Chemistry

HSC Board Exam February–March 2027 – Practice Paper

Model Answer Paper

Time: 3 hours **Max. Marks: 70**

Model answers show one correct method; any other correct method gets full marks.

SECTION A – Q.1 Select and write the correct answer for the following multiple choice type of questions. **[10]**

(i) The coordination number of each atom in a body-centred cubic (bcc) crystal lattice is _____.

(A) 4 (B) 6

(C) 8 (D) 12

Answer (1 mark)

(C) 8

In bcc, the body-centre atom touches the 8 corner atoms of the cube.

(ii) Which of the following 0.1 m aqueous solutions has the highest boiling point?

(A) Glucose (B) Urea

(C) NaCl (D) K_2SO_4

Answer (1 mark)

(D) K_2SO_4

$\Delta T_b = i\, K_b\, m$. At equal molality, the solute with the largest van't Hoff factor raises the boiling point most: $K_2SO_4 \rightarrow 2K^+ + SO_4^{2-}$ gives i = 3 (NaCl i = 2; glucose and urea i = 1).

(iii) The SI unit of molar conductivity is _____.

(A) $\Omega^{-1}\ m^{-1}$ (B) $\Omega^{-1}\ m^2\ mol^{-1}$

(C) $\Omega\ m$ (D) $\Omega^{-1}\ cm\ mol^{-1}$

Answer (1 mark)

(B) $\Omega^{-1}\ m^2\ mol^{-1}$

$\Lambda = \kappa/c$; κ is in $\Omega^{-1}\ m^{-1}$ and c in $mol\ m^{-3}$, so Λ is in $\Omega^{-1}\ m^2\ mol^{-1}$ ($S\ m^2\ mol^{-1}$).

(iv) The unit of the rate constant of a first order reaction is _____.

(A) $mol\ dm^{-3}\ s^{-1}$ (B) $dm^3\ mol^{-1}\ s^{-1}$

(C) s^{-1} (D) $mol^{-1}\ s$

Answer (1 mark)

(C) s^{-1}

For a first order reaction, k = rate/[A] = $(mol\ dm^{-3}\ s^{-1})/(mol\ dm^{-3}) = s^{-1}$.

(v) The oxidation state of sulfur in peroxodisulfuric acid ($H_2S_2O_8$) is _____.

(A) +5 (B) +6

(C) +7 (D) +8

Answer (1 mark)
(B) +6
Two of the eight O atoms form a peroxide (–O–O–) link and have oxidation state −1, so 2(+1) + 2x + 6(−2) + 2(−1) = 0 gives x = +6.

(vi) The spin-only magnetic moment of Ti^{3+} (Z = 22) is _____.

(A) 1.73 BM (B) 2.84 BM
(C) 3.87 BM (D) 0 BM

Answer (1 mark)
(A) 1.73 BM
Ti^{3+} is $3d^1$, so n = 1 and $\mu = \sqrt{(n(n+2))} = \sqrt{3} = 1.73$ BM.

(vii) The coordination number of iron in $K_3[Fe(C_2O_4)_3]$ is _____.

(A) 3 (B) 4
(C) 6 (D) 9

Answer (1 mark)
(C) 6
Oxalate ($C_2O_4^{2-}$) is a bidentate ligand, so 3 × 2 = 6 donor atoms are bonded to Fe.

(viii) Which of the following alkyl halides undergoes S_N1 reaction most readily?

(A) CH_3Br (B) CH_3CH_2Br
(C) $(CH_3)_2CHBr$ (D) $(CH_3)_3CBr$

Answer (1 mark)
(D) $(CH_3)_3CBr$
It forms the most stable (tertiary) carbocation, $(CH_3)_3C^+$.

(ix) Which of the following compounds gives a positive iodoform test?

(A) HCHO (B) CH_3CH_2CHO
(C) C_6H_5CHO (D) $CH_3COCH_2CH_3$

Answer (1 mark)
(D) $CH_3COCH_2CH_3$
Only butanone contains the $CH_3CO–$ (methyl ketone) group needed for the iodoform test.

(x) The monomer used for the manufacture of nylon-6 is _____.

(A) adipic acid (B) caprolactam
(C) hexamethylenediamine (D) vinyl chloride

Answer (1 mark)
(B) caprolactam
Nylon-6 is made by heating caprolactam with a trace of water (ring-opening polymerisation).

SECTION A – Q.2 Answer the following questions. **[8]**

(i) Calculate the pH of 0.001 M HCl solution.

Answer (1 mark)
HCl is a strong acid: $[H_3O^+] = 1 \times 10^{-3}$ M
$pH = -\log_{10}[H_3O^+] = -\log(10^{-3}) = 3$

(ii) What is the value of ΔU for an isolated system?

Answer (1 mark)
ΔU = 0, because an isolated system exchanges neither heat nor work with its surroundings (q = 0, W = 0).

(iii) Write the IUPAC name of $CH_3–CH_2–O–CH(CH_3)_2$.

Answer (1 mark)
2-Ethoxypropane (ethyl isopropyl ether)

(iv) Name the test in which a primary amine, on warming with chloroform and alcoholic KOH, gives an offensive smell.

Answer (1 mark)
Carbylamine test (isocyanide test). The foul smell is of the isocyanide (R–N≡C) formed.

(v) Name the linkage that joins two monosaccharide units in a disaccharide.

