

ISC Class 12 Chemistry Specimen Paper 2

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Maximum Marks: 70 | Time Allowed: Three hours | Reading Time: 15 minutes

Paper 1 (Theory) carries 70 marks. Sections A and B are compulsory. Attempt any three questions from Section C.

General Instructions

Write your answers on the separate answer paper provided. The first 15 minutes are for reading the paper, and you may not write during that time. Section A and Section B are compulsory, and from Section C you must attempt any three of the four questions. Marks for each question, or part of a question, are shown in brackets. All working for numerical questions must be shown on the same sheet as the answer, and the final answer must carry its unit. Every constant and every relative atomic mass you need is given inside the question that needs it. No structures, graphs or flow charts are printed in this paper, and where a question asks for one you are expected to draw it yourself in pencil and label it. Equations must be balanced. This paper carries 70 of the 100 marks for the subject, the remaining 30 being for the practical work.

SECTION A (14 Marks)

Attempt all parts of Question 1.

Question 1 [14]

Each part carries 1 mark. For the parts that offer four choices, write only the option you choose. For the rest, answer in a single sentence or give the single word, name or value asked for.

- (i) The packing efficiency of a body centred cubic lattice is close to:
(a) 52.4 per cent (b) 68 per cent
(c) 74 per cent (d) 60 per cent
- (ii) Name the colligative property on which the working of a reverse osmosis plant for the desalination of sea water depends.
- (iii) On diluting the solution of a strong electrolyte, the molar conductivity:
(a) rises slowly towards a limiting value (b) stays unchanged
(c) falls steadily (d) first falls and then rises
- (iv) Write the unit of the rate constant of a zero order reaction.
- (v) Of the following, the one that is an emulsion of water dispersed in oil is:
(a) milk (b) butter (c) soap lather (d) smoke
- (vi) In the extraction of iron in a blast furnace, the substance obtained as slag is:
(a) CaO (b) SiO₂ (c) CaSiO₃ (d) FeSiO₃
- (vii) Give a reason why bleaching powder loses its strength when it is left in an open container.
- (viii) Name the ore of chromium from which potassium dichromate is manufactured.
- (ix) Explain what is meant by the denticity of a ligand, and give the denticity of the ethylenediamine molecule.
- (x) The reagent that converts an alcohol into the corresponding alkyl chloride in the best yield, the only other products being gases that escape, is:
(a) concentrated hydrochloric acid (b) phosphorus pentachloride
(c) chlorine (d) thionyl chloride
- (xi) Name the product formed when anisole is treated with hydroiodic acid, and state the position at which the ether linkage breaks.

- (xii) Of the four polymers named below, the one that is biodegradable is:
 (a) polythene (b) Bakelite (c) PHBV (d) polystyrene
- (xiii) Arrange ammonia, methylamine and aniline in order of their increasing basic strength in aqueous solution.
- (xiv) The drug that relieves hyperacidity by blocking the histamine H_2 receptors of the stomach wall is:
 (a) aspirin (b) paracetamol
 (c) sodium hydrogen carbonate (d) ranitidine

SECTION B (26 Marks)

Attempt all parts of Question 2. Each part carries 2 marks.

Question 2 [26]

- (i) A metal crystallises in a face centred cubic lattice whose edge length is 400 pm. Calculate the radius of the metal atom, and state the number of atoms contained in one unit cell. [2]
- (ii) 20 g of sodium hydroxide is dissolved in 500 g of water, and the density of the solution so formed is 1.04 g cm^{-3} . Calculate the molality and the molarity of the solution. (Na = 23, O = 16, H = 1.) [2]
- (iii) 3.0 g of a non volatile, non electrolyte solute is dissolved in 100 g of water, and the freezing point of the water falls by 0.279 K. Calculate the molar mass of the solute. (K_f for water = $1.86 \text{ K kg mol}^{-1}$.) [2]
- (iv) Calculate the standard emf of the cell $\text{Mg} | \text{Mg}^{2+} || \text{Cu}^{2+} | \text{Cu}$ and the standard free energy change for the cell reaction. (E° for $\text{Mg}^{2+}/\text{Mg} = -2.37 \text{ V}$, E° for $\text{Cu}^{2+}/\text{Cu} = +0.34 \text{ V}$ and $F = 96500 \text{ C mol}^{-1}$.) [2]
- (v) A current of 1.5 A is passed through a solution of copper sulphate for 20 minutes using inert electrodes. Calculate the mass of copper deposited at the cathode. (Cu = 63.5 and $F = 96500 \text{ C mol}^{-1}$.) [2]
- (vi) The rate constant of a first order reaction is $1.15 \times 10^{-3} \text{ s}^{-1}$. Calculate the half life of the reaction and the time in which three quarters of the reactant will have been used up. (Take $\log 2 = 0.3010$.) [2]
- (vii) Explain what is meant by the activation energy of a reaction, and state the effect of a catalyst on it. [2]
- (viii) Explain what the Ellingham diagram is used for, and state what it tells you about the temperature at which carbon will reduce zinc oxide. [2]
- (ix) Explain why the +5 state of bismuth is far less stable than the +5 state of antimony. Draw the structure of the ozone molecule and state the bond order of each oxygen to oxygen bond in it. [2]
- (x) Explain why potassium dichromate solution turns yellow on the addition of alkali, and write the equation for the change. [2]
- (xi) Write the IUPAC names of $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ and $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, and state the kind of isomerism each of them can show. [2]
- (xii) Arrange the four compounds chlorobenzene, 2-chlorotoluene, 4-chloronitrobenzene and 2,4-dinitrochlorobenzene in order of increasing ease of nucleophilic substitution of the chlorine atom, and give the reason for the order. [2]
- (xiii) Explain why the boiling point of ethanol is much higher than that of ethoxyethane, although the two have nearly the same molar mass. [2]

SECTION C (30 Marks)

Attempt any three questions from this Section. Each question carries 10 marks.

Question 3 [10]

- (a) Distinguish between a stoichiometric defect and a non-stoichiometric defect in an ionic crystal. Explain why a crystal of sodium chloride heated in sodium vapour acquires a yellow colour. [3]
- (b) 30 g of urea, $\text{CO}(\text{NH}_2)_2$, is dissolved in 180 g of water at 298 K. Calculate the vapour pressure of the solution and the lowering of the vapour pressure, given that the vapour pressure of pure water at this temperature is 23.8 mm Hg. (C = 12, O = 16, N = 14, H = 1.) [3]

- (c) Calculate the emf at 298 K of the cell $\text{Fe} | \text{Fe}^{2+} (0.001 \text{ M}) || \text{Ag}^+ (0.1 \text{ M}) | \text{Ag}$. (E° for $\text{Fe}^{2+}/\text{Fe} = -0.44 \text{ V}$, E° for $\text{Ag}^+/\text{Ag} = +0.80 \text{ V}$ and $2.303RT/F = 0.0591 \text{ V}$.) Write the reaction taking place at each electrode, and state whether the cell reaction is feasible as written. [4]

Question 4 [10]

- (a) The half life of a first order reaction is 30 minutes. Calculate its rate constant, and calculate the fraction of the reactant left unchanged after 90 minutes. [3]
- (b) The rate constant of a reaction is found to double when the temperature is raised from 300 K to 310 K. Calculate the activation energy of the reaction. ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\log 2 = 0.3010$.) [3]
- (c) Define the adsorption isotherm. Write the Freundlich adsorption isotherm, explain what each symbol in it stands for, and describe the shape of the graph of $\log (x/m)$ against $\log p$ that it predicts. State what the graph shows at very high pressure and give a reason. [4]

Question 5 [10]

- (a) Define crystal field splitting energy. Explain, using the crystal field theory, why $[\text{Co}(\text{NH}_3)_6]^{3+}$ is diamagnetic while $[\text{CoF}_6]^{3-}$ is paramagnetic. Calculate the spin only magnetic moment of the second complex. (Take $\mu = \sqrt{n(n+2)}$ BM.) [3]
- (b) Explain what is meant by the chelate effect. Draw the two geometrical isomers of $[\text{Co}(\text{en})_2\text{Cl}_2]^+$, label each, and state which of the two can be resolved into optical isomers. [3]
- (c) Describe the manufacture of sulphuric acid by the contact process. Name the catalyst, give the conditions of temperature and pressure, write the balanced equation for the catalysed step, and explain why the sulphur trioxide is not absorbed directly in water. [4]

Question 6 [10]

- (a) Describe how aniline is converted into each of the following, naming the reagents and the conditions in every case: chlorobenzene, phenol, iodobenzene. State the single intermediate common to all three routes. [3]
- (b) Distinguish between an alpha amino acid and a peptide. Explain what is meant by the zwitterion form of an amino acid and by the isoelectric point. Name the two kinds of secondary structure found in proteins. [3]
- (c) Write the reagents, the conditions and the organic product for each of the following. (1) Toluene is oxidised to benzoic acid. (2) Benzene is converted into acetophenone. (3) Propanoic acid is converted into 2-bromopropanoic acid. (4) Ethanenitrile is reduced to ethanamine. [4]

ANSWER KEY AND MARKING SCHEME

Full working is given for every numerical, and every numerical answer is quoted to three significant figures unless the figures work out exactly. Marks shown in *italics* are the step marks an examiner would award. Accept any correct alternative method that reaches the same answer, accept a correctly balanced equation written with any reasonable set of state symbols, and accept a correctly drawn structure or mechanism in any reasonable style.

Question 1 [14]

- (i) (b) 68 per cent. In a body centred cubic cell the atoms touch along the body diagonal, so $r = \sqrt{3}a/4$, and with two atoms to the cell the fraction of the volume filled works out at 0.680.
- (ii) Osmotic pressure. In reverse osmosis a pressure greater than the osmotic pressure of the sea water is applied to it, so that pure water is driven the wrong way through a semipermeable membrane and is collected.
- (iii) (a) rises slowly towards a limiting value. A strong electrolyte is already fully dissociated, so the number of ions does not change on dilution. The rise is only the small one that comes from the weakening of the interionic attractions as the ions move further apart.
- (iv) $\text{mol dm}^{-3} \text{ s}^{-1}$, that is concentration divided by time, since the rate of a zero order reaction is equal to k and does not depend on concentration at all.
- (v) (b) butter. Butter is an emulsion of the water in oil type, droplets of water being dispersed through fat. Milk is the other way round, oil in water.
- (vi) (c) CaSiO_3 . The limestone of the charge breaks down to calcium oxide, which acts as a basic flux and combines with the silica impurity to give the fusible calcium silicate that runs down as slag.
- (vii) Bleaching powder reacts slowly with the carbon dioxide of the air, which sets free chlorine and leaves calcium carbonate behind. The available chlorine is thereby lost, and the powder becomes useless. This gradual loss is called auto-oxidation.
- (viii) Chromite, FeCr_2O_4 , also known as chrome iron ore.
- (ix) The denticity of a ligand is the number of donor atoms by which a single molecule or ion of that ligand is attached to the central metal atom. Ethylenediamine has two donor nitrogen atoms, so its denticity is two and it is called bidentate.
- (x) (d) thionyl chloride. In the Darzens procedure the other two products are sulphur dioxide and hydrogen chloride, both gases, so they escape and leave the alkyl chloride pure.
- (xi) The products are phenol and iodomethane. The linkage breaks on the side of the alkyl group, not of the ring, because the attack of the iodide ion needs an sp^3 carbon and because the partial double bond character of the bond from oxygen to the ring makes that bond the stronger of the two.
- (xii) (c) PHBV. It is a copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid, and the ester linkages along its chain are broken down by bacteria in the soil. The other three carry only carbon to carbon chains, which microorganisms cannot attack.
- (xiii) Aniline, then ammonia, then methylamine. In aniline the lone pair of the nitrogen is drawn into the ring by resonance and is the least available of the three, while in methylamine the methyl group pushes electrons towards the nitrogen and makes the lone pair the most available.
- (xiv) (d) ranitidine. Histamine makes the stomach wall pour out hydrochloric acid, and ranitidine stops it from reaching the receptor, so the acid is never released. Sodium hydrogen carbonate only neutralises the acid already present and does nothing to the receptor.

1 mark for each correct part. No mark is deducted for a wrong option, and a one-line answer that carries the correct chemistry gains the mark even if it is loosely worded.

Question 2 [26]

- (i) In a face centred cubic lattice the atoms touch along the face diagonal, so $4r = \sqrt{2}a$ and $r = a/(2\sqrt{2}) = 400/(2 \times 1.414) = 400/2.828 = 141 \text{ pm}$. The unit cell holds 8 corner atoms counted as one eighth each and 6 face centre atoms counted as one half each, that is $8 \times 1/8 + 6 \times 1/2 = 1 + 3 = 4$ atoms.

Relation $4r = \sqrt{2}a$ used to give $r = 141 \text{ pm}$ 1. Four atoms per unit cell 1.

- (ii) Moles of sodium hydroxide = $20/40 = 0.500$ mol. Molality = $0.500/0.500$ kg of water = 1.00 mol kg^{-1} . Mass of the solution = $20 + 500 = 520$ g, so its volume = $520/1.04 = 500 \text{ cm}^3 = 0.500 \text{ dm}^3$. Molarity = $0.500/0.500 = 1.00 \text{ mol dm}^{-3}$.

Molality 1.00 m 1. Volume 500 cm³ from the density, giving molarity 1.00 M 1.

- (iii) From $\Delta T_f = K_f w_2 \times 1000/(M_2 w_1)$, $M_2 = K_f w_2 \times 1000/(\Delta T_f w_1) = (1.86 \times 3.0 \times 1000)/(0.279 \times 100) = 5580/27.9 = 200 \text{ g mol}^{-1}$.

Correct rearrangement of the depression formula 1. Molar mass 200 g mol⁻¹ 1.

- (iv) Magnesium is the anode and copper the cathode, so $E^\circ_{\text{cell}} = 0.34 - (-2.37) = 2.71 \text{ V}$. The cell reaction $\text{Mg} + \text{Cu}^{2+} \rightarrow \text{Mg}^{2+} + \text{Cu}$ transfers 2 electrons, so $n = 2$ and $\Delta G^\circ = -nFE^\circ_{\text{cell}} = -2 \times 96500 \times 2.71 = -523030 \text{ J mol}^{-1}$, that is -523 kJ mol^{-1} .

$E^\circ_{\text{cell}} = 2.71 \text{ V}$ 1. $\Delta G^\circ = -523 \text{ kJ mol}^{-1}$ 1.

- (v) Charge passed $Q = It = 1.5 \times 20 \times 60 = 1800 \text{ C}$. Moles of electrons = $1800/96500 = 0.01865 \text{ mol}$. The cathode reaction is $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$, so two electrons give one atom of copper and moles of copper = $0.01865/2 = 0.009326 \text{ mol}$. Mass of copper = $0.009326 \times 63.5 = 0.592 \text{ g}$.

Charge 1800 C with moles of electrons 0.01865 1. Mass of copper 0.592 g 1.

- (vi) $t_{1/2} = 0.693/k = 0.693/1.15 \times 10^{-3} = 603 \text{ s}$, that is 10.0 minutes. When three quarters has gone, one quarter remains, which is two half lives, so $t = 2 \times 603 = 1206 \text{ s}$, that is about 20.1 minutes. The same answer follows from $t = (2.303/k) \log 4 = (2.303/1.15 \times 10^{-3}) \times 0.6020 = 1206 \text{ s}$.

Half life 603 s 1. Time for three quarters 1206 s 1.

- (vii) Activation energy is the minimum extra energy, over and above the average energy that the reactant molecules already have, which a colliding pair must possess if the collision is to lead to reaction. It is the difference between the energy of the reactants and the energy of the activated complex at the top of the energy barrier. A catalyst lowers the activation energy. It provides a fresh path of lower energy, usually through an intermediate complex with the catalyst, so that a much larger fraction of the collisions carries enough energy and the rate rises. The catalyst does not alter ΔH for the reaction, and it lowers the barrier for the forward and the backward reaction alike.

Activation energy defined as the minimum energy over the average needed for a fruitful collision 1. Catalyst lowers it by offering a path of lower energy, ΔH unchanged 1.

- (viii) An Ellingham diagram is a plot of the standard free energy change of formation of the oxides against temperature, and it is used to decide whether one element will reduce the oxide of another, and above what temperature. The reduction is feasible when the line for the oxide of the reducing agent lies below the line for the oxide to be reduced at that temperature, because ΔG° for the coupled reaction is then negative. The line for carbon turning into carbon monoxide slopes downwards, since gas is produced and the entropy rises, while the line for zinc oxide slopes upwards. The two cross a little above 1200 K, so carbon can reduce zinc oxide only above roughly that temperature, which is why the reduction of zinc oxide by coke is carried out at about 1673 K.

Use of the diagram to judge feasibility from the lower line 1. Carbon reduces zinc oxide only above about 1200 K 1.

- (ix) Bismuth comes after the first row of the transition series and the lanthanoids, so its 6s electrons are poorly shielded and are drawn so close to the nucleus that they are very reluctant to take part in bonding. This inert pair effect is far more marked in bismuth than in antimony, so bismuth prefers the +3 state and its +5 compounds are strong oxidising agents that readily revert to +3. Ozone should be drawn as a bent molecule with the central oxygen sp^2 hybridised, the bond angle close to 117 degrees, and the two resonance structures shown, one with a double bond on the left and one with it on the right. Because the two structures contribute equally, both bonds are alike and each has a bond order of 1.5.

Inert pair effect, stronger in bismuth, with the +5 state acting as an oxidant 1. Bent structure with resonance drawn and bond order 1.5 1.

- (x) The dichromate ion and the chromate ion exist together in equilibrium, the position of which is governed by the hydrogen ion concentration. Alkali removes hydrogen ions, so by Le Chatelier's principle the equilibrium shifts towards the yellow chromate ion and the orange colour of the dichromate is replaced by yellow. $\text{Cr}_2\text{O}_7^{2-}$

$+ 2\text{OH}^- \rightarrow 2\text{CrO}_4^{2-} + \text{H}_2\text{O}$. Adding acid drives the equilibrium back and the orange colour returns.

Shift of the chromate to dichromate equilibrium on removal of hydrogen ions 1. Correct balanced equation 1.

- (xi) $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ is tetraamminedichloridochromium(III) chloride. Being an octahedral complex of the type MA_4B_2 , it shows geometrical isomerism, the two chloride ligands lying either next to each other in the cis form or opposite each other in the trans form. $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ is diamminedichloridoplatinum(II). It is square planar of the type MA_2B_2 and shows geometrical isomerism, the cis form being the anticancer drug cisplatin. Neither complex is optically active, because each has a plane of symmetry.

Both IUPAC names correct 1. Geometrical isomerism identified for each, with cis and trans described 1.

- (xii) The order of increasing ease is 2-chlorotoluene, then chlorobenzene, then 4-chloronitrobenzene, then 2,4-dinitrochlorobenzene. Nucleophilic substitution on an aryl halide goes through an intermediate in which the negative charge sits on the ring, so anything that spreads that charge helps the reaction. The nitro group withdraws electrons strongly, both inductively and by resonance, and when it stands at the ortho or para position the charge is carried right onto its oxygen atoms, so one nitro group speeds the reaction greatly and two speed it still more. The methyl group of 2-chlorotoluene works the other way, releasing electrons into the ring and so raising the charge density, which makes the attack by the nucleophile harder than in chlorobenzene itself.

Correct order of the four compounds 1. Reason given in terms of the withdrawal of electrons by the nitro groups and release by the methyl group 1.

- (xiii) Ethanol has its hydrogen atom attached to a strongly electronegative oxygen, so molecules of ethanol are held to one another by intermolecular hydrogen bonds, and a good deal of energy must be supplied to break that network before the liquid can boil. In ethoxyethane both bonds of the oxygen go to carbon, so there is no hydrogen on an electronegative atom and the molecules cannot hydrogen bond to each other. They are held only by weak dipole and van der Waals forces, so ethoxyethane boils at about 308 K against 351 K for ethanol. Ethoxyethane can still accept a hydrogen bond from water, which is why it is slightly soluble.

Hydrogen bonding between ethanol molecules identified as the cause 1. Absence of such bonding in the ether, only weak forces, with the comparison made 1.

Question 3 [10]

- (a) A stoichiometric defect is one in which the ratio of the cations to the anions remains exactly that of the chemical formula, so the crystal stays electrically neutral and its composition is unchanged. The Schottky defect, in which equal numbers of cations and anions are missing, and the Frenkel defect, in which an ion leaves its site and squeezes into an interstitial position, are the two kinds. A non-stoichiometric defect is one in which that ratio is disturbed, so the crystal has a small excess of metal or of non-metal and its composition no longer answers exactly to the formula, the neutrality being preserved instead by a change in the oxidation state of some of the ions or by trapped electrons. When sodium chloride is heated in sodium vapour, sodium atoms settle on the surface of the crystal, give up their electrons to form Na^+ ions, and chloride ions diffuse out to the surface to meet them. The anion sites they leave behind are occupied by the released electrons, and such a site is called an F-centre. These trapped electrons absorb light from the visible region as they are excited, and the crystal appears yellow. This is a metal excess defect, which also makes the crystal conduct electricity to a small extent.

Stoichiometric and non-stoichiometric defects distinguished 1. Formation of the F-centre by electrons in the vacant anion sites 1. Absorption of visible light by the trapped electrons giving the yellow colour 1.

- (b) Moles of urea = $30/60 = 0.500$ mol, and moles of water = $180/18 = 10.0$ mol. Mole fraction of water = $10.0/(10.0 + 0.500) = 10.0/10.5 = 0.952$. Urea is non volatile, so by Raoult's law the vapour pressure of the solution is $p = x_{\text{water}} \times p^\circ = 0.952 \times 23.8 = 22.7$ mm Hg. Lowering of vapour pressure = $23.8 - 22.7 = 1.13$ mm Hg.

Mole fractions with $x_{\text{water}} = 0.952$ 1. Vapour pressure of the solution 22.7 mm Hg 1. Lowering 1.13 mm Hg 1.

- (c) Iron is the anode, since it has the lower reduction potential, and silver the cathode. $E^\circ_{\text{cell}} = 0.80 - (-0.44) = 1.24$ V. Anode: $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$. Cathode: $2\text{Ag}^+ + 2\text{e}^- \rightarrow 2\text{Ag}$. The cell reaction is $\text{Fe} + 2\text{Ag}^+ \rightarrow \text{Fe}^{2+} + 2\text{Ag}$, for which $n = 2$ and $Q = [\text{Fe}^{2+}]/[\text{Ag}^+]^2 = 0.001/(0.1)^2 = 0.001/0.01 = 0.1$. By the Nernst equation $E = E^\circ - (0.0591/2) \log Q = 1.24 - 0.02955 \times (-1) = 1.24 + 0.0296 = 1.27$ V. The emf is positive, so ΔG is negative and

the cell reaction is feasible as written.

$E_{\text{cell}}^{\circ} = 1.24 \text{ V}$ 1. Both electrode reactions with silver correctly balanced 1. $Q = 0.1$ with $n = 2$ 1. $E_{\text{cell}} = 1.27 \text{ V}$ and the reaction declared feasible 1.

Question 4 [10]

- (a) For a first order reaction $k = 0.693/t_{1/2} = 0.693/30 = 0.0231 \text{ min}^{-1}$, that is $2.31 \times 10^{-2} \text{ min}^{-1}$. In 90 minutes the reaction runs for $90/30 = 3$ half lives, and each half life leaves half of what was there before, so the fraction left is $(1/2)^3 = 1/8 = 0.125$, that is 12.5 per cent of the original amount.

Rate constant 0.0231 min^{-1} 1. Recognition of three half lives in 90 minutes 1. Fraction left $1/8$ or 0.125 1.

- (b) By the Arrhenius equation in its two temperature form, $\log(k_2/k_1) = (E_a/2.303R) \times (T_2 - T_1)/(T_1 T_2)$. Here $k_2/k_1 = 2$, so $\log(k_2/k_1) = 0.3010$, $T_1 = 300 \text{ K}$, $T_2 = 310 \text{ K}$ and $T_2 - T_1 = 10 \text{ K}$. Hence $E_a = 2.303 \times R \times 0.3010 \times T_1 T_2 / (T_2 - T_1) = 2.303 \times 8.314 \times 0.3010 \times (300 \times 310)/10 = 5.763 \times 9300 = 53600 \text{ J mol}^{-1}$, that is 53.6 kJ mol^{-1} .

Correct two temperature form of the Arrhenius equation 1. Substitution with $\log 2 = 0.3010$ and $T_1 T_2 / \Delta T = 9300$ 1. Activation energy 53.6 kJ mol^{-1} 1.

- (c) An adsorption isotherm is the curve obtained when the extent of adsorption on a given adsorbent is plotted against the pressure of the gas, or the concentration of the solute, the temperature being held constant throughout. The Freundlich isotherm is $x/m = kp^{1/n}$, where x is the mass of gas adsorbed, m is the mass of the adsorbent, so that x/m is the extent of adsorption per unit mass, p is the equilibrium pressure of the gas, k is a constant that depends on the adsorbent, the gas and the temperature, and n is a constant greater than one. Taking logarithms gives $\log(x/m) = \log k + (1/n) \log p$, so the graph of $\log(x/m)$ against $\log p$ is a straight line of slope $1/n$ with an intercept of $\log k$ on the vertical axis. At very high pressure the straight line fails and the plot bends over and runs flat, because the surface of the adsorbent has become completely covered. No further adsorption is then possible however high the pressure is raised, so x/m reaches a saturation value and no longer depends on p , which is the region the equation does not describe.

Adsorption isotherm defined at constant temperature 1. Freundlich equation written with every symbol explained 1. Straight line of slope $1/n$ and intercept $\log k$ 1. Departure at high pressure with saturation of the surface as the reason 1.

Question 5 [10]

- (a) Crystal field splitting energy, written Δ_o for an octahedral field, is the difference in energy between the two sets of d orbitals into which the five degenerate d orbitals of the free metal ion are separated by the electrostatic field of the ligands, that is between the upper e_g pair and the lower t_{2g} trio. In both complexes cobalt is in the +3 state with the configuration $3d^6$. Ammonia is a strong field ligand, so Δ_o is larger than the energy needed to pair two electrons in the same orbital. All six electrons therefore crowd into the three t_{2g} orbitals, giving the low spin arrangement $t_{2g}^6 e_g^0$ with no unpaired electron, so the complex is diamagnetic. Fluoride is a weak field ligand and Δ_o is smaller than the pairing energy, so the arrangement is the high spin one $t_{2g}^4 e_g^2$, which leaves four unpaired electrons and makes the complex paramagnetic. For the fluoro complex $n = 4$, so $\mu = \sqrt{4 \times (4 + 2)} = \sqrt{24} = 4.90 \text{ BM}$.

Crystal field splitting energy defined 1. Low spin diamagnetic d^6 with ammonia against high spin paramagnetic d^6 with fluoride 1. Magnetic moment 4.90 BM for four unpaired electrons 1.

- (b) The chelate effect is the extra stability a complex gains when a polydentate ligand binds the metal through two or more donor atoms at once and so closes a ring with it. Replacing several unidentate ligands by one chelating ligand sets free more particles than it uses up, so the entropy of the system rises, and the ring itself must be broken at two points at once if the ligand is to leave. The complex is therefore much harder to pull apart than one of comparable unidentate ligands, five and six membered rings being the most stable. The two geometrical isomers of $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ should be drawn as octahedra. In the cis isomer the two chloride ligands occupy adjacent corners, the two ethylenediamine rings spanning the remaining four positions. In the trans isomer the two chloride ligands lie at opposite corners, along the same axis, with the two rings in the plane between them. Only the cis isomer can be resolved into optical isomers, because it has no plane of symmetry and so exists as a pair of non superimposable mirror images. The trans isomer has a plane of symmetry and is optically inactive.

Chelate effect explained with the ring and the entropy gain 1. Both isomers drawn and labelled cis and trans 1. Cis isomer identified as the resolvable one, with the absence of a plane of symmetry 1.

- (c) Sulphur, or a sulphide ore such as iron pyrites, is first burnt in air to give sulphur dioxide. The gas is freed of dust in an electrostatic precipitator, dried over concentrated sulphuric acid and purified in a scrubber, because arsenic compounds would poison the catalyst. The dry purified sulphur dioxide is then mixed with air and passed over the catalyst, which is vanadium pentoxide, V_2O_5 , spread on a support. The temperature is held at about 720 K and the pressure at about 2 atmospheres. The catalysed step is $2SO_2 + O_2 \rightarrow 2SO_3$, a reversible and exothermic reaction, so a moderate temperature and an excess of air push the yield up. The sulphur trioxide is not absorbed directