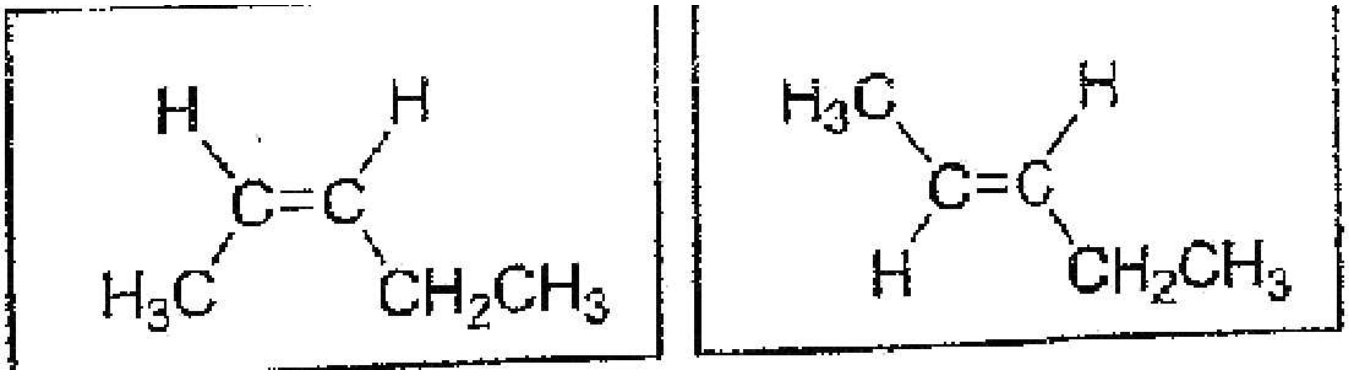
3

trans

3

2

3



Diastereoisomers of G (marking scheme)

(04 marks × 12 = 48 marks)

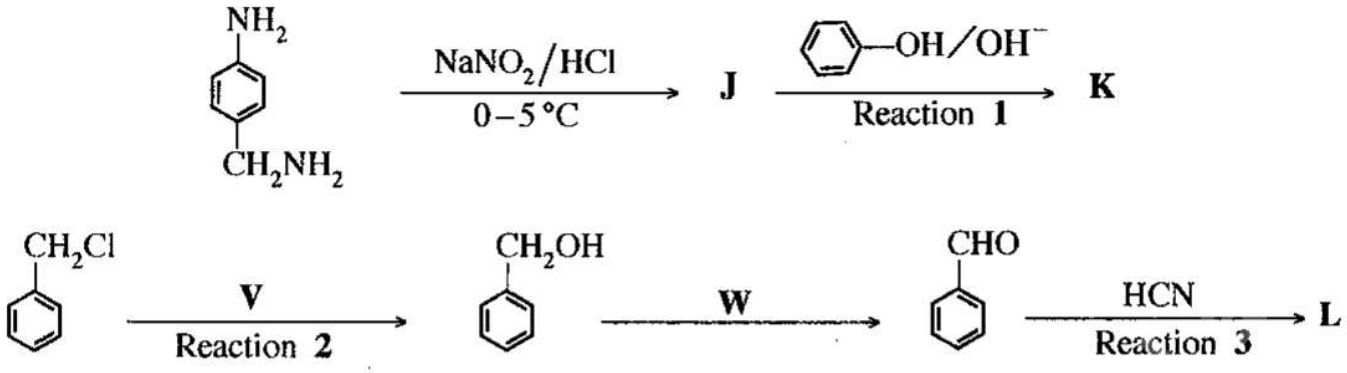
4(a): 48 marks

Review.

Principle: structure deduction of $C_5H_{12}O$ alcohols from chirality, oxidation and dehydration. Only three $C_5H_{12}O$ alcohols are chiral (pentan-2-ol, 3-methylbutan-2-ol, 2-methylbutan-1-ol). B, C and D are secondary alcohols: acidified dichromate gives ketones (X, Y, Z), which $NaBH_4$ reduces back to the same alcohols. A must be the chiral primary alcohol, 2-methylbutan-1-ol (it would be oxidized to a carboxylic acid, which $NaBH_4$ does not reduce). D is the achiral secondary alcohol pentan-3-ol, which dehydrates to pent-2-ene (G), as does pentan-2-ol (C, major Saytzeff product); G has cis/trans isomers. A gives 2-methylbut-1-ene (E) and B gives 2-methylbut-2-ene (F); both add HBr (Markovnikov) through the same tertiary carbocation to give 2-bromo-2-methylbutane (H). Common mistakes: choosing pentan-3-ol or 3-methylbutan-1-ol as a chiral alcohol, and drawing pent-1-ene for G (it has no geometric isomers).

(b) [40 marks]

(b) Consider the two reaction schemes given below.



Reaction schemes

(i) Draw the structures of **J**, **K** and **L** in the boxes given below.

Answer

J

2

2

2

6

4

2

K

2

6

4

6

4

–

L

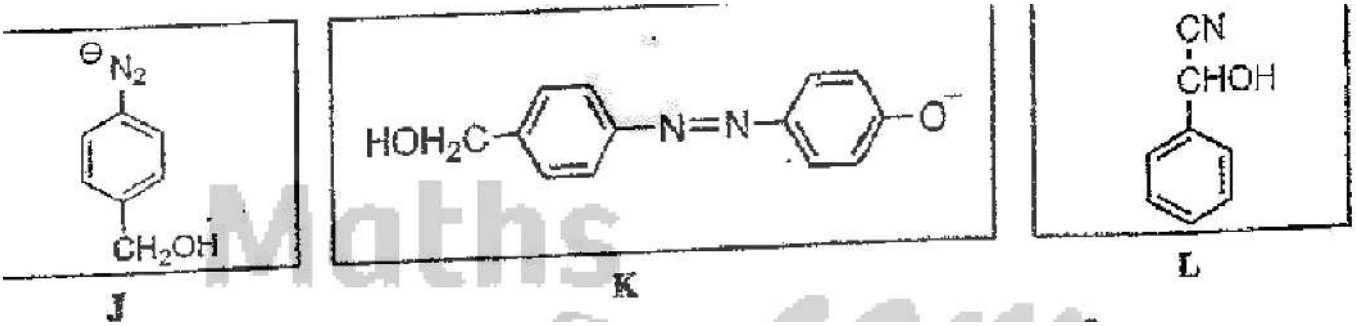
6

5

2

2

–



Structures of J, K and L, and reagents V and W (marking scheme)

(ii) Write the reagents **V** and **W** in the boxes given below.

Answer

V

–

W

(iii) Writing A_E, A_N, S_E, S_N or E in the appropriate box, classify each of the reactions **1**, **2** and **3** as electrophilic addition (A_E), nucleophilic addition (A_N), electrophilic substitution (S_E), nucleophilic substitution (S_N) or elimination (E) reaction.

Answer

Reaction 1: S_E
Reaction 2: S_N
Reaction 3: A_N (05 marks × 8 = 40 marks) 4(b): 40 marks

Review.

Principle: reactions of amines, diazonium salts, alkyl halides and aldehydes. $NaNO_2$/HCl at 0–5 °C converts the aromatic $–NH_2$ to a diazonium ion, while the aliphatic $–CH_2NH_2$ gives an unstable aliphatic diazonium ion that loses N_2 and forms $–CH_2OH$; so J carries both $–N_2$^+ and $–CH_2OH$. In alkaline phenol (phenoxide), the diazonium ion acts as an electrophile and couples at the para position (electrophilic substitution, S_E) to give the azo dye K. Benzyl chloride is hydrolysed by aqueous NaOH (S_N), PCC oxidizes the primary alcohol only to the aldehyde, and HCN adds to C=O (nucleophilic addition, A_N) to give the cyanohydrin L. Common mistakes: leaving $–CH_2NH_2$ unchanged in J, using acidified $KMnO_4$/$K_2Cr_2O_7$ for W (these over-oxidize to benzoic acid), and calling the coupling reaction an addition. (The scheme's J is printed with a circled charge on N_2 that looks like ⊖; it should be the positive diazonium ion.)

(c) [12 marks]

(c) (i) What is the structure of the **major** product of the reaction between $CH_3CH=CH_2$ and HBr?

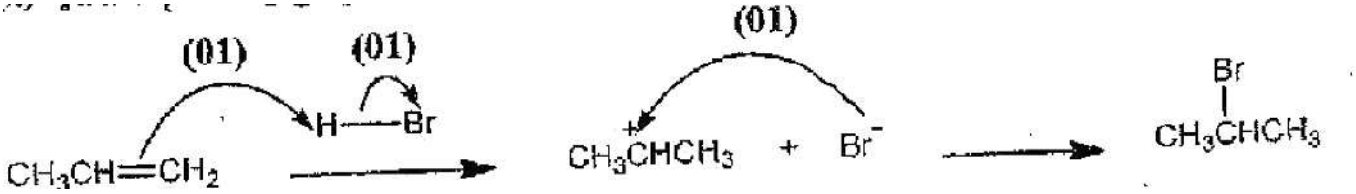
Answer

$CH_3CHBrCH_3$ (03)

(ii) Write the mechanism of the above reaction.

Answer

Step 1: the π electrons of the C=C bond attack the H of H–Br (curved arrow from the double bond to H) (01), and the H–Br bond electrons move onto Br (curved arrow) (01), giving the secondary carbocation CH_3C^+HCH_3 (03) and Br^- (03).
Step 2: Br^- attacks the carbocation (curved arrow from Br^- to C^+) (01), giving $CH_3CHBrCH_3$.
Note: marks may be awarded if δ+ and δ− are written on H and Br in HBr. 4(c): 12 marks



Mechanism of addition of HBr to propene (marking scheme)

Review.

Principle: electrophilic addition of HBr to an unsymmetrical alkene (Markovnikov's rule). H^+ adds to the terminal CH_2 so that the more stable secondary carbocation forms; Br^- then bonds to that carbon, giving 2-bromopropane rather than 1-bromopropane. Curved arrows must start from the electron source (the π bond, the H–Br bond, the Br^- lone pair) and point to the electron sink. Common mistakes: drawing the primary carbocation, arrows pointing the wrong way, and omitting the charges on the carbocation and bromide ion.

Read: RB U9 §3.1 · p. 54 RB U7 §1.4 · p. 21 RB U8 §2.2 · p. 33 RB U10 §4.3 · p. 78

Answer two from each part

Essay · Paper II Parts B and C

Part B

Question 5 · Part B · essay

−1

−1

A

23

−1

(a) [75 marks]

The following reaction occurs when $NaHCO_3(s)$ is heated to a temperature above 100 °C.
$2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$
A sample of $NaHCO_3(s)$ was placed in an evacuated closed rigid container of 5.00 dm^3 volume and heated to 328 °C. After the equilibrium was reached, a small amount of $NaHCO_3(s)$ still remained in the container. The pressure of the container was found to be 1.0×10^6 Pa. Assume that the volume of the solids remaining in the container is negligible. RT = 5000 J mol^{-1} at 328 °C.

(i) Calculate the number of moles of $H_2O(g)$ in the container when the equilibrium is reached at 328 °C.

Answer

Only $CO_2(g)$ and $H_2O(g)$ are present in the gas phase. Assuming ideal gas behaviour (PV = nRT) (03):
$n_{total} = P_{total}\ V/RT = (1.0 \times 10^6\ Pa \times 5.00 \times 10^{-3}\ m^3)/(8.314\ J\ K^{-1}\ mol^{-1} \times 601\ K)$ (02) $= (1.0 \times 10^6 \times 5.00 \times 10^{-3})/(5000\ J\ mol^{-1}) = 1.0$ mol (05)
$n_{total} = n_{H2O(g)} + n_{CO2(g)}$; by the stoichiometry $n_{H2O(g)} = n_{CO2(g)}$ (02)
$\therefore n_{H2O(g)} =$ **0.50 mol** (03)

(ii) Calculate K_p for the above equilibrium at 328 °C, and **hence** calculate K_c.

Answer

$K_p = P_{H2O(g)} \times P_{CO2(g)}$ (05)
In the system, $P_{total} = P_{H2O(g)} + P_{CO2(g)} = 1.0 \times 10^6$ Pa (05) and $P_{H2O(g)} = P_{CO2(g)}$
$\therefore P_{H2O(g)} = P_{CO2(g)} = 5.0 \times 10^5$ Pa (04 + 01)
$\therefore K_p = (5.0 \times 10^5 \text{ Pa})^2 =$ **2.5×10^{11} Pa^2** (04 + 01)
$K_p = K_c(RT)^{\Delta n}$ (05); $\Delta n = 2 - 0 = 2$ (03)
$\therefore K_c = K_p/(RT)^2 = 2.5 \times 10^{11}$ Pa^2/(8.314 J K^{-1} mol^{-1} × 601 K)^2 (02) = 2.5×10^{11} Pa^2/(5000 J mol^{-1})^2 = **1.0×10^4 mol^2 m^{-6}** (1.0×10^{-2} mol^2 dm^{-6}) (04 + 01)
Note: K_c must be calculated using the value of K_p. Other answers are not accepted.

(iii) An extra amount of $CO_2(g)$ was added into the container described above at 328 °C. When the equilibrium is re-established, the partial pressure of $CO_2(g)$ was four (4) times the partial pressure of $H_2O(g)$. Calculate the partial pressures of $CO_2(g)$ and $H_2O(g)$ under this condition.

Answer

Take $P_{H2O(g)} = x$ Pa, so $P_{CO2(g)} = 4x$ Pa. $K_p = P_{H2O(g)} \times P_{CO2(g)} = x \cdot 4x = 4x^2$ (05)
Since the temperature is constant, K_p is unchanged (05): 2.5×10^{11} Pa$^2 = 4x^2$ (05); $x^2 = 6.25 \times 10^{10}$ Pa^2; $x = 2.5 \times 10^5$ Pa
$\therefore P_{H2O(g)} =$ **2.5×10^5 Pa** (04 + 01)
$P_{CO2(g)} =$ **1.0×10^6 Pa** (04 + 01) · 5(a): 75 marks

Review.

Principle: for a heterogeneous equilibrium the solids ($NaHCO_3$, Na_2CO_3) do not appear in K, so $K_p = P_{CO2} \cdot P_{H2O}$, and K_p depends on temperature only (Resource Book 12 §2.1). Method: (i) get total moles from PV = nRT, using RT = 5000 J mol^{-1} directly, then split equally because the gases are formed 1 : 1; (ii) K_p from the two equal partial pressures, then convert with $K_p = K_c(RT)^{\Delta n}$, where Δn counts gaseous moles only (2 − 0 = 2); (iii) after extra CO_2 the temperature, hence K_p, is unchanged, so put $P_{CO2} = 4x$ and solve $4x^2 = K_p$. Common mistakes: including the solids in Δn (giving Δn = 1 or 3), using volume in dm^3 with Pa (use m^3), taking $K_c = K_p$, and forgetting units (Pa^2, mol^2 m^{-6}). Check: $(2.5 \times 10^5)(1.0 \times 10^6) = 2.5 \times 10^{11}$ Pa$^2 = K_p$.

(b) [75 marks]

In order to determine the standard enthalpy change (ΔH°) of the reaction, $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(l) + CO_2(g)$, the following experiment consisting of two steps (I and II) was carried out at room temperature.
Step I: 0.08 mol of $NaHCO_3(s)$ was added to 100.00 cm^3 of 1.0 mol dm^{-3} HCl acid solution in a beaker. The maximum temperature **fall** was found to be 5.0 °C.
[The reaction taking place: $NaHCO_3(s) + HCl(aq) \rightarrow Na^+(aq) + Cl^-(aq) + H_2O(l) + CO_2(g)$]
Step II: 0.04 mol of $Na_2CO_3(s)$ was added to 100.00 cm^3 of 1.0 mol dm^{-3} HCl acid solution in a beaker. The maximum temperature **rise** was found to be 3.5 °C.
[The reaction taking place: $Na_2CO_3(s) + 2HCl(aq) \rightarrow 2Na^+(aq) + 2Cl^-(aq) + H_2O(l) + CO_2(g)$]
Specific heat capacity at constant pressure and density of HCl acid solution are 4.0 J g^{-1} K^{-1} and 1.0 g cm^{-3} respectively. Assume that the changes in volume and density of the solutions after the addition of solids in the above two steps are negligible.

(i) Calculate the enthalpy changes (in kJ mol^{-1}) of the reactions given in steps I and II above.

Answer

Step I

3

(05)

−1

−1

(04 + 01)

(05)

−1

(04 + 01)

(02 marks for expressing it as a positive value)

Step II

2

3

−1

−1

(04 + 01)

−1

(04 + 01)

(02 marks for expressing it as a negative value)

(ii) Using the values obtained in (i) above and a **thermochemical cycle**, calculate ΔH° of the reaction, $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(l) + CO_2(g)$.

Answer

Cycle (the cycle must be balanced to earn its marks):
$2HCl(aq) + 2NaHCO_3(s) \xrightarrow{-\Delta H_1\ (05)} Na_2CO_3(s) + CO_2(g) + H_2O(l) + 2HCl(aq)$ (or without HCl)
$2HCl(aq) + 2NaHCO_3(s) \xrightarrow{-\Delta H_2\ (05)} 2NaCl(aq) + 2CO_2(g) + 2H_2O(l)$
$Na_2CO_3(s) + CO_2(g) + H_2O(l) + 2HCl(aq) \xrightarrow{-\Delta H_3\ (05)} 2NaCl(aq) + 2CO_2(g) + 2H_2O(l)$
By Hess's law, $\Delta H_1 = \Delta H_2 - \Delta H_3$ (05)
$\Delta H_1 = 25 \times 2 - (-35)$ kJ mol^{-1} (05)
ΔH_1 = **+85 kJ mol^{-1}** (04 + 01)

(iii) State the condition under which a heat change of a reaction is equal to its enthalpy change.

Answer

At constant pressure. (05)

(iv) Identify **two** sources of error in the above experimental procedure.

Answer

Any two of: no calorimeter was used (its heat capacity was not taken into account); the heat effects associated with dissolution of the solid in the solution were ignored/differ (enthalpy of dissolution values differ); heat loss to the surroundings. (03 × 2) · 5(b): 75 marks

Review.

Principle: Hess's law with a thermochemical cycle, and calorimetry Q = msθ (Resource Book 5 §2.2). Method: Q is for the 100 g of solution and is then scaled to one mole of the limiting solid; $NaHCO_3$ + HCl is endothermic (temperature falls, ΔH positive) and Na_2CO_3 + HCl is exothermic (temperature rises, ΔH negative). Two moles of $NaHCO_3$ are needed in the cycle, so $\Delta H_2 = 2 \times 25 = +50$ kJ and $\Delta H_1 = 50 - (-35) = +85$ kJ mol^{-1}. Common mistakes: using the mass of the solid instead of 100 g of solution, forgetting the sign

(a fall in temperature means a positive ΔH), forgetting to double the +25 kJ mol^{-1} for 2 mol $NaHCO_3$, and unbalanced cycles. Heat change equals ΔH only at constant pressure. The remark on the second error source is taken from the Sinhala scheme and may be loosely phrased in translation; the other two (no calorimeter, heat loss) are unambiguous. Topic is within the current syllabus.

Read: RB U12 §2.1 · p. 76 RB U5 §2.2 · p. 36 RB U5 §2.4 · p. 53

Question 6 · Part B · essay

(a) [50 marks]

(i) Explain why the rate of a reaction increases when the concentrations of the reactants are increased.

Answer

The number of reactant particles per unit volume increases (with the increase in concentration). (05) This increases the frequency of collisions (the number of collisions per unit time). (05)

(ii) Give **two** reasons to explain why in general, the rate of a reaction increases with increasing temperature.

Answer

The collision frequency increases, and the fraction of reactant molecules with energy greater than the activation energy increases with temperature. (05 + 05) (In the scheme the key phrases are "collision frequency" and "fraction of molecules with energy greater than the activation energy"; each is underlined for 05 marks.)

(iii) What is the relationship between order and molecularity of an elementary reaction?

Answer

Molecularity = order of the reaction. (10)

(iv) Sketch the structure of the activated complex of the elementary reaction, NO + O_2 → NO_2 + O. Label the bonds that are being formed as 'forming' and the bonds that are being broken as 'breaking'.

Answer

Activated complex: O·····O·····N=O, drawn with dotted (partial) bonds. The O···O bond (the O–O bond of O_2 being broken) is labelled 'breaking' and the O···N bond (the new bond between N of NO and O of O_2) is labelled 'forming'. Either the structure O---O---N=O or the equivalent one with the O=O double bond partly retained is accepted. (10) (Correct structure 04; labelling 03 + 03.)

2

2

(v) Write the rate expression for the elementary reaction, xA + yB → zC, where the rate constant is k, and stoichiometric coefficients are x, y, z.

Answer

Rate = k[A]^x[B]^y, or (1/x)(−Δ[A]/Δt) = k[A]^x[B]^y, or (1/x)(−d[A]/dt) = k[A]^x[B]^y, or −Δ[A]/Δt = k[A]^x[B]^y, or −d[A]/dt = k[A]^x[B]^y. (10) · 6(a): 50 marks

Review.

Principle: collision theory — rate depends on the frequency of effective collisions, which rises with concentration (more particles per volume) and with temperature (mainly through the larger fraction of molecules having $E \geq E_a$, plus more frequent collisions) (Resource Book 11 §1.5). For an elementary reaction the rate law follows the stoichiometry, so order = molecularity, and the activated complex shows partial (dotted) bonds, with the breaking bond and forming bond labelled (11 §1.10). Common mistakes: saying temperature only increases the 'speed' of molecules without mentioning the fraction with $E \geq E_a$, drawing complete bonds in the activated complex, and writing the rate law with exponents that are not the stoichiometric coefficients (this is allowed here only because the reaction is elementary). Topic is within the current syllabus.

(b) [50 marks]

The reaction xA + yB → zC was studied in a two phase system consisting of an organic solvent and water. The compound A is soluble in both phases while compounds B and C are soluble only in the aqueous phase. The partition coefficient for the distribution of A between phases, $K_D = [A_{(org)}]/[A_{(aq)}] = 4.0$.
The compound A was added to the two phase system and allowed to reach equilibrium. The reaction was started by injecting the compound B to the aqueous phase. Temperature of the system was maintained at a constant value. The results of the experiments carried out are given below.

Experiment No.	Volume of the organic phase (cm^3)	Volume of the aqueous phase (cm^3)	Amount of A added to the system (mol)	Amount of B injected (mol)	Initial rate, $(-\Delta C_A/\Delta t)$ (mol dm^{-3} s^{-1})
I	–	100.00	1.00×10^{-2}	1.00×10^{-2}	1.20×10^{-5}
II	100.00	100.00	1.25×10^{-1}	1.00×10^{-2}	7.50×10^{-5}
III	50.00	50.00	6.25×10^{-2}	1.00×10^{-2}	1.50×10^{-3}

Note:

(i) Calculate the initial concentration of A in the aqueous phase in experiments I, II and III above.

Answer

Experiment I:

aq

−2

−3

3

−3

(01 + 01)

Experiment II:

D

org

aq

aq

org

(03)

−1

−3

3

−3

3

(02 + 01)

−1

−2

(02 + 01)

aq

−2

−3

3

−1

−3

(02 + 01)

Experiment III:

aq

−2

(02 + 01)

−2

−2

(02 + 01)

aq

−3

3

−1

−3

(02 + 01)

(ii) Find the order of the reaction with respect to A.

Answer

The order with respect to A is obtained from experiments I and II, in which [B] in the aqueous phase is the same (0.1 mol dm^{-3}). (01)
1.2×10^{-5} mol dm^{-3} s^{-1} = k[0.1 mol dm^{-3}]^x[0.1 mol dm^{-3}]^y (02 + 01)
7.5×10^{-5} mol dm^{-3} s^{-1} = k[0.25 mol dm^{-3}]^x[0.1 mol dm^{-3}]^y (02 + 01)
Dividing: $(7.5 \times 10^{-5})/(1.2 \times 10^{-5})$ = (0.25/0.1)^x; 6.25 = 2.5^x (03); 2.5^2 = 6.25, so **x = 2** (02)

(iii) Find the order of the reaction with respect to B.

Answer

The order with respect to B is obtained from experiments II and III, in which [A] in the aqueous phase is the same (0.25 mol dm^{-3}). [B] in III = 1.00×10^{-2} mol/(50×10^{-3} dm^3) = 0.2 mol dm^{-3}.
$1.5 \times 10^{-3}/7.5 \times 10^{-5}$ = (0.2/0.1)^y (03); 20 = 2^y; log 20 = y log 2; 1.3010 = y × 0.3010; **y = 4.32 (≈ 4)** (02)

(iv) Calculate the rate constant of the reaction.

Answer

The rate constant is calculated using the data of experiment I: k = Rate(I)/([A(I)]^2[B(I)]^4) (03) (4.32 may be used instead of 4).
k = (1.20×10^{-5} mol dm^{-3} s^{-1})/[(1.00×10^{-1} mol dm^{-3})^2 (1.00×10^{-1} mol dm^{-3})^4] (02 + 01)
k = **1.2×10^{1} mol^{-4} dm^{12} s^{-1}** (as printed in the scheme) (01)

(v) In the experiment III above, after adding A and allowing the system to reach equilibrium, if a volume of 10.00 cm^3 was removed from the organic phase, what can be stated about the initial rate of the reaction? Give reason/reasons for your answer.

Answer

The initial rate of the reaction does not change. (02) The concentration of A in the aqueous phase does not change. (02) · 6(b): 50 marks

Review.

Principle: the rate law must be written with the concentrations in the phase where the reaction occurs (the aqueous phase), and the partition coefficient converts the total amount of A into $[A]_{aq}$ (Resource Book 12 §2.7; rate law and order in 11 §1.6). Method: $[A]_{aq} = n_A/(V_{aq}(1 + K_D\ V_{org}/V_{aq}))$; compare experiments with one concentration held constant (I and II for A; II and III for B); k from experiment I. In (v), removing some of the organic layer after equilibrium does not alter the concentration in either layer, so the rate is unchanged. Issues in the official answer: with the printed rate 1.50×10^{-3} the calculation gives y = 4.32, which the scheme accepts as ≈ 4; the data appear designed for y = 4 (a rate of 1.20×10^{-3} would give exactly 4). The scheme's unit for k (mol^{-4} dm^{12} s^{-1}) does not match the overall order 6, which gives mol^{-5} dm^{15} s^{-1}; the numerical value 12 is correct for x = 2, y = 4. Also, one line of the scheme prints the rate of experiment III as 1.5×10^{-5}, a typing slip for 1.5×10^{-3}. Common mistakes: using concentrations based on the total volume or on A added rather than $[A]_{aq}$, and using the organic-phase concentration. Topic is within the current syllabus.

(c) [50 marks]

A mixture of liquids X and Y behaves ideally. At a constant temperature, when the liquid phase in equilibrium with the vapour phase in a closed rigid vessel contains 1.2 moles of X and 2.8 moles of Y, the total vapour pressure is 3.4×10^4 Pa. At the same temperature, when the composition of the liquid phase in equilibrium with the vapour phase is 1.2 moles of X and 4.8 moles of Y, the total vapour pressure is 3.6×10^4 Pa. Calculate the saturated vapour pressures of X and Y at this temperature.

Answer

By Raoult's law, $p_i = x_i\, p_i\text{^}0$ (05); $p_{total} = p_X + p_Y = x_X\, p_X\text{^}0 + x_Y\, p_Y\text{^}0$ (05)
First composition: x_X = 1.2 mol/(1.2 mol + 2.8 mol) (04 + 01); x_X = 0.3 and therefore x_Y = 0.7 (02 + 02 + 01)
Second composition: x_X = 1.2 mol/(1.2 mol + 4.8 mol) (04 + 01); x_X = 0.2 and therefore x_Y = 0.8 (02 + 02 + 01)
Two equations for the two compositions:
3.4×10^4 Pa = $0.3p_X\text{^}0 + 0.7p_Y\text{^}0$ (1) (05)
3.6×10^4 Pa = $0.2p_X\text{^}0 + 0.8p_Y\text{^}0$ (2) (05)
Solving: $p_X\text{^}0$ = **2.0×10^4 Pa** (04 + 01); $p_Y\text{^}0$ = **4.0×10^4 Pa** (04 + 01) · 6(c): 50 marks

Review.

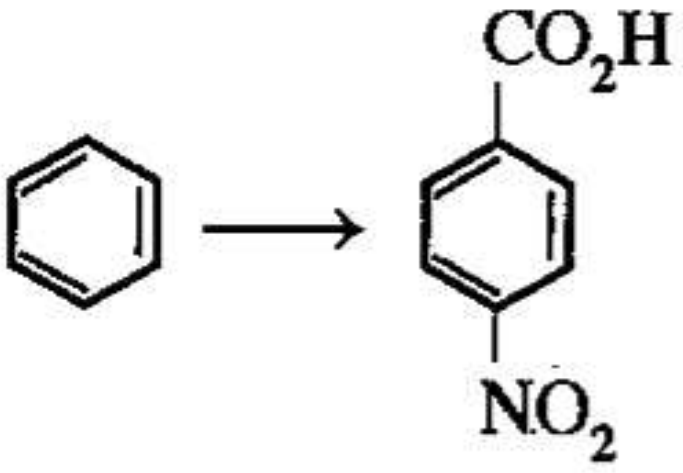
Principle: Raoult's law for an ideal binary liquid mixture, $P_{total} = x_X\, P_X\text{^}0 + x_Y\, P_Y\text{^}0$ (Resource Book 12 §2.6). Method: convert moles to mole fractions in each liquid composition (0.3/0.7 and 0.2/0.8), write one equation per composition and solve the simultaneous equations: multiply (1) by 2 and (2) by 3 to get $0.6p_X\text{^}0 + 1.4p_Y\text{^}0 = 6.8 \times 10^4$ and $0.6p_X\text{^}0 + 2.4p_Y\text{^}0 = 10.8 \times 10^4$, so $p_Y\text{^}0 = 4.0 \times 10^4$ Pa and $p_X\text{^}0 = 2.0 \times 10^4$ Pa. Common mistakes: using mole fractions in the vapour instead of the liquid, and forgetting that the composition of the liquid phase (not the total mixture) is what is given. The scheme's second mole-fraction line is labelled with the symbol for Y but gives the value for X (0.2), a labelling slip; the values used are correct. Topic is within the current syllabus.

Read: RB U11 §1.5 · p. 15 RB U11 §1.6 · p. 16 RB U11 §1.10 · p. 57 RB U12 §2.7 · p. 229 RB U12 §2.6 · p. 216

Question 7 · Part B · essay

(a) [30 marks]

Show how you would carry out the following conversion in **not more than five (5) steps**.

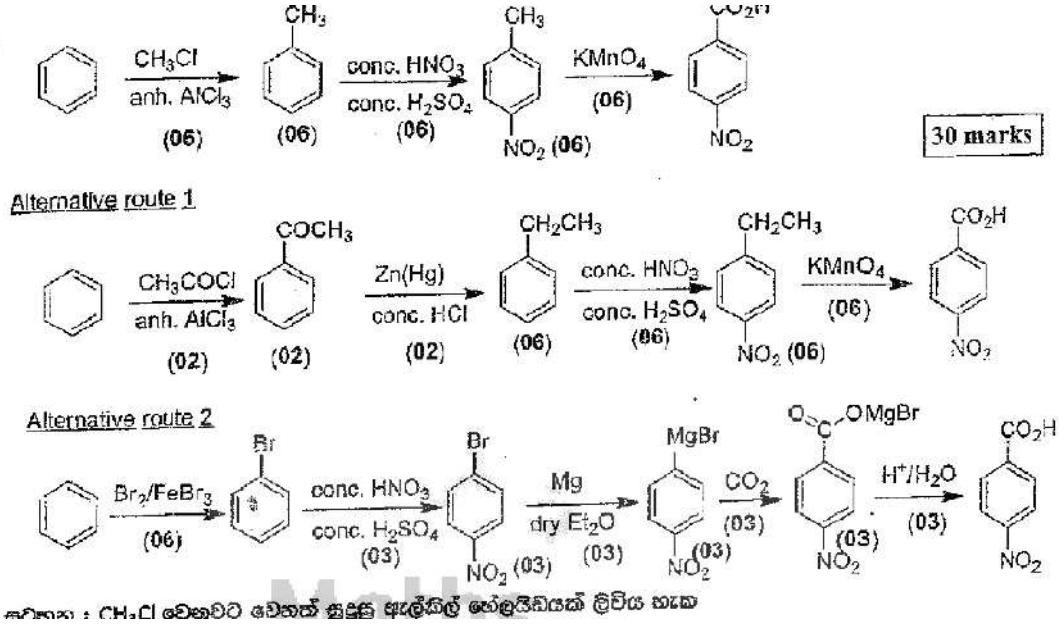


compounds A and B are required

Benzene → 4-nitrobenzoic acid

Answer

Route (30 marks, 06 for each reagent/product shown): benzene —CH_3Cl, anhydrous $AlCl_3$→ toluene (methylbenzene) (06 + 06) —conc. HNO_3/conc. H_2SO_4→ 4-nitrotoluene (06 + 06) —$KMnO_4$→ 4-nitrobenzoic acid (06).
Alternative route 1: benzene —CH_3COCl, anh. $AlCl_3$ (02)→ acetophenone (02) —Zn(Hg)/conc. HCl (02)→ ethylbenzene (06) —conc. HNO_3/conc. H_2SO_4→ 4-nitroethylbenzene (06) —$KMnO_4$→ 4-nitrobenzoic acid (06).
Alternative route 2: benzene —Br_2/$FeBr_3$ (06)→ bromobenzene —conc. HNO_3/conc. H_2SO_4 (03)→ 4-bromonitrobenzene (03) —Mg, dry Et_2O (03)→ 4-nitrophenylmagnesium bromide (03) —CO_2 (03)→ the magnesium carboxylate (O=C–OMgBr) (03) —H^+/H_2O (03)→ 4-nitrobenzoic acid. (30 marks)
Scheme notes: another suitable alkyl halide may be written in place of CH_3Cl; $(CH_3)_3CCl$ is not accepted; RCH_2Cl is accepted if the final product obtained is suitable (the side chain must be oxidisable to –CO_2H).



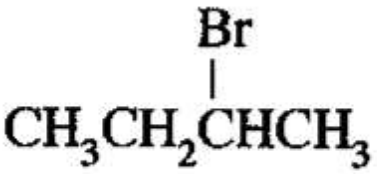
Routes for benzene → 4-nitrobenzoic acid (scheme)

Review.

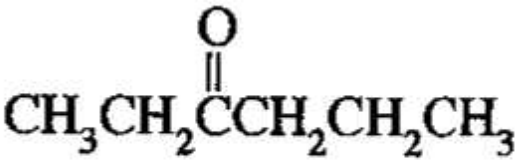
Principle: –CH_3 and –CH_2R are ortho/para-directing, so the alkyl group must be introduced before nitration and then oxidised to –CO_2H (which is meta-directing, so the reverse order would give 3-nitrobenzoic acid) (Resource Book 8 §2.4, §2.5). Mistakes: nitrating first (gives nitrobenzene, then Friedel–Crafts fails on a deactivated ring), or oxidising before nitration.

(b) [90 marks]

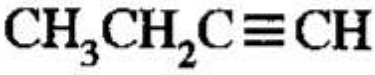
Two compounds A and B are required to be prepared in the laboratory.



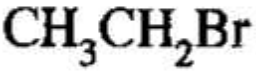
A



B



X



Y

Target compounds A and B and the starting compounds X and Y

(i) Show how you would prepare A and B in **not more than five (5) steps in each case**, using X and Y as required.

Answer

Preparation of A

3

2

(05)

2

4

2

(05)

3

2

2

(05)

(05)

3

2

3

Alternative route for A

(05)

2+

+

2

(03)

3

2

3

(03)

4

4

+

2

(03)

3

2

3

(03)

3

(03)

Preparation of B

(05)

2

(05)

3

2

+

3

2

(05)

3

2

(05)

3

2

2

3

(05)

2+

+

2

(05)

3

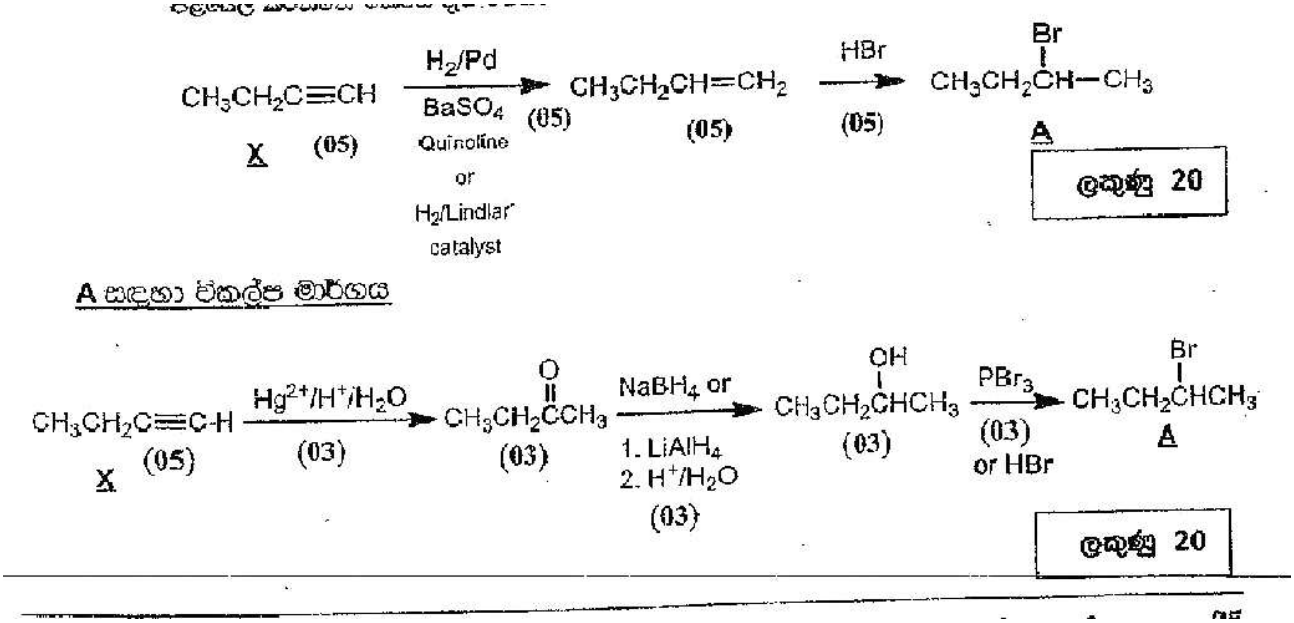
2

2

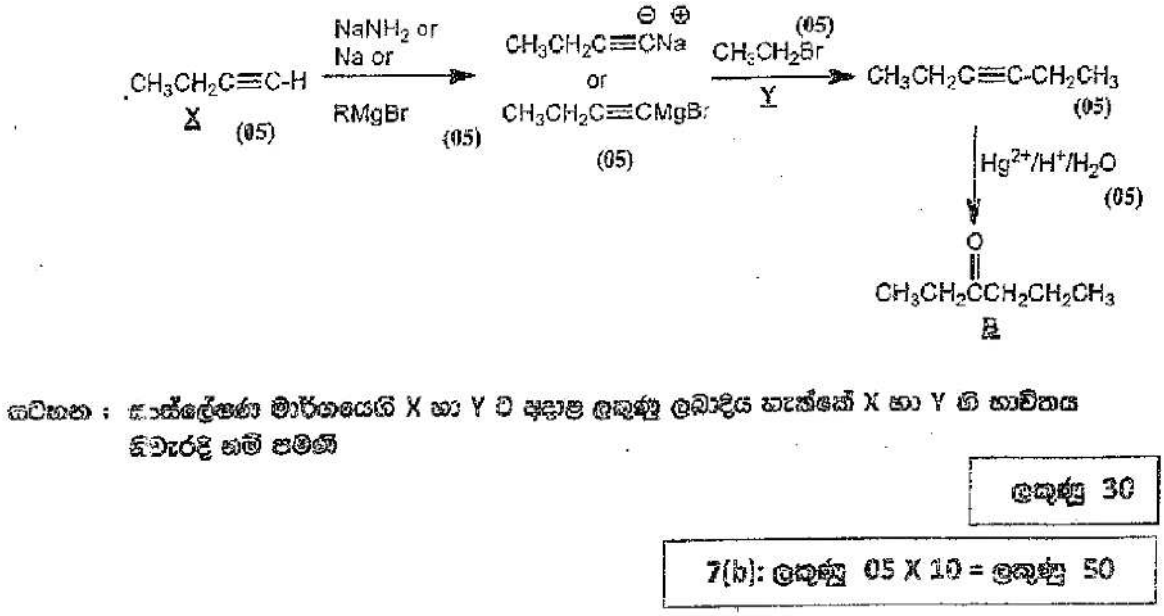
2

3

Scheme note: marks for X and Y in the synthetic route are given only if X and Y are used correctly. 7(b)(i): 5 × 10 = 50 marks.



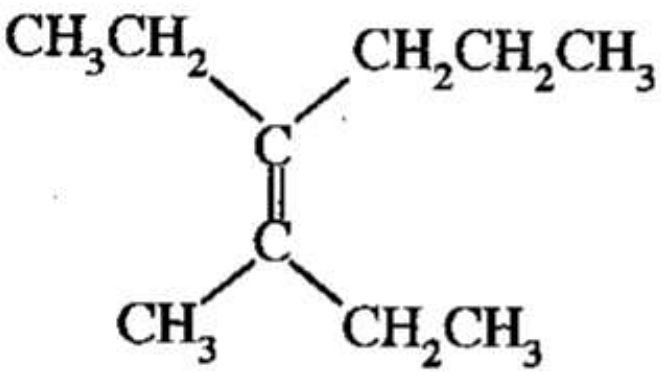
Preparation of A: two routes (scheme)



Preparation of B (scheme)

(ii) Show how you would prepare the compound C using A and B given above, in not more than five (5) steps.

i.

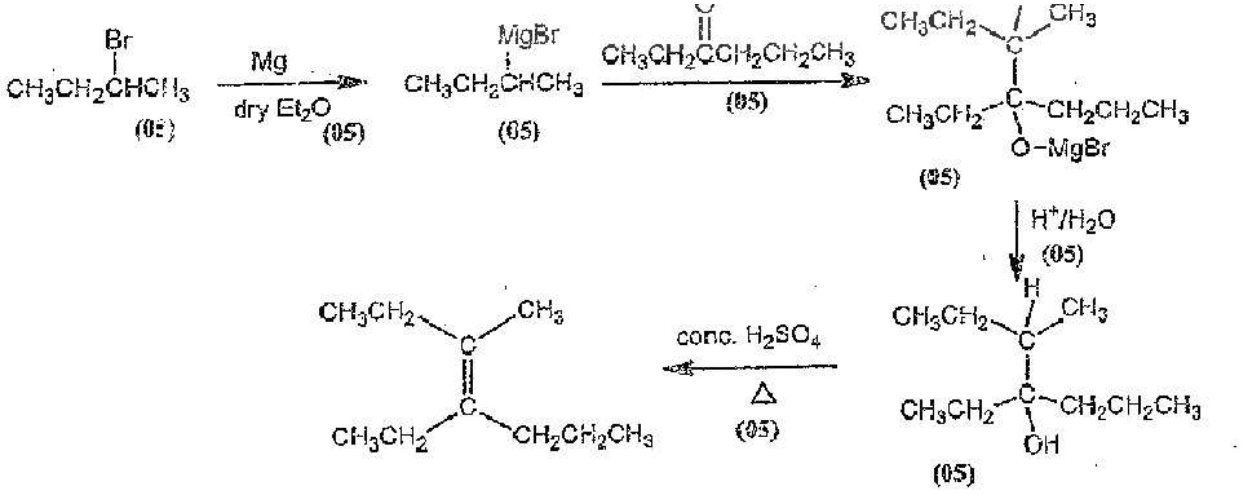


C

Compound C

Answer

A —Mg, dry Et_2O (05 + 05)→ $CH_3CH_2CH(MgBr)CH_3$ (05) —B ($CH_3CH_2COCH_2CH_2CH_3$) (05)→ the magnesium alkoxide, $(CH_3CH_2)(CH_3)CH–C(CH_2CH_3)(CH_2CH_2CH_3)–OMgBr$ (05) —H^+/H_2O (05)→ the tertiary alcohol $(CH_3CH_2)(CH_3)CH–C(OH)(CH_2CH_3)(CH_2CH_2CH_3)$ (05) —conc. H_2SO_4, Δ (05)→ C, $(CH_3CH_2)(CH_3)C=C(CH_2CH_3)(CH_2CH_2CH_3)$ (05). 7(b)(ii): 05 × 8 = 40 marks
Scheme notes: steps may be combined where appropriate, and marks should be awarded accordingly for correct answers; no marks for 'Cu/300 °C' or 'heat' (alone) as the dehydration conditions.



Preparation of C from A and B (scheme)

Review.

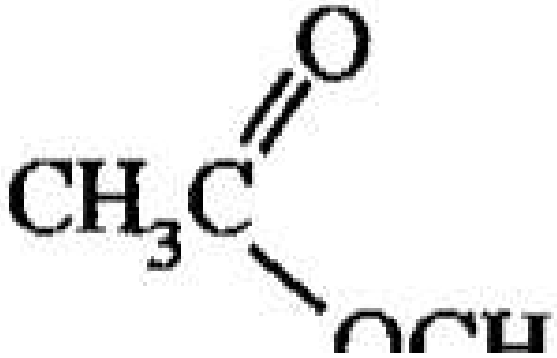
Principle: building a carbon skeleton with Grignard chemistry and alkyne chemistry (Resource Book 8 §2.3, §2.7; 9 §3.4). The terminal alkyne ($pK_a \approx 25$) is deprotonated and alkylated with Y (CH_3CH_2Br) to give 3-hexyne, then Markovnikov hydration ($Hg^{2+}/H^+/H_2O$) gives a ketone, B. A (2-bromobutane) is formed by Lindlar (cis) partial hydrogenation of X to 1-butene and Markovnikov addition of HBr, or by hydration → reduction → bromination. C comes from the secondary Grignard reagent of A + ketone B, then acid work-up and dehydration. Common mistakes: using full H_2/Pd (gives butane), anti-Markovnikov HBr (peroxides), reacting a Grignard reagent in the presence of water or –OH/–C≡C–H groups, and missing the acid work-up step. Note: the current syllabus treats Grignard reagents and alkyne hydration in the Resource Book units

cited; multi-step synthesis questions are still tested.

(c) [30 marks]

Using your knowledge of the mechanism of the reaction between acetyl chloride and NaOH, propose a mechanism for the reaction between

mechanism for the reactic



and

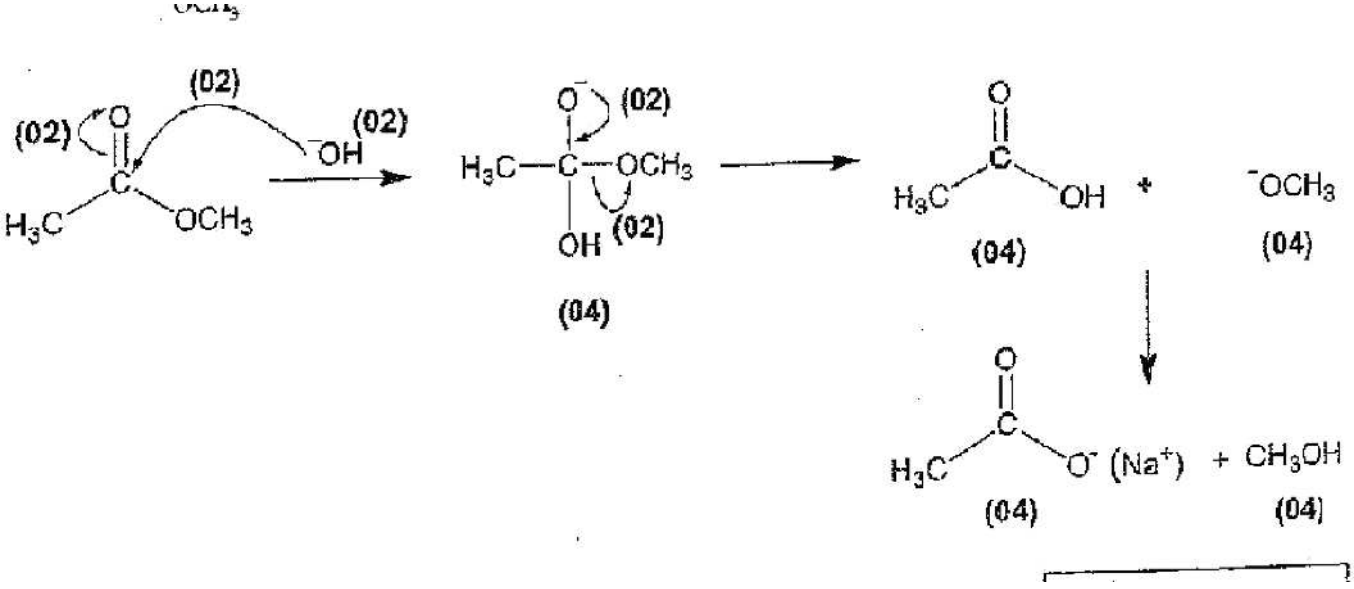
3

3

and NaOH.

Answer

Nucleophilic acyl substitution (addition–elimination): the OH^- attacks the carbonyl carbon (curved arrow from OH^- to C, and the C=O π electrons move onto oxygen) (02 + 02 + 02) to give the tetrahedral intermediate CH_3–C(O^-)(OH)–OCH_3 (04); the lone pair on O^- reforms the C=O and the CH_3O^- leaves (curved arrows) (02 + 02) to give CH_3COOH (04) + CH_3O^- (04); proton transfer from the acid to the methoxide gives $CH_3COO^-(Na^+)$ (04) + CH_3OH (04). 7(c): 30 marks



Mechanism of the base hydrolysis of methyl ethanoate (scheme)

Review.

Principle: the carbonyl carbon of an acid derivative is electrophilic; nucleophilic attack gives a tetrahedral intermediate from which the best leaving group departs (Resource Book 9 §3.6). The final proton transfer

makes the overall reaction irreversible (acetate ion is not attacked by CH_3O^-/CH_3OH). Common mistakes: writing a one-step SN2 displacement, omitting the intermediate, and ending with the carboxylic acid instead of its salt in excess NaOH.

Read: RB U8 §2.4 · p. 44 RB U8 §2.7 · p. 50 RB U9 §3.4 · p. 60 RB U9 §3.6 · p. 70

Part C

Question 8 · Part C · essay

Part C – Essay. Answer two questions only. (Each question carries 15 marks; 150 marks on the scheme's scale.)

(a) [75 marks]

Solution **Y** contains **three** cations.

 The following tests were carried out to identify these cations.

	Test	Observation
①	Dilute HCl was added to a small portion of **Y**.	A white precipitate (**P_1**)
②	**P_1** was separated by filtration and H_2S was bubbled through the solution.	A black precipitate (**P_2**)
③	**P_2** was separated by filtration. The filtrate was boiled to remove the H_2S, cooled, and NH_4OH/NH_4Cl was added.	No precipitate
④	H_2S was bubbled through the solution.	A black precipitate (**P_3**)

 The following tests were carried out for precipitates **P_1**, **P_2** and **P_3**.

Precipitate	Test	Observation
P_1	I. Water was added to **P_1** and the mixture was boiled.	**Part** of **P_1** dissolved.
II. The mixture from I above was filtered while warm and the following tests were carried out on the filtrate (**F_1**) and residue (**R_1**). **Filtrate (**F_1**)** • Dilute H_2SO_4 was added to warm **F_1**. **Residue (**R_1**)** • **R_1** was washed thoroughly with warm water and dilute NH_4OH was added. • Thereafter, a KI solution was added.	A white precipitate **R_1** dissolved. A dark yellow precipitate	
P_2	**P_2** was dissolved in warm dil. HNO_3 and a potassium chromate solution was added.	A yellow precipitate

Precipitate	Test	Observation
P_3	I. **P_3** was dissolved in warm conc. HNO_3.	A pink coloured solution (**solution 1**)
II. The following were added to **solution 1** above. • conc. HCl • dil. NH_4OH	A blue coloured solution (**solution 2**) A yellow-brown coloured solution (**solution 3**)	

(i) Identify the **three** cations. (Reasons are **not** required.)

Answer

Pb^{2+}, Co^{2+}, Ag^{+} (08 × 3)

(ii) Identify,
I. precipitates **P_1**, **P_2** and **P_3**
II. species responsible for the colours of **solutions, 1, 2** and **3**.
(**Note:** Write chemical formulae **only**.)

Answer

I. **P_1**: $PbCl_2$ and AgCl; **P_2**: PbS; **P_3**: CoS (05 × 4)
II. Solution 1: Co^{2+} or $Co(NO_3)_2$ or $[Co(H_2O)_6]^{2+}$ (05)
Solution 2: $[CoCl_4]^{2-}$ (05)
Solution 3: $[Co(NH_3)_6]^{2+}$ (05)

(iii) Explain **briefly** why the cation/s that precipitate/s in ④ above does not/do not precipitate in acidic medium.

Answer

For a cation to precipitate from solution as its sulphide, $[M^{2+}][S^{2-}] > K_{sp}$ (04)
In acidic medium $[S^{2-}]$ is reduced (03), because the equilibrium $H_2S(aq) \rightleftharpoons 2H^{+}(aq) + S^{2-}(aq)$ is pushed to the left (03).
K_{sp} of the sulphides of group (iv) cations (Mn^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}) > K_{sp} of the sulphides of group (ii) cations (03).
Since $[S^{2-}]$ is low in acidic medium, it is not sufficient to precipitate the group (iv) sulphides; therefore they remain in solution. (03) · 8(a): 75 marks

Review.

Principle: classical group separation of cations (Resource Book 12 §2.4; colours and complexes of Co in 6 §4.10). Dilute HCl precipitates the group I chlorides AgCl and $PbCl_2$; $PbCl_2$ is fairly soluble in hot water, so it is separated from AgCl and confirmed as white $PbSO_4$, while AgCl dissolves in NH_3 as $[Ag(NH_3)_2]^{+}$ and gives yellow AgI with KI. Because $PbCl_2$ is only partly precipitated by cold dilute HCl, the remaining Pb^{2+} comes down with H_2S in acid as black PbS (group II), confirmed as yellow $PbCrO_4$. Group III gives nothing; the black sulphide in alkaline medium (group IV) is CoS: pink $[Co(H_2O)_6]^{2+}$, blue $[CoCl_4]^{2-}$ with conc. HCl, and an ammine complex with NH_3. In (iii) the key idea is the common-ion suppression of S^{2-} by H^{+}, so only the very insoluble group II sulphides exceed K_{sp}. Common mistakes: forgetting that Pb^{2+} appears in both group I and group II, and giving Ni^{2+} (green) instead of Co^{2+}.

(b) [75 marks]

A solid sample was found to contain $(NH_4)_2SO_4$, NH_4NO_3 and non-reactive substances. The following procedures were used to determine the amount of ammonium salts present in this sample.
A 1.00 g portion of the solid sample was dissolved in water and diluted to 250.00 cm^3 in a volumetric flask (hereafter referred to as solution **S**).

Procedure 1

A 50.00 cm^3 portion of solution **S** was treated with an excess amount of a strong alkali (NaOH) and the **gas** liberated was passed into 30.00 cm^3 of 0.10 mol dm^{-3} HCl. The volume of 0.10 mol dm^{-3} NaOH required to neutralize the remaining HCl (using phenolphthalein as the indicator) was 10.20 cm^3.

Procedure 2

To a 25.00 cm^3 portion of solution **S**, Al powder was added followed by an excess of strong alkali, and the mixture was heated. The **gas** liberated was passed into 30.00 cm^3 of 0.10 mol dm^{-3} HCl. The volume of 0.10 mol dm^{-3} NaOH required to neutralize the remaining HCl (using phenolphthalein as the indicator) was 15.00 cm^3.

(**Note:** Completion of gas evolution in procedures **1** and **2** was checked using litmus paper.)

(i) Identify the **gas** liberated in procedure **1**.

Answer

NH_3 (03)

(ii) Identify the **gas** liberated in procedure **2**.

Answer

NH_3 (03)

(iii) Write balanced chemical equations for the reactions taking place in procedures **1** and **2**.

Answer

Reactions in procedure 1

4

2

4

2

4

3

2

(04)

4

3

3

3

2

(04)

Reactions in procedure 2

4

2

4

2

4

3

2

(03)

4

3

3

3

2

(03)

–

3

2

2

3

(05)

Note: since it was not stated that the reactions of procedures 1 and 2 must be written separately, candidates may write only the last three reactions (procedure 2). In that case award 07 marks each for the reactions with NaOH (reactions 3 and 4).

(iv) Calculate the mass percentage of each of the compounds $(NH_4)_2SO_4$ and NH_4NO_3 in the solid sample. (H = 1, N = 14, O = 16, S = 32)

Answer

Let the mass of $(NH_4)_2SO_4$ in the sample = x g (01); mass of NH_4NO_3 in the sample = y g (01)
Molar mass of $(NH_4)_2SO_4$ = 132 (01); molar mass of NH_4NO_3 = 80 (01)
Moles of $(NH_4)_2SO_4$ = x/132 (01); moles of NH_4NO_3 = y/80 (01)
Procedure 1
Moles of NaOH = (0.10/1000) × 10.20 (01)
∴ moles of HCl that reacted with NaOH = (0.10/1000) × 10.20 (01)
∴ moles of HCl that reacted with NH_3 = (0.10/1000) × 30.0 − (0.10/1000) × 10.20 (01) = (0.10/1000) × 19.80 (01)
∴ moles of NH_3(g) liberated = (0.10/1000) × 19.80 (01)
Moles of $(NH_4)_2SO_4$ in 50.00 cm^3 = (x/132) × (1/5) (01)
Moles of NH_4NO_3 in 50.00 cm^3 = (y/80) × (1/5) (01)
∴ moles of NH_3 liberated from 50.00 cm^3 of the solution (equations 1 and 2):
(x/132) × (1/5) × 2 + (y/80) × (1/5) = (0.10/1000) × 19.80 ……(6) (07)
Similarly for procedure 2
Moles of NaOH = (0.10/1000) × 15.00 (01)
∴ moles of HCl that reacted with NaOH = (0.10/1000) × 15.00 (01)
∴ moles of HCl that reacted with NH_3 = (0.10/1000) × 30.0 − (0.10/1000) × 15.00 (01) = (0.10/1000) × 15.00 (01)
∴ moles of NH_3(g) liberated = (0.10/1000) × 15.00 (01)
Moles of $(NH_4)_2SO_4$ in 25.00 cm^3 = (x/132) × (1/10) (01)
Moles of NH_4NO_3 in 25.00 cm^3 = (y/80) × (1/10) (01)
Moles of NH_3 liberated from 25.00 cm^3 of the solution (equations 3, 4 and 5):
(x/132) × (1/10) × 2 + (y/80) × (1/10) + (y/80) × (1/10) = (0.10/1000) × 15.00 ……(7) (07)
(x/132) × (1/10) × 2 + (2y/80) × (1/10) = (0.10/1000) × 15.00
(x/132) × (1/5) + (y/80) × (1/5) = (0.10/1000) × 15.00 ……(8) (01)
Equation (6) [÷ 2]: (x/132) × (1/5) + (y/80) × (1/10) = (0.10/1000) × 19.80 × ½ ……(6)
Equation (8) − (6): (y/80) × (1/10) = (0.10/1000) × 15.00 − (0.10/1000) × 9.90 (01)
y = (0.10/1000) × 5.10 × 800; **y = 0.408** (02)
Substituting y = 0.408 in equation (8) (y = 0.408 may also be substituted in equation (6)):
(x/132) × (1/5) + (0.408/80) × (1/5) = (0.10/1000) × 15.00
x/660 = (0.10/1000) × 15.00 − 0.408/400 = (6.0 − 4.08)/4000
x = 0.317 (02)
% of $(NH_4)_2SO_4$ = (0.317/1.0) × 100 = **31.7%** (05)
% of NH_4NO_3 = (0.408/1.0) × 100 = **40.8%** (05)

Alternative answer 1

Procedure 1

3

−3

(02)

−3

(01)

3

−3

(01)

−3

(01)

Procedure 2

3

−3

(02)

−3

(01)

3

−3

(01)

−3

(01)

4

3

4

2

4

3

4

3

4

2

4

−3

(07)

3

3

3

4

3

4

2

4

−3

(07)

−3

−3

(02)

−3

(02)

−3

(02)

4

3

−3

−1

(04 + 01 for mol. mass)

40.8%

(05)

4

2

4

−3

−1

(04 + 01 for mol. mass)

31.7%

(05)

Alternative answer 2

Procedure 1

(01)

(01)

(02)

(02)

4

4

2

3

4

3

4

2

4

3

(01)

Procedure 2

(01)

(01)

(02)

3

3

(01)

3

3

(07)

4

3

(01)

4

3

−1

as printed; the factor × 5 is missing – see review

(04 + 01 for mol. mass)

40.8%

(05)

3

4

3

3

3

4

2

4

(07)

4

2

4

3

4

2

4

(01)

4

2

4

(01)

4

2

4

−1

(04 + 01 for mol. mass)

31.7%

(05) · 8(b): 75 marks

Review.

Principle: indirect (back) titration of liberated ammonia, combined with the Al/alkali reduction of nitrate to NH_3 (Resource Book 6 §4.5; 3 §3.8). Procedure 1 releases NH_3 only from NH_4^+ ions; procedure 2 releases NH_4^+-nitrogen **plus** nitrate-nitrogen, so the difference (scaled to the same volume) gives the nitrate. Per 50.00 cm^3: total NH_4^+ = 1.98×10^{-3} mol; NH_4^+ + NO_3^− = $2 \times 1.50 \times 10^{-3} = 3.00 \times 10^{-3}$ mol, so NO_3^− = n(NH_4NO_3) = 1.02×10^{-3} mol (× 5 × 80 = 0.408 g, 40.8%), and $(1.98 - 1.02) \times 10^{-3}/2 = 4.8 \times 10^{-4}$ mol $(NH_4)_2SO_4$ (× 5 × 132 = 0.317 g, 31.7%). Common mistakes: forgetting the different aliquot volumes (50.00 vs 25.00 cm^3, i.e. ×5 vs ×10), forgetting that $(NH_4)_2SO_4$ gives 2 NH_3, and counting NH_4NO_3 only once in procedure 2. Notes on the official scheme: in alternative answer 2 the first heading is printed as "Procedure 2" but refers to procedure 1, and the first 40.8% fraction is printed without the factor 5 (0.00102 × 80 × 100/1.0 alone would give 8.16%; the mass line above it correctly includes × 5). The RB writes the aluminate as $[Al(OH)_4]^-$: $3NO_3$^− + 8Al + $5OH^-$ + $18H_2O \rightarrow 3NH_3 + 8[Al(OH)_4]^-$, equivalent to the scheme's AlO_2^− equation.

Read: RB U12 §2.4 · p. 175 RB U6 §4.10 · p. 160 RB U6 §4.5 · p. 136 RB U3 §3.8 · p. 115

Question 9 · Part C · essay

(a) [75 marks]

Consider the following industrial processes.
I. Manufacture of bleaching powder
II. Manufacture of calcium carbide
III. Manufacture of urea
IV. Manufacture of sulphuric acid (contact process)

(i) State the starting materials used in each process.

Answer

I. Bleaching powder – $CaCO_3$ (limestone), CaO (quicklime), $Ca(OH)_2$ (slaked lime) and Cl_2 gas
II. Calcium carbide – CaO (quicklime), $CaCO_3$ (limestone) and coke (C)
III. Urea – NH_3 (l or gas) and CO_2 (l or gas)
IV. H_2SO_4 – sulphur (s)/FeS_2 (iron pyrites), air and water
(02 × 9 = 18 marks) · 9(a)(i): 18 marks

(ii) Write balanced chemical equations for the reactions taking place in each process, along with proper conditions wherever necessary.

Answer

I. Bleaching powder

3

2

(03)

2

2

(03)

2

2

(01)

(01)

2

2

2

2

(03)

9(a)(ii)I: 11 marks

II. Calcium carbide

(02)

2

(03)

2

2

3

2

2

9(a)(ii)II: 05 marks

III. Urea

3

2

(01)

(01)

2

4

(03)

(01)

2

2

2

(02)

(01)

2

2

(01)

(The (03) and (02) marks are for the balanced equations.)

9(a)(ii)III: 10 marks

IV. Sulphuric acid

2

2

2

2

2

2

3

(03)

2

2

2

5

(01)

(01)

(01)

3

(03)

3

2

4

2

2

7

(03)

2

2

7

2

2

4

(03)

9(a)(ii)IV: 15 marks · 9(a)(ii): 41 marks

Note: physical states are not required for (a)(i) and (ii).

(iii) State **two** uses for each of the following:
bleaching powder, calcium carbide, urea and sulphuric acid

Answer

Bleaching powder

Calcium carbide

Urea

2

4

4

2

4

(02 + 02) × 4 = 16 marks

Note: marks may be awarded for acceptable uses not included in the scheme with the approval of the Chief Examiner.

9(a)(iii): 16 marks · 9(a): 75 marks

Review.

Principle: raw materials, chemistry and conditions of industrial processes (Resource Book 14 §1.8 contact process; urea via NH_3 from 14 §1.6). For the contact process, remember the V_2O_5 catalyst, ~450 °C and ~1 atm (a compromise between rate and the exothermic equilibrium), and that SO_3 is absorbed in conc. H_2SO_4 (oleum) rather than water, which would form an acid mist. Urea is made from NH_3 and CO_2 through

ammonium carbamate, which is dehydrated. **Syllabus note:** the manufacture of bleaching powder and of calcium carbide is not in the current syllabus/Resource Book, and urea manufacture is only mentioned there as a use of ammonia. **Scheme error:** the third alternative for calcium carbide, $CaCO_3 + 3C \rightarrow 2CaC_2 + CO + CO_2$, is not balanced (1 Ca and 4 C on the left, 2 Ca and 6 C on the right); a balanced version is $CaCO_3(s) + 4C(s) \rightarrow CaC_2(s) + 3CO(g)$. The scheme also accepts it "for this year only".

(b) [75 marks]

The major environmental problems we are facing at present are ozone layer depletion (OLD), global warming (GW) and acid rain (AR). The questions given below are related to the environment and the problems mentioned above.

(i) The carbon and nitrogen cycles are two important chemical cycles that operate in the environment.
I. With regard to the carbon cycle, state **one** main form of carbon that is present in each of the following: atmosphere, plants, water, Earth's crust
II. State briefly how N_2 gas in the atmosphere is removed and replenished in the nitrogen cycle.
III. State **two** ways by which microorganisms participate in the carbon cycle.

Answer

I.
• Atmosphere – CO_2 (02)
• Plants – glucose/starch/cellulose/lignin (02)
• Water – HCO_3^−/CO_3^{2-} (CO_2(aq)) (02)
• Earth's crust – $CaCO_3$/$CaCO_3$·$MgCO_3$/fossil fuels (coal, petroleum)/graphite (02)

II. Ways of removal
• Industrial fixation (Haber process)/internal combustion engines/combustion at high temperatures (02)
• Biological fixation (nitrogen-fixing bacteria) (02)
• Atmospheric fixation (by lightning) (02)
Way of replenishment
• Denitrifying bacteria that convert NO_3^− into N_2 (02)

III. Under aerobic conditions, organic compounds in the soil are decomposed (by microorganisms) to CO_2 (02), while under anaerobic conditions they are converted to CH_4 and CO (02). 9(b)(i): 20 marks

(ii) Identify the **two** main nitrogen containing compounds present in the atmosphere that contribute to acid rain. With the aid of balanced chemical equations show how these compounds make rain water acidic.

Answer

NO, NO_2 (02 + 02)
$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ (02)
$4NO_2(g) + 2H_2O(l) + O_2(g) \rightarrow 4HNO_3(aq)$ (02)
or $2NO_2(g) + H_2O(l) \rightarrow HNO_2(aq) + HNO_3(aq)$
HNO_3 is a strong acid that gives H^+, or ($HNO_3 \rightarrow H^+ + NO_3$^−) (02) · 9(b)(ii): 10 marks

(iii) Identify **two** contributing industrial processes **per** environmental problem stated above (OLD, GW, AR). Identify **one** chemical compound that is liberated to the atmosphere by **each** of these industrial processes.

Answer

Ozone layer depletion

2

3

2

(industry (02), chemical species (01)) × 2

Global warming

4

2

4

2

3

(industry (02), chemical species (01)) × 2

Acid rain

2

2

2

(industry (02), chemical species (01)) × 2 · 9(b)(iii): 18 marks

(iv) Identify the main industrial process that contributes significantly to the addition of nitrogen compounds to water and soil. Comment on the pathways by which these compounds are added to water and soil.

Answer

Haber process (production of NH_3) (04)
NH_3 is converted to fertilizers (01):
I. NH_3 is converted to HNO_3 (03) by the Ostwald process (02). HNO_3 (02) is used to make fertilizers such as KNO_3 (02), NH_4NO_3 (02) and urea (02). These are added to the soil.
or
II. Liquid NH_3 is used directly as a fertilizer (01):
NH_3 (01) —H_2O→ NH_4^+ (02) —nitrifying bacteria (02)→ NO_2^- (03) —nitrifying bacteria (02)→ NO_3^- (03)
9(b)(iv): 18 marks

(v) Inappropriate disposal of solid municipal waste as in the Meethotamulla event contributes significantly to one of the three environmental issues stated above. Identify this environmental issue and state briefly how the disposal of solid municipal waste contributes to it.

Answer

Because the waste is dumped without control or sorting, under anaerobic conditions (02) methane gas (02) is produced in large amounts (between the layers of solid waste) by the activity of bacteria (01). Methane is a greenhouse gas (01); it contributes to **global warming** (03). 9(b)(v): 09 marks · 9(b): 75 marks

Review.

Principle: sources and chemistry of air and water pollutants (Resource Book 14 §1.13 for acid rain, ozone depletion and the greenhouse effect; 14 §1.14 for nitrogen compounds in water; 14 §1.6 for the Haber and Ostwald processes). Acid rain from nitrogen comes from NO formed in high-temperature combustion, oxidised to NO_2 and then to HNO_3; ozone depletion is linked to CFC/HCFC, halons, CH_3Br and NO_x from high-flying aircraft; greenhouse gases include CO_2, CH_4, N_2O and CFCs. Landfills and garbage heaps decompose anaerobically to give CH_4, which the RB names explicitly as a cause of global warming. Common mistakes: giving SO_2 as a nitrogen compound, naming CO_2 as an ozone-depleting gas, and stating a process without the specific compound it releases. **Syllabus note:** the carbon and nitrogen cycles in (i) are not taught as separate topics in the current Resource Book, which covers these ideas only within the pollution sections.

Read: RB U14 §1.8 · p. 27 RB U14 §1.6 · p. 21 RB U14 §1.13 · p. 58 RB U14 §1.14 · p. 80

Question 10 · Part C · essay

(a) [75 marks]

(i) $TiCl_3$ is a violet coloured solid. In water, two hydrated species of $TiCl_3$, **A** and **B** are formed. **A** and **B** are coordination compounds of titanium with an octahedral geometry, containing H_2O and Cl^- as ligands.
A and **B** were separated and their atomic compositions were determined. The compounds were further analysed using the procedures given below.

Analysis of A

When excess $AgNO_3(aq)$ was added to 50.00 cm^3 of a 0.20 mol dm^{-3} solution of **A**, a white precipitate that was soluble in dilute ammonia was obtained. The mass of the precipitate after washing and oven drying (to a constant mass) was 4.305 g.

Analysis of B

When excess $AgNO_3(aq)$ was added to 50.00 cm^3 of a 0.30 mol dm^{-3} solution of **B**, the same white precipitate was obtained as in analysis, **A**. The mass of the precipitate after washing and oven drying (to a constant mass) was also 4.305 g.
(H = 1, O = 16, Cl = 35.5, Ti = 48, Ag = 108)

I. Write the electronic configuration of titanium in **A** and **B**.

Answer

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^1$ or $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1$ (02)
or [Ar] $3d^1\ 4s^0$ (accepted for this year only)
Note: the oxidation state of Ti is the same in A and B.

II. Deduce the structures of **A** and **B**.

Answer

Structure of A

(02)

(02)

(02)

–

(02)

(02)

(02)

(02)

(02)

2

6

3

(07)

Structure of B

(02)

(02)

–

(02)

(02)

–

(02)

(02)

2

5

2

2

5

2

(07)

2

2

III. Give the IUPAC names of **A** and **B**.

Answer

A – hexaaquatitanium(III) chloride (03)
B – pentaaquachloridotitanium(III) chloride (03) · 10(a)(i): 50 marks

(ii) **X**, **Y** and **Z** are coordination compounds of the metal ion M(II). They have a square planar geometry. **X** is a neutral compound. On addition of $BaCl_2$(aq) to an aqueous solution of **Y**, a white precipitate that is insoluble in dilute acids is obtained. **Z** gives three ions in aqueous solution.
Write the structural formulae of **X**, **Y** and **Z** selecting the appropriate species from the list given below.
K^+, NH_3, CN^-, SO_4^{2-}

Answer

X

2

3

2

3

2

2

(08)

Y

3

4

4

(08)

Z

2

4

+

4

2−

3

4

2

3

3

2

4

3

3

2

4

3

3

4

3

3

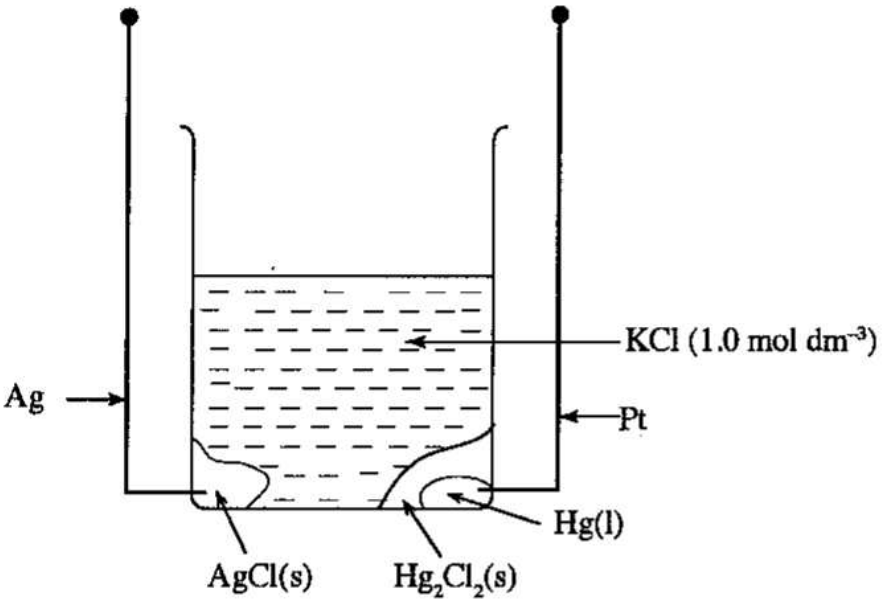
4

(09) · 10(a)(ii): 25 marks · 10(a): 75 marks

Review.

Principle: counting ionisable (outer-sphere) chloride by precipitation as AgCl to fix the formula of a complex, and matching charges and coordination number (Resource Book 6 §4.10, §4.10.6). n(AgCl) = 4.305/143.5 = 0.0300 mol in both cases; per mole of complex this is 0.0300/0.010 = 3 for A and 0.0300/0.015 = 2 for B, so A = $[Ti(H_2O)_6]Cl_3$ and B = $[TiCl(H_2O)_5]Cl_2$ (hydration isomers). Ti^{3+} is $3d^1$, which explains the colour. In (ii), the neutral complex needs two CN^- with two NH_3; Y needs SO_4^{2-} outside the sphere ($BaSO_4$ is insoluble in acids), so the cation is $[M(NH_3)_4]^{2+}$; Z must give three ions, e.g. $K_2[M(CN)_4] \rightarrow 2K^+ + [M(CN)_4]^{2-}$. Common mistakes: writing the configuration of the Ti atom ($3d^2\ 4s^2$) instead of Ti^{3+}, putting all chlorides inside the coordination sphere, and ignoring the ligand order (alphabetical: aqua before chlorido) in IUPAC names. Note: the scheme's printed configurations read "$1s^2\ 2s^2\ sp^6$…", an obvious misprint for $2p^6$ (corrected above).

(b) [75 marks]



The electrochemical cell

An electrochemical cell is made as shown in the diagram above.
The following data are provided.
Ag(s), AgCl(s) | Cl^-(aq) E° = 0.22 V
Hg(l) | Hg_2Cl_2(s) | Cl^-(aq) E° = 0.27 V

(i) Write the reduction half reaction of the above cell.

Answer

Reduction half reaction:
$Hg_2Cl_2(s) + 2e \rightarrow 2Hg(l) + 2Cl^-(aq)$ (05)

(ii) Write the oxidation half reaction of the above cell.

Answer

Oxidation half reaction:
$Ag(s) + Cl^-(aq) \rightarrow AgCl(s) + e$ (05)

(iii) Construct the cell reaction.

Answer

Cell reaction:
$Hg_2Cl_2(s) + 2Ag(s) \rightarrow 2AgCl(s) + 2Hg(l)$ (10)

(iv) Using the E° values given, calculate the electromotive force of the cell.

Answer

emf of the cell:
$E_{cell} = E°_{Hg/Hg2Cl2} - E°_{Ag/AgCl} = 0.27\ V - 0.22\ V$ (04 + 01) = **0.05 V** (04 + 01)

(v) Give the standard cell notation of the above electrochemical cell.

Answer

Cell notation:
$Ag(s) \mid AgCl(s) \mid Cl^{-}(aq, 1.0 \text{ mol dm}^{-3}) \mid Hg_2Cl_2(s) \mid Hg(l), Pt$ or
$Ag(s), AgCl(s) \mid Cl^{-}(aq, 1.0 \text{ mol dm}^{-3}) \mid Hg_2Cl_2(s), Hg(l)\ Pt$ (10)
Notes: do not deduct marks if Pt is written. Physical states must be written for parts (i) to (v).

(vi) Does the electromotive force of the above electrochemical cell depend on the chloride ion concentration? Give reason/s for your answer.

Answer

The emf of the cell does not depend on the chloride ion concentration. The chloride ion concentration does not appear in the cell reaction. (05 + 05)

(vii) Calculate the change in the mass of Ag(s) + AgCl(s), when a current of 0.10 A was drawn for a period of 60 minutes from the cell.

Answer

A current of 0.10 A was drawn for 60 minutes.
Amount of charge passed through the cell = $0.10 \text{ A} \times 60 \text{ min} \times 60 \text{ s min}^{-1} = 360 \text{ C}$ (04 + 01)
The electrode reaction at the negative electrode is $Ag(s) + Cl^{-}(aq) \rightarrow AgCl(s)$.
For each electron passing through the cell, one Ag atom combines with a Cl^{-} to form AgCl(s); so the mass increases by the mass of chloride taken up:
$= 35.5 \text{ g mol}^{-1} \times 360 \text{ C}/96500 \text{ C mol}^{-1}$ (04 + 01) = **0.132 g** (increase) (04 + 01)

(viii) What would be the chloride ion concentration in the solution after drawing the current in (vii) above? (Faraday constant, F = 96,500 C mol^{-1}, Cl = 35.5, Ag = 108)

Answer

The chloride ion concentration does not change, i.e. chloride ion concentration = **1.0 mol dm^{-3}**. (10) · 10(b): 75 marks

Review.

Principle: a cell built from two electrodes of the second kind sharing one KCl electrolyte (Resource Book 13 §3.2, §3.3; Faraday's laws 13 §3.4). The electrode with the higher reduction potential (calomel, 0.27 V) is the cathode; the Ag/AgCl electrode is the anode, so $E_{cell} = 0.27 - 0.22 = 0.05$ V. Adding the half reactions (Ag half ×2) the $2Cl^{-}$ released at the cathode exactly cancels the $2Cl^{-}$ consumed at the anode, so Cl^{-} does not appear in the overall reaction: the emf is independent of $[Cl^{-}]$ and $[Cl^{-}]$ stays at 1.0 mol dm^{-3}. In (vii), n(e) = $360/96500 = 3.73 \times 10^{-3}$ mol; each electron converts one Ag into AgCl, so the Ag + AgCl electrode gains $3.73 \times 10^{-3} \times 35.5 = 0.132$ g. Common mistakes: reversing anode/cathode, using 108 (Ag) instead of 35.5 for the mass change, forgetting to convert minutes to seconds, and thinking $[Cl^{-}]$ falls because AgCl forms.

Read: RB U6 §4.10.6 · p. 169 RB U6 §4.10 · p. 160 RB U13 §3.3 · p. 250 RB U13 §3.4 · p. 261

2016 · Chemistry Digital Paper

50 questions · 2 hours

MCQ · Paper I

Question 1 · Q1–30 · single answer

Green light of wave length 4.42×10^{-7} m is observed in the emission spectrum of hydrogen. The energy of one photon of this green light is

- (1)4.5×10^{-19} kJ
- (2)2×10^{-19} kJ
- (3)1.5×10^{-19} kJ
- (4)4.5×10^{-22} kJ
- (5)19.9×10^{-26} kJ

Answer and review

Answer **(4)** Official Evaluation Report

$E = hc/\lambda = (6.626 \times 10^{-34}\ \text{J s})(3 \times 10^{8}\ \text{m s}^{-1})/(4.42 \times 10^{-7}\ \text{m}) = 4.5 \times 10^{-19}\ \text{J} = 4.5 \times 10^{-22}$ kJ. The trap is the unit: the options are in kJ, and 42% of candidates chose (1), which is the value in J (correct answer chosen by 43%).

RB U1 §1.2 · p. 13

Question 2 · Q1–30 · single answer

Which one of the following atoms in its gaseous state will liberate the largest amount of energy when it gains an electron?

- (1)S
- (2)P
- (3)Na
- (4)Mg
- (5)Ne

Answer and review

Answer **(1)** Official Evaluation Report

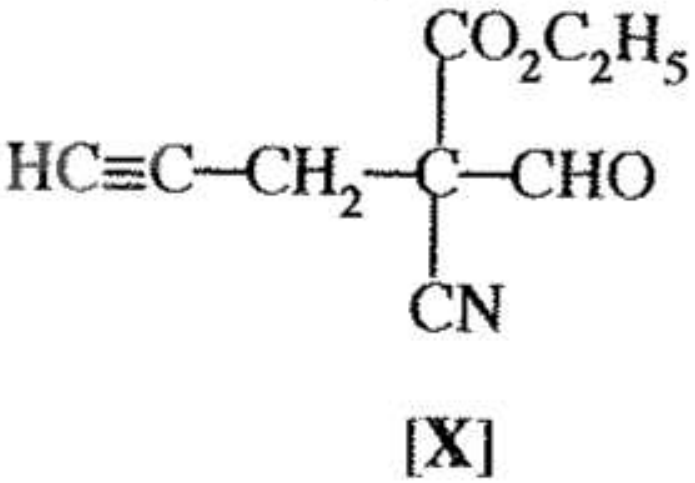
Energy released on gaining an electron (electron gain enthalpy) is largest for the most electronegative atom that ends up with a more stable configuration. S (about −200 kJ mol^{-1}) is far more exothermic than P (about −72, half-filled 3p, so a weaker tendency), Na (about −53), while Mg (full 3s) and Ne (full shell) do not release energy (the electron must go into a higher level). The Evaluation Report records only 20% correct, with 29% choosing Na and 33% choosing Ne.

RB U1 §1.6 · p. 32

Question 3 · Q1–30 · single answer

What is the IUPAC name of the compound X?

: name of the compound **X**?



[X]

- (1)ethyl 2-formyl-2-nitrile-4-pentynoate
- (2)2-cyano-2-ethoxycarbonyl-4-pentynal
- (3)2-ethoxycarbonyl-2-nitrile-4-pentynal
- (4)ethyl-2-cyano-2-formyl-4-pentynoate
- (5)ethyl 2-cyano-2-formyl-4-pentynoate

Answer and review

Answer **(5)** Official Evaluation Report

The ester is the principal group (priority ester > nitrile > aldehyde), so the name is an alkyl alkanoate: ethyl ...pent-4-ynoate, with the CHO and CN prefixes written as formyl and cyano in alphabetical order (cyano before formyl) and the nitrile never called "nitrile" as a prefix. Option (4) has the right parts but an incorrect hyphen after "ethyl".

RB U7 §1.3 · p. 7

Question 4 · Q1–30 · single answer

Which of the following statements regarding sizes of ions formed by s and p block elements is **false**?

- (1)Cations are always smaller than their neutral atoms.
- (2)Anions are always larger than their neutral atoms.
- (3)The size of cations decreases from left to right across a period.
- (4)The size of anions increases from left to right across a period.
- (5)The size of anions formed by elements of second period are larger than cations formed by elements of third period.

Answer and review

Answer **(4)** Official Evaluation Report

Anions of a period become smaller from left to right (e.g. $P^{3-} > S^{2-} > Cl^{-}$) because the nuclear charge rises while the electrons are added to the same shell. The other statements are true: cations lose a shell or gain nuclear pull, anions gain electron repulsion, cations such as Na^{+}, Mg^{2+}, Al^{3+} shrink across the period, and N^{3-}–F^{-} (second period) are larger than Na^{+}–Al^{3+}. The Evaluation Report data show 43% chose (4) and 40% chose (5).

RB U1 §1.6 · p. 32

Question 5 · Q1–30 · single answer

The sets of quantum numbers associated with the last two electrons of an atom in an element are (3, 0, 0, +½) and (3, 0, 0, − ½). The element is

- (1)Li
- (2)Na
- (3)Mg
- (4)Al
- (5)K

Answer and review

Answer **(3)** Official Evaluation Report

The last two electrons are in the 3s orbital (n = 3, l = 0, m_l = 0) with opposite spins, so the configuration ends $3s^2$: $1s^2\ 2s^2\ 2p^6\ 3s^2$ = Mg (Z = 12). Na would have only one electron ($3s^1$) in this orbital. 56% answered correctly.

RB U1 §1.3 · p. 17 RB U1 §1.4 · p. 23

Question 6 · Q1–30 · single answer

A 0.60 g sample of KIO_3 was dissolved in water and excess KI was added to it. The minimum amount of 3.0 mol dm^{-3} HCl required to completely convert KIO_3 to I_3^− is, (O = 16, K = 39, I = 127)

- (1)1.0 cm^3
- (2)4.7 cm^3
- (3)5.6 cm^3
- (4)10.2 cm^3
- (5)33.6 cm^3

Answer and review

Answer **(3)** Official Evaluation Report

$M(KIO_3)$ = 214 g mol^{-1}, so n = 0.60/214 = 2.8×10^{-3} mol. IO_3^− + $8I^{-}$ + $6H^{+}$ → $3I_3$^− + $3H_2O$ needs 6 mol H^{+} per mol IO_3^−: $n(H^{+}) = 1.68 \times 10^{-2}$ mol, V = $1.68 \times 10^{-2}/3.0 = 5.6 \times 10^{-3}$ dm^3 = 5.6 cm^3. Using the I_2 equation ($5I^{-}$ + IO_3^− + $6H^{+}$ → $3I_2$) gives the same 6 H^{+}; the 4.7 cm^3 distractor (21% chose it) comes from using 5 H^{+}. 43% answered correctly.

RB U3 §3.8 · p. 115 RB U3 §3.4 · p. 99

Question 7 · Q1–30 · single answer

At 25 °C, the solubility product, K_{sp} of MnS(s) is 5.0×10^{-15} mol^2 dm^{-6}. The acid dissociation constants K_1 and K_2 for H_2S(aq) are 1.0×10^{-7} mol dm^{-3} and 1.0×10^{-13} mol dm^{-3} respectively. The equilibrium constant, K_c for the reaction, MnS(s) + $2H^+$(aq) ⇌ Mn^{2+}(aq) + H_2S(aq) is

- (1)2.0×10^{-16}
- (2)5.0×10^{-8}
- (3)20
- (4)5.0×10^{5}
- (5)2.0×10^{7}

Answer and review

Answer **(4)** Official Evaluation Report

The reaction is the sum of MnS ⇌ Mn^{2+} + S^{2-} (K_{sp}) and S^{2-} + $2H^+$ ⇌ H_2S ($1/(K_1K_2)$). $K_c = K_{sp}/(K_1K_2) = 5.0 \times 10^{-15}/(1.0 \times 10^{-7} \times 1.0 \times 10^{-13}) = 5.0 \times 10^{5}$. Forgetting to invert K_1K_2 gives the wrong answers. 53% answered correctly.

RB U12 §2.4 · p. 175 RB U12 §2.2 · p. 118

Question 8 · Q1–30 · single answer

An organic compound A contains 39.97% of C, 6.73% of H and 53.30% of O, by weight. What is the empirical formula of A? (H = 1, C = 12, O = 16)

- (1)$C_6H_8O_2$
- (2)$C_2H_4O_2$
- (3)$C_3H_7O_3$
- (4)$C_3H_6O_3$
- (5)CH_2O

Answer and review

Answer **(5)** Official Evaluation Report

Moles per 100 g: C 39.97/12 = 3.33; H 6.73/1 = 6.73; O 53.30/16 = 3.33. The ratio C : H : O = 1 : 2 : 1, so the empirical formula is CH_2O. Options (2) and (4) are molecular formulae that are multiples of it ($C_2H_4O_2$, $C_3H_6O_3$). 72% answered correctly, the highest facility among the general chemistry questions.

RB U3 §3.4 · p. 99

Question 9 · Q1–30 · single answer

Which of the following statements is **false** with regard to the chemistry of Lithium (Li) and its compounds?

- (1)Lithium reacts with oxygen gas to give Li_2O.
- (2)Lithium has the highest melting point among the group I metals.
- (3)The basicity of LiOH is less than that of NaOH.
- (4)Li_2CO_3 has the lowest thermal stability among the group I carbonates.
- (5)LiCl gives a blue colour when subjected to the flame test.

Answer and review

Answer **(5)** Official Evaluation Report

Lithium salts give a crimson (red) flame, not blue. The other statements are true: Li forms the normal oxide Li_2O, has the highest melting point of group 1 (strongest metallic bonding), LiOH is the weakest base of the group and Li_2CO_3 (small, highly polarising Li^+) is the only carbonate that decomposes easily on heating. 73% answered correctly.

RB U6 §4.1 · p. 122

Question 10 · Q1–30 · single answer

The oxidation states of N^① and N^② in the most stable Lewis structure of the F_2NNO molecule respectively are (skeleton, F–N^①(–F)–N^②–O, in which N^① is bonded to two F atoms, to N^② and has no bond to O)

- (1)+2 and +2
- (2)+1 and +3
- (3)+2 and +3
- (4)+1 and +2
- (5)+3 and +1

Answer and review

Answer **(1)** Official Evaluation Report

In the most stable structure (octets, formal charges zero) N^① makes single bonds to 2 F and to N^② and carries a lone pair; N^② is doubly bonded to O and singly to N^①, with one lone pair. N^① : two bonds to the more electronegative F give +2, the N–N bond counts 0, so +2. N^② : the N=O bond gives +2, the N–N bond 0, so +2. 70% answered correctly.

RB U3 §3.1 · p. 88 RB U2 §2.1 · p. 44

Question 11 · Q1–30 · single answer

Consider the reaction, $CH_4(g) + CO_2(g) \rightleftharpoons 2CO(g) + 2H_2(g)$. When 0.60 mol of $CH_4(g)$ and 1.00 mol of $CO_2(g)$ were introduced into a closed rigid container of volume 1.00 dm^3 at 25 °C and the system was allowed to reach equilibrium, 0.40 mol of CO(g) was formed. The value of the equilibrium constant, K_c ($mol^2\ dm^{-6}$) for the reaction is

- (1)0.04
- (2)0.08
- (3)0.67
- (4)1.20
- (5)8.00

Answer and review

Answer **(2)** Official Evaluation Report

0.40 mol CO means 0.20 mol CH_4 and 0.20 mol CO_2 reacted and 0.40 mol H_2 formed. At equilibrium (V = 1.00 dm^3): $[CH_4] = 0.40$, $[CO_2] = 0.80$, $[CO] = 0.40$, $[H_2] = 0.40$ mol dm^{-3}. $K_c = (0.40)^2(0.40)^2/(0.40 \times 0.80) = 0.0256/0.32 = 0.08$ $mol^2\ dm^{-6}$. 61% answered correctly.

RB U12 §2.1 · p. 76

Question 12 · Q1–30 · single answer

The chemical formula of diamminebromidodicarbonylhydridocobalt(III) chloride according to IUPAC rules is

- (1)$[Co(CO)_2BrH(NH_3)_2]Cl$
- (2)$[CoBr(CO)_2(NH_3)_2H]Cl$
- (3)$[Co(NH_3)_2Br(CO)_2H]Cl$
- (4)$[CoBr(CO)_2H(NH_3)_2]Cl$
- (5)$[CoHBr(CO)_2(NH_3)_2]Cl$

Answer and review

Answer **(4)** Official Evaluation Report

In the formula the metal symbol is written first and the ligands follow in alphabetical order of their donor (valence) atom: Br, C (CO), H, N (NH_3), giving $[CoBr(CO)_2H(NH_3)_2]Cl$. Charge check: Co(III) + Br^- + H^- = +1, so the complex cation is balanced by Cl^-. The Evaluation Report notes only 26% answered correctly and attributes this to not knowing the ordering rule (the name uses alphabetical order of ligand names, the formula uses donor atoms).

RB U6 §4.10.6 · p. 169 RB U3 §3.2 · p. 93

Question 13 · Q1–30 · single answer

The following procedure was used to determine the sulphur content in a coal sample. A coal sample of mass 1.60 g was burned in oxygen gas. The SO_2 gas formed was collected in a solution of H_2O_2. This solution was then titrated with 0.10 mol dm^{-3} NaOH. The volume of NaOH required to reach the end point was 20.0 cm^3. The percentage of sulphur in the coal sample is (S = 32)

- (1)1.0
- (2)2.0
- (3)4.0
- (4)6.0
- (5)8.0

Answer and review

Answer **(2)** Official Evaluation Report

S → SO_2; SO_2 + H_2O_2 → H_2SO_4, a dibasic acid that needs 2 NaOH. n(NaOH) = 0.10 × 0.0200 = 2.0 × 10^{-3} mol, so n(H_2SO_4) = n(S) = 1.0 × 10^{-3} mol = 0.032 g; % S = 0.032/1.60 × 100 = 2.0%. Treating H_2SO_4 as monobasic gives 4.0% (option 3, chosen by 29%). 40% answered correctly.

RB U3 §3.8 · p. 115 RB U6 §4.6 · p. 141

Question 14 · Q1–30 · single answer

Combustion of ethylene, $C_2H_4(g)$ is shown in the following reaction. $C_2H_4(g)$ + $3O_2(g)$ → $2CO_2(g)$ + $2H_2O(g)$ ΔH = − 1323 kJ mol^{-1}. What is the value of ΔH (in kJ mol^{-1}) if the combustion produces water in the liquid state, $H_2O(l)$ rather than water in the gaseous state, $H_2O(g)$? (ΔH for $H_2O(g)$ → $H_2O(l)$ is − 44 kJ mol^{-1})

- (1)−1235

- (2)−1279
- (3)−1323
- (4)−1367
- (5)−1411

Answer and review

Answer **(5)** Official Evaluation Report

The reaction forms 2 mol of water, so 2 × (−44) = −88 kJ must be added by Hess's law: −1323 − 88 = −1411 kJ mol^{-1}. Using only one condensation (−1367, chosen by 26%) or adding +88 (−1235) are the typical slips. Only 39% answered correctly.

RB U5 §2.2 · p. 36

Question 15 · Q1–30 · single answer

The vapour pressure of benzene at 25 °C is 12.5 kPa. When an unknown non-volatile substance was dissolved in 100 cm^3 of benzene at this temperature, the vapour pressure of the solution was found to be 11.25 kPa. The mole fraction of the unknown substance in the above solution is

- (1)0.05
- (2)0.10
- (3)0.50
- (4)0.90
- (5)0.95

Answer and review

Answer **(2)** Official Evaluation Report

Raoult's law: $(P° - P)/P° = x_{solute}$. (12.5 − 11.25)/12.5 = 0.10. The ratio P/P° = 0.90 is the mole fraction of the benzene, not of the solute (option 4, chosen by 20%). 48% answered correctly.

RB U12 §2.6 · p. 216

Question 16 · Q1–30 · single answer

A buffer solution can be prepared by mixing a weak acid (K_a = 4.0 × 10^{-7} mol dm^{-3}) and a strong base. The ratio of the concentrations of acid to base (acid : base) needed to prepare a buffer solution at pH = 6 is

- (1)1 : 1
- (2)2 : 1
- (3)2 : 5
- (4)5 : 1
- (5)5 : 2

Answer and review

Answer **(All)** Official Evaluation Report

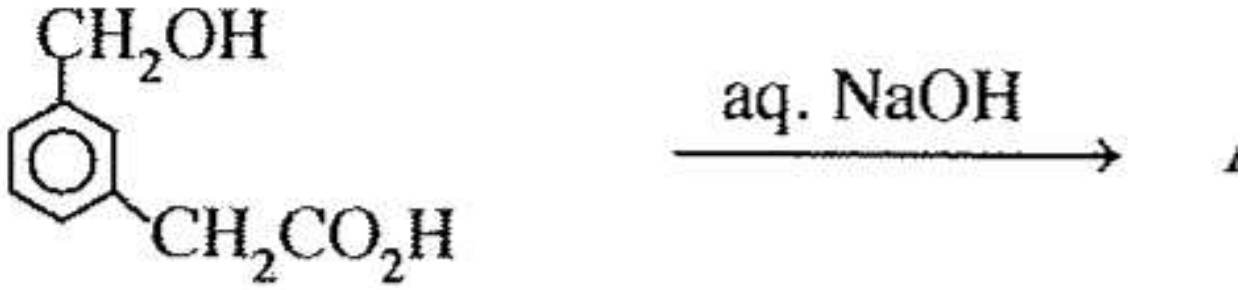
The official key is "All": all five options were accepted. At pH 6, $[H^+]$ = 1.0 × 10^{-6}, so $[A^-]/[HA] = K_a/[H^+]$ = 0.40. The strong base converts part of the acid to salt, so with x mol acid and y mol base, y/(x − y) = 0.40,

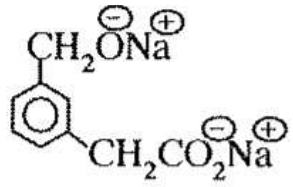
giving x : y = 3.5 : 1 = 7 : 2. None of the five options equals this ratio, so the question has no correct option as printed and every response was credited (answers were spread over all five options, 11–27%).

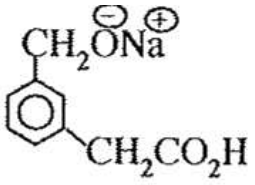
RB U12 §2.3 · p. 167

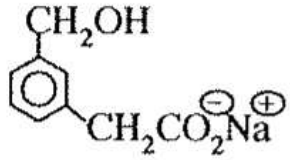
Question 17 · Q1–30 · single answer

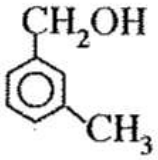
The major product A obtained from the reaction given above is

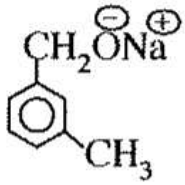


(1) 

(2) 

(3) 

(4) 

(5) 

Answer and review

Answer **(3)** Official Evaluation Report

Aqueous NaOH deprotonates only the acidic –CO_2H (pK_a about 4.5) to give the sodium carboxylate. The benzylic –CH_2OH is an alcohol (pK_a about 16), much less acidic than water, so it is not converted to the alkoxide, and the CH_2 groups are not changed. Option (3) is correct; 49% answered correctly, and 23% chose (1), the double sodium salt.

RB U9 §3.3 · p. 59 RB U9 §3.5 · p. 66

Question 18 · Q1–30 · single answer

The rate law for the reaction $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ is, Rate = $k[NO_2]^2$. If a small amount of CO(g) is introduced to a closed rigid container in which this reaction is taking place at a given temperature, which of the following statements is **true** regarding the changes that would take place?

- (1)Both k and reaction rate increase.

- (2)Both k and reaction rate remain unchanged.
- (3)Both k and reaction rate decrease.
- (4)k increases and reaction rate remains unchanged.
- (5)k remains unchanged and reaction rate increases.

Answer and review

Answer **(2)** Official Evaluation Report

The rate constant depends only on temperature (and catalyst), so k is unchanged. The rate law is zero order in CO, so adding CO does not change the rate. Option (5) (31% chose it) wrongly assumes more reactant always raises the rate. 45% answered correctly.

RB U11 §1.6 · p. 16

Question 19 · Q1–30 · single answer

At 25 °C, given that, $M(s) + 3Ag^{+}(aq) \rightarrow 3Ag(s) + M^{3+}(aq)$ $E°_{cell} = 2.46$ V and $Ag^{+}(aq) + e \rightarrow Ag(s)$ $E° = 0.80$ V. The standard reduction potential for the half-reaction, $M^{3+}(aq) + 3e \rightarrow M(s)$ at 25 °C is

- (1)−1.66 V
- (2)−0.06 V
- (3)0.06 V
- (4)1.66 V
- (5)3.26 V

Answer and review

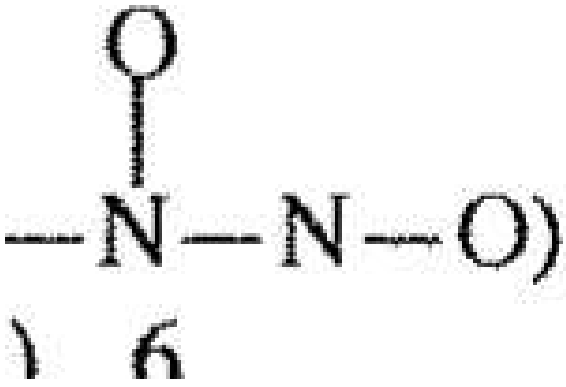
Answer **(1)** Official Evaluation Report

Silver is reduced (cathode) and M is oxidised (anode), so $E°_{cell} = E°_{cathode} - E°_{anode} = 0.80 - E°(M^{3+}/M) = 2.46$, giving $E°(M^{3+}/M) = -1.66$ V. The potential of Ag^{+}/Ag is intensive and is NOT multiplied by 3. The Evaluation Report notes 35% answered correctly, 26% chose +1.66 V (cathode and anode confused) and recommends practice in identifying anodes and cathodes.

RB U13 §3.3 · p. 250 RB U13 §3.2 · p. 238

Question 20 · Q1–30 · single answer

How many resonance structures can be drawn for the molecule N_2O_3? (skeleton as shown)



- (1)2

- (2)3
- (3)4
- (4)5
- (5)6

Answer and review

Answer **(3)** Official Evaluation Report

The official key is option (3), 4 resonance structures. The Evaluation Report notes that facility was only 32% (26% chose 3, 21% chose 5) and recommends drawing resonance structures systematically from the Lewis rules: fix the skeleton, give every atom an octet, place formal charges, then move multiple bonds and charges to generate each distinct contributor.

RB U2 §2.3 · p. 52

Question 21 · Q1–30 · single answer

Which of the following statements is **true** with regard to transition metals and their compounds?

- (1)The electronic configuration of copper is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$.
- (2)All elements that have d-electrons are 'transition elements'.
- (3)The electronic configuration of Ti in TiO_2 is the same as that of Sc in $ScCl_3$.
- (4)Acidity of the oxides of a given transition metal decreases with increase in oxidation state of the metal ion.
- (5)Transition metals in the 3d series can have the quantum number $m_l = \pm 3$.

Answer and review

Answer **(3)** Official Evaluation Report

Ti in TiO_2 is Ti(IV) and Sc in $ScCl_3$ is Sc(III); both are [Ar]. (1) omits the 4s electron: Cu is [Ar] $3d^{10}\ 4s^1$. (2) is false because Zn (d^{10}) is not a transition element. (4) is reversed: acidity increases with oxidation state (e.g. MnO is basic, Mn_2O_7 is acidic). (5) is false because d-orbitals have $m_l = -2$ to $+2$ only. 51% answered correctly.

RB U6 §4.10 · p. 160 RB U1 §1.4 · p. 23

Question 22 · Q1–30 · single answer

The equilibrium $PCl_3(g) + 3NH_3(g) \rightleftharpoons P(NH_2)_3(g) + 3HCl(g)$ exists in a closed container at a constant temperature. If the volume of the container is increased by keeping the temperature constant, which of the following is **true** regarding the changes that could take place in the rates of forward and reverse reactions?

- (1)Forward reaction: increases; reverse reaction: decreases
- (2)Forward reaction: decreases; reverse reaction: increases
- (3)Forward reaction: decreases; reverse reaction: decreases
- (4)Forward reaction: increases; reverse reaction: increases
- (5)Forward reaction: no change; reverse reaction: no change

Answer and review

Answer **(3)** Official Evaluation Report

Increasing the volume at constant T lowers every concentration, so collisions per unit time fall and both rates decrease at once. The Evaluation Report notes the lowest facility of the paper (13%): 60% chose (5), probably because the moles of gas are equal on both sides (4 mol each), so the position of equilibrium does not shift, but the rates still fall.

RB U11 §1.5 · p. 15 RB U12 §2.1 · p. 76

Question 23 · Q1–30 · single answer

When solid ammonium chloride, $NH_4Cl(s)$ is dissolved in water at 25 °C, the temperature of the solution decreases. Which of the following is **true** of ΔH° and ΔS° for the process?

- (1)ΔH° positive, ΔS° positive
- (2)ΔH° positive, ΔS° negative
- (3)ΔH° positive, ΔS° zero
- (4)ΔH° negative, ΔS° positive
- (5)ΔH° negative, ΔS° negative

Answer and review

Answer **(1)** Official Evaluation Report

The solution cools because the process absorbs heat from the surroundings: ΔH° is positive (endothermic). It occurs spontaneously only because the entropy rises as the ordered crystal becomes freely moving hydrated ions, so ΔS° is positive and TΔS° outweighs ΔH° (ΔG° < 0). Only 40% answered correctly.

RB U5 §2.4 · p. 53

Question 24 · Q1–30 · single answer

Which of the following statements is **false** regarding 3d transition metals and their compounds?

- (1)Oxides of some metals are amphoteric.
- (2)Some metals and metal oxides are used in industry as catalysts.
- (3)Electronegativity of 3d transition metals is higher than 4s metals.
- (4)Only one element shows the oxidation state of +7.
- (5)Oxoions such as MnO_4^−, $Cr_2O_7^{2-}$ are resistant to reduction.

Answer and review

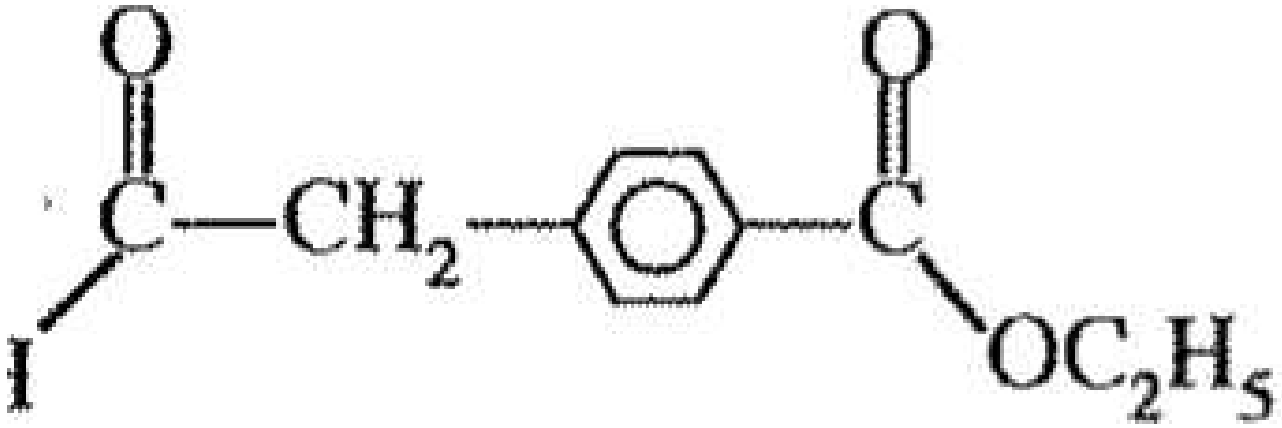
Answer **(5)** Official Evaluation Report

MnO_4^− and $Cr_2O_7^{2-}$ are strong oxidising agents that are readily reduced (to Mn^{2+} and Cr^{3+}), so (5) is false. The others are true: ZnO and Cr_2O_3 are amphoteric; Fe, V_2O_5, MnO_2 and Ni are catalysts; 3d metals are more electronegative than the s-block metals; only Mn reaches +7. 60% answered correctly.

RB U6 §4.10 · p. 160

Question 25 · Q1–30 · single answer

The major product obtained, when the compound shown below is reacted with excess CH_3MgBr, and then hydrolyzed is



IS

(1) $HOCH_2CH_2$–C6H4–C(OH)(CH_3)(CH_3)

(2) CH_3–CH(OH)–CH_2–C6H4–C(=O)–CH_3

(3) $HOCH_2CH_2$–C6H4–C(=O)–CH_3

(4) CH_3–CH(OH)–CH_2–C6H4–C(=O)–OC_2H_5

(5) CH_3–CH(OH)–CH_2–C6H4–C(OH)(CH_3)(CH_3)

Answer and review

Answer **(5)** Official Evaluation Report

The compound is a para-disubstituted benzene bearing –CH_2CHO and –$CO_2C_2H_5$. Excess Grignard reagent attacks both carbonyl groups: the aldehyde gives a secondary alcohol, $CH_3CH(OH)CH_2$–, and the ester adds two CH_3 groups (the ketone formed first reacts again, with loss of $C_2H_5O^-$) to give a tertiary alcohol, –$C(OH)(CH_3)_2$. This is option (5). 54% answered correctly.

RB U8 §2.7 · p. 50 RB U9 §3.6 · p. 70 RB U9 §3.4 · p. 60

Question 26 · Q1–30 · single answer

In the reaction scheme below, the structures of X and Y respectively are
$CH_3COCH_2CONH_2$ —((1) $LiAlH_4$, (2) H^+/H_2O)→ X —(CH_3COCH_3)→ Y

- (1)X = $CH_3CH(OH)CH_2CONH_2$; Y = $CH_3CH(OH)CH_2CON{=}C(CH_3)_2$
- (2)X = $CH_3CH(OH)CH_2CH_2NH_2$; Y = $CH_3CH(OH)CH_2CH_2N{=}C(CH_3)_2$
- (3)X = $CH_3COCH_2CH_2NH_2$; Y = $CH_3COCH_2CH_2N{=}C(CH_3)_2$
- (4)X = $CH_3COCH_2CH_2NH_2$; Y = $CH_3COCH_2CH_2NHCOCH_3$
- (5)X = $CH_3CH(OH)CH_2CH_2NH_2$; Y = $CH_3CH(OH)CH_2CH_2NHCOCH_3$

Answer and review

Answer **(2)** Official Evaluation Report

$LiAlH_4$ reduces both the ketone (to a secondary alcohol) and the amide (C=O to CH_2, giving the primary amine), so X = $CH_3CH(OH)CH_2CH_2NH_2$. A primary amine condenses with a ketone (acetone) to give an imine (Schiff base), >C=N–, with loss of water. An amide (options 1) is not formed, and an N-acetyl amide (options 4 and 5) would need an acyl derivative, not acetone. 67% answered correctly.

RB U9 §3.6 · p. 70 RB U9 §3.4 · p. 60 RB U10 §4.1 · p. 75

Question 27 · Q1–30 · single answer

Which of the following statements is **false** with regard to NH_3?

- (1)NH_3 can act only as a base.
- (2)NH_3 burns in oxygen to give N_2 gas.
- (3)NH_3 gives a brown colour with Nessler's reagent.
- (4)NH_3 reacts with Li to give Li_3N and H_2 gas.
- (5)NH_3 has a bond angle less than 109° 28′ but greater than that in NF_3.

Answer and review

Answer **(1)** Official Evaluation Report

NH_3 is a weak base (lone pair) but it can also act as an acid (it loses H^+ to give NH_2^−, e.g. with Li to give Li_3N + H_2, statement 4), so "only a base" is false. NH_3 burns in O_2 to N_2 and H_2O, the lone pair repels the bonds so the angle is about 107° (less than 109.5°) and larger than in NF_3 (about 102°) because the electronegative F atoms draw the bonding pairs away from N. Nessler's reagent test for NH_3/NH_4^+ (brown colour or precipitate) is not in the current Resource Book. 56% answered correctly.

RB U6 §4.5 · p. 136

Question 28 · Q1–30 · single answer

An electrochemical cell was constructed using Zn^{2+}(aq)/Zn(s) and Sn^{2+}(aq)/Sn(s) electrodes. Which of the following statements correctly describes the operation of the cell? $E°_{Zn^{2+}(aq)/Zn(s)}$ = −0.76 V, $E°_{Sn^{2+}(aq)/Sn(s)}$ = −0.14 V

- (1)Zn electrode is the cathode, Zn is oxidized, electrons flow from Sn to Zn.
- (2)Zn electrode is the cathode, Sn is oxidized, electrons flow from Sn to Zn.
- (3)Sn electrode is the anode, Zn^{2+}(aq) is reduced, electrons flow from Zn to Sn.
- (4)Zn electrode is the anode, Zn is oxidized, electrons flow from Zn to Sn.
- (5)Zn electrode is the anode, Sn^{2+}(aq) is reduced, electrons flow from Sn to Zn.

Answer and review

Answer **(4)** Official Evaluation Report

The couple with the more negative E° (Zn^{2+}/Zn, −0.76 V) is the stronger reductant, so Zn is oxidised at the anode and releases electrons; they flow through the external circuit to the Sn electrode (cathode), where Sn^{2+} is reduced. $E°_{cell}$ = −0.14 − (−0.76) = +0.62 V. Options (1), (2), (3), (5) each contain a contradiction (anode/cathode, oxidised/reduced or electron-flow direction). 64% answered correctly; this was the highest facility among the physical chemistry questions.

RB U13 §3.3 · p. 250

Question 29 · Q1–30 · single answer

Which one of the following statements about $C_6H_5NH_2$ is **false**?

- (1)Reacts with CH_3COCl to form an amide.
- (2)Evolves ammonia when heated with aqueous NaOH.
- (3)Reacts with bromine water to give a white precipitate.
- (4)Gives a phenol when reacted with nitrous acid.
- (5)Less basic than $C_6H_5CH_2NH_2$.

Answer and review

Answer **(2)** Official Evaluation Report

Aniline is a primary aromatic amine: it is acylated by CH_3COCl to N-phenylethanamide, brominated by bromine water to 2,4,6-tribromoaniline (white precipitate), diazotised by HNO_2 (the diazonium salt gives phenol on warming) and is less basic than benzylamine because its lone pair is delocalised into the ring. The C–N bond in aniline is not hydrolysed by hot aqueous NaOH, so no NH_3 is evolved (an amide would do this). The Evaluation Report lists 29 among the questions below 40% facility (37% correct, answers widely spread).

RB U10 §4.1 · p. 75 RB U10 §4.2 · p. 77 RB U10 §4.3 · p. 78

Question 30 · Q1–30 · single answer

Four saturated solutions of silver acetate in contact with $CH_3COOAg(s)$ are placed in four beakers. How does the solubility of silver acetate change, when the following solutions are added separately to each of the beakers? CH_3COONa, dil. HNO_3, NH_4OH, $AgNO_3$. The changes in solubility for the four additions respectively are

- (1)increases, increases, increases, increases
- (2)decreases, decreases, decreases, decreases
- (3)decreases, increases, increases, decreases
- (4)decreases, increases, decreases, decreases
- (5)decreases, decreases, increases, decreases

Answer and review

Answer **(3)** Official Evaluation Report

CH_3COONa and $AgNO_3$ add a common ion (CH_3COO^- or Ag^+), so the solubility decreases. Dilute HNO_3 protonates acetate ($CH_3COO^- + H^+ \rightarrow CH_3COOH$, a weak acid), removing it from solution, so more solid dissolves. NH_4OH forms the soluble complex $[Ag(NH_3)_2]^+$, removing Ag^+, so solubility increases. Hence: decreases, increases, increases, decreases. 49% answered correctly.

RB U12 §2.4 · p. 175

Questions 31–40: response code

(1)	(2)	(3)	(4)	(5)
Only (a) and (b) are correct	Only (b) and (c) are correct	Only (c) and (d) are correct	Only (d) and (a) are correct	Any other number or combination of responses is correct

Question 31 · Q31–40 · response code

Consider the reaction given below.
$2HI(g) \rightleftharpoons I_2(s) + H_2(g)$ $\Delta H° = -52.96$ kJ mol^{-1}
Which of the following statements is/are **correct** when the reaction takes place in a closed container?

- Increasing the temperature and decreasing the pressure drives the equilibrium to the right.
- Increasing the temperature and decreasing the pressure drives the equilibrium to the left.
- Decreasing the temperature and increasing the pressure drives the equilibrium to the right.
- Decreasing the temperature and increasing the pressure drives the equilibrium to the left.

Answer and review

Answer **(2)** Official Evaluation Report

The forward reaction is exothermic and reduces the number of gas molecules (2 mol gas → 1 mol gas, since I_2 is a solid). By Le Chatelier's principle, raising T favours the endothermic (backward) reaction and lowering P favours the side with more gas molecules (left), so (b) is correct; lowering T and raising P both favour the right, so (c) is correct. The trap is to forget that I_2 is solid and count it as a gas. 58% answered correctly; 22% chose (4).

RB U12 §2.1 · p. 76

Question 32 · Q31–40 · response code

Which of the following statements is/are **true** regarding the molecule CH_2=CHCHO ?

- All three carbon atoms are sp^2 hybridized.
- All three carbon atoms lie in a straight line.
- All three carbon atoms do not lie in the same plane.
- All three carbon atoms lie in the same plane.

Answer and review

Answer **(4)** Official Evaluation Report

In propenal (acrolein) every carbon forms one π bond (two in C=C, one in C=O), so all three are sp^2 with trigonal planar geometry. Bond angles of about 120° mean the carbons are not collinear, but the conjugated system is planar, so all three carbons (indeed all atoms) lie in one plane: (a) and (d). Any three points always lie in one plane anyway, so (c) can never be true. 66% answered correctly.

RB U2 §2.3 · p. 52

Question 33 · Q31–40 · response code

Some of the reactions associated with the Solvay process are

- $CaCO_3$ —Δ→ CaO + CO_2

- $NaCl + NH_3 + H_2O + CO_2 \rightarrow NaHCO_3 + NH_4Cl$
- $Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$
- $Ca(OH)_2 + 2NH_4Cl \rightarrow CaCl_2 + 2NH_4OH$

Answer and review

Answer **(1/5)** Official Evaluation Report

The Evaluation Report accepts (1) or (5). In the Solvay process limestone is heated to give CO_2 and CaO (a), CO_2 is passed into ammoniated brine to precipitate $NaHCO_3$ (b), the $NaHCO_3$ is heated to give Na_2CO_3 (the reverse of (c)), and NH_3 is recovered by treating NH_4Cl with slaked lime (d). So (a), (b) and (d) are true, code (5); (1) was also accepted, probably because (d) is written with "NH_4OH" instead of $2NH_3 + 2H_2O$. Statement (c) is the trap: it runs in the wrong direction. Only 29% chose (1) and 38% (5).

RB U14 §1.5 · p. 18

Question 34 · Q31–40 · response code

Which of the following statements is/are **always true** regarding the rate of an elementary reaction?

- The rate can be increased by increasing temperature.
- The rate can be increased by removing the products from the reaction medium.
- The rate of the reaction depends on the rate of the slowest step.
- Rate of the reaction can be increased by making $\Delta G < 0$.

Answer and review

Answer **(5)** Official Evaluation Report

Raising the temperature increases the fraction of collisions with energy $\geq E_a$, so the rate rises (a). The rate of the forward reaction depends on reactant concentrations, not products (b is false); an elementary reaction occurs in a single step, so there is no "slowest step" (c is false); ΔG is a thermodynamic quantity that says nothing about rate (d is false). Only (a) is true, so code (5). 51% answered correctly; 18% chose (1).

RB U11 §1.5 · p. 15 RB U11 §1.8 · p. 53 RB U11 §1.10 · p. 57

Question 35 · Q31–40 · response code

Which of the following statements is/are **true** regarding 4−pentenal?

- Shows geometric isomerism.
- The compound obtained when reacted with HBr does not show optical isomerism.
- The compound obtained when reacted with HBr shows optical isomerism.
- The compound obtained when reacted with CH_3MgBr shows optical isomerism.

Answer and review

Answer **(3)** Official Evaluation Report

4-Pentenal is $CH_2{=}CHCH_2CH_2CHO$; the C=C carbon at the end carries two H atoms, so there is no geometric isomerism (a false). Markovnikov addition of HBr gives $CH_3CHBrCH_2CH_2CHO$, with a chiral C (H, Br, CH_3, CH_2CH_2CHO): (c) true, (b) false. CH_3MgBr adds to the C=O to give $CH_2{=}CHCH_2CH_2CH(OH)CH_3$, also chiral: (d) true. 51% answered correctly; 25% chose (5).

RB U7 §1.4 · p. 21 RB U8 §2.2 · p. 33 RB U9 §3.4 · p. 60

Question 36 · Q31–40 · response code

Which of the following statements is/are **false** with regard to nitric acid?

- Pure nitric acid is a light yellow liquid.
- All N−O bond lengths in nitric acid are equal.
- Nitric acid cannot act as a reducing agent.
- It is used in the manufacture of an important fertilizer, ammonium nitrate.

Answer and review

Answer **(1)** Official Evaluation Report

Pure HNO_3 is colourless; it turns yellow on standing only because it decomposes to NO_2 (a false). In HNO_3 the two terminal N–O bonds are equal (resonance) but the N–OH bond is longer, so not all N–O bonds are equal (b false). N is already in its highest oxidation state (+5), so HNO_3 cannot be oxidised and cannot act as a reducing agent (c true); NH_4NO_3 is made from HNO_3 and NH_3 (d true). The false statements are (a) and (b). Only 21% answered correctly; 30% chose (2), wrongly treating (c) as false.

RB U6 §4.5 · p. 136

Question 37 · Q31–40 · response code

C(s) reacts with O_2(g) to produce 0.40 mol of CO_2(g), with the release of 40 kJ of heat. Which of the following statements is/are **true** for the above system? (C = 12, O = 16)

- 100 kJ of heat is required to decompose one mole of CO_2(g) into C(s) and O_2(g).
- 25 kJ of heat is required to form 11 g of CO_2(g).
- Sum of enthalpies of products is less than the sum of enthalpies of reactants.
- Sum of enthalpies of products is greater than the sum of enthalpies of reactants.

Answer and review

Answer **(5)** Official Evaluation Report

For 1 mol CO_2, $\Delta H = -40$ kJ / 0.40 mol = -100 kJ mol^{-1}, so decomposing 1 mol CO_2 requires +100 kJ (a true). 11 g CO_2 = 11/44 = 0.25 mol, whose formation releases 25 kJ, it does not require it (b false). The reaction is exothermic, so H(products) < H(reactants) (c true, d false). (a) and (c) are not one of the listed pairs, so code (5). 46% answered correctly.

RB U5 §2.2 · p. 36

Question 38 · Q31–40 · response code

Which of the following statements is/are **true** for a balanced chemical equation of an elementary reaction?

- The order of reaction is the same as molecularity.
- The order of reaction is less than the molecularity.
- The order of reaction is higher than the molecularity.
- Molecularity cannot be zero.

Answer and review

Answer **(4)** Official Evaluation Report

For an elementary reaction the rate law follows directly from the balanced equation, so the order equals the molecularity, the number of reacting species colliding in that step (a). At least one particle must take part, so molecularity is always a positive whole number (1, 2 or rarely 3) and cannot be zero (d). (b) and (c) contradict (a). 59% answered correctly; 21% chose (5).

RB U11 §1.10 · p. 57

Question 39 · Q31–40 · response code

Which of the following statements is/are **true** regarding the molecule given below?
$CH_2{=}CH(CH_2)_3{-}CO{-}NH_2$

- Decolourizes bromine water.
- Liberates ammonia when warmed with an aqueous NaOH solution.
- Gives an orange coloured precipitate with 2,4−DNP reagent.
- Gives a primary amine when treated with $NaBH_4$.

Answer and review

Answer **(1)** Official Evaluation Report

The C=C bond adds Br_2, so bromine water is decolourised (a), and an amide is hydrolysed by warm aqueous NaOH to the carboxylate with loss of NH_3 (b). The amide C=O does not give the aldehyde/ketone reactions: no 2,4-DNP precipitate (c), and $NaBH_4$ does not reduce amides ($LiAlH_4$ would give the amine) (d). The Evaluation Report notes that only 37% chose (1) while 28% chose (5), and stresses that the C=O in amides does not show aldehyde/ketone reactions.

RB U9 §3.6 · p. 70 RB U9 §3.4 · p. 60 RB U8 §2.2 · p. 33

Question 40 · Q31–40 · response code

Consider the compounds given below.
(A) HCHO (B) NH_2CONH_2 (C) C_6H_5OH
(D) $HO_2C(CH_2)_4CO_2H$ (E) $H_2N(CH_2)_6NH_2$
Which of the pairs given below will produce thermosetting polymers when reacted under the appropriate conditions?

- A and B
- A and C
- C and D
- D and E

Answer and review

Answer **(1)** Official Evaluation Report

Formaldehyde condenses with urea (urea-formaldehyde resin) and with phenol (bakelite) to give cross-linked, three-dimensional networks that set permanently on heating, i.e. thermosetting polymers: (a) and (b). Hexanedioic acid and hexane-1,6-diamine give nylon-6,6, a linear thermoplastic (d is the trap), and phenol with a diacid does not give a thermoset. Bakelite is in the current Resource Book; urea-formaldehyde is not described there. 40% answered correctly.

RB U14 §1.11 · p. 37

Questions 41–50: statement pairs

Response	First statement	Second statement
(1)	True	True, and correctly explains the first statement
(2)	True	True, but does not explain the first statement correctly
(3)	True	False
(4)	False	True
(5)	False	False

Question 41 · Q41–50 · statement pair

Statement 1

Sucrose when treated with concentrated H_2SO_4 gives a black mass.

Statement 2

Concentrated H_2SO_4 is a strong oxidizing agent.

Answer and review

Answer **(2)** Official Evaluation Report

Both statements are true, but the charring of sucrose is due to the dehydrating action of concentrated H_2SO_4, which removes the elements of water and leaves carbon: $C_{12}H_{22}O_{11} \rightarrow 12C + 11H_2O$. Its oxidizing property is real (e.g. with Cu or C) but does not explain the black mass. 44% answered correctly; 30% chose (1).

RB U6 §4.6 · p. 141

Question 42 · Q41–50 · statement pair

Statement 1

In the addition reaction between $CH_3CH{=}CH_2$ and HX, the $CH_3CH_2CH_2$^+ carbocation is formed easily as an intermediate.

Statement 2

Alkyl groups attached to a positively charged carbon atom release electrons through C−C, σ-bonds towards the positively charged carbon and increase the stability of the carbocation.

Answer and review

Answer **(4)** Official Evaluation Report

Electrophilic addition of H^+ to propene gives mainly the secondary carbocation CH_3CH^+CH_3, which is stabilised by two electron-releasing alkyl groups; the primary $CH_3CH_2CH_2$^+ (one alkyl group) is much less stable and is not formed easily. This is why Markovnikov's rule gives CH_3CHXCH_3. First statement false, second true. 48% answered correctly.

RB U8 §2.2 · p. 33

Question 43 · Q41–50 · statement pair

Statement 1

The average molecular speed of H_2(g) at 80 °C is lower than that of N_2(g) at 40 °C.

Statement 2

Average molecular speed is directly proportional to the square root of temperature and inversely proportional to the square root of molar mass.

Answer and review

Answer **(5)** Official Evaluation Report

$\bar{c} \propto \sqrt{(T/M)}$ with T in kelvin: for H_2, $\sqrt{(353/2)} \approx 13.3$; for N_2, $\sqrt{(313/28)} \approx 3.3$, so H_2 at 80 °C is about four times faster and the first statement is false. The official key treats the second statement as false as well, presumably because the proportionality holds only for absolute (kelvin) temperature, whereas the statement says just "temperature" in a question that gives temperatures in °C. Many teachers would read it as true, and 50% of candidates chose (4), against 24% for the key (5); students should state "absolute temperature" explicitly.

RB U4 §1.4 · p. 19

Question 44 · Q41–50 · statement pair

Statement 1

Reactivity of alkali metals with water increases on going down the group.

Statement 2

Strong metallic bonds are formed when the size of the metal atom increases.

Answer and review

Answer **(3)** Official Evaluation Report

Down Group 1 the atoms get larger and the ionization energy falls, so the outer electron is lost more easily and the reaction with water becomes more vigorous (true). As the atoms get larger the delocalised electrons are further from the nuclei, so metallic bonding becomes weaker (melting points fall from Li to Cs); the second statement is false. 49% answered correctly; 23% chose (2).

RB U6 §4.1 · p. 122 RB U2 §2.5 · p. 78

Question 45 · Q41–50 · statement pair

Statement 1

$CH_3C{\equiv}CH$ gives a red precipitate when treated with ammoniacal Cu_2Cl_2.

Statement 2

The acidic terminal hydrogen in alkynes can be displaced by metals.

Answer and review

Answer **(1/2/4)** Official Evaluation Report

The Evaluation Report accepts (1), (2) or (4). Propyne is a terminal alkyne; its weakly acidic ≡C–H is replaced by Cu^+ to give the red copper(I) propynide, $CH_3C{\equiv}CCu$, a test for terminal alkynes, and the same H is displaced by Na (giving $CH_3C{\equiv}CNa + H_2$). The intended answer is (1); (2) and (4) were also accepted, presumably because the precipitate is often described as red-brown and because the test involves metal ions rather than metals. 84% chose one of the accepted responses.

RB U8 §2.3 · p. 41

Question 46 · Q41–50 · statement pair

Statement 1

All spontaneous reactions are exothermic.

Statement 2

For any reaction $\Delta G = \Delta H + T\Delta S$

Answer and review

Answer **(5)** Official Evaluation Report

A reaction is spontaneous when $\Delta G < 0$; endothermic processes such as dissolving NH_4Cl or melting ice above 0 °C are spontaneous because $T\Delta S$ outweighs a positive ΔH, so the first statement is false. The correct relation is $\Delta G = \Delta H - T\Delta S$, so the second is also false. 51% answered correctly.

RB U5 §2.4 · p. 53

Question 47 · Q41–50 · statement pair

Statement 1

The reaction between $N_2(g)$ and $H_2(g)$ to produce $NH_3(g)$ is endothermic.

Statement 2

$NH_3(g)$ is used in the synthesis of nitric acid and urea.

Answer and review

Answer **(4)** Official Evaluation Report

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is exothermic ($\Delta H \approx -92$ kJ mol^{-1}), which is why the Haber process uses a moderate temperature with a catalyst; the first statement is false. NH_3 is oxidised to HNO_3 in the Ostwald process and reacted with CO_2 to make urea, so the second is true. 51% answered correctly; 31% chose (2).

RB U14 §1.6 · p. 21 RB U5 §2.2 · p. 36

Question 48 · Q41–50 · statement pair

Statement 1

Mirror images of bromochloromethane are enantiomers.

Statement 2

Enantiomers are non superimposable mirror images of each other.

Answer and review

Answer **(4)** Official Evaluation Report

CH_2BrCl has two identical H atoms on the carbon, so it has no chiral centre; its mirror image is superimposable on it (the same molecule), and the first statement is false. The second statement is the correct definition of enantiomers. Only 34% answered correctly; 22% chose (1).

RB U7 §1.4 · p. 21

Question 49 · Q41–50 · statement pair

Statement 1

The solubility of barium oxalate, $BaC_2O_4(s)$ is less in acidic aqueous medium than in water.

Statement 2

The conjugate acid of $C_2O_4^{2-}$ is the weak acid $H_2C_2O_4$.

Answer and review

Answer **(5)** Official Evaluation Report

In acid, H^+ combines with $C_2O_4^{2-}$ (the anion of a weak acid) to form HC_2O_4^−, lowering $[C_2O_4^{2-}]$, so more BaC_2O_4 dissolves: the solubility is greater in acid and the first statement is false. A conjugate acid differs from its base by one H^+, so the conjugate acid of $C_2O_4^{2-}$ is HC_2O_4^−, not $H_2C_2O_4$; the second statement is also false. The lowest facility in this section: only 18% chose (5), while 36% chose (4); the Evaluation Report stresses the stepwise dissociation of the dibasic acid $H_2C_2O_4$.

RB U12 §2.4 · p. 175 RB U12 §2.2 · p. 118

Question 50 · Q41–50 · statement pair

Statement 1

Enzymes present in root nodules of certain plants are capable of fixing N_2.

Statement 2

N_2 molecule is unreactive mainly because of the presence of the N−N triple bond.

Answer and review

Answer **(2/4)** Official Evaluation Report

The Evaluation Report accepts (2) or (4). The N≡N triple bond is very strong (about 945 kJ mol^{-1}), which makes N_2 unreactive (second true), but this does not explain the first statement. Nitrogen is fixed by the enzyme nitrogenase of Rhizobium bacteria living in the root nodules of legumes; the first statement is true if read as "enzymes in the nodules" and false if read as "enzymes of the plant", hence both codes are accepted. Biological nitrogen fixation is not covered in the current Resource Book. 75% chose an accepted response.

RB U6 §4.5 · p. 136

Structured essay · answer all four

SEQ · Paper II Part A

Question 1 · Part A · structured essay

Paper II Part A (2016, old syllabus): each question carries 10 marks on the paper; the Evaluation Report's scheme below is marked out of 100 per question (the 100 marks are divided by 10 for the paper). A further note for 1(a): if more than one answer is given for a question, award zero marks for that question.

(a) [24 marks]

You are provided with the following list of some p-block elements in the Periodic Table.

B	C	N	O	F	Ne
Al	Si	P	S	Cl	Ar

Answer

(i) C (ii) N / S / P / Cl / C (any one of these is accepted) (iii) Ne (iv) Al (v) O (vi) F (04 marks × 6 = 24 marks)
Note: if more than one answer is given for a question, award zero marks for that question. 1(a): 24 marks

Review.

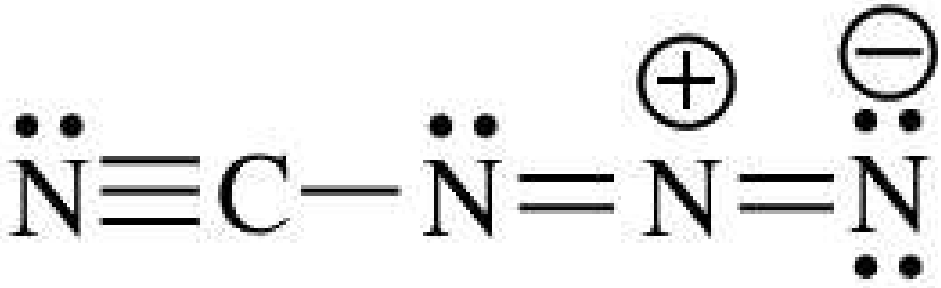
Report comments: in (i) four facts must all be considered together: high hardness, homoatomic (one kind of atom), covalent lattice and non-metallic character, which gives carbon (diamond); only 69% of candidates scored, so not all four facts were being weighed. Facilities were (ii) 83% (the easiest part of the question), (iii) 80%, (iv) 82%, (v) 70%; (vi) was only 41% although F, not O or Cl, is the strongest oxidizing agent in the list (largest electron gain tendency and weak F–F bond, giving the highest reduction potential for F_2). Neon has the highest first ionization energy because it has the smallest radius and a full octet of the elements listed. O_2 and O_3 are the two gaseous allotropes. $Al(OH)_3$ and Al_2O_3 react with both acids and bases. See the Resource Book sections on periodic trends and on the p-block groups.

(b) [56 marks]

The following parts (i) to (v) are based on the molecule CN_4. It has the following skeleton.
N–C–N–N–N
(i) Assuming that N–N bond lengths are approximately equal, draw the **most** acceptable Lewis structure for this molecule.

Answer

ure for this molecule.



4

+

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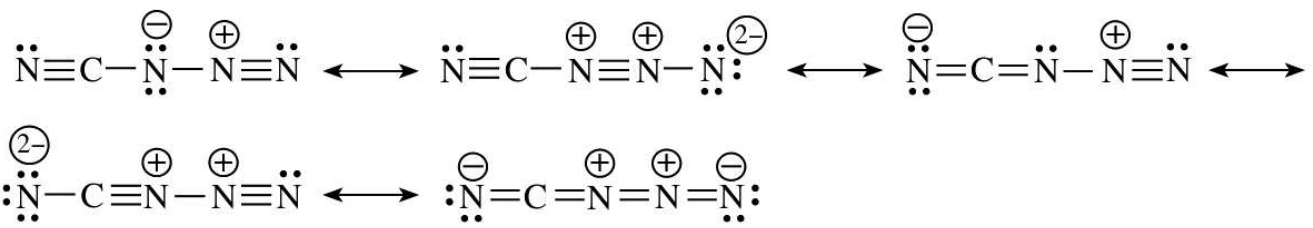
$N{\equiv}C{-}\overset{\ominus}{\underset{\cdot\cdot}{N}}{-}\overset{\oplus}{N}{\equiv}\underset{\cdot\cdot}{N}$ ($N{\equiv}C{-}N{-}N{\equiv}N$) (with one lone pair on each of the end N^1 and on N^2, and two lone pairs on the terminal N^-): formal charge +1 on N^3 and −1 on N^4. The two N–N bonds are both double, so they are equal in length. (10 marks)

(ii) Draw **three** resonance structures for this molecule (excluding the structure drawn in part (i) above).

Answer



Note : Consider first three responses.

Resonance structures given in the scheme (five are shown; only the first three responses are marked)

Any three of: $N\equiv C–N^{-}–N^{+}\equiv N$; $N\equiv C–N^{+}\equiv N^{+}–N^{2-}$; $N^{-}=C=N–N^{+}\equiv N$; $N^{2-}–C\equiv N^{+}–N^{+}\equiv N$; $N^{-}=C=N^{+}=N^{+}=N^{-}$ (the last is the form with all N–N and C–N bonds double). Note: consider the first three responses only. (05 marks × 3 = 15 marks)

(iii) Based on the Lewis structure drawn in (i) above, state the following regarding the C and N atoms given in the table below.
I. VSEPR pairs around the atom. II. electron pair geometry around the atom. III. shape around the atom. IV. hybridization of the atom.
The nitrogen atoms of CN_4 are numbered as follows: $N^1–C–N^2–N^3–N^4$

Answer

	C	N^2	N^3
I. VSEPR pairs	2	3	2
II. electron pair geometry	linear	trigonal planar	linear
III. shape	linear	angular / V	linear
IV. hybridization	sp	sp^2	sp

(01 mark × 12 = 12 marks)

(iv) In the Lewis structure drawn in part (i) above, indicate whether N^2 or N^3 has the **higher** electronegativity. Give reasons for your choice. [Numbering of atoms is as in part (iii).]

Answer

$N^3 > N^2$, i.e. N^3 has the higher electronegativity (05)
N^3 is sp hybridized and carries a positive charge, or its oxidation state is +1 (01 + 01)
N^2 is sp^2 hybridized and carries zero charge, or its oxidation state is −1 (01 + 01)
The higher the positive charge / the higher the positive oxidation state, the higher the electronegativity (01)
The higher the s-character, the higher the electronegativity (01)

(v) Identify the atomic/hybrid orbitals involved in the formation of the following σ bonds in the Lewis structure drawn in part (i) above. [Numbering of atoms is as in part (iii).]
I. N^1–C: N^1 ....., C .....
II. C–N^2: C ....., N^2 .....
III. N^2–N^3: N^2 ....., N^3 .....
IV. N^3–N^4: N^3 ....., N^4 .....

Answer

I. N^1–C: N^1 sp (or 2p), C sp
II. C–N^2: C sp, N^2 sp^2
III. N^2–N^3: N^2 sp^2, N^3 sp
IV. N^3–N^4: N^3 sp, N^4 sp^2 (or 2p) (01 mark × 8 = 08 marks)
Note: even if the Lewis structure drawn in (b)(i) is wrong, award marks for the pair geometry in the central atom / around the atom as given. 1(b): 56 marks

Review.

Report comments: (b) was the weakest part of the question. Facilities were (i) 25%, (ii) 25%, (iii) 33–41% for the four rows, (iv) only 12% (the lowest in the question) and (v) 44%, 44%, 33%, 27%. One reason given is

that nothing was credited in some parts when the Lewis structure in (i) was wrong, so the later parts suffered. Method: write the skeleton, count valence electrons (4 + 4 × 5 = 24), complete octets, then minimise formal charges; N^2 has two σ bonds and one π bond plus one lone pair (3 electron pairs, sp^2, bent) while N^3 has two double bonds (2 pairs, sp, linear). For (iv) the point to stress, according to the report, is that electronegativity rises with higher oxidation number and with greater s-character of the hybrid orbital, so the sp, +1 atom N^3 is more electronegative than the sp^2, −1 atom N^2. In (v) use the hybrid on each atom (sp for the central C, sp^2 for N^2, sp for N^3); the end atoms N^1 and N^4 may be given as sp or sp^2 or plain 2p as accepted. Resonance forms must keep the same atom skeleton and total charge, differing only in electron positions.

(c) [20 marks]

State whether the following statements are **true** or **false**. (Reasons are **not** required.)
(i) SF_6 and OF_6 are both stable molecules.
(ii) Although the electron pair geometry of $SiCl_4$, NCl_3 and SCl_2 is tetrahedral, their bond angles are different.
(iii) The boiling point of Kr is greater than that of Xe.
(iv) The solubility of group II sulphates decreases down the group primarily due to decrease in hydration enthalpy of the cations.

Answer

(i) False (ii) True (iii) False (iv) True (05 marks × 4 = 20 marks) 1(c): 20 marks · Total for 1: 100 marks

Review.

Report comments: facilities were (i) 80%, (ii) 80%, (iii) 60%, (iv) 56%. (i) SF_6 exists because sulphur can expand its octet, but oxygen (period 2, no d orbitals) cannot, so OF_6 does not exist. (ii) The bond angles depend on the number of lone pairs: $SiCl_4$ 109.5° (no lone pairs), NCl_3 pyramidal (one lone pair, about 107°), SCl_2 angular (two lone pairs, about 103°). (iii) London forces increase with size and number of electrons, so Xe boils higher than Kr. (iv) Down group 2 the lattice enthalpy of the sulphates changes little (the large sulphate ion dominates), while the hydration enthalpy of the cation falls as the cation gets bigger, so solubility decreases.

Read: RB U2 §2.3 · p. 52 RB U2 §2.1 · p. 44 RB U1 §1.6 · p. 32 RB U6 §4.5 · p. 136

Question 2 · Part A · structured essay

Marks below are out of 100 for the question (10 marks on the paper). Notes to examiners in the scheme: if only one answer in (a)(i) is correct, award marks for the respective correct answers of (a)(ii) and (a)(iii); award marks for (a)(iv) only if both X and Y are correctly identified. If the answer is given as X = KOH, Y = $Ca(OH)_2$, do not award marks for (a)(i) and (a)(iv), but award marks for the correct answers of (a)(ii) and (a)(iii).

(a) [50 marks]

X and Y are s-block elements of the Periodic Table. They react with water to form hydroxides. The hydroxide of X is more basic than that of Y. The hydroxide of X is used in the manufacture of baby soap. The hydroxide of Y is commonly used to identify the gas Z that is one of the main gases responsible for global warming.
(i) Identify X and Y.

Answer

X: K or potassium · Y: Ca or calcium (03 + 03)

(ii) Write the electronic configurations of X and Y.

Answer

X = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$
Y = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$ (03 + 03)

(iii) Write the colour of the flame given by salts of X and Y in the flame test.

Answer

X: lilac / violet / reddish-violet
Y: brick red / yellow-red / orange red (note: marks could be awarded for 'orange' colour) (03 + 03)

(iv) Indicate the relative magnitudes of the following in respect of X and Y.
I. Atomic size
II. Density
III. Melting point
IV. First ionization energy
(Write X or Y in each pair of boxes: [ ] > [ ].)

Answer

I. Atomic size: X > Y
II. Density: Y > X
III. Melting point: Y > X
IV. First ionization energy: Y > X (03 × 4)

(v) Identify Z.

Answer

CO_2 (03)

(vi) Using balanced chemical equations **only**, indicate how the hydroxide of Y could be used to identify Z.
Note: Indicate precipitates, if any, using "↓" and colours of precipitates/solutions used in the identification.

Answer

$CO_2 + Ca(OH)_2 \rightarrow CaCO_3\downarrow + H_2O$ (white / milky white precipitate) (01 + 01 + 01)
$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$ (colourless solution) (02 + 01)
Note: if Y has been identified correctly, Y could be used instead of Ca.

(vii) A natural source of Y in which it is present as a carbonate is used as a raw material in the manufacture of a disinfectant.
I. Name the natural source.
II. Identify the disinfectant.
III. Write the steps in the manufacturing process of the disinfectant, using balanced chemical equations **only**.

Answer

I. Limestone / marble / oyster shells (03)
II. Bleaching powder: $Ca(OCl)_2{\cdot}Ca(OH)_2{\cdot}CaCl_2{\cdot}2H_2O(s)$ / $Ca(OCl)_2$ (03)
III. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ (02)
$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$ (02)
$3Ca(OH)_2(s) + 2Cl_2(g) \rightarrow Ca(OCl)_2{\cdot}Ca(OH)_2{\cdot}CaCl_2{\cdot}2H_2O(s)$ (01)
Note: physical states are not required. 2(a): 50 marks

Review.

Report comments: facilities were (i) 65%, (ii) 61%, (iii) 47%, (iv) 40%, (v) 71% (the easiest part), (vi) 21%, (vii) I 30%, II 27%, III 24%. In (i) the name of the element is required, but most candidates wrote the name of the hydroxide; the report stresses reading the question carefully, and in (vii) I the name of the source is

asked, so a formula should be given only when it is requested. It also reminds teachers that potassium compounds in baby (soft) soap are mentioned even in the Ordinary Level syllabus. Reasoning: KOH is a strong base used in soft soap; lime water, $Ca(OH)_2$, turns milky with CO_2 (a greenhouse gas) and the milkiness clears with excess CO_2 because soluble $Ca(HCO_3)_2$ forms. K and Ca are in the same period: K has one valence electron and Ca two, so K has the larger atom, lower density, lower melting point and lower first ionization energy (weaker metallic bonding, lower effective nuclear charge). Flame colours: K lilac, Ca brick red. Outside the current syllabus: the manufacture of bleaching powder from limestone (quicklime, slaked lime, chlorine) does not appear in the present Resource Book; this is an old-syllabus paper.

(b) [50 marks]

(i) Complete the reactions given below by selecting the appropriate solution from the given list and writing in the box.

List of solutions (not in order)

$Na_2S_2O_3(aq)$, $AgNO_3(aq)$, $K_2SO_4(aq)$, $(NH_4)_2CO_3(aq)$, $BaCl_2(aq)$, $KI(aq)$

Note: A solution should be used **only once**.

I. $BaCl_2(aq)$ + [ ] → **A** (White precipitate that dissolves in dil. HCl to give a clear solution)
II. $Pb(NO_3)_2(aq)$ + [ ] → **B** (Yellow precipitate that dissolves in hot water)
III. $AgNO_3(aq)$ + [ ] → **C** (White precipitate that turns black on standing)
IV. $K_2SO_3(aq)$ + [ ] → **D** (White precipitate that dissolves in dil. HCl)
V. NaBr(aq) + [ ] → **E** (Pale yellow precipitate that dissolves completely in conc. ammonia)
VI. $Ba(NO_3)_2(aq)$ + [ ] → **F** (White precipitate that does **not** dissolve in dil. HCl)

Answer

I. $(NH_4)_2CO_3$ · II. KI · III. $Na_2S_2O_3$ · IV. $BaCl_2$ · V. $AgNO_3$ · VI. K_2SO_4 (04 marks × 6 = 24 marks)

(ii) Write the chemical formulae of the precipitates **A** to **F**.

Answer

A $BaCO_3$ · B PbI_2 · C $Ag_2S_2O_3$ · D $BaSO_3$ · E AgBr · F $BaSO_4$ (03 marks × 6 = 18 marks)

(iii) Write balanced chemical equations for the dissolution of precipitates **A**, **D** and **E** in (b)(i) above.

Answer

(A) $BaCO_3 + 2HCl \rightarrow BaCl_2 + H_2O + CO_2$ (or H_2CO_3) (03)
(D) $BaSO_3 + 2HCl \rightarrow BaCl_2 + H_2O + SO_2$ (or H_2SO_3) (03)
(E) $AgBr + 2NH_3 \rightarrow [Ag(NH_3)_2]Br$ or $[Ag(NH_3)_2]^+ + Br^-$ (02)
Note: mark (b)(iii) independently. 2(b): 50 marks · Total for 2: 100 marks

Review.

Report comments: facilities for (b)(i) I–VI were 42%, 55%, 48%, 53%, 56% and 58%; (ii) 40%; (iii) only 18%, the lowest in the question. The report stresses understanding what is asked: (iii) wanted the equation for the dissolving of the precipitate (acid dissolution of the carbonate and sulphite with release of CO_2 and SO_2; ammonia dissolution of AgBr to the diammine complex), not the precipitation equation. Selection logic: A is $BaCO_3$ and D is $BaSO_3$ (barium salts of weak acids, which dissolve in HCl), whereas $BaSO_4$ (F) is insoluble in acid; PbI_2 (B) is yellow and dissolves in hot water; $Ag_2S_2O_3$ (C) is white and decomposes to black Ag_2S on standing; AgBr (E) is pale yellow and soluble in conc. NH_3. Because each solution is used once, fix the unambiguous ones first (E needs $AgNO_3$, so C must use thiosulphate). See the Resource Book sections on thiosulphate and on solubility and precipitation reactions.

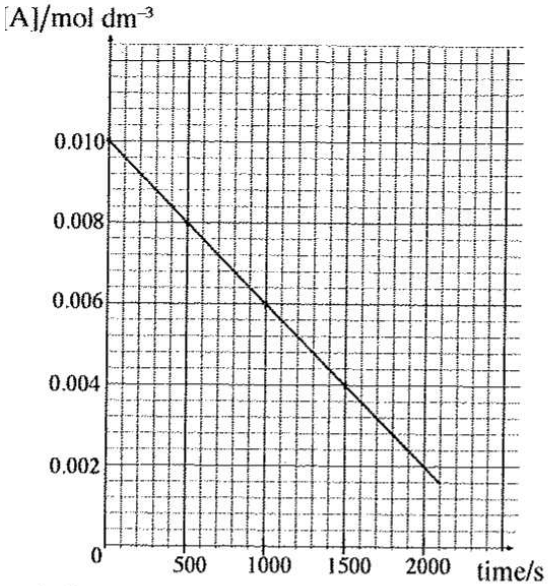
Read: RB U6 §4.1 · p. 122 RB U6 §4.2 · p. 126 RB U14 §1.13 · p. 58 RB U12 §2.4 · p. 175

Question 3 · Part A · structured essay

Marks below are out of 100 for the question (10 marks on the paper). The report notes that this question is on chemical kinetics and gas laws together; units are not required in 3(b).

(a) [60 marks]

When 0.010 moles of gas **A** is placed in a 1.0 dm^3 evacuated closed rigid container in the presence of a small amount of a solid catalyst, at 227 °C, it decomposes as shown below.
A(g) → B(g) + C(g)
The concentration of A(g) was measured over time. The results are shown in the following graph.



and the rate constant of the reaction as **a** and ***k***

−3

−3

−3

(i) Taking the order and the rate constant of the reaction as **a** and k, respectively, write the rate expression for the above reaction.

Answer

Rate = k[A]^a (10)
or −Δ[A]/Δt = k[A]^a, or −d[A]/dt = k[A]^a (if the (−) sign is not included, do not award marks)

(ii) Giving reasons, determine the value of **a**.

Answer

Rate = $k[A]^0$, or order = a = 0 (10)
Rate = constant (the gradient is constant), or the rate is independent of concentration (05)

(iii) Calculate the rate constant, k at 227 °C.

Answer

Rate constant, k = |Rate| (05)
k = |(0.002 − 0.010) mol dm^{-3} / 2000 s|, or any two points (04 + 01)
k = 4.0 × 10^{-6} mol dm^{-3} (as printed in the scheme; for a zero-order reaction the unit is mol dm^{-3} s^{-1}) (04 + 01)

(iv) Calculate the pressure in the container when half the initial amount of A(g) has decomposed. Assume that the volume of the catalyst can be neglected.

Answer

Volume of the container = 1.0 dm^3
A → B + C: after 50% completion, 0.01(1 − x) : 0.01x : 0.01x [concentrations in mol dm^{-3}]
Amount of gas at t = 0 = 0.01 mol
Amount of gas after 50% is decomposed = (0.005 + 0.005 + 0.005) mol = 0.015 mol (05)
Assuming ideal gas behaviour, apply PV = nRT:
Pressure = 0.015 mol × 8.314 J K^{-1} mol^{-1} × 500 K / 10^{-3} m^3 (08 + 02)
= 6.23 × 10^4 Pa (as printed; 62 355 Pa rounds to 6.24 × 10^4 Pa) (04 + 01) 3(a): 60 marks

(b) [40 marks]

In the presence of a solid catalyst, the gas **X** decomposes according to the following chemical equation.
X(g) → 2Y(g) + Z(g) (catalyst, Δ)
1.0 mole of gas **X** was introduced to an evacuated container. The initial volume of the gas was measured to be V_0. The reaction was initiated by introducing a small amount of catalyst (volume is negligible). The rate constant of the catalysed reaction is k_1 and order of the reaction with respect to **X** is **b**. The initial rate of the reaction was measured as R_0. The pressure of the system was maintained at a constant value by allowing the container to expand. The temperature of the system was also maintained at a constant value.
(i) Write an expression for R_0 using the terms **b**, k_1 and V_0.

Answer

Initial rate, $R_0 = k_1[X]^b$
$R_0 = k_1(1.0 \text{ mol} / V_0)^b$ ——— (1) (10) (units are not required)

(ii) It was observed that the rate of the reaction was $0.25R_0$ and the volume of the container was doubled when 50% of X(g) was consumed. Calculate the order **b** of the reaction.

Answer

After 50% decomposition, [X] = 0.5 mol / $2V_0$ (05)
At this stage, Rate = $0.25R_0$
$0.25R_0 = k_1(0.5 \text{ mol} / 2V_0)^b$ ——— (2) (10)
From (2)/(1): $0.25R_0 / R_0 = k_1(0.5 \text{ mol} / 2V_0)^b / k_1(1.0 \text{ mol} / V_0)^b$ (10)
0.25 = 0.25^b
b = 1 (05) (units are not required) 3(b): 40 marks · Total for 3: 100 marks

Review.

Report comments: this was the least successful question in Paper II (overall facility about 29%; the report calls the competency in chemical kinetics unsatisfactory). Facilities: (a)(i) 68% (the easiest part), (a)(ii) 11%, (a)(iii) 8% (the lowest), (a)(iv) 15%, (b)(i) 45%, (b)(ii) 29%. The graph is a straight line, so the rate (the gradient) is constant and the order is zero; candidates did not read the axes of the graph, and a wrong answer in (a)(ii) carried through to (a)(iii). Method for (iii): for a zero-order reaction k equals the magnitude of the gradient, 0.008 mol dm^{-3} / 2000 s = 4.0 × 10^{-6} mol dm^{-3} s^{-1}. For (iv) the amount of gas rises from 0.010 to 0.015 mol (A 0.005 + B 0.005 + C 0.005) in the rigid 1.0 dm^3 vessel at 500 K, and P = nRT/V = 6.24 × 10^4 Pa (the printed 6.23 × 10^4 is a truncation). In (b), at constant P and T the volume is proportional to the amount of gas: 1.0 mol X becomes 0.5 mol X + 1.0 mol Y + 0.5 mol Z = 2.0 mol, so the volume doubles, which gives [X] = 0.5 mol / $2V_0$ at 50% reaction and (0.25)^b = 0.25, b = 1. The report adds that students must practise combining kinetics with gas laws, and must substitute the given symbols into the right expressions (b(i), b(ii) had facilities of only 45% and 29%).

Read: RB U11 §1.6 · p. 16 RB U11 §1.7 · p. 26 RB U4 §1.2 · p. 5 RB U11 §1.3 · p. 9

Question 4 · Part A · structured essay

Marks below are out of 100 for the question (10 marks on the paper). Structures in the scheme are condensed formulae; they are typed here, with the larger ones shown as figures from the Evaluation Report.

(a) [50 marks]

(i) **A**, **B**, **C** and **D** are structural isomers with the molecular formula $C_4H_{10}O$. All four isomers reacted with metallic sodium to evolve H_2 gas. Of the four isomers, only **A** exhibited optical isomerism. When **B**, **C** and **D** were added separately to conc. HCl, containing $ZnCl_2$, the mixture containing **B** became turbid very rapidly. The development of turbidity with **C** and **D** was very slow. When **C** and **D** were heated with conc. H_2SO_4, **E** and **F** were respectively obtained. **E** and **F** are structural isomers with the molecular formula C_4H_8. Neither **E** nor **F** exhibited geometric isomerism. When **E** and **F** were treated with HBr, **G** and **H** were respectively obtained. Only **G** exhibited optical isomerism. Draw the structures of **A**, **B**, **C**, **D**, **E**, **F**, **G** and **H** in the boxes given below. (It is **not necessary** to draw stereoisomeric forms.) (4.0 marks)

Answer

Compound	Structure
A	$CH_3CH_2CH(OH)CH_3$ (butan-2-ol)
B	$(CH_3)_3C-OH$ (2-methylpropan-2-ol)
C	$CH_3CH_2CH_2CH_2OH$ (butan-1-ol)
D	$(CH_3)_2CH-CH_2OH$ (2-methylpropan-1-ol)
E	$CH_3CH_2CH=CH_2$ (but-1-ene)
F	$CH_3-C(CH_3)=CH_2$ (2-methylpropene)
G	$CH_3CH_2CH(Br)CH_3$ (2-bromobutane)
H	$(CH_3)_3C-Br$ (2-bromo-2-methylpropane)

(05 × 8 = 40 marks)

A

I

C

J

B

3

3

3

4

10

(ii) When **A** and **C** were reacted with PCC, **I** and **J** were respectively obtained. Draw the structures of **I** and **J** in the boxes given below. (PCC = Pyridinium chlorochromate) (1.0 mark)

Answer

I

2

5

3

J

3

2

2

(05 × 2 = 10 marks)

4(a): 50 marks

Review.

Principle: deducing isomeric alcohols from chemical evidence. All four react with Na, so all are alcohols ($C_4H_{10}O$ has four alcohols). Only butan-2-ol has a chiral carbon, so it is A. In the Lucas test (conc. HCl/$ZnCl_2$) tertiary alcohols go turbid at once (stable tertiary carbocation), so B is 2-methylpropan-2-ol; C and D, slow, are the two primary alcohols. Their dehydration gives the two C_4H_8 alkenes without geometric isomers, but-1-ene and 2-methylpropene; Markovnikov addition of HBr gives 2-bromobutane (chiral, G) from but-1-ene and 2-bromo-2-methylpropane (achiral, H) from 2-methylpropene, which fixes C = butan-1-ol and D = 2-methylpropan-1-ol. PCC stops oxidation of a primary alcohol at the aldehyde (J = butanal) and oxidises the secondary alcohol to the ketone (I = butanone). Report comments: facilities A 63%, B 59%, C 46%, D 42%, E 49%, F 45%, G 57%, H 44%, I 52%, J 41%; only 4 of the 10 structures were above 50% even though the report calls these basic, familiar concepts. Common errors: swapping C and D (the HBr/optical-activity clue decides it), drawing but-2-ene for E (it shows geometric isomerism), and letting PCC oxidise butan-1-ol to the acid.

(b) [30 marks]

Draw the structure of the **major** organic products **K**, **L**, **M**, **N**, **O**, **P**, **Q**, **R**, **S** and **T** of the following reactions in the relevant boxes given on page 8. (3.0 marks)

(i) $CH_3CH{=}CH_2$ —(HBr, peroxide)→ **K**

Answer

K

3

2

2

(03)

(ii) C_6H_5CHO —(① 2,4-DNP, ② dehydration)→ **L**

Answer

L

6

5

6

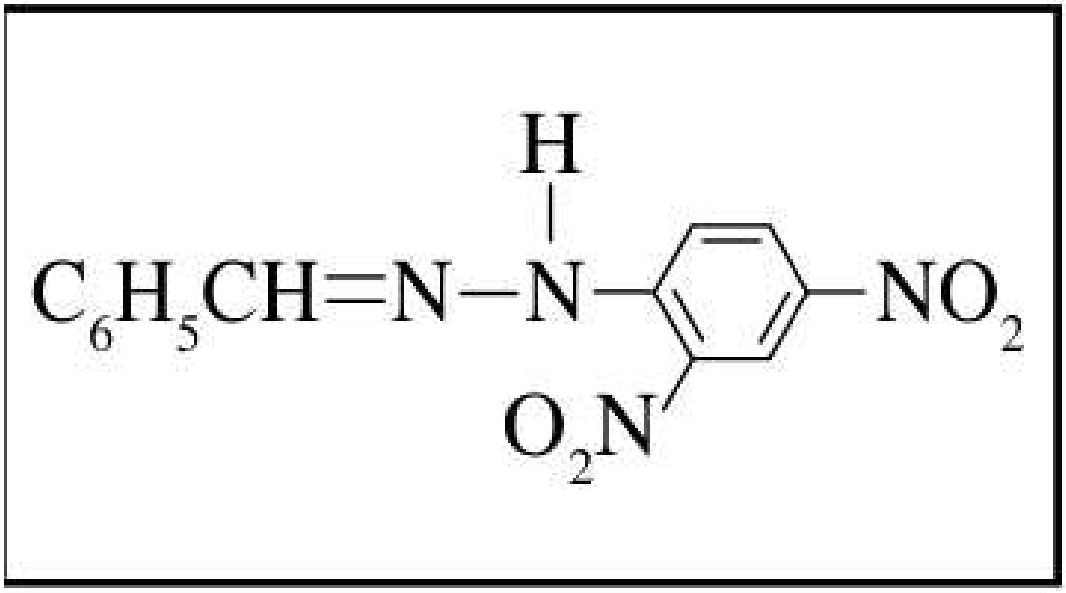
3

2

2

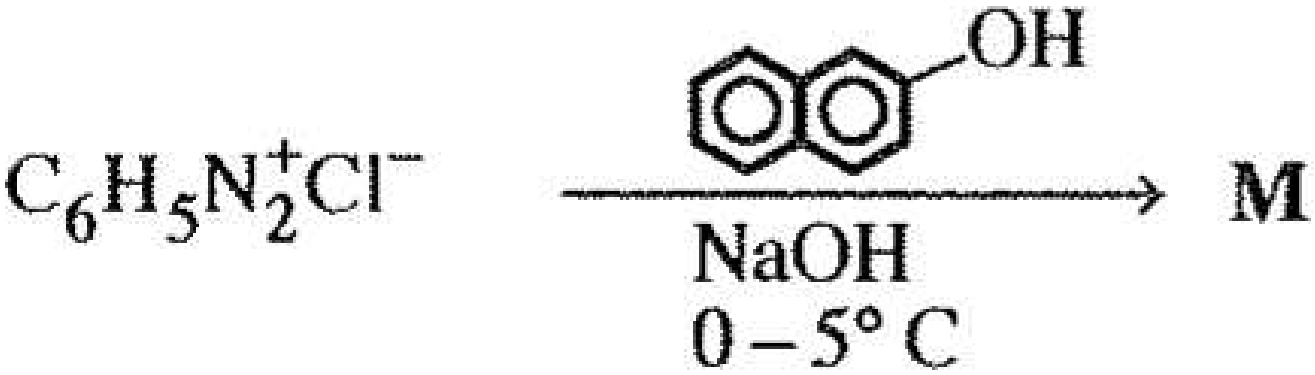
2

(03)



L (scheme)

(iii) $C_6H_5N_2^+Cl^-$ —(2-naphthol, NaOH, 0–5 °C)→ **M**



reaction (iii): the reagent is 2-naphthol (naphthalen-2-ol)

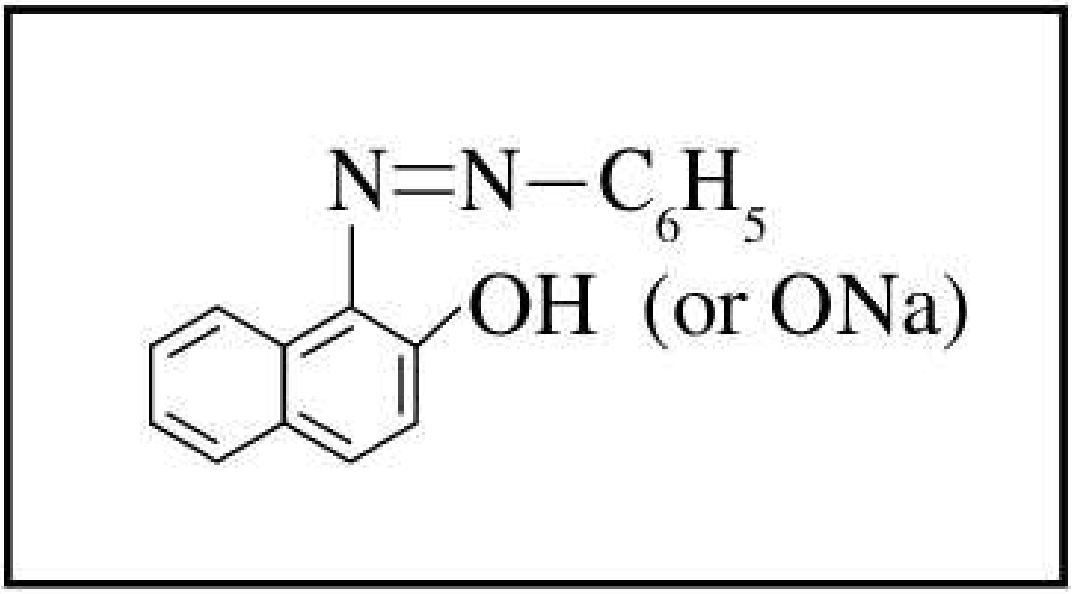
Answer

M

6

5

(03)



M (scheme)

(iv) C_6H_5COCl —(NH_3)→ **N**

Answer

N

6

5

2

(03)

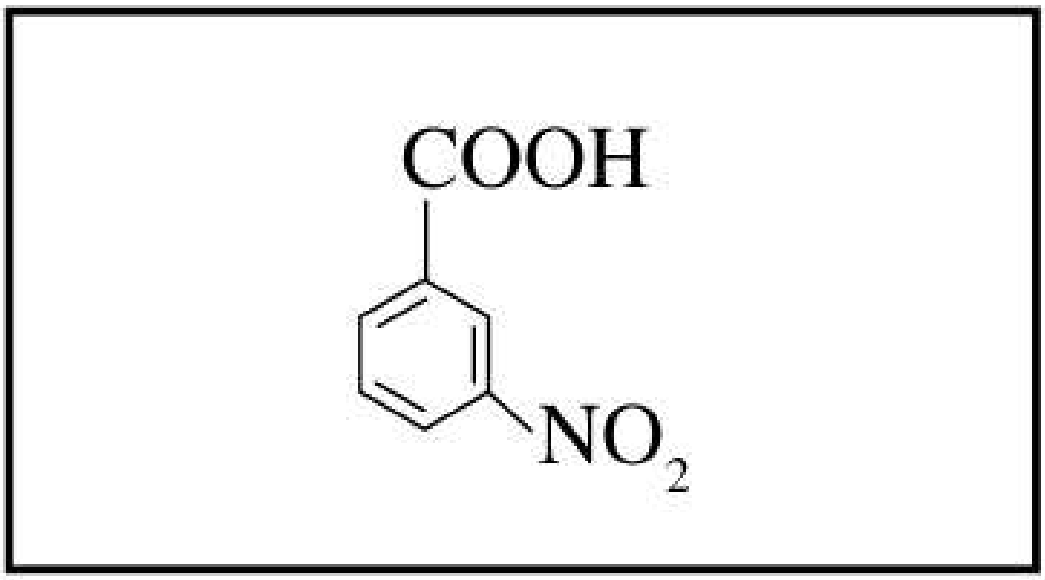
(v) $C_6H_5CO_2H$ —(conc. HNO_3, conc. H_2SO_4)→ **O**

Answer

O

2

(03)



O (scheme)

(vi) $CH_3COC_2H_5$ —(Zn|Hg, conc. HCl)→ **P**

Answer

P

3

2

2

5

(03)

(vii) CH_3CHO —($Ag(NH_3)_2$^+OH^-)→ **Q**

Answer

Q

3

2

or

3

3

2

(03)

(viii) $CH_3C{\equiv}CH$ —($NaNH_2$)→ **R**

Answer

R

3

+

+

(03)

3

+

3

(ix) $CH_3C{\equiv}CCH_3$ —$(H_2|Pd)$→ **S**

Answer

S

3

2

2

3

(03)

(x) C_6H_5OH —(Br_2)→ **T**

Answer

T

6

2

3

(03)

(03 × 10 = 30 marks)

4(b): 30 marks

Review.

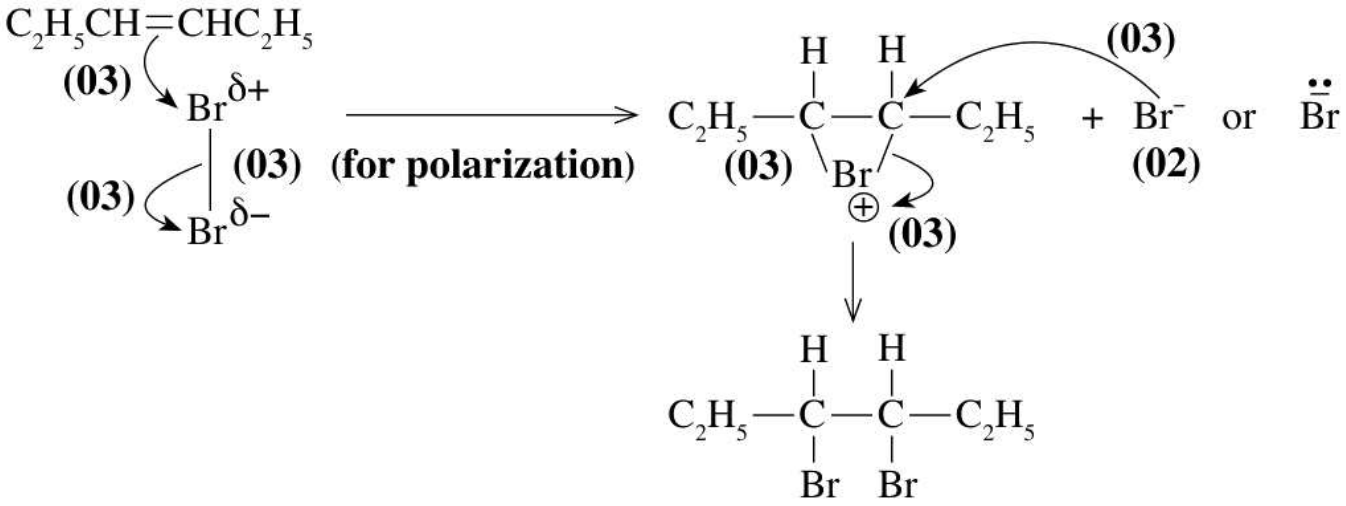
Principle: recall of standard reactions from the reagent. (i) peroxide reverses the HBr orientation (anti-Markovnikov, free radical) to 1-bromopropane. (ii) carbonyl + 2,4-DNP (2,4-dinitrophenylhydrazine) is addition then loss of water to the hydrazone. (iii) diazonium coupling with 2-naphthol in alkali at 0–5 °C gives the orange-red azo dye, coupling at C-1. (iv) acid chloride + NH_3 gives the amide. (v) COOH is a meta director, so nitration gives 3-nitrobenzoic acid. (vi) Clemmensen reduction (Zn(Hg)/conc. HCl) turns C=O into CH_2, giving butane. (vii) Tollens' reagent oxidises the aldehyde to the carboxylate (ethanoic acid after acidification). (viii) the terminal alkyne is acidic and $NaNH_2$ forms the sodium alkynide. (ix) H_2 over Pd reduces the alkyne fully to butane (the Resource Book uses poisoned Pd only for stopping at the alkene). (x) bromine water substitutes all three activated o/p positions of phenol. Report comments: facilities (i) 64%, (ii) 22% (lowest in the question), (iii) 24%, (iv) 65% (the easiest with (i)), (v) 51%, (vi) 61%, (vii) 31%, (viii) 55%, (ix) 59%, (x) 54%. Low marks in (ii) came from not knowing the formula of 2,4-DNP when it is given only by name, and in (iii) from the large azo product being hard to remember. The scheme's note for R is self-contradictory as printed (the first "not accepted" structure is the same as the accepted one); the point intended is that the negative charge must be on the terminal carbon and the product shown as the ionic sodium alkynide.

(c) [20 marks]

Write the mechanism for the reaction between $C_2H_5CH{=}CHC_2H_5$ and $Br_2(CCl_4)$. (2.0 marks)

Answer

Electrophilic addition via a cyclic bromonium ion:
1. As the Br_2 molecule approaches the C=C π bond it is polarised, $Br^{\delta+}{-}Br^{\delta-}$ (03, for polarization); curly arrow from the π bond to $Br^{\delta+}$ (03) and curly arrow from the Br−Br bond to $Br^{\delta-}$ (03).
2. Cyclic bromonium ion: $C_2H_5{-}CH{-}CH{-}C_2H_5$ bridged by Br^+ (three-membered ring) (03), formed together with Br^- (or $:Br^-$) (02).
3. Br^- attacks a ring carbon (curly arrow from Br^- to C) (03) and the $C{-}Br^+$ bond electrons move onto Br (curly arrow) (03), giving $C_2H_5CH(Br)CH(Br)C_2H_5$ (3,4-dibromohexane).
Note: if the cyclic intermediate is not drawn, do not award 06 marks.



Mechanism with mark allocation (scheme)

4(c): 20 marks · Total for 4: 100 marks

Review.

Principle: electrophilic addition of a halogen to an alkene. The π electrons induce a dipole in Br_2 and attack $Br^{\delta+}$; the Br−Br bond breaks heterolytically, giving a cyclic bromonium ion and Br^-, which then opens the ring by attacking a carbon from the opposite side to give the vicinal dibromide (3,4-dibromohexane). Marks are for the polarisation, each correctly placed curly arrow (tail at the electron source, head at the atom receiving the pair), the bromonium ion with its charge, and Br^-. Report comments: facility only 39% although it is a familiar mechanism; the report urges repeated practice of the same mechanism. Common mistakes: drawing an open carbocation instead of the cyclic bromonium ion (loses 6 marks), arrows starting from atoms instead of bonds or lone pairs, and omitting charges. Overall facility for Q4 was 48%, the highest in Paper II (25% of candidates scored 76–100, 40% scored 25 or below).

Read: RB U9 §3.1 · p. 54 RB U7 §1.4 · p. 21 RB U8 §2.2 · p. 33 RB U9 §3.4 · p. 60

Answer two from each part

Essay · Paper II Parts B and C

Part B

Question 5 · Part B · essay

Paper II Part B (2016, old syllabus). Universal gas constant R = 8.314 J K^{-1} mol^{-1}; Avogadro constant N_A = 6.022 × 10^{23} mol^{-1}. Each Part B/C question carries 15 marks on the paper; the Evaluation Report's scheme is marked out of 150.

(a) [40 marks]

The procedure given below was followed to determine the partition coefficient, K_D of butanedioic acid (BDA, $HOOCCH_2CH_2COOH$) between ether and water at 25 °C.
Initially, 20 g of solid BDA was shaken well with a mixture of approximate volumes of 100 cm^3 of ether and 100 cm^3 of water in a reagent bottle and the layers were allowed to separate. At this stage, some undissolved BDA was seen remaining at the bottom of the reagent bottle. Thereafter, a 50.00 cm^3 volume of ether layer and a 25.00 cm^3 volume of water layer were titrated with 0.05 mol dm^{-3} NaOH solution. The volumes taken from the ether and water layers required 4.80 cm^3 and 16.00 cm^3 of the NaOH solution respectively.
(i) Calculate the partition coefficient, K_D for the distribution of butanedioic acid between ether and water at 25 °C.

Answer

$n_{butanedioic\ acid}/n_{NaOH}$ = 1/2, or any identification of the stoichiometry (05)
Ether layer: $C_{BDA_{ether}}$ = ½ × 0.05 mol dm^{-3} × 4.8 cm^3/50.00 cm^3 (03) = 2.4 × 10^{-3} mol dm^{-3} (04 + 01)
Aqueous layer: $C_{BDA_{aq}}$ = ½ × 0.05 mol dm^{-3} × 16.0 cm^3/25.00 cm^3 (02) = 1.6 × 10^{-2} mol dm^{-3} (04 + 01)
$K_D = [BDA]_{ether}/[BDA]_{aqueous}$ (05) = 2.4 × 10^{-3} mol dm^{-3}/1.6 × 10^{-2} mol dm^{-3} = **0.15** or 3/20 (04 + 01)
or $K_D = [BDA]_{aqueous}/[BDA]_{ether}$ = 1.6 × 10^{-2} mol dm^{-3}/2.4 × 10^{-3} mol dm^{-3} = 6.67 or 20/3
Note: steps can be combined; award marks accordingly.

(ii) Calculate the solubility of butanedioic acid in ether, given that the solubility of this acid in water is 8.0 g dm^{-3}.

Answer

Solubility: $[BDA]_{ether} = K_D[BDA]_{water}$ (03) (= 2.4 × 10^{-3} mol dm^{-3}) (04 + 01)
Consider a mixture having 1.0 dm^3 of ether layer and 1.0 dm^3 of aqueous layer: x/M_{BDA} = 0.15(8.0 g dm^{-3})/M_{BDA} (05); x = **1.2 g dm^{-3}** (04 + 01)
Note: the equation can be accepted without M_{BDA}. (4.0 marks on the paper) · 5(a): 40 marks

Review.

Principle: the partition (distribution) law — at constant temperature the ratio of the concentrations of a solute in two immiscible solvents in contact is constant, $K_D = [BDA]_{ether}/[BDA]_{water}$. The undissolved solid shows both layers are saturated, so the same ratio links the two solubilities: solubility in ether = 0.15 × 8.0 = 1.2 g dm^{-3}. Butanedioic acid is diprotic, so n(acid) = ½ n(NaOH) — forgetting the ½ changes both concentrations but not their ratio. The ratio must be quoted with the solvents in the order stated (0.15 for ether/water, or 6.67 for water/ether). The report notes facilities of only 37% for (i) and 22% for (ii): although this is a basic idea, it comes late in the syllabus and appears to have received little attention. (The scheme's line "$[BDA]_{ether} = K_D[BDA]_{water}$ = 2.4 × 10^{-3} mol dm^{-3}" simply restates the titration result; the solubility step is the 1.2 g dm^{-3} line.)

(b) [40 marks]

Consider the following reactions. Thermodynamic data supplied are **not** for the standard state.

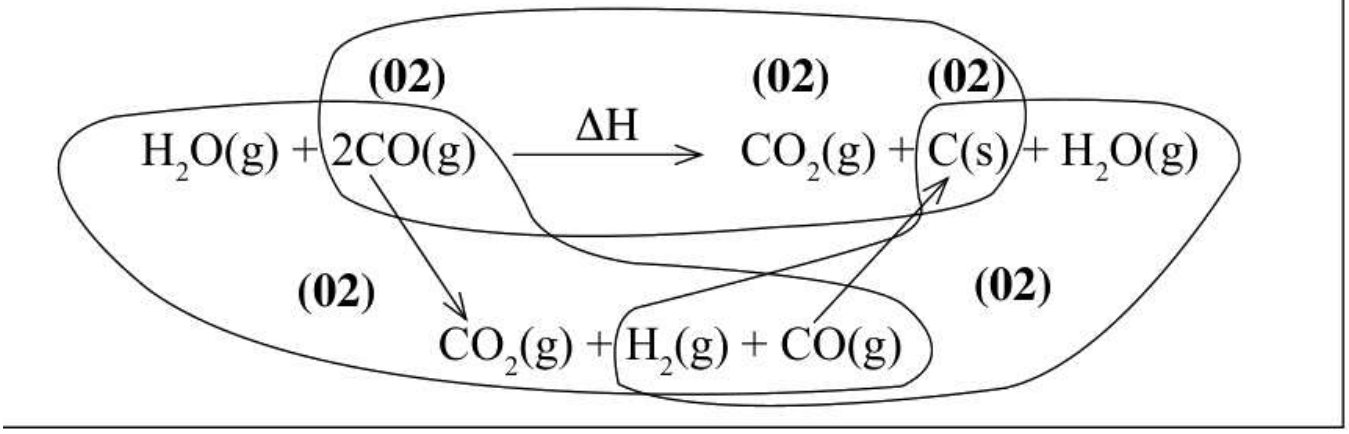
Reaction	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$	130	140
$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$	40	50

2

Answer

Write the two reactions as follows and add:
$CO(g) + H_2(g) \rightarrow C(s) + H_2O(g)$ (02)
$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$ (02)
$2CO(g) \rightarrow C(s) + CO_2(g)$ (02 + 02 + 02)
(The overall reaction must be generated by adding the two reactions for awarding marks.) (Physical states are required.)

Alternate calculation using a thermodynamic cycle



2

2

2

2

2

$\Delta H = -130$ kJ $mol^{-1} - 40$ kJ $mol^{-1} =$ **-170 kJ mol^{-1}** (04 + 01)
$\Delta S = -140$ J K^{-1} $mol^{-1} - 50$ J K^{-1} $mol^{-1} =$ **-190 J K^{-1} mol^{-1}** (04 + 01)
(If standard states are written, do not award marks.)
The sign of ΔS is negative. This agrees with the reduction of entropy, mainly due to the reduction of the number of moles of gases as the forward reaction progresses (2 mol gas → 1 mol gas). (05)

(ii) By means of a suitable calculation, predict whether the reaction given in part (i) above is spontaneous at 27 °C.

Answer

Find ΔG at 27 °C: $\Delta G = \Delta H - T\Delta S$ (02) (if standard states are written, do not award marks)
$\Delta G = -170$ kJ $mol^{-1} - 300$ K × (-190×10^{-3} kJ K^{-1} mol^{-1}) (04 + 01)
$\Delta G =$ **-113 kJ mol^{-1}** (04 + 01)
The forward reaction is spontaneous. (03) (The calculation must be shown for the last 03 marks.) (4.0 marks on the paper) · 5(b): 40 marks

Review.

Principle: Hess's law applies to ΔH and to ΔS because both are state functions. Reverse the first equation (signs change: −130, −140) and reverse the second (−40, −50), then add: $2CO(g) \rightarrow C(s) + CO_2(g)$, $\Delta H = -170$ kJ mol^{-1}, $\Delta S = -190$ J K^{-1} mol^{-1}. $\Delta S < 0$ agrees with 2 mol of gas becoming 1 mol of gas plus a solid. At 300 K, $\Delta G = -170 - 300(-0.190) = -113$ kJ mol^{-1} < 0, so spontaneous. Common mistakes: not converting ΔS from J to kJ (or T to kelvin), and writing ΔH°/ΔS° symbols when the question says the data are not standard (the scheme withholds marks for that). The report gives 37% facility for both parts and says that, although the required equation is obtained just by adding the two given equations, candidates clearly neglected this. Note: in the scheme the second added equation is printed as "$CO(g) + H_2(g) \rightarrow CO_2(g) + H_2(g)$"; it should read $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$ (the reverse of the second given reaction), as transcribed above, and the scheme's "300 K^{-1} mol^{-1}" should read 300 K.

(c) [70 marks]

An excess amount of C(s) and 0.15 mol of $CO_2(g)$ were placed in a closed rigid 2.0 dm^3 container and the system was allowed to reach equilibrium at a temperature of 689 °C. Once the equilibrium was achieved, the pressure in the container was found to be 8.0×10^5 Pa. (Take RT = 8000 J mol^{-1} at 689 °C)
(i) Write an expression for the equilibrium constant, K_p for the reaction $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$.

Answer

$K_p = P_{CO}\text{^}2/P_{CO2}$ (05)

(ii) Calculate K_p and K_c at 689 °C.

Answer

$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$: initial (mol) CO_2 0.15; at equilibrium (mol) CO_2 0.15 − x, CO 2x (05)
Total number of gas moles = 0.15 + x (04 + 01)
Apply PV = nRT assuming ideal behaviour: $0.15 + x = (8.0 \times 10^5 \text{ Pa} \times 2.0 \times 10^{-3} \text{ m}^3)/(8.0 \times 10^3 \text{ J mol}^{-1})$ (04 + 01); x = 0.05 mol (04 + 01)
$n_{CO} = 0.1$ mol (03); $n_{CO2} = (0.15 - 0.05)$ mol = 0.10 mol (02)
Therefore, $P_{CO} = 2 \times 0.05 \times 8.0 \times 10^5$ Pa/0.2 = 4.0×10^5 Pa (04 + 01); $P_{CO2} = 0.1 \times 8.0 \times 10^5$ Pa/0.2 = 4.0×10^5 Pa (04 + 01)
$K_p = (4.0 \times 10^5 \text{ Pa})^2/4.0 \times 10^5$ Pa (04 + 01) = **4.0×10^5 Pa** (04 + 01)
Alternate calculation: $n_{total} = 0.20$ mol, ∴ $X_{CO} = X_{CO2} = ½$ (05); $P_{CO} = 8 \times 10^5$ Pa × ½ = 4×10^5 Pa (04 + 01); $P_{CO2} = 8 \times 10^5$ Pa × ½ = 4×10^5 Pa (04 + 01); $K_p = (4 \times 10^5 \text{ Pa})^2/4 \times 10^5$ Pa (04 + 01); $K_p = 4 \times 10^5$ Pa (04 + 01)
$K_c = K_p(RT)^{-\Delta n}$ or $K_p = K_c(RT)^{\Delta n}$ (03); Δn = 1 (02)
$K_c = 4.0 \times 10^5 \text{ Pa} \times (8 \times 10^3 \text{ J mol}^{-1})^{-1}$; K_c = **50 mol m^{-3} or 0.05 mol dm^{-3}** (04 + 01)
Alternate calculation: $K_c = [CO]^2/[CO_2]$ (05) = $[0.10/(2 \times 10^{-3})]^2/[0.10/(2 \times 10^{-3})] = 50$ mol m^{-3} (0.05 mol dm^{-3}) (04 + 01)

(iii) In another experiment, the container described above contains an excess of C(s) together with CO(g) and $CO_2(g)$ at 689 °C. The initial partial pressure of each gas is 2.0×10^5 Pa. Explain, with the aid of a calculation, the change in partial pressure of $CO_2(g)$ when the system reaches equilibrium.

Answer

Calculate Q using the pressures: Q = $(2.0 \times 10^5 \text{ Pa})^2/2.0 \times 10^5$ Pa = 2.0×10^5 Pa (05)
Q is smaller than K_p. Therefore, **P_{CO2} decreases** and P_{CO} increases until Q = K_p. (05)
Alternate calculation: $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$; pressures (Pa): CO_2 $2 \times 10^5 - x$, CO $2 \times 10^5 + 2x$; $K_p = 4.0 \times 10^5 = (2 \times 10^5 + 2x)^2/(2.0 \times 10^5 - x)$ (05). Solving the quadratic equation and predicting that P_{CO2} decreases and P_{CO} increases. (05) (7.0 marks on the paper) · 5(c): 70 marks · Total for 5: 150 marks

Review.

Principle: heterogeneous equilibrium — the solid C does not appear in K_p or K_c; $K_p = K_c(RT)^{\Delta n}$ with $\Delta n(gas) = 2 - 1 = 1$. Method: the ideal gas equation gives the total amount of gas at equilibrium, $n = PV/RT = (8.0 \times 10^5 \times 2.0 \times 10^{-3})/8000 = 0.20$ mol $= 0.15 + x$, so $x = 0.05$ mol and $n(CO) = n(CO_2) = 0.10$ mol; each partial pressure is 4.0×10^5 Pa, $K_p = 4.0 \times 10^5$ Pa and $K_c = K_p/RT = 50$ mol $m^{-3} = 0.05$ mol dm^{-3}. In (iii) compare the reaction quotient with K_p: $Q = 2.0 \times 10^5$ Pa $< K_p$, so the forward reaction proceeds and P_{CO2} falls (solving the quadratic gives $x \approx 3.4 \times 10^4$ Pa, so $P_{CO2} \approx 1.7 \times 10^5$ Pa). Common mistakes: including C(s) in the expression, writing the total moles as $0.15 - x$ (the scheme itself prints "0.15 − x" for the total, a slip for $0.15 + x$, corrected above; its alternate also prints "$8 \times 10^3 \times ½$" where 8×10^5 Pa × ½ is meant, and "J mol^{-2}" for J mol^{-1}), and forgetting to convert dm^3 to m^3 when using SI units. The report: (c)(i) was the easiest part of the question (81%) because it only asks for the K_p expression, but (c)(ii) was 35% and (c)(iii) only 13%, the lowest of the question — "though the question is simple it has not been understood correctly". Overall facility of Q5 was 36%, although it was the most popular Part B question (71%). The report stresses practising the basic concepts in the syllabus rather than very complicated problems.

Read: RB U12 §2.7 · p. 229 RB U5 §2.4 · p. 53 RB U12 §2.1 · p. 76 RB U4 §1.2 · p. 5

Question 6 · Part B · essay

(a) [50 marks]

A 0.10 mol dm^{-3} solution of a weak acid, **HA** was prepared by diluting an appropriate amount of the pure weak acid to 25.00 cm^3 with distilled water in a volumetric flask at 25 °C. The pH of this solution was 3.0.
(i) Considering the equation, $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$, calculate the dissociation constant, K_a of the weak acid.

Answer

pH = 3.0; $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3} (04 + 01)
$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$
$K_a = [H_3O^+(aq)][A^-(aq)]/[HA(aq)]$ (02) (physical states are required)
$= (1.0 \times 10^{-3}$ mol $dm^{-3})^2/0.10$ mol dm^{-3} (02 + 01) = **1.0×10^{-5} mol dm^{-3}** (02 + 01)

(ii) A dilute solution of this weak acid, **HA** was titrated with a strong base, **BOH**. It was found that the pH of the titration mixture after reaching the equivalence point was 9.0. Calculate the concentration of the salt, **AB** in the titration mixture. ($K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6} at 25 °C)

Answer

The pH at the equivalence point is determined by the degree of hydrolysis of the salt. Consider $A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$ (05)
$K_a/K_w = \{[H_3O^+(aq)][A^-(aq)]/[HA(aq)]\}/\{[H_3O^+(aq)][OH^-(aq)]\}$
At the equivalence point $[HA(aq)] \approx [OH^-(aq)]$, so $K_a/K_w = [A^-(aq)]/[OH^-(aq)]^2$
$[OH^-(aq)] = \{[A^-(aq)]K_w/K_a\}^{1/2}$ ——— (1) (05)
At the equivalence point $[A^-(aq)]$ = [salt]. Since pH = 9.0 at the equivalence point, $[OH^-] = 10^{-5}$ mol dm^{-3} (02)
[salt] $= ([OH^-(aq)])^2 K_a/K_w = (1.0 \times 10^{-5}$ mol $dm^{-3})^2 \times (1.0 \times 10^{-5}$ mol $dm^{-3})/(1.0 \times 10^{-14}$ mol^2 $dm^{-6})$ (04 + 01) = **0.1 mol dm^{-3}** (04 + 01)

(iii) The above titration mixture was diluted hundred times by adding distilled water. Calculate the pH of the diluted titration mixture.

Answer

When the titration mixture at the equivalence point is 100 times diluted, the salt concentration is decreased by 100 times. Using equation (1):
$[OH^-(aq)]_{new} = \{([A^-(aq)]/100)(K_w/K_a)\}^{1/2}$ (05) $= (1/10)\{[A^-(aq)]K_w/K_a\}^{1/2} = (1/10)\{(0.1\ mol\ dm^{-3})(1 \times 10^{-14}\ mol^2\ dm^{-6})/(1 \times 10^{-5}\ mol\ dm^{-3})\}^{1/2}$ (04 + 01)
$[OH^-(aq)] = 1.0 \times 10^{-6}\ mol\ dm^{-3}$; $[H_3O^+(aq)] = 1.0 \times 10^{-8}\ mol\ dm^{-3}$; therefore **pH = 8.0** (05)
Alternate calculation: $A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$, with $c(1 - \alpha)$, $c\alpha$, $c\alpha$. By Ostwald's law, $K_b = \alpha^2c = \alpha^2c^2/c = [OH^-]^2/c$; $[OH^-] = \sqrt{(K_{bc})} = \sqrt{((K_w/K_a)c)}$ (05); [salt] $= [A^-] = c = 0.1\ mol\ dm^{-3}/100$; $[OH^-] = \sqrt{\{(1 \times 10^{-14}\ mol^2\ dm^{-6}/1 \times 10^{-5}\ mol\ dm^{-3}) \times (1 \times 10^{-1}\ mol\ dm^{-3}/100)\}} = 1 \times 10^{-6}\ mol\ dm^{-3}$ (04 + 01); pOH = 6.0; pH = 8.0 (05) (5.0 marks on the paper) · 6(a): 50 marks

Review.

Principle: weak-acid equilibrium and salt hydrolysis. With pH 3.0, $[H_3O^+] = [A^-] = 10^{-3}\ mol\ dm^{-3}$ and $[HA] \approx 0.10\ mol\ dm^{-3}$ (dissociation only 1%), so $K_a = 1.0 \times 10^{-5}\ mol\ dm^{-3}$. At the equivalence point the solution contains only the salt AB; A^- hydrolyses ($K_b = K_w/K_a = 10^{-9}\ mol\ dm^{-3}$) and $[OH^-] = \sqrt{(K_{bc})}$. From pH 9.0, $[OH^-] = 10^{-5}$, so $c = (10^{-5})^2/10^{-9} = 0.1\ mol\ dm^{-3}$. Diluting 100 times lowers $[OH^-]$ by $\sqrt{100} = 10$, so pOH = 6 and pH = 8.0 — not pH 7 and not a fall of 2 pH units, the usual errors. The report gives facilities of 53%, 12% and only 6% (the lowest of the whole question) for (i)–(iii) and asks for more attention to salt hydrolysis. Note: in the scheme's alternate the square root is printed as $\sqrt{((K_a/K_w)c)}$; it should be $\sqrt{((K_w/K_a)c)}$, as the numbers substituted in the next line show (corrected above).

(b) [50 marks]

AgBr(s) is a pale-yellow coloured salt sparingly soluble in water. Its solubility product, K_{sp} is $5.0 \times 10^{-13}\ mol^2\ dm^{-6}$ at 25 °C.
(i) Calculate the concentration of $Ag^+(aq)$ in a saturated solution of AgBr in equilibrium with solid AgBr at 25 °C.

Answer

$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$ (05)
$K_{sp} = [Ag^+(aq)][Br^-(aq)]$ (03); $[Ag^+(aq)] = [Br^-(aq)] = x$; $K_{sp} = x^2$ (02)
Therefore, $[Ag^+(aq)] = (5.0 \times 10^{-13})^{1/2} =$ **$7.07 \times 10^{-7}\ mol\ dm^{-3}$** or $7.1 \times 10^{-7}\ mol\ dm^{-3}$ (04 + 01)

(ii) Solid AgBr together with 100.0 cm^3 of the solution described in part (i) above were placed in a beaker. A volume of 100.0 cm^3 of distilled water was added to the beaker and the mixture was stirred well until the equilibrium is reached. At this stage, some solid AgBr was still left at the bottom of the beaker. What could be the concentration of $Ag^+(aq)$ in this solution? Explain your answer.

Answer

The solution is a saturated solution of AgBr. (05) Therefore, $[Ag^+(aq)]$ is the same as above, **$7.07 \times 10^{-7}\ mol\ dm^{-3}$**. (05)

(iii) Using a suitable calculation, predict the observation expected when 10.0 cm^3 of a $1.5 \times 10^{-4}\ mol\ dm^{-3}$ $AgNO_3$ solution and 5.0 cm^3 of a $6.0 \times 10^{-4}\ mol\ dm^{-3}$ NaBr solution are mixed at 25 °C.

Answer

The product of the concentrations of Ag^+ and Br^- must be calculated and compared with K_{sp}.
$[Ag^+(aq)] = 1.5 \times 10^{-4}\ mol\ dm^{-3} \times 10.00\ cm^3/15.00\ cm^3 = 1.0 \times 10^{-4}\ mol\ dm^{-3}$ (04 + 01)
$[Br^-(aq)] = 6.0 \times 10^{-4}\ mol\ dm^{-3} \times 5.00\ cm^3/15.00\ cm^3 = 2.0 \times 10^{-4}\ mol\ dm^{-3}$ (04 + 01)
$[Ag^+(aq)] \times [Br^-(aq)] = 2.0 \times 10^{-8}\ mol^2\ dm^{-6} > K_{sp}$ (10) [or any other correct approach]
Therefore, **AgBr will precipitate** (a pale yellow precipitate will form). (05) (5.0 marks on the paper) · 6(b): 50 marks

Review.

Principle: solubility product. For a 1:1 salt the solubility s = $\sqrt{K_{sp}}$ = 7.1 × 10^{-7} mol dm^{-3}. In (ii) the key word is that solid AgBr is still present: the solution is saturated at the same temperature, so [Ag^{+}] is unchanged — halving it for the dilution is the common wrong answer. In (iii) first find the concentrations after mixing (total volume 15.0 cm^3), then compare the ionic product with K_{sp}; 2.0 × 10^{-8} > 5.0 × 10^{-13}, so a pale-yellow precipitate of AgBr forms. Forgetting the dilution on mixing is the main slip here (it does not change the conclusion in this case). The report: (b)(i) was the easiest part of the question (56%), but (ii) only 21% and (iii) 16%.

(c) [50 marks]

(i) The pressure of the vapour phase in equilibrium with an ideal binary solution is P. The liquid phase mole fractions of the two components are X_1 and X_2, and their respective saturated vapour pressures are P_1^0 and P_2^0. Show that X_1 = (P − P_2^0)/(P_1^0 − P_2^0).

Answer

Applying Raoult's law to the ideal binary mixture: P_i = x_{iPi}^0 (05); P = P_1 + P_2 (05); P = x_1P_1^0 + x_2P_2^0 (05); x_2 = 1 − x_1; P = x_1P_1^0 + (1 − x_1)P_2^0; x_1 = (P − P_2^0)/(P_1^0 − P_2^0) (05)

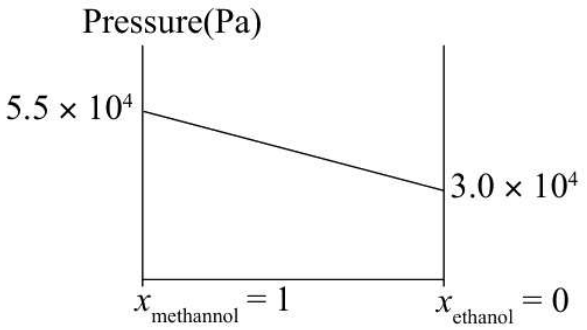
(ii) The pressure of the vapour phase in equilibrium with a binary solution containing methanol and ethanol is 4.5 × 10^4 Pa at 50 °C. At this temperature the saturated vapour pressures of methanol and ethanol are 5.5 × 10^4 Pa and 3.0 × 10^4 Pa respectively. Consider that the solutions behave ideally.
I. Calculate the mole fractions of methanol and ethanol in the liquid phase.
II. Calculate the mole fractions of methanol and ethanol in the vapour phase.

Answer

I. Mole fractions in the liquid phase: x_{MeOH} = (4.5 − 3.0) × 10^4 Pa/(5.5 − 3.0) × 10^4 Pa = **0.6** (04 + 01); x_{EtOH} = 1 − 0.6 = **0.4** (04 + 01)
II. Mole fractions in the gas phase: $x_{methanol,\ gas}$ = 0.6 × 5.5 × 10^4 Pa/4.5 × 10^4 Pa = **0.73** (04 + 01); $x_{ethanol,\ gas}$ = 1.0 − 0.73 = **0.27** (04 + 01) (Answers can be given as fractions: 11/15 and 4/15.)

(iii) Based on the above calculations and given information, draw the vapour pressure - composition diagram of the methanol - ethanol mixture at 50 °C. Consider that the solutions behave ideally.

Answer



mole fractions on horizontal axis	**(02)**
Saturated vapour pressures corresponding to mole fractions	**(04)**
Straight line showing P total with correct slope	**(04)**

Pressure–composition diagram (ideal mixture), as given in the scheme

Pressure (Pa) on the vertical axis; a straight line for the total vapour pressure from 5.5 × 10^4 Pa (pure methanol) to 3.0 × 10^4 Pa (pure ethanol).
Mole fractions on the horizontal axis (02); saturated vapour pressures corresponding to the mole fractions (04); straight line showing P_{total} with the correct slope (04)
Note: if more than one line is drawn, the P_{total} line must be labelled. (5.0 marks on the paper) · 6(c): 50 marks · Total for 6: 150 marks

Review.

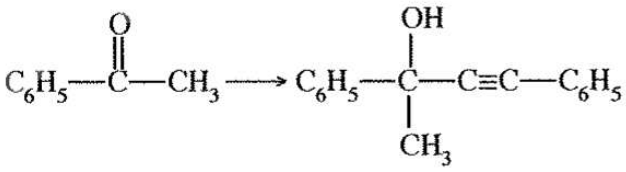
Principle: Raoult's law for an ideal binary solution, $P_i = x_{iPi}$^0, with Dalton's law $P = P_1 + P_2$ and, for the vapour, $y_i = P_i/P$. Liquid: x(MeOH) = (4.5 − 3.0)/(5.5 − 3.0) = 0.60; vapour: y(MeOH) = 0.60 × 5.5/4.5 = 0.73, so the vapour is richer in the more volatile component (methanol). The total-pressure line of an ideal mixture is straight between the two pure vapour pressures; the point (x = 0.6, 4.5 × 10^4 Pa) lies on it. Common mistakes: using the liquid mole fraction for the vapour, and unlabelled axes. The report gives facilities of 42%, 28% and 26% for (c)(i)–(iii); (iii) was easy but marks were lost because the earlier parts were wrong, and it asks for more attention to phase equilibrium. Overall facility was low (selected by 58%; 50% scored 37/150 or less); the report blames lack of practice with calculations. Note on the scheme: its last line of (i) prints "($P_1 - P_2$^0)" where $P - P_2$^0 is meant, and the axis of its diagram labels both ends as pure methanol ($x_{methanol} = 1$ at the left, "$x_{ethanol} = 0$" at the right); the right-hand end should be $x_{ethanol} = 1$ ($x_{methanol} = 0$), where P = 3.0 × 10^4 Pa.

Read: RB U12 §2.2 · p. 118 RB U12 §2.4 · p. 175 RB U12 §2.6 · p. 216

Question 7 · Part B · essay

(a) [60 marks]

Using **only** the chemicals given in the list, show how you would carry out the following conversion. List of chemicals: H_2O, alcoholic KOH, Br_2, Conc. H_2SO_4, $NaBH_4$, C_2H_5MgBr/dry ether.
Your conversion should not exceed 9 steps.



List of chemicals

H_2O, alcoholic KOH, Br_2, Conc. H_2SO_4, $NaBH_4$, C_2H_5MgBr/dry ether

6

5

3

6

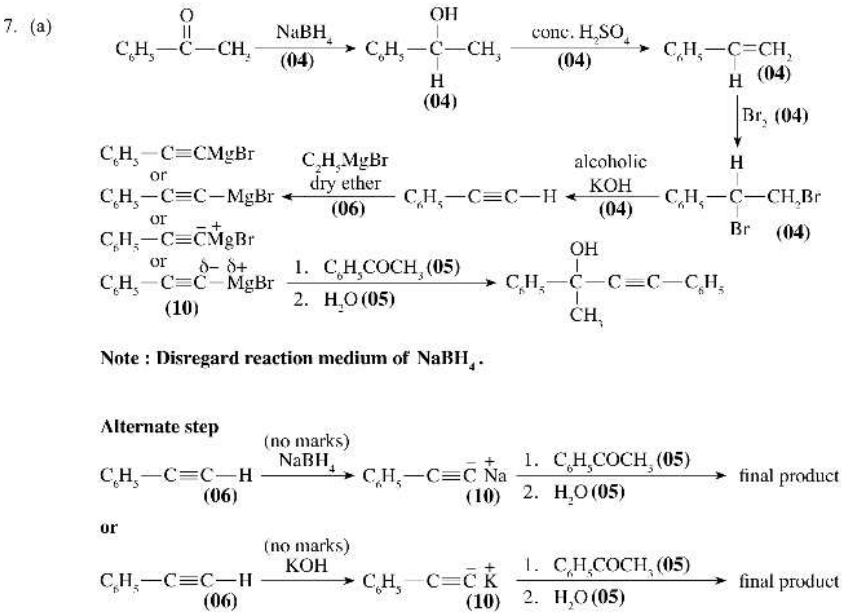
5

3

6

5

Answer



Scheme answer for 7(a), with the alternate step

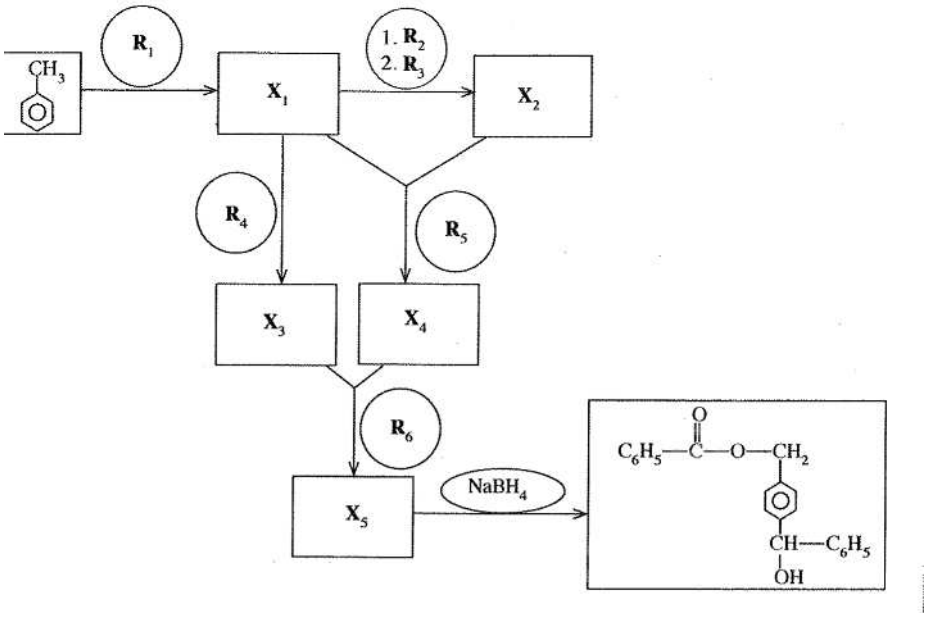
$C_6H_5COCH_3$ —$NaBH_4$ (04)→ $C_6H_5CH(OH)CH_3$ (04) —conc. H_2SO_4 (04)→ $C_6H_5CH{=}CH_2$ (04) —Br_2 (04)→ $C_6H_5CHBrCH_2Br$ (04) —alcoholic KOH (04)→ $C_6H_5C{\equiv}CH$ —C_2H_5MgBr/dry ether (06)→ $C_6H_5C{\equiv}CMgBr$ (or $C_6H_5C{\equiv}C{-}MgBr$, or $C_6H_5C{\equiv}C^{\wedge}{-}Mg^{\wedge}{+}Br$, or $C_6H_5C{\equiv}C^{\delta-}{-}MgBr^{\delta+}$) (10) —1. $C_6H_5COCH_3$ (05), 2. H_2O (05)→ $C_6H_5C(OH)(CH_3)C{\equiv}CC_6H_5$
Note: disregard the reaction medium of $NaBH_4$.
Alternate step: $C_6H_5C{\equiv}CH$ (06) —$NaBH_4$ (no marks)→ $C_6H_5C{\equiv}C^{\wedge}{-}Na^{+}$ (10) —1. $C_6H_5COCH_3$ (05), 2. H_2O (05)→ final product; or $C_6H_5C{\equiv}CH$ (06) —KOH (no marks)→ $C_6H_5C{\equiv}C^{\wedge}{-}K^{+}$ (10) —1. $C_6H_5COCH_3$ (05), 2. H_2O (05)→ final product (6.0 marks on the paper) · 7(a): 60 marks

Review.

Principle: building a C–C bond with an alkynyl Grignard reagent. Work backwards: the target is a tertiary alcohol formed when $C_6H_5C{\equiv}C^{-}$ (as $C_6H_5C{\equiv}CMgBr$) adds to the C=O of the starting ketone $C_6H_5COCH_3$, so some of the starting material is kept aside as the electrophile. The phenylethyne is made from the same ketone: reduce ($NaBH_4$) to the secondary alcohol, dehydrate (conc. H_2SO_4) to styrene, add Br_2 to give the vicinal dibromide, and do a double dehydrobromination with alcoholic KOH. The terminal alkyne is acidic enough to be deprotonated by C_2H_5MgBr (ethane is released), giving the alkynyl Grignard reagent; this addition followed by H_2O work-up gives the product (8 steps). The report notes that the key idea — using the given Grignard reagent to make another Grignard reagent from the terminal alkyne — was the difficulty, and recommends more practice with such conversions. Note on marks: the marks printed in the main route add to 54 of the 60; the alternate step awards (06) for $C_6H_5C{\equiv}CH$, which suggests the alkyne itself also carries (06) in the main route.

(b) [70 marks]

Identify **R_1 – R_6** and **X_1 – X_5** in order to complete the following reaction scheme.



1

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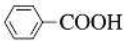
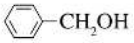
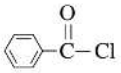
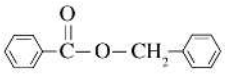
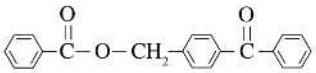
Answer

(b)

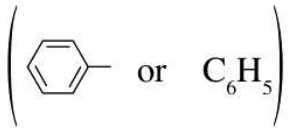
R_1	$KMnO_4/H^+$ or $K_2Cr_2O_7/H^+$ or CrO_3	(06)	X_1		(07)
R_2	$LiAlH_4$	(06)	X_2		(07)
R_3	H^+ or dil. HCl or dil. H_2SO_4 or H_2O	(05)	X_3		(07)
R_4	PCl_5 or PCl_3 or $SOCl_2$	(06)	X_4		(07)
R_5	conc. H_2SO_4 or $SOCl_2$	(06)	X_5		(07)

1

5

1

5

R_6 anhydrous $AlCl_3$ **(06)**  (or C_6H_5) **(07)**

Note : For X_1 to X_4, if is given instead of penalize only once.
For X_5, all aromatic rings must be shown for award of marks.

6

R_1: $KMnO_4/H^+$ or $K_2Cr_2O_7/H^+$ or CrO_3 (06); X_1: C_6H_5COOH (benzoic acid) (07)
R_2: $LiAlH_4$ (06); X_2: $C_6H_5CH_2OH$ (benzyl alcohol) (07)
R_3: H^+ or dil. HCl or dil. H_2SO_4 or H_2O (05); X_3: C_6H_5COCl (benzoyl chloride) (07)
R_4: PCl_5 or PCl_3 or $SOCl_2$ (06); X_4: $C_6H_5COOCH_2C_6H_5$ (benzyl benzoate) (07)
R_5: conc. H_2SO_4 or $SOCl_2$ (06); X_5: $C_6H_5COOCH_2$–C_6H_4–COC_6H_5 (the benzoyl group para to the CH_2 on the benzyl ring) (07)
R_6: anhydrous $AlCl_3$ (06) (phenyl may be drawn as a benzene ring or written C_6H_5)
Note: for X_1 to X_4, if a cyclohexane ring is given instead of a benzene ring, penalize only once. For X_5, all aromatic rings must be shown for award of marks. (7.0 marks on the paper) · 7(b): 70 marks

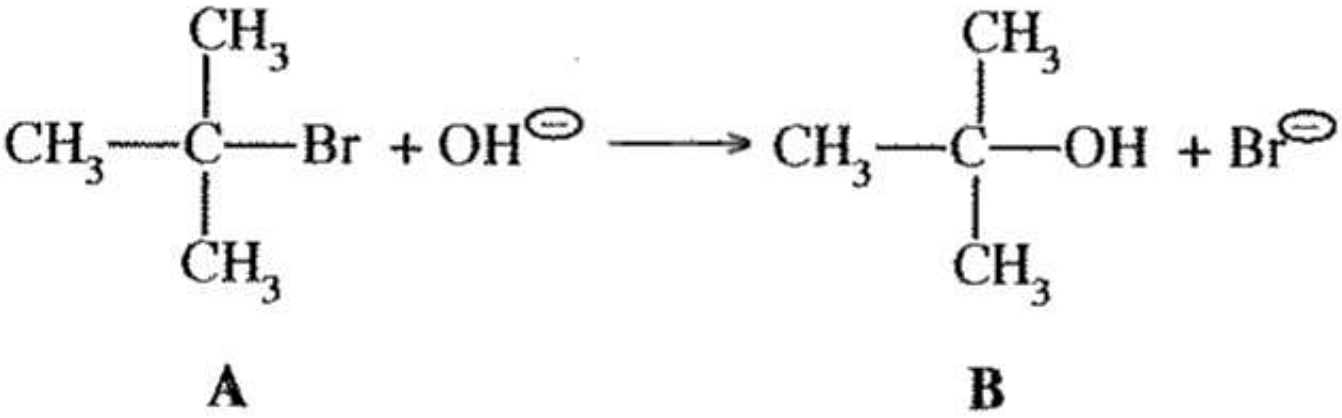
Review.

Principle: interconversions of aromatic side chains and carboxylic acid derivatives. Side-chain oxidation of toluene gives benzoic acid (X_1); $LiAlH_4$ then aqueous acid work-up reduces it to benzyl alcohol (X_2); PCl_5 (or $PCl_3/SOCl_2$) converts the acid to benzoyl chloride (X_3); benzoic acid and benzyl alcohol esterify (conc. H_2SO_4) to benzyl benzoate (X_4). Friedel–Crafts acylation of X_4 with X_3/anhydrous $AlCl_3$ puts a C_6H_5CO– group para to the –CH_2– on the activated (alkyl-substituted) ring, and $NaBH_4$ reduces only the ketone C=O to CH(OH), leaving the ester untouched, which gives the boxed product — this fixes the structure of X_5. Common mistakes: using $NaBH_4$ for the acid → alcohol step (it does not reduce –COOH), and drawing the acyl group on the benzoate ring (deactivated by the ester C=O). The report gives a facility of 50% for (b). Note on the

scheme: R_5 lists "$SOCl_2$" as an alternative; strictly, the esterification step is the acid-catalysed reaction of X_1 with X_2. The scheme also prints a stray "(07)" beside R_6 (the part total of 70 is reached with 06 for R_6), so the R_6 line carries 06 marks.

(c) [20 marks]

(i) Give the mechanism for the following reaction.



3

3

–

3

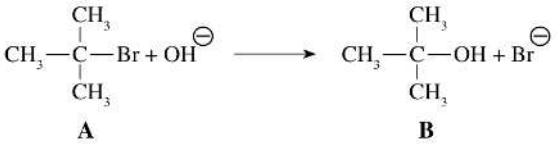
3

–

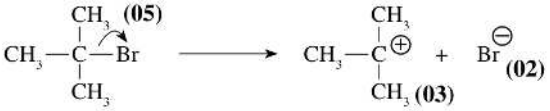
(ii) The reaction of **A** with NaOH, gives in addition to **B** another product **C**. Give the structure of **C**.

Answer

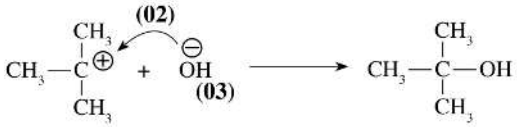
c) (i)



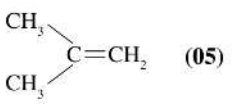
Step I



Step II



(ii)



N1

(i) Step I: the C–Br bond breaks heterolytically (curved arrow from the C–Br bond to Br) (05), giving the tertiary carbocation $(CH_3)_3C^+$ (03) and Br^- (02).

Step II: OH^- (03) attacks the carbocation (curved arrow from OH^- to C^+) (02) to give $(CH_3)_3C–OH$.
(ii) C: $(CH_3)_2C=CH_2$ (2-methylpropene) (05) (2.0 marks on the paper) · 7(c): 20 marks · Total for 7: 150 marks

Review.

Principle: nucleophilic substitution of a tertiary alkyl halide goes by the S_{N1} route — slow ionisation to a stable tertiary carbocation, then fast attack by OH^-; curved arrows must start at the bond or lone pair and end at the atom receiving the electrons. In the presence of OH^- (a base) elimination of HBr competes, giving 2-methylpropene. The report gives facilities of 50% for (c)(i) and only 28% for (c)(ii), the lowest of the question, because candidates forgot that alkyl halides undergo elimination of HX as well as nucleophilic substitution with OH^-. The Resource Book (alkyl halides) describes this two-step carbocation route for tertiary halides and the competition between substitution (aqueous KOH) and elimination (ethanolic KOH). Q7 was the least-chosen Part B question (51%), overall facility 46%.

Read: RB U9 §3.4 · p. 60 RB U8 §2.6 · p. 49 RB U8 §2.7 · p. 50 RB U8 §2.4 · p. 44

Part C

Question 8 · Part C · essay

Paper II Part C (2016, old syllabus). Answer two questions only (each question carries 15 marks on the paper; the scheme is marked out of 150).

(a) [50 marks]

The compound **A** (**A** = MX_n, M = a transition element that belongs to the 3d-block, X = ligands of the same type) when treated with excess dilute NaOH followed by H_2O_2 gives a compound **B**. When an aqueous solution of **B** is acidified with dil. H_2SO_4 compound **C** is produced. **C** when reacted with NH_4Cl gives compound **D** as one of the products. Heating solid **D** gives a blue coloured compound **E**, water vapour and an inert diatomic gas **F**. Ca metal when burnt in gas **F** gives a white solid **G**. The reaction of **G** with water liberates a gas **H**. This gas forms white fumes with HCl gas. The metal Na reacts with liquid **H** to give a colourless diatomic gas **I** as one of the products. When an aqueous solution of **A** is treated with excess Na_2CO_3, a coloured precipitate is formed. The precipitate is filtered and the filtrate is acidified with dil HNO_3. Addition of $AgNO_3$(aq) to this solution gives a white precipitate which is soluble in dilute NH_4OH.
(i) Identify **A**, **B**, **C**, **D**, **E**, **F**, **G**, **H** and **I**.

Answer

A: $CrCl_3$ or $CrCl_3·H_2O$ or $[Cr(H_2O)_6]Cl_3$
B: Na_2CrO_4
C: $Na_2Cr_2O_7$
D: $(NH_4)_2Cr_2O_7$
E: Cr_2O_3 (award (05) for any chromium compound)
F: N_2
G: Ca_3N_2
H: NH_3
I: H_2 (05 × 9 = 45 marks)

(ii) What will you observe when a solution containing **C** is treated with dil. NaOH? Give the balanced chemical equation relevant to this observation.

Answer

The orange solution C turns yellow. (01 + 01)
$Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$ (03) 8(a): 50 marks

Review.

Principle: chromium chemistry and the nitrogen cycle of reactions. Cr^{3+} is oxidised by H_2O_2 in alkali to yellow chromate (B, Na_2CrO_4); acid converts chromate to orange dichromate (C, $Na_2Cr_2O_7$) — the $2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$ equilibrium, which OH^- pushes back to yellow chromate in (ii). With NH_4Cl, ammonium dichromate D forms; on heating it decomposes to Cr_2O_3, H_2O and N_2 (F). Ca burns in N_2 to give Ca_3N_2 (G), which hydrolyses to NH_3 (H, white fumes of NH_4Cl with HCl); Na in liquid NH_3 gives $NaNH_2$ and H_2 (I). The white precipitate soluble in dilute NH_4OH is AgCl, so the ligands X are Cl^-. Note: Cr_2O_3 is **green**, not blue as the question states; the scheme allows (05) for any chromium compound for E, presumably for this reason. The scheme's printed formula "$[Cr(H_2O)_6]3Cl^-$" means $[Cr(H_2O)_6]Cl_3$, and its equation omits the 2− charge on $Cr_2O_7^{2-}$ (both corrected above). The report gives facilities of 40% for (i) and 24% for (ii) and stresses learning the colours of d-block compounds.

(b) [50 marks]

An aqueous solution **T** contains **three** metal ions. The following experiments were carried out to identify these metal ions.

Experiment	Observation
1. T was acidified with dilute HCl, and H_2S was bubbled through the clear solution obtained.	A black precipitate Q_1 was formed.
2. Q_1 was removed by filtration. The filtrate was boiled till all the H_2S was removed. The solution was cooled, and NH_4Cl and NH_4OH were added.	A clear solution was obtained.
H_2S was bubbled through the solution.	A black precipitate Q_2 was formed.
3. Q_2 was removed by filtration. The filtrate was boiled till all the H_2S was removed, and a solution of $(NH_4)_2CO_3$ was added.	A white precipitate Q_3 was formed.

1

2

3

Experiment	Observation
1. Q_1 was dissolved in hot dilute HNO_3. After cooling, the solution was neutralized and KI was added.	A precipitate and a brown solution were formed.
2. Q_2 was dissolved in warm dilute HCl. The solution was cooled, and dilute NH_4OH was added.	A green precipitate was formed.
More dilute NH_4OH was added to this mixture.	The green precipitate dissolved giving a deep blue solution.
3. Q_3 was dissolved in conc. HCl and the solution was subjected to the flame test.	A green flame was obtained.

three

T

Reasons are not required.

Answer

T contains: **Cu^{2+}, Ni^{2+}, Ba^{2+}** (10 + 10 + 10)

(ii) Write the chemical formulae of the precipitates **Q_1**, **Q_2**, and **Q_3**.

Answer

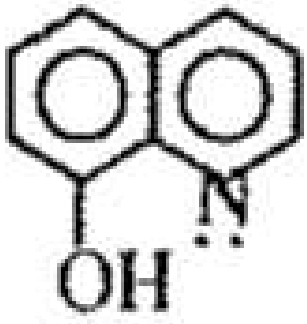
Q_1: **CuS**; Q_2: **NiS**; Q_3: **$BaCO_3$** (07 + 07 + 06)
Note: (i) charges are required. (ii) mark independently. 8(b): 50 marks

Review.

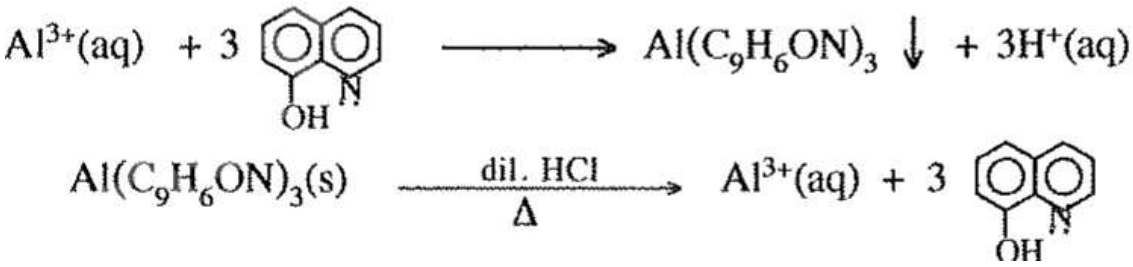
Principle: separation of cations by controlled sulfide precipitation (Resource Book, solubility product and qualitative analysis). In acid, $[S^{2-}]$ is very low so only the very insoluble sulfides precipitate — black CuS (Q_1). In NH_4Cl/NH_4OH, $[S^{2-}]$ rises and NiS (black, Q_2) precipitates. The remaining alkaline-earth ion is precipitated by $(NH_4)_2CO_3$ as white $BaCO_3$ (Q_3). Confirmations: $Cu^{2+} + I^-$ gives a CuI precipitate and I_2 (brown, as I_3^−); Ni^{2+} gives green $Ni(OH)_2$ that dissolves in excess NH_3 to give deep blue $[Ni(NH_3)_6]^{2+}$; Ba^{2+} gives a green flame. A common trap is to read "deep blue with excess NH_3" as Cu^{2+} — but the hydroxide precipitate here is green, which marks Ni^{2+}. Facilities were 49% for (i) (the easiest part of the question) and 48% for (ii).

(c) [50 marks]

The following procedure was used to determine the concentration of Al^{3+} ions in solution **U**.
Excess 8-hydroxyquinoline (commonly known as oxine, C_9H_7ON) was added to 25.0 cm^3 of solution **U** at pH = 5 to precipitate Al^{3+} ions as aluminium oxinate, $Al(C_9H_6ON)_3$. The precipitate was filtered, washed with distilled water and dissolved in warm dilute HCl containing excess KBr. Thereafter, 25.0 cm^3 of 0.025 mol dm^{-3} $KBrO_3$ was added to this solution. The reactions taking place in the above procedure are as follows:



Oxine (8-hydroxyquinoline)



3+

9

6

3

+

9

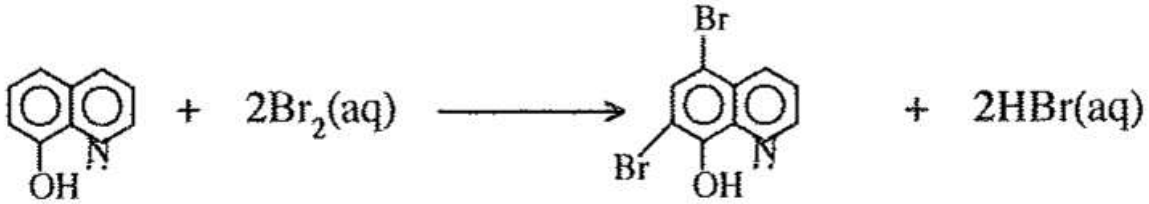
6

3

3+

$KBrO_3$ is a primary standard for the generation of Br_2 in acidic medium.

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \longrightarrow 3\ Br_2(aq) + 3H_2O(l)$$



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2

2

The excess Br_2 is reacted with KI to give I_3^−. Then I_3^− was titrated with 0.05 mol dm^{-3} $Na_2S_2O_3$ using starch as the indicator. The volume of $Na_2S_2O_3$ required to reach the end point was 15.00 cm^3. Calculate the concentration of Al^{3+} in solution **U** in mg dm^{-3}. (Al = 27)

Answer

I_3^− + $2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 3I^-$ or $I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$ (02)
$Br_2 + 2I^- \rightarrow I_2 + 2Br^-$ (02)
Moles of $S_2O_3^{2-}$ = (0.05/1000) × 15.0 (03)
Therefore, moles of I_2 = ½ × (0.05/1000) × 15.0 (03)
Therefore, moles of excess Br_2 = ½ × (0.05/1000) × 15.0 (03) = 3.75×10^{-4} (02)
BrO_3^− + $5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$
Moles of BrO_3^− = (0.025/1000) × 25.0 (03)
Therefore, moles of Br_2 produced by the above reaction = 3 × (0.025/1000) × 25.0 (03) = 18.75×10^{-4} (02)
Amount of Br_2 reacted with oxine = $(18.75 \times 10^{-4}) - (3.75 \times 10^{-4})$ (03) = 15×10^{-4} (02)
Therefore, moles of oxine = ½ × 15×10^{-4} (03) = 7.5×10^{-4} (02)
Therefore, moles of Al^{3+} = ⅓ × 7.5×10^{-4} (03) = 2.5×10^{-4} (02)
$[Al^{3+}]$ = $(2.5 \times 10^{-4}/25.0) \times 1000$ mol dm^{-3} (03) = $(2.5 \times 10^{-4}/25.0) \times 1000 \times 27$ g dm^{-3} (03) = $(2.5 \times 10^{-4}/25.0) \times 1000 \times 27 \times 1000$ mg dm^{-3} (03) = **270 mg dm^{-3}** (03) 8(c): 50 marks · Total for 8: 150 marks

Review.

Principle: a back titration chained through several stoichiometric ratios. Br_2 generated: 3 × n(BrO_3^−) = 3 × 6.25×10^{-4} = 1.875×10^{-3} mol. Excess Br_2 = n(I_2) = ½ n($S_2O_3^{2-}$) = ½ × 7.5×10^{-4} = 3.75×10^{-4} mol. Br_2 used = 1.50×10^{-3} mol; each oxine takes $2Br_2$, so oxine = 7.5×10^{-4} mol; each Al^{3+} binds 3 oxine, so Al^{3+} = 2.5×10^{-4} mol in 25.0 cm^3 = 0.010 mol dm^{-3} = 0.27 g dm^{-3} = 270 mg dm^{-3}. Common mistakes: using the 1:2 thiosulfate ratio the wrong way, forgetting the factor 3 in the bromate reaction, and forgetting to subtract the excess. The report gives only 18% facility (the lowest in the question) and says the complex formula and compound put candidates off: Q8 was the least-chosen question in Paper II (41%), although read carefully it needed only a calculation using the stoichiometric ratios.

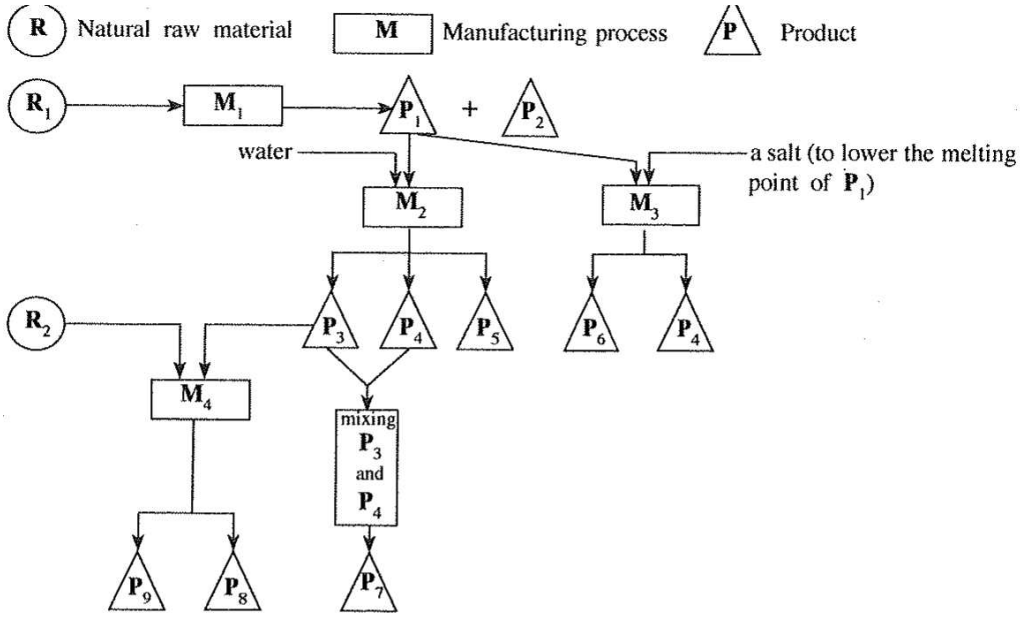
Read: RB U6 §4.10 · p. 160 RB U6 §4.5 · p. 136 RB U12 §2.4 · p. 175 RB U3 §3.8 · p. 115

Question 9 · Part C · essay

(a) [75 marks]

A flow chart drawn by a final year university student to establish a chemical industry in the future in Sri Lanka is given below.

The following symbols are used to represent natural raw materials, manufacturing processes and products:
(R) natural raw material, [M] manufacturing process, /P\ product.



1

1

1

2

1

2

3

4

5

1

1

3

6

4

2

3

4

9

8

3

4

7

P_2 is used to produce a halogen that exists as a liquid at room temperature.
P_7 is used as a bleaching agent/strong oxidizing agent.
P_8 is used daily to maintain good hygiene.
(i) Identify the **two** natural raw materials $\mathbf{R_1}$ and $\mathbf{R_2}$.

Answer

R_1: Sea water (03)
R_2: Oil / Fats / Coconut oil / Vegetable oil (03)

(ii) Identify the **four** manufacturing processes $\mathbf{M_1}$, $\mathbf{M_2}$, $\mathbf{M_3}$ and $\mathbf{M_4}$ [e.g. manufacture of ammonia or Haber process]

Answer

M_1: Manufacture of salt (03)
M_2: Manufacture of NaOH (03)
M_3: Manufacture / extraction of Na (Downs cell method) (03)
M_4: Manufacture of soap (03)

(iii) Identify the products $\mathbf{P_1}$ to $\mathbf{P_9}$.

Answer

P_1: NaCl (03)
P_2: Bittern solution / Mother liquor / $MgBr_2$ (03)
P_3: NaOH (03)
P_4: Cl_2 (03)
P_5: H_2 (03)
P_6: Na (03)
P_7: NaOCl / Milton solution (03)
P_8: Soap (03)
P_9: Glycerol / Glycerine (03)

(iv) Briefly describe the steps involved in processes $\mathbf{M_1}$ and $\mathbf{M_3}$. (diagrams of equipment **not** required.)

Answer

1

(01)

3

(01)

(01)

4

(01)

(01)

(01)

(01)

3

2

(01)

+

(02)

−

2

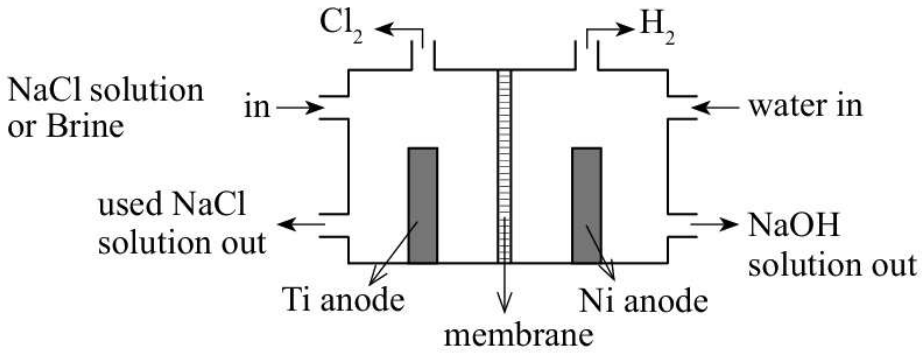
(02)

2

(02)

(v) Draw and label the equipment used in the process **M_2**.

Answer



Note : Mark independently.

(01 marks × 9 + 01 for correct sketch of cell = 10 marks)

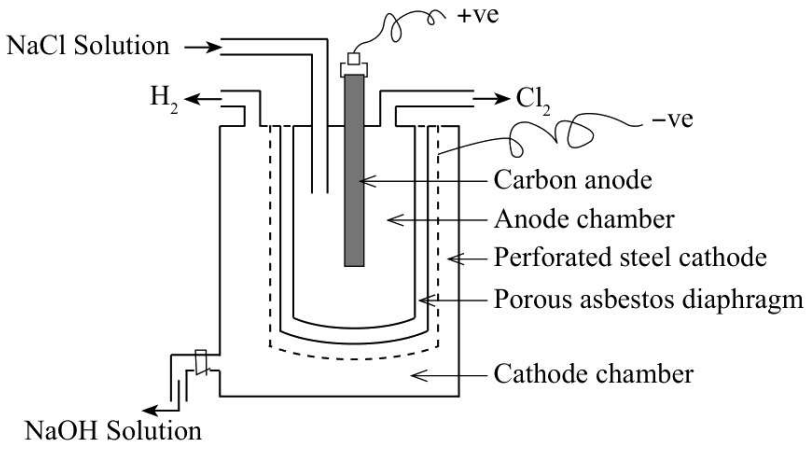
2

2

Membrane cell with labels: NaCl solution or brine in; used NaCl solution out; Cl_2 out (anode side); water in; NaOH solution out; H_2 out (cathode side); Ti anode; membrane; Ni cathode (printed "Ni anode" in the scheme). Note: mark independently. (01 mark × 9 + 01 for correct sketch of cell = 10 marks)

Alternate answer :

Diaphragm Cell



(01 marks × 9 + 01 for correct sketch of cell = 10 marks)

Alternate answer: diaphragm cell

Alternate answer:

2

2

(01 mark × 9 + 01 for correct sketch of cell = 10 marks)

(vi) Identify the salt used in the process **M_3**.

Answer

$CaCl_2$ (03)

(vii) Give **one** use for each of **P_5**, **P_6** and **P_9**.

Answer

P_5 (H_2): fuel / to manufacture HCl / to manufacture margarine / in weather balloons / manufacture of NH_3 (01)
P_6 (Na): sodium vapour lamps / synthesis of $NaNH_2$ / to dry organic solvents / as a coolant in nuclear reactors (01)
P_9 (glycerol): to manufacture cosmetics / to manufacture TNG (explosives) (01) (7.5 marks on the paper) · 9(a): 75 marks

Review.

Principle: reading an integrated industrial flow chart from clues. Sea water (R_1) gives salt (P_1) and bittern (P_2, the source of Br_2 — the halogen liquid at room temperature). Brine electrolysis (M_2) gives NaOH, Cl_2 and H_2; electrolysis of molten NaCl with $CaCl_2$ to lower the melting point (M_3, Downs cell) gives Na and Cl_2; NaOH + Cl_2 gives NaOCl (P_7, bleach); NaOH saponifies oils/fats (R_2) to soap (P_8) and glycerol (P_9). In the membrane cell, Cl^- is oxidised at the titanium anode and water is reduced at the nickel cathode (H_2 + OH^-), while only Na^+ crosses the cation-exchange membrane. Syllabus note: the current Resource Book covers NaOH by the membrane cell, soap, and the use of bittern (for Mg), and mentions the Downs cell only under electrolysis; salt production by fractional evaporation of sea water (the three-tank answer to (iv)) and the extraction of sodium are no longer prescribed industries. Errors in the scheme: P_7 is printed "NOCl" — it must be NaOCl (sodium hypochlorite), as transcribed above; the membrane-cell sketch labels both electrodes "anode" — the Ni electrode is the cathode. The report: facilities were 38, 33, 28, 20, 33, 47 and 25% for (a)(i)–(vii); (a)(iv) was the weakest (about 20%) because the production processes were not identified correctly, and a proper study of the prescribed industries is recommended.

(b) [75 marks]

Answer these questions using the list given below.
CO_2, CH_4, volatile hydrocarbons, NO, NO_2, N_2O, NO_3^−, SO_2, H_2S, CFC, $CaCO_3$, liquid petroleum and coal
(i) Identify **two** gaseous species that are responsible for acid rain and briefly explain, with the aid of balanced chemical equations, how these species cause acid rain.

Answer

NO_2, SO_2, NO (any two) (02 + 02)
From NO: $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ (02); $4NO_2(g) + O_2(g) + 2H_2O(l) \rightarrow 4HNO_3(aq)$ (02); $HNO_3(aq) \rightarrow H^+(aq) + NO_3$^−(aq) (01)
From NO_2: $4NO_2(g) + O_2(g) + 2H_2O(l) \rightarrow 4HNO_3(aq)$ (03); $HNO_3(aq) \rightarrow H^+(aq) + NO_3$^−(aq) (02)
From SO_2: $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ (02); $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$ (02); $H_2SO_4(aq) \rightarrow 2H^+(aq) + SO_4^{2-}(aq)$ (01)
or $2SO_2(g) + O_2(g) + 2H_2O(l) \rightarrow 2H_2SO_4(aq)$ (03); $H_2SO_4(aq) \rightarrow 2H^+(aq) + SO_4^{2-}(aq)$ (02)
(Generation of acid rain by any two sets of reactions given above, 05 marks × 2 = 10 marks.) Note: physical states are not required.

(ii) Acid rain has harmful effects on the environment. Briefly discuss this statement

Answer

Points to be included:
• Damage to plants
• HNO_3/H_2SO_4 dissolves aluminosilicates on Earth to give free Al^{3+}, which leaches into water and interferes with the operation of fish gills, resulting in the death of fish
• Washes out nutrients from soil
• Degrades metallic structures (e.g. vehicles, bridges, buildings, statues)
• Hardness of water increases
• Concentration of heavy metals in water increases
• Composition of Earth's surface changes (e.g. due to solubility of dolomite, limestone, marble, sand and rock / oxidation of minerals such as sulfides)
Any five (02 marks × 5 = 10 marks)

(iii) Identify **three** species that are emitted to the environment due to the burning of fossil fuel, along with one adverse environmental issue for each.

Answer

SO_2, NO, NO_2, CO_2, volatile hydrocarbons (any three) (02 + 02 + 02)
Global warming — CO_2, volatile hydrocarbons (02 + 01)
Acid rain — SO_2, NO (02 + 01)
Photochemical smog — NO, hydrocarbons (02 + 01)

(iv) "The existence of trace amounts of industrial synthetic species in the atmosphere can cause adverse environmental issues." Explain this statement using CFC as an example.

Answer

• CFCs are industrial gases that are used as coolants in refrigerators, air conditioners and spray cans.
• CFCs are released into the atmosphere during usage and repair of this equipment.
• CFCs are highly stable trace gases in the atmosphere.
• Therefore, CFCs are persistent gases in the atmosphere.
and
• CFCs produce Cl· (chlorine radicals) in the higher atmosphere (stratosphere) in the presence of high energy UV radiation.
• These increase the rate of depletion of ozone by acting as a catalyst.
• The reduction of ozone allows harmful UV rays to reach the surface of the planet.
• Exposure to harmful UV radiation results in cancers, gene mutations and cataracts.
or
• CFC is a strong greenhouse gas.
• CFCs contribute to global warming.
• CFCs absorb IR radiation emitted from the surface of the planet.
• Global warming results in climate change. (02 × 8 = 10 marks)

(v) Identify **five** greenhouse gases and state a human activity by which each of these gases enters the atmosphere.

Answer

CO_2: (fossil) fuel burning (01 + 01)
CH_4: wet land agriculture / animal farms / improper waste disposal (01 + 01)
NO_2: burning at high temperatures (01 + 01)
CFCs: air conditioners / refrigerators / spray guns (01 + 01)
N_2O: agriculture (use of nitrogen fertilizer) (01 + 01)
H_2S: anaerobic digestion of sulfur-containing substances such as coconut husks (01 + 01)
SO_2: fossil fuel burning (01 + 01)
Volatile hydrocarbons: fossil fuel burning, natural gas extraction, transportation (01 + 01)
Any five (02 × 5 = 10 marks)

(vi) Briefly explain using balanced chemical equations, how a natural substance (select from the list) can be used to remove acidic gases emitted during the burning of fossil fuel.

Answer

Limestone ($CaCO_3$) decomposes to give CaO (lime) and CO_2 (02): $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$ (03)
CaO then reacts with the SO_2 (02): $CaO + SO_2 \rightarrow CaSO_3$ (03)
Note: if only the equation is given, 05 marks.
or A slurry of limestone is used to absorb or scrub SO_2 (05): $CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2$ (05) (7.5 marks on the paper) · 9(b): 75 marks · Total for 9: 150 marks

Review.

Principle: chemistry of air pollution (Resource Book: acid rain, global warming, ozone depletion, photochemical smog). Acid rain comes from oxides of S and N being oxidised and dissolving to give H_2SO_4 and HNO_3 (CO_2 alone makes rain only weakly acidic, pH about 5.6, and is not counted). CFCs are inert in the lower atmosphere, so even trace amounts survive to reach the stratosphere, where UV releases Cl· radicals that catalytically destroy O_3; they are also powerful greenhouse gases. Limestone removes SO_2 from flue gases, giving $CaSO_3$ (which can be oxidised further to $CaSO_4$, gypsum). Note that the scheme's (iv) bullet reads "CFCs produce in the higher atmosphere…" — the word lost is chlorine radicals (Cl·), supplied above; and its (v) list accepts NO_2, H_2S and SO_2, but the current Resource Book states that SO_2, NO_2, NO and CO are not reckoned as greenhouse gases (short atmospheric lifetime); its main greenhouse gases are water vapour, CO_2, CH_4, N_2O and volatile halogenated hydrocarbons (CFC, HFC, HCFC), so choose from these today. Volatile hydrocarbons in (iii) are likewise better linked to photochemical smog than to global warming. The report:

answers to (b) were satisfactory overall (facilities 39, 47, 52, 22, 58 and 18% for (b)(i)–(vi)), (b)(v) being the easiest part of the question; (b)(vi) was the weakest (18%) because it concerns modern technology. Q9 was the most popular Part B/C question (76%) but the overall facility was only about 35%.

Read: RB U14 §1.2 · p. 6 RB U14 §1.4 · p. 14 RB U13 §3.4 · p. 261 RB U14 §1.13 · p. 58

Question 10 · Part C · essay

(a) [75 marks]

X

Y

Z

X

Y

Z

10

5

8

2

2

4

2

6

3

3

3

3

two types

non-coordinated

S

X

Y

Z

each

S

−3

3

3

S

4

X

Y

Z

Answer

SCN^- / NCS^- and H_2O (05 + 05)

(ii) Write the chemical formula of the yellow precipitate.

Answer

AgI (05)

(iii) Giving reasons, determine the structures of **X**, **Y** and **Z**.

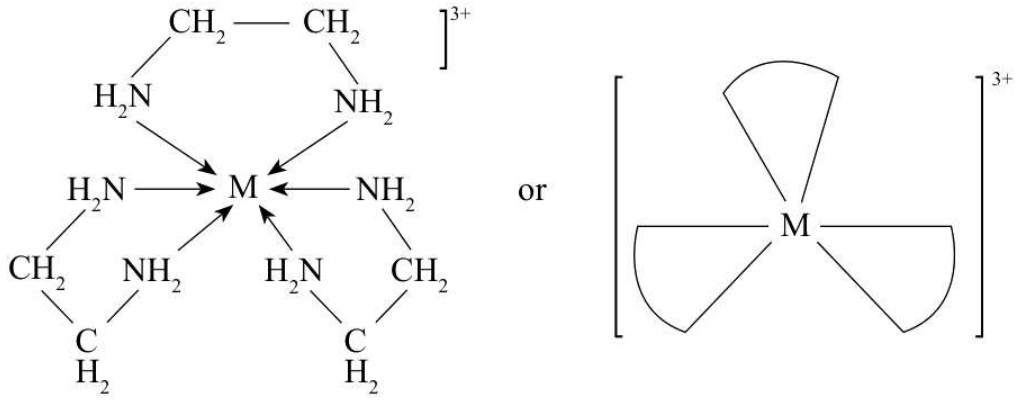
Answer

Based on the atomic composition:
coordination sphere of X: $[Fe(H_2O)_5(SCN)]$ or $[Fe(SCN)(H_2O)_5]$ (05)
coordination sphere of Y: $[Fe(H_2O)_4(SCN)_2]$ or $[Fe(SCN)_2(H_2O)_4]$ (05)
coordination sphere of Z: $[Fe(H_2O)_3(SCN)_3]$ or $[Fe(SCN)_3(H_2O)_3]$ (05)
Note: (NCS) could be used instead of (SCN). Could be written as either H_2O or OH_2.
Number of moles of each compound (i.e. X, Y, Z) in 100 cm^3 = (0.1/1000) × 100 = 0.01 (05)
Relative molecular mass of AgI = 235. Therefore, number of moles of AgI (or I^-) in the precipitate = 7.05/235 = 0.03 (05)
If the oxidation state of Fe is +3: X: charge of complex is +2, hence two I^- (02); Y: charge of complex is +1, hence one I^- (02); Z: complex has no charge, hence no I^- (02). (Total I^- = 0.01 × 3 = 0.03 mol, as found.)
Therefore, the oxidation state of Fe has to be +3. (04)
or If the oxidation state of Fe is +2: X: charge of complex is +1, hence one I^- (02); Y: charge of complex is zero, hence will not have any I^- (02); Z: charge of complex is −1, hence will not have any I^- (02). Therefore, the oxidation state of Fe cannot be +2; it has to be +3. (04)
Structural formulae:
X: **$[Fe(H_2O)_5(SCN)]I_2$** or $[Fe(SCN)(H_2O)_5]I_2$ (05)
Y: **$[Fe(H_2O)_4(SCN)_2]I$** or $[Fe(SCN)_2(H_2O)_4]I$ (05)
Z: **$[Fe(H_2O)_3(SCN)_3]$** or $[Fe(SCN)_3(H_2O)_3]$ (05)
Note: • (NCS) could be used instead of (SCN). No marks for (CNS) / (CSN). H_2O could be written as OH_2. • If the coordination spheres of X, Y, Z are not written but the structural formulae of X, Y, Z are written, award the (05 + 05 + 05) for the correct structural formulae and the marks allocated for the respective coordination spheres (05 + 05 + 05).

(iv) Given below is the structure of ethylenediamine (en): $H_2\ddot{N}–CH_2–CH_2–\ddot{N}H_2$
Ethylenediamine coordinates to the metal ion M^{3+} through the two nitrogen atoms, to form the complex ion **Q** (i.e. metal ion and ligands coordinated to it). **Q** has an octahedral geometry. Write the structural formula of **Q** and draw its structure.
Note: Consider that only ethylenediamine is coordinated to the metal ion. Use the abbreviation 'en' to denote ethylenediamine in your structural formula.

Answer

iv) $(M(en_3)^{3+}$ **(05)**



(05)

3

3+

$[M(en)_3]^{3+}$ (05)
Structure: M bonded to six N atoms from three $H_2N–CH_2–CH_2–NH_2$ ligands, each forming a five-membered chelate ring (or the simplified drawing of three arcs around M), with the overall charge 3+ shown (05)
Note: the charge of the complex is required for the award of marks. (7.5 marks on the paper) · 10(a): 75 marks

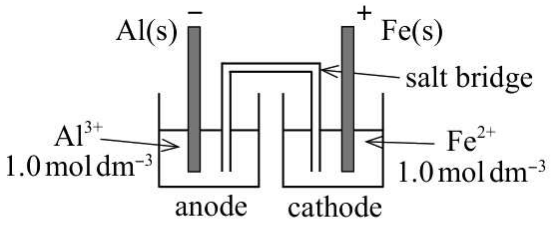
Review.

Principle: deducing complex formulae from atomic composition and a precipitation stoichiometry. Split each formula into ligands: $FeH_{10}CNO_5S$ = Fe + $5H_2O$ + SCN, and similarly $4H_2O$ + 2SCN and $3H_2O$ + 3SCN. The yellow precipitate insoluble in conc. NH_3 with M_r 235 is AgI, so the counter-ions are I^-. 0.010 mol of each complex gives 0.030 mol AgI; with Fe^{3+} the complex charges are +2, +1 and 0 (2 + 1 + 0 = 3 I^- per set), which fits, while Fe^{2+} would give only one I^- per set. Only the free (non-coordinated) I^- ions are precipitated — ligands inside the coordination sphere are not. The report: all four sub-parts of (a) were below 20% (facilities 17, 8, 4 and 9%; (a)(iii) at 4% was the lowest in the question): candidates could not pick out the ligands from atomic compositions instead of familiar formulae, and could not apply their knowledge to the bidentate ligand in (iv). Syllabus note: the current Resource Book uses $[Fe(SCN)(H_2O)_5]^{2+}$ as the test for Fe^{3+}, but chelating (bidentate) ligands such as ethylenediamine are not covered, so (a)(iv) is outside the current syllabus. The scheme's "$(M(en_3)^{3+}$" is written $[M(en)_3]^{3+}$ above.

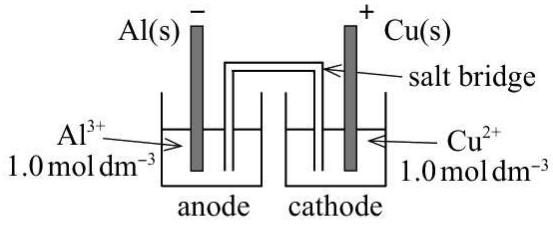
(b) [75 marks]

You are provided with the following.
• 1.0 mol dm^{-3} aqueous solutions of $Al(NO_3)_3$, $Cu(NO_3)_2$ and $Fe(NO_3)_2$
• Al, Cu and Fe metal rods
• Chemicals required to use in salt bridges
• Conducting wires and beakers
In addition to the above, the following data is also provided.
$E°_{Fe2+/Fe}$ = −0.44 V, $E°_{Al3+/Al}$ = −1.66 V, $E°_{Cu2+/Cu}$ = +0.34 V
(i) Diagram the **three** electrochemical cells that can be constructed using the above materials. Indicate the anode and cathode along with their signs in each cell.

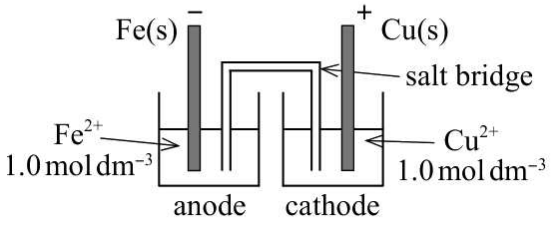
Answer



A



B



C

Scheme: cells A (Al|Fe), B (Al|Cu) and C (Fe|Cu)

Cell A: Al(s) (−, anode) in Al^{3+} 1.0 mol dm^{-3} and Fe(s) (+, cathode) in Fe^{2+} 1.0 mol dm^{-3}, joined by a salt bridge.
Cell B: Al(s) (−, anode) in Al^{3+} 1.0 mol dm^{-3} and Cu(s) (+, cathode) in Cu^{2+} 1.0 mol dm^{-3}, salt bridge.
Cell C: Fe(s) (−, anode) in Fe^{2+} 1.0 mol dm^{-3} and Cu(s) (+, cathode) in Cu^{2+} 1.0 mol dm^{-3}, salt bridge.
For each electrode: display and identification of metal strip (01); identification of the solution (01); display of correct charge (01); correct labelling as anode or cathode (01); display of the salt bridge (01)
Note: mark each electrode individually. If a voltmeter is drawn, do not deduct marks. If a battery or an external voltage source is connected, do not award marks. If the electrodes are connected by a wire, deduct 02 marks. (27 marks for 3 cells)

(ii) For each electrochemical cell drawn in part (i) above
I. give the cell notation,
II. determine $E°_{cell}$,
III. give balanced chemical equations with physical states for the electrode reactions.

Answer

I. Cell A: Al(s) | Al^{3+}(aq, 1.0 mol dm^{-3}) || Fe^{2+}(aq, 1.0 mol dm^{-3}) | Fe(s) (02)
Cell B: Al(s) | Al^{3+}(aq, 1.0 mol dm^{-3}) || Cu^{2+}(aq, 1.0 mol dm^{-3}) | Cu(s) (02)
Cell C: Fe(s) | Fe^{2+}(aq, 1.0 mol dm^{-3}) || Cu^{2+}(aq, 1.0 mol dm^{-3}) | Cu(s) (02)
II. $E°_{cell} = E°_{cathode} - E°_{anode}$ or $E°_{cell} = E°_{RHS} - E°_{LHS}$ (03)
Cell A: $E°_{cell}$ = −0.44 V − (−1.66 V) (02) = **1.22 V** (01 + 01)
Cell B: $E°_{cell}$ = 0.34 V − (−1.66 V) (02) = **2.00 V** (01 + 01)
Cell C: $E°_{cell}$ = 0.34 V − (−0.44 V) (02) = **0.78 V** (01 + 01)
III. Cell A: Al(s) ⇌ Al^{3+}(aq) + 3e (01); Fe^{2+}(aq) + 2e ⇌ Fe(s) (01)
Cell B: Al(s) ⇌ Al^{3+}(aq) + 3e (01); Cu^{2+}(aq) + 2e ⇌ Cu(s) (01)
Cell C: Fe(s) ⇌ Fe^{2+}(aq) + 2e (01); Cu^{2+}(aq) + 2e ⇌ Cu(s) (01)
Note: do not award marks if → is used instead of ⇌. Physical states are required.

(iii) Giving reasons, explain which of the following compounds is/are appropriate to use in salt bridges. NaOH, $NaNO_3$, acetic acid

Answer

NaOH — not suitable, metal hydroxides can be formed. (02)
$NaNO_3$ — suitable, good ionic conductivity OR (not suitable because the ionic conductivities of Na^+ and NO_3^− are different) (02)
Acetic acid — not suitable, weakly ionized, low conductivity (02)
Alternate answer 1: None of the given compounds is suitable (03). NaOH — metal hydroxide can be formed (01); $NaNO_3$ — mobility / conductivity of the two ions are different (01); acetic acid — weakly ionized / low conductivity (01)
Alternate answer 2: Only $NaNO_3$ is suitable (03), due to its good ionic conductivity; it does not participate in the electrode reactions (03)

(iv) Consider the electrochemical cell which shows the highest $E°_{cell}$ initially. Assume that this electrochemical cell has been constructed using equal volumes of the relevant solutions in each compartment and their volumes do not change during the experiment.
The two electrodes of this cell were connected using a conducting wire and after some time, the concentration of metal ions in the anode compartment was found to be **C** mol dm^{-3}. Express the concentration of metal ions in the cathode compartment in terms of **C**.

Answer

Selection of the correct pair of electrodes (Al/Cu, cell B) (03)
$2Al(s) + 3Cu^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Cu(s)$ (02) (physical states and stoichiometry must be correct)
Initial (mol dm^{-3}): Cu^{2+} 1.0, Al^{3+} 1.0; after time t (mol dm^{-3}): Cu^{2+} (1 − 3x/V) (02), Al^{3+} (1 + 2x/V) (02), where V = volume
$[Al^{3+}] = 1 + 2x/V = C$ (03); $x/V = (C - 1)/2$
$[Cu^{2+}] = 1 - 3(C - 1)/2$ (03) = **(5 − 3C)/2 mol dm^{-3}**
or Selection of the correct pair of electrodes (03). Assume $[Al^{3+}]$ increased during time t by c_1 mol dm^{-3}. Then $[Al^{3+}] = 1 + c_1 = C$ (03). The concentration of Cu^{2+} decreased during this time by $3c_1/2$ mol dm^{-3} (03). Therefore $[Cu^{2+}] = 1 - 3c_1/2$ (03) = 1 − 3(C − 1)/2 (03) = (5 − 3C)/2 (7.5 marks on the paper) · 10(b): 75 marks · Total for 10: 150 marks

Review.

Principle: galvanic cells from standard reduction potentials. In each pair the electrode with the more negative E° is the anode (negative terminal, oxidation) and the other is the cathode (positive, reduction); $E°_{cell} = E°_{cathode} - E°_{anode}$, never multiplied by the electron numbers. Al/Cu gives the largest $E°_{cell}$, 2.00 V. A salt bridge electrolyte must be a strong electrolyte whose ions do not react with the electrode solutions (OH^- would precipitate metal hydroxides; acetic acid conducts poorly); $NaNO_3$ is the usable choice here, but the scheme also credits the answer that it is not ideal because Na^+ and NO_3^− have different ionic mobilities (KNO_3 or KCl, whose ions move at similar speeds, are preferred). In (iv), with equal volumes, every 2 mol Al^{3+} formed matches 3 mol Cu^{2+} removed: if $[Al^{3+}] = C$ then the rise is C − 1, so $[Cu^{2+}]$ falls by 3(C − 1)/2 to (5 − 3C)/2. The report: facilities for (b)(i)–(iv) were 42%, 54/64/47% (I–III; (b)(ii)II was the easiest part of the question) and 28%; (b)(iv) fell below 5% because candidates did not identify the anode, cathode and cell reaction correctly. Q10 was chosen by about 50% with an overall facility of 26%. Notes on the scheme: its third $E°_{cell}$ calculation is headed "Cell B" again but is cell C (corrected above); in the alternate for (iv) "$[Cu^{2+}]$ increased" should read decreased (corrected above); and the scheme's equation line uses "fyda" (Sinhala "or") between the two forms of the $E°_{cell}$ formula.

Read: RB U6 §4.10.6 · p. 169 RB U6 §4.10 · p. 160 RB U13 §3.3 · p. 250 RB U13 §3.2 · p. 238

Sources

References

- National Institute of Education. (2018). G.C.E. (Advanced Level) Chemistry Resource Book, Grade 12 · Units 1–3. Department of Science, Faculty of Science and Technology, NIE, Maharagama, Sri Lanka. Open
- National Institute of Education. (2018). G.C.E. (Advanced Level) Chemistry Resource Book, Grade 12 · Units 4–5. Department of Science, Faculty of Science and Technology, NIE, Maharagama, Sri Lanka. Open
- National Institute of Education. (2018). G.C.E. (Advanced Level) Chemistry Resource Book, Grade 12 · Unit 6. Department of Science, Faculty of Science and Technology, NIE, Maharagama, Sri Lanka. Open
- National Institute of Education. (2019). G.C.E. (Advanced Level) Chemistry Resource Book, Grade 12 · Units 7–10. Department of Science, Faculty of Science and Technology, NIE, Maharagama, Sri Lanka. Open
- National Institute of Education. (2019). G.C.E. (Advanced Level) Chemistry Resource Book, Grade 13 · Units 11–13. Department of Science, Faculty of Science and Technology, NIE, Maharagama, Sri Lanka. Open
- National Institute of Education. (2019). G.C.E. (Advanced Level) Chemistry Resource Book, Grade 13 · Unit 14. Department of Science, Faculty of Science and Technology, NIE, Maharagama, Sri Lanka. Open
- Department of Examinations, Sri Lanka. G.C.E. (A/L) Examination, 02 – Chemistry, English medium question papers: 2016, 2017, 2018 (old syllabus); 2019, 2020, 2021(2022), 2022(2023), 2023(2024) Part B & C, 2024, 2025, 2026.
- Department of Examinations, Sri Lanka. 02 – Chemistry marking schemes: 2018, 2019, 2020, 2021(2022), 2024 and 2025 (partial), English; 2017 and 2023(2024), Sinhala medium.
- Research and Development Branch, National Evaluation and Testing Service, Department of Examinations. (2016). G.C.E. (A.L.) Examination 2016: Evaluation Report, 02 – Chemistry. Part III, pp. 68–71.

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