Answer (1 mark)
Glycosidic linkage (C–O–C link formed between two monosaccharide units with loss of a water molecule).

(vi) What is the size range of nanoparticles?

Answer (1 mark)
1 nm to 100 nm (1 nm = 10^{-9} m).

(vii) Name the point defect in ionic solids that decreases the density of the crystal.

Answer (1 mark)
Schottky defect (equal numbers of cations and anions are missing from their lattice sites).

(viii) What is the shape of the ClF_3 molecule?

Answer (1 mark)
T-shaped (Cl is sp^3d hybridised with 3 bond pairs and 2 lone pairs).

SECTION B Attempt any EIGHT of the following questions. (Q.3 to Q.14) **[16]**

Q.3 Air contains 80 % nitrogen by volume. The Henry's law constant for nitrogen in water at 25 °C is 6.5×10^{-4} mol dm^{-3} bar^{-1}. Calculate the solubility of nitrogen in water at 25 °C exposed to air at a total pressure of 1.0 bar.

Answer (2 marks)
Given: $K_H = 6.5 \times 10^{-4}$ mol dm^{-3} bar^{-1}; $P_{total} = 1.0$ bar; mole fraction of $N_2 = 80/100 = 0.80$
Partial pressure of N_2, $P = 0.80 \times 1.0 = 0.80$ bar
By Henry's law, $S = K_H \times P$
$S = 6.5 \times 10^{-4} \times 0.80$
$= 5.2 \times 10^{-4}$ mol dm^{-3}
Ans: Solubility of $N_2 = 5.2 \times 10^{-4}$ mol dm^{-3}

Marking: Partial pressure of N_2 = 0.80 bar – ½ mark · Formula $S = K_H P$ with substitution – ½ mark · Answer 5.2×10^{-4} – ½ mark · Correct unit mol dm^{-3} (mol L^{-1}) – ½ mark

Examiner tip: Henry's law uses the partial pressure of the gas, not the total pressure. Using 1.0 bar directly loses a mark.

Q.4 The dissociation constant (K_a) of a weak monobasic acid HA is 4.0×10^{-6}. Calculate its degree of dissociation and the pH of its 0.01 M solution. (log 2 = 0.3010)

Answer (2 marks)

Given: $K_a = 4.0 \times 10^{-6}$, c = 0.01 M

For a weak acid, $\alpha = \sqrt{(K_a/c)} = \sqrt{(4.0 \times 10^{-6}/0.01)} = \sqrt{(4.0 \times 10^{-4})} = 2 \times 10^{-2} = 0.02$

$[H_3O^+] = \alpha c = 0.02 \times 0.01 = 2 \times 10^{-4}$ M

$pH = -\log(2 \times 10^{-4}) = 4 - \log 2 = 4 - 0.3010 = 3.699$

Ans: $\alpha = 0.02$ (2 %); pH = 3.699 ≈ 3.70

Marking: Formula $\alpha = \sqrt{(K_a/c)}$ and $\alpha = 0.02$ – 1 mark · $[H_3O^+] = 2 \times 10^{-4}$ M – ½ mark · pH = 3.699 – ½ mark

Examiner tip: Use $\alpha = \sqrt{(K_a/c)}$ only for a weak acid; then $[H_3O^+] = \alpha c$, not α.

Q.5 1.5 mol of an ideal gas expands isothermally from 12 dm^3 to 27 dm^3 against a constant external pressure of 2.0 bar. Calculate the work done in joules. (1 dm^3 bar = 100 J)

Answer (2 marks)

Given: $P_{ext} = 2.0$ bar, $V_1 = 12$ dm^3, $V_2 = 27$ dm^3

$W = -P_{ext}\,\Delta V = -P_{ext}\,(V_2 - V_1)$

$= -2.0 \times (27 - 12) = -30$ dm^3 bar

$= -30 \times 100$ J $= -3000$ J $= -3.0$ kJ

Ans: W = −3000 J (negative sign: work is done by the system on the surroundings)

Marking: Formula $W = -P_{ext}\Delta V$ – ½ mark · Substitution and −30 dm^3 bar – ½ mark · Conversion to −3000 J – 1 mark

Examiner tip: The number of moles is not needed for expansion against constant pressure. Keep the negative sign for expansion work.

Q.6 State Kohlrausch's law of independent migration of ions. Write the expression for the limiting molar conductivity (Λ_0) of $CaCl_2$ in terms of the limiting molar conductivities of its ions.

Answer (2 marks)

Kohlrausch's law: At infinite dilution, when dissociation of the electrolyte is complete, each ion migrates independently of its co-ion and makes a definite contribution to the molar conductivity of the electrolyte. Λ_0 is the sum of the limiting molar conductivities of the cation and the anion.

For $CaCl_2 \rightarrow Ca^{2+} + 2Cl^-$:

$\Lambda_0(CaCl_2) = \lambda_0(Ca^{2+}) + 2\lambda_0(Cl^-)$

Marking: Correct statement of the law – 1 mark · Expression for $\Lambda_0(CaCl_2)$ with factor 2 – 1 mark

Examiner tip: Multiply each ionic conductivity by the number of ions in the formula; $2\lambda_0(Cl^-)$ is the common slip.

Q.7 The rate constant of a first order reaction is 6.93×10^{-3} s^{-1}. Calculate (a) its half-life and (b) the time required for 75 % of the reaction to be completed.

Answer (2 marks)

(a) $t_{1/2} = 0.693/k = 0.693/(6.93 \times 10^{-3}\ s^{-1}) = 100$ s

(b) For 75 % completion, $[A] = [A]_0/4$, i.e. two half-lives.

$t = 2 \times t_{1/2} = 2 \times 100 = 200$ s

(Or $t = (2.303/k)\log([A]_0/[A]) = (2.303/6.93 \times 10^{-3}) \times \log 4 = 332.3 \times 0.6021 \approx 200$ s)

Ans: (a) 100 s (b) 200 s

Marking: (a) Formula and $t_{1/2}$ = 100 s – 1 mark · (b) 75 % = two half-lives, t = 200 s – 1 mark

Examiner tip: For first order reactions, 75 % completion = 2 half-lives and 87.5 % = 3 half-lives; this saves time.

Q.8 Write balanced chemical equations for:
(a) Chlorine reacts with cold and dilute sodium hydroxide.
(b) Complete hydrolysis of xenon hexafluoride.

Answer (2 marks)

(a) $Cl_2 + 2NaOH$ (cold, dilute) $\rightarrow NaCl + NaOCl + H_2O$

(b) $XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$

Marking: (a) Correct balanced equation – 1 mark · (b) Correct balanced equation – 1 mark

Examiner tip: With hot, concentrated NaOH the products change ($NaCl + NaClO_3$). Read the conditions carefully.

Q.9 Why are most compounds of transition metals coloured? Explain why Zn^{2+} salts are white. (Zn: Z = 30)

Answer (2 marks)

Transition metal ions have partially filled d orbitals. In the presence of ligands, the d orbitals split into two sets of slightly different energy. An electron absorbs light of a particular wavelength from the visible region and jumps from the lower to the higher set (d–d transition). The complementary colour of the light that is not absorbed is seen, so the compound appears coloured.

Zn^{2+} has the configuration [Ar] $3d^{10}$. Its d orbitals are completely filled, so no d–d transition is possible. Hence Zn^{2+} salts do not absorb visible light and are white.

Marking: Partially filled d orbitals and d–d transition – 1 mark · $Zn^{2+} = 3d^{10}$, no d–d transition, so colourless – 1 mark

Examiner tip: Write the configuration $3d^{10}$; just saying 'fully filled' without it often gets only ½ mark.

Q.10 Write the IUPAC names of:
(a) $[Co(NH_3)_4(H_2O)Cl]SO_4$
(b) $K_2[Zn(OH)_4]$

Answer (2 marks)

(a) Tetraammineaquachlorocobalt(III) sulfate
(IUPAC 2005 form 'tetraammineaquachloridocobalt(III) sulfate' is also accepted.)
(Charge on complex ion = +2; x + 0 + 0 − 1 = +2, so x = +3. Ligands alphabetically: ammine, aqua, chloro.)
(b) Potassium tetrahydroxozincate(II)
('tetrahydroxidozincate(II)' is also accepted; x + 4(−1) = −2, so x = +2.)

Marking: (a) Correct name with ligand order and (III) – 1 mark · (b) Correct name with '-ate' and (II) – 1 mark

Examiner tip: List ligands alphabetically (ammine, aqua, chloro) ignoring prefixes like tetra-. In an anionic complex the metal name ends in '-ate' (zincate).

Q.11 Write chemical equations for:
(a) Finkelstein reaction, using 1-bromopropane.
(b) Swarts reaction, using 2-bromopropane.

Answer (2 marks)
(a) $CH_3CH_2CH_2Br + NaI \xrightarrow{\text{(dry acetone)}} CH_3CH_2CH_2I + NaBr\downarrow$
(1-iodopropane; NaBr is insoluble in acetone and precipitates, which drives the reaction forward.)
(b) $CH_3–CHBr–CH_3 + AgF \xrightarrow{\text{(heat)}} CH_3–CHF–CH_3 + AgBr$
(2-fluoropropane; Hg_2F_2, AsF_3 or SbF_3 can also be used.)
Marking: (a) Correct equation with dry acetone – 1 mark · (b) Correct equation with metallic fluoride – 1 mark
Examiner tip: Mention the reagent condition (dry acetone). Without it the Finkelstein equation gets only ½ mark.

Q.12 Phenol is more acidic than ethanol. Explain.

Answer (2 marks)
On losing H^+, phenol gives the phenoxide ion, $C_6H_5O^-$. Its negative charge is delocalised over the benzene ring by resonance (charge at the ortho and para positions), so the phenoxide ion is stabilised.
Ethanol gives the ethoxide ion, $C_2H_5O^-$. Its charge stays on the oxygen atom, and the +I (electron-releasing) effect of the ethyl group increases the charge density further, destabilising the ion.
Since phenoxide is more stable than ethoxide, phenol loses H^+ more easily and is more acidic.
Marking: Resonance stabilisation of phenoxide ion – 1 mark · No resonance plus +I effect destabilising ethoxide ion – 1 mark
Examiner tip: Compare the stability of the two anions, not of phenol and ethanol themselves.

Q.13 Distinguish between DNA and RNA (any four points).

Answer (2 marks)

DNA	RNA
Sugar is 2-deoxyribose.	Sugar is ribose.
Bases: A, G, C and thymine (T).	Bases: A, G, C and uracil (U).
Double-stranded helix.	Usually single-stranded.
Carries genetic information; replicates itself.	Helps in protein synthesis; does not replicate.

Marking: Each correct point of difference – ½ mark (4 × ½ = 2 marks)
Examiner tip: Write the points in a table, pair by pair. Mixed lists lose marks.

Q.14 State any four principles of green chemistry.

Answer (2 marks)
Any four of the twelve principles:
(1) Prevention of waste: it is better to prevent waste than to treat it after it is formed.
(2) Atom economy: design syntheses so that most atoms of the reactants end up in the product.
(3) Less hazardous chemical syntheses.
(4) Use of safer solvents and auxiliaries (e.g. water, supercritical CO_2).
(5) Design for energy efficiency (reactions at room temperature and pressure).
(6) Use of renewable feedstocks.
(7) Use of catalysts in place of stoichiometric reagents.
(8) Design for degradation (products break down into harmless substances).

Marking: Any four correct principles – ½ mark each

Examiner tip: A one-line explanation with each principle's name earns the full ½ mark; a bare name may not.

SECTION C Attempt any EIGHT of the following questions. (Q.15 to Q.26) **[24]**

Q.15 An element crystallises in a face-centred cubic (fcc) lattice with unit cell edge length 389 pm. The density of the element is 12.0 g cm^{-3}. Calculate (a) the molar mass of the element and (b) the radius of its atom. (N_A = 6.022 × 10^{23} mol^{-1}; $\sqrt{2}$ = 1.414)

Answer (3 marks)

Given: fcc, so n = 4 atoms per unit cell; a = 389 pm = 3.89 × 10^{-8} cm; ρ = 12.0 g cm^{-3}

(a) $\rho = nM/(a^3 N_A)$, so $M = \rho a^3 N_A/n$

$a^3 = (3.89 \times 10^{-8}\ cm)^3 = 58.86 \times 10^{-24}\ cm^3 = 5.886 \times 10^{-23}\ cm^3$

$M = (12.0 \times 5.886 \times 10^{-23} \times 6.022 \times 10^{23})/4 = (12.0 \times 35.45)/4 = 425.4/4 = 106.3$ g mol^{-1} (the element is palladium, Pd)

(b) For fcc, $r = a/(2\sqrt{2}) = 389/(2 \times 1.414) = 389/2.828 = 137.6$ pm

Ans: (a) M ≈ 106.3 g mol^{-1} (b) r ≈ 137.6 pm

Marking: n = 4 for fcc and formula $M = \rho a^3 N_A/n$ – ½ mark · Conversion of a to cm and a^3 – ½ mark · M ≈ 106.3 g mol^{-1} – 1 mark · $r = a/(2\sqrt{2}) \approx 137.6$ pm – 1 mark

Examiner tip: Convert pm to cm (1 pm = 10^{-10} cm) before cubing. Many answers go wrong by a factor of 10^6 here. Answers from 106 to 106.5 g mol^{-1} (log-table rounding) are accepted.

Q.16 (a) A solution containing 3.0 g of a non-volatile non-electrolyte in 50 g of water freezes at −0.62 °C. Calculate the molar mass of the solute. (K_f for water = 1.86 K kg mol^{-1}; freezing point of water = 0 °C) [2]

(b) Define cryoscopic constant. [1]

Answer (3 marks)

(a) $\Delta T_f = 0 - (-0.62) = 0.62$ K; W_2 = 3.0 g; W_1 = 50 g

$M_2 = (1000 \times K_f \times W_2)/(\Delta T_f \times W_1)$

$= (1000 \times 1.86 \times 3.0)/(0.62 \times 50) = 5580/31 = 180$ g mol^{-1}

(b) Cryoscopic constant (K_f) is the depression in freezing point produced when one mole of a non-volatile solute is dissolved in 1 kg of solvent (i.e. for a 1 molal solution). Unit: K kg mol^{-1}.

Marking: (a) Formula – ½ mark; substitution – ½ mark; M_2 = 180 g mol^{-1} – 1 mark · (b) Correct definition – 1 mark

Examiner tip: A change of 0.62 °C equals 0.62 K. Do not add 273 to ΔT_f.

Q.17 (a) Define solubility product. [1]

(b) The solubility product of lead(II) fluoride (PbF_2) at 298 K is 3.2 × 10^{-8}. Calculate its molar solubility. [2]

Answer (3 marks)

(a) Solubility product (K_{sp}) of a sparingly soluble salt is the product of the molar concentrations of its ions in a saturated solution, each raised to the power equal to the number of those ions produced by one formula unit of the salt, at constant temperature.

(b) $PbF_2(s) \rightleftharpoons Pb^{2+}(aq) + 2F^-(aq)$

If S is the molar solubility: $[Pb^{2+}] = S$, $[F^-] = 2S$

$K_{sp} = [Pb^{2+}][F^-]^2 = S(2S)^2 = 4S^3$

$S^3 = K_{sp}/4 = 3.2 \times 10^{-8}/4 = 8 \times 10^{-9}$

$S = \sqrt[3]{(8 \times 10^{-9})} = 2 \times 10^{-3}$ mol dm^{-3}

Ans: Molar solubility of $PbF_2 = 2 \times 10^{-3}$ mol dm^{-3}

Marking: (a) Correct definition – 1 mark · (b) Equilibrium and $K_{sp} = 4S^3$ – 1 mark · (b) $S = 2 \times 10^{-3}$ mol dm^{-3} – 1 mark

Examiner tip: Write the dissociation equation first; it shows why $[F^-] = 2S$ and gives the $4S^3$ relation.

Q.18 For a reaction at 300 K, $\Delta H = +40$ kJ mol^{-1} and $\Delta S = +120$ J K^{-1} mol^{-1}. Calculate ΔG and predict whether the reaction is spontaneous at 300 K. Above what temperature will the reaction become spontaneous? (Assume ΔH and ΔS do not change with temperature.)

Answer (3 marks)

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

$\Delta H = 40$ kJ mol^{-1} $= 40000$ J mol^{-1}

$\Delta G = 40000 - (300 \times 120) = 40000 - 36000 = +4000$ J mol^{-1} $= +4$ kJ mol^{-1}

Since ΔG is positive, the reaction is non-spontaneous at 300 K.

At equilibrium $\Delta G = 0$, so $T = \Delta H/\Delta S = 40000/120 = 333.3$ K

Ans: $\Delta G = +4$ kJ mol^{-1} (non-spontaneous); the reaction becomes spontaneous above 333.3 K.

Marking: $\Delta G = +4$ kJ mol^{-1} with formula – 1 mark · Prediction: non-spontaneous – 1 mark · $T = \Delta H/\Delta S = 333.3$ K – 1 mark

Examiner tip: Convert ΔH to J (or ΔS to kJ) before subtracting. Mixing units is the commonest error.

Q.19 Write the cell reaction and calculate the emf of the following cell at 298 K:

Ni(s) | Ni^{2+}(0.10 M) || Ag^+(0.010 M) | Ag(s)

($E°_{Ni} = -0.25$ V, $E°_{Ag} = 0.80$ V)

Answer (3 marks)

At anode: $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$

At cathode: $2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$

Cell reaction: $Ni(s) + 2Ag^+(aq) \rightarrow Ni^{2+}(aq) + 2Ag(s)$; $n = 2$

$E°_{cell} = E°_{cathode} - E°_{anode} = 0.80 - (-0.25) = 1.05$ V

$E_{cell} = E°_{cell} - (0.0592/n) \log ([Ni^{2+}]/[Ag^+]^2)$

$= 1.05 - (0.0592/2) \log (10^{-1}/(10^{-2})^2)$

$= 1.05 - 0.0296 \times \log 10^3 = 1.05 - 0.0296 \times 3$

$= 1.05 - 0.0888 = 0.9612$ V

Ans: $E_{cell} \approx 0.961$ V

Marking: Correct cell reaction with $n = 2$ – 1 mark · $E°_{cell} = 1.05$ V – ½ mark · Nernst equation with $[Ag^+]^2$ – ½ mark · $E_{cell} = 0.961$ V – 1 mark

Examiner tip: Do not double E° of silver when you balance the electrons; E° is an intensive property. Square only $[Ag^+]$ in the Nernst term.

Q.20 The rate constant of a reaction becomes four times when the temperature is raised from 300 K to 320 K. Calculate the energy of activation of the reaction. ($R = 8.314$ J K^{-1} mol^{-1}; $\log 4 = 0.6021$)

Answer (3 marks)

$\log (k_2/k_1) = (E_a/2.303R) \times (T_2 - T_1)/(T_1T_2)$

$k_2/k_1 = 4$; $T_1 = 300$ K; $T_2 = 320$ K

$E_a = 2.303\ R \log(k_2/k_1) \times T_1T_2/(T_2 - T_1)$

= 2.303 × 8.314 × 0.6021 × (300 × 320)/20

= 2.303 × 8.314 × 0.6021 × 4800

= 55336 J mol^{-1} ≈ 55.3 kJ mol^{-1}

Ans: E_a ≈ 55.3 kJ mol^{-1}

Marking: Arrhenius two-temperature equation – 1 mark · Correct substitution – 1 mark · E_a ≈ 55.3 kJ mol^{-1} with unit – 1 mark

Examiner tip: Use log tables step by step (2.303 × 8.314 = 19.15). Small rounding differences, e.g. 55.3 to 55.4 kJ mol^{-1}, are accepted.

Q.21 Optically active (R)-2-bromobutane reacts with aqueous NaOH by the S_N2 mechanism. Explain the mechanism with the transition state, and state the configuration of the product formed. Why is this reaction called bimolecular?

Answer (3 marks)

$CH_3CH_2CHBrCH_3 + OH^- \rightarrow CH_3CH_2CH(OH)CH_3 + Br^-$

(1) The nucleophile OH^- attacks C-2 from the side opposite to the C–Br bond (backside attack).

(2) The reaction takes place in a single step through a transition state in which the C–OH bond is partly formed and the C–Br bond is partly broken:

$HO^{\delta-}\cdots\cdots C(H)(CH_3)(C_2H_5)\cdots\cdots Br^{\delta-}$ (H, CH_3 and C_2H_5 lie in one plane around C-2; HO and Br on opposite sides)

(3) Br^- leaves and the three other groups flip over like an umbrella turned inside out, so the configuration is inverted (Walden inversion). (R)-2-bromobutane therefore gives (S)-butan-2-ol (OH takes the priority position that Br had, but on the opposite side).

Rate = $k[CH_3CH_2CHBrCH_3][OH^-]$. Two species (alkyl halide and nucleophile) take part in the single, rate-determining step, so the reaction is bimolecular (second order).

Marking: Backside attack and one-step process with transition state – 1 mark · Inversion of configuration: (S)-butan-2-ol – 1 mark · Rate law and reason for 'bimolecular' – 1 mark

Examiner tip: Show the transition state with partial (dotted) bonds and say clearly that the product has inverted, (S), configuration; 'butan-2-ol' alone loses a mark.

Q.22 The atomic radii of zirconium (Zr, 160 pm) and hafnium (Hf, 159 pm) are almost equal, although Hf lies one period below Zr in the same group. Name the effect responsible for this. Explain its cause and state one other consequence of this effect.

Answer (3 marks)

Effect: Lanthanoid contraction – the steady decrease in atomic and ionic (M^{3+}) radii of the lanthanoids from lanthanum (La) to lutetium (Lu) with increasing atomic number.

Cause: across the lanthanoid series electrons enter the inner 4f orbitals. The 4f electrons shield the outer electrons poorly from the increasing nuclear charge, so the effective nuclear charge increases and the electron cloud is pulled inward.

Why Zr ≈ Hf: Hf (5d series) comes after the fourteen lanthanoids. The size increase expected on going from period 5 to period 6 is cancelled by the lanthanoid contraction, so Hf has almost the same radius as Zr (and very similar properties).

Other consequence (any one): lanthanoids have very similar properties, so their separation is difficult; or basic strength of hydroxides decreases from $La(OH)_3$ to $Lu(OH)_3$.

Marking: Naming lanthanoid contraction with meaning – 1 mark · Cause (poor shielding by 4f electrons) – 1 mark · Explaining Zr ≈ Hf – ½ mark; one other consequence – ½ mark

Examiner tip: Say 'poor shielding by 4f electrons'; 'increase in nuclear charge' alone is incomplete.

Q.23 Write chemical equations for:
(a) Reimer–Tiemann reaction
(b) Preparation of ethyl methyl ether by Williamson synthesis
(c) Action of hot concentrated HI on anisole

Answer (3 marks)
(a) $C_6H_5OH + CHCl_3 + 4NaOH(aq) \xrightarrow{-(340\ K)} o\text{-}NaO\text{–}C_6H_4\text{–}CHO + 3NaCl + 3H_2O$
$o\text{-}NaO\text{–}C_6H_4\text{–}CHO + HCl(dil.) \rightarrow o\text{-}HO\text{–}C_6H_4\text{–}CHO + NaCl$
(salicylaldehyde, 2-hydroxybenzaldehyde)
(b) $C_2H_5ONa + CH_3Br \rightarrow C_2H_5\text{–}O\text{–}CH_3 + NaBr$
(sodium ethoxide + bromomethane → ethyl methyl ether, i.e. methoxyethane; $CH_3ONa + C_2H_5Br$ is also accepted)
(c) $C_6H_5\text{–}O\text{–}CH_3 + HI \xrightarrow{-(heat)} C_6H_5OH + CH_3I$
(phenol + iodomethane)
Marking: (a) Correct reaction giving salicylaldehyde – 1 mark · (b) Correct equation – 1 mark · (c) Correct products phenol and CH_3I – 1 mark
Examiner tip: In (c), the O–C_6H_5 bond is not broken (it has partial double-bond character), so phenol, not iodobenzene, is formed.

Q.24 Write chemical equations for:
(a) Cannizzaro reaction of benzaldehyde
(b) Clemmensen reduction of acetophenone
(c) Action of thionyl chloride on propanoic acid

Answer (3 marks)
(a) $2C_6H_5CHO + NaOH\ (conc.) \xrightarrow{-(heat)} C_6H_5CH_2OH + C_6H_5COONa$
(benzyl alcohol + sodium benzoate)
(b) $C_6H_5COCH_3 + 4[H] \xrightarrow{-(Zn\text{–}Hg,\ conc.\ HCl)} C_6H_5CH_2CH_3 + H_2O$
(ethylbenzene)
(c) $CH_3CH_2COOH + SOCl_2 \xrightarrow{-(heat)} CH_3CH_2COCl + SO_2\uparrow + HCl\uparrow$
(propanoyl chloride; the –OH of –COOH is replaced by –Cl, and both by-products are gases)
Marking: Each correct equation with reagent – 1 mark (3 × 1)
Examiner tip: Write the reagent/condition on the arrow; a bare equation gets only ½ mark.

Q.25 (a) Write the Hofmann bromamide degradation of propanamide. [1]
(b) Write the reaction for the diazotisation of aniline. [1]
(c) Aniline is a weaker base than methylamine. Give reason. [1]

Answer (3 marks)
(a) $CH_3CH_2CONH_2 + Br_2 + 4NaOH \rightarrow CH_3CH_2NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$
(ethanamine; one carbon less than the amide)
(b) $C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{-(273\text{–}278\ K)} C_6H_5N_2^+Cl^- + NaCl + 2H_2O$
(benzenediazonium chloride)
(c) In aniline, the lone pair on nitrogen is delocalised into the benzene ring by resonance, so it is less available for accepting a proton. In methylamine, the +I effect of the CH_3 group increases the electron density on nitrogen. Hence methylamine is the stronger base.
Marking: (a) Balanced equation – 1 mark · (b) Equation with temperature 273–278 K – 1 mark · (c) Resonance in aniline vs +I effect in methylamine – 1 mark
Examiner tip: In (b), the low temperature (0–5 °C) is essential; diazonium salts decompose on warming.

Q.26 (a) What are biodegradable polymers? Give one example. [1]
(b) Write the names and structures of the monomers of PHBV. [1]
(c) Write the names and structures of the monomers of Buna-S. [1]

Answer (3 marks)
(a) Polymers that are broken down by micro-organisms (bacteria, fungi) in the environment, within a reasonable time, into harmless products are called biodegradable polymers. Example: PHBV (or nylon-2-nylon-6, PGA).
(b) 3-Hydroxybutanoic acid, $CH_3–CH(OH)–CH_2–COOH$, and 3-hydroxypentanoic acid, $CH_3–CH_2–CH(OH)–CH_2–COOH$
(c) Buta-1,3-diene, $CH_2=CH–CH=CH_2$, and styrene (vinylbenzene), $C_6H_5–CH=CH_2$

Marking: (a) Definition and example – ½ + ½ mark · (b) Both monomers – ½ mark each · (c) Both monomers – ½ mark each
Examiner tip: Give both name and structure; only one of the two earns half credit.

SECTION D Attempt any THREE of the following questions. (Q.27 to Q.31) **[12]**

Q.27 (a) On the basis of valence bond theory, explain the hybridisation, geometry and magnetic behaviour of $[Mn(CN)_6]^{3-}$. Also calculate its spin-only magnetic moment. (Mn: Z = 25) [3]
(b) What is an ambidentate ligand? Give one example. [1]

Answer (4 marks)
(a) Oxidation state of Mn: x + 6(−1) = −3, so x = +3
Mn (ground state): [Ar] $3d^5\ 4s^2$; Mn^{3+}: [Ar] $3d^4$
Mn^{3+} (free ion), 3d: [↑][↑][↑][↑][ ] 4s: [ ] 4p: [ ][ ][ ] (4 unpaired electrons)
CN^- is a strong field ligand, so the 3d electrons pair up as far as needed, leaving two 3d orbitals empty:
3d: [↑↓][↑][↑][ ][ ] 4s: [ ] 4p: [ ][ ][ ]
Two 3d, one 4s and three 4p orbitals hybridise to give six d^2sp^3 hybrid orbitals, which accept six lone pairs from six CN^- ions:
3d: [↑↓][↑][↑][××][××] 4s: [××] 4p: [××][××][××] (×× = electron pair from CN^-)
Hybridisation: d^2sp^3 (inner orbital, low spin complex)
Geometry: octahedral
Magnetic behaviour: two unpaired electrons, so paramagnetic.
$\mu = \sqrt{(n(n+2))} = \sqrt{(2 \times 4)} = \sqrt{8} = 2.83$ BM
(b) A ligand that has two different donor atoms and can bind to the metal through either of them (but only one at a time) is an ambidentate ligand. Example: NO_2^- (through N: nitro, or through O: nitrito); SCN^- (S or N).

Marking: (a) Oxidation state +3 and $3d^4$ configuration – ½ mark · (a) Pairing due to strong field CN^- and d^2sp^3 with orbital diagram – 1 mark · (a) Octahedral – ½ mark; paramagnetic (2 unpaired) – ½ mark · (a) μ = 2.83 BM – ½ mark · (b) Definition with example – 1 mark
Examiner tip: Show the electron boxes before and after pairing. With $3d^4$, only one pair forms – two electrons stay unpaired, so the complex is paramagnetic, not diamagnetic.

Q.28 (a) Write the aldol condensation of ethanal. Name the products formed. [2]
(b) Arrange the following in increasing order of acid strength and explain: CH_3COOH, $Cl_2CHCOOH$, $ClCH_2COOH$ [2]

Answer (4 marks)

(a) $2CH_3CHO$ –(dil. NaOH)→ $CH_3–CH(OH)–CH_2–CHO$ (3-hydroxybutanal, aldol)

$CH_3–CH(OH)–CH_2–CHO$ –(heat, $-H_2O$)→ $CH_3–CH=CH–CHO$ (but-2-enal, crotonaldehyde)

(b) Increasing acid strength: $CH_3COOH < ClCH_2COOH < Cl_2CHCOOH$

Reason: Cl is an electron-withdrawing group (−I effect). It disperses the negative charge of the carboxylate ion and stabilises it. The greater the number of Cl atoms on the α-carbon, the greater the stabilisation, so the acid strength increases. The CH_3 group has a +I effect that destabilises the acetate ion, so acetic acid is the weakest.

Marking: (a) Formation of aldol with name – 1 mark · (a) Dehydration to but-2-enal – 1 mark · (b) Correct order – 1 mark · (b) Explanation using −I effect and anion stability – 1 mark

Examiner tip: Aldol condensation needs an α-hydrogen; mention dil. NaOH as the reagent.

Q.29 (a) Calculate the standard enthalpy of formation of propane, $C_3H_8(g)$, from the following data: [3]

(i) $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$; $\Delta_cH° = -2220.0$ kJ mol^{-1}

(ii) C(graphite) + $O_2(g) \rightarrow CO_2(g)$; $\Delta_fH° = -393.5$ kJ mol^{-1}

(iii) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$; $\Delta_fH° = -285.8$ kJ mol^{-1}

(b) Predict the sign of ΔS when steam condenses to liquid water. Give reason. [1]

Answer (4 marks)

(a) Required: $3C(graphite) + 4H_2(g) \rightarrow C_3H_8(g)$; $\Delta_fH° = ?$

By Hess's law: 3 × (ii) + 4 × (iii) − (i)

$\Delta_fH° = 3(-393.5) + 4(-285.8) - (-2220.0)$

$= -1180.5 - 1143.2 + 2220.0$

$= -103.7$ kJ mol^{-1}

(Or: $\Delta_cH° = \Sigma\Delta_fH°(products) - \Sigma\Delta_fH°(reactants)$: $-2220.0 = [3(-393.5) + 4(-285.8)] - \Delta_fH°(C_3H_8)$, giving the same result.)

Ans: $\Delta_fH°(C_3H_8) = -103.7$ kJ mol^{-1}

(b) ΔS is negative. Molecules in a liquid are more ordered (less random) than in the gaseous state, so the entropy decreases on condensation.

Marking: (a) Correct target equation and combination 3(ii) + 4(iii) − (i) – 1 mark · (a) Correct substitution – 1 mark · (a) Answer −103.7 kJ mol^{-1} – 1 mark · (b) Negative sign with reason – 1 mark

Examiner tip: Reverse equation (i) and change the sign of its ΔH. Forgetting the sign change is the commonest mistake.

Q.30 (a) In the contact process for the manufacture of sulfuric acid:
(i) Write the equation for the catalytic oxidation of SO_2, name the catalyst and state the temperature and pressure used. Using Le Chatelier's principle, explain why the temperature is not kept very low although the reaction is exothermic. [2]
(ii) Why is SO_3 absorbed in concentrated H_2SO_4 and not in water? Write the equations for the formation of oleum and its conversion to sulfuric acid. [1]
(b) Fluorine is a stronger oxidising agent than chlorine. Give reason. [1]

Answer (4 marks)
(a)(i) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$; $\Delta H = -196.6$ kJ
Catalyst: V_2O_5; temperature about 720 K; pressure about 2 bar.
The forward reaction is exothermic and occurs with a decrease in the number of moles of gas (3 → 2). By Le Chatelier's principle, low temperature and high pressure favour the formation of SO_3. But at a very low temperature the rate of reaction is too slow, so an optimum temperature of about 720 K is used with a catalyst to get a good yield at a reasonable rate.
(ii) SO_3 reacts with water very vigorously and forms a dense mist (fog) of acid that is difficult to condense, so it is absorbed in conc. H_2SO_4:
$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$ (oleum)
$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$
(b) F_2 has a low bond dissociation enthalpy (weak F–F bond) and F^- has a very high hydration enthalpy because of its small size. So F_2 is reduced to F^- more easily ($E° = +2.87$ V, higher than that of Cl_2), which makes fluorine the stronger oxidising agent.
Marking: (a)(i) Balanced equation with V_2O_5, 720 K, 2 bar – 1 mark · (a)(i) Le Chatelier explanation (low T favours SO_3 but rate too slow; optimum T) – 1 mark · (a)(ii) Reason (acid mist) – ½ mark; oleum formation and dilution equations – ½ mark · (b) Correct reason – 1 mark
Examiner tip: Yield and rate pull in opposite directions here: say both. 'Low temperature favours SO_3' alone does not explain why 720 K is used.

Q.31 (a) Finely divided MnO_2 (pyrolusite) is fused with KOH and potassium chlorate ($KClO_3$) to give a dark green compound X. When X is dissolved in water and the solution is acidified, it gives a purple solution of Y and a brown precipitate Z. Identify X, Y and Z and write balanced equations for both steps. [2]
(b) What happens when glucose is treated with (i) HI on prolonged heating (ii) bromine water? Write chemical equations. [2]

Answer (4 marks)
(a) X = potassium manganate, K_2MnO_4; Y = potassium permanganate, $KMnO_4$ (MnO_4^-); Z = manganese dioxide, MnO_2
Step 1 (fusion): $3MnO_2 + 6KOH + KClO_3 \xrightarrow{\text{(heat)}} 3K_2MnO_4 + KCl + 3H_2O$
($2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$, with air as oxidant, is also accepted.)
Step 2 (disproportionation of manganate in acidic solution):
$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2\downarrow + 2H_2O$
(Mn changes from +6 to +7 in MnO_4^- and to +4 in MnO_2. Commercially, MnO_4^{2-} is oxidised electrolytically: $MnO_4^{2-} \rightarrow MnO_4^- + e^-$.)
(b) (i) $CHO–(CHOH)_4–CH_2OH + HI \xrightarrow{\text{–(prolonged heating)}} CH_3–CH_2–CH_2–CH_2–CH_2–CH_3$ (n-hexane)

This shows that the six carbon atoms of glucose are in a straight chain.

(ii) $CHO–(CHOH)_4–CH_2OH + [O] –(Br_2 \text{ water})\rightarrow COOH–(CHOH)_4–CH_2OH$ (gluconic acid)

This shows that glucose contains an aldehyde (–CHO) group.

Marking: (a) X, Y, Z correctly identified – ½ mark · (a) Balanced fusion equation – ½ mark · (a) Balanced disproportionation equation – 1 mark · (b)(i) n-hexane – 1 mark · (b)(ii) Gluconic acid – 1 mark

Examiner tip: Check the charge balance of the disproportionation equation (−2 on both sides). In (b), name the products and state what each reaction proves about glucose's structure.

All the best for your exam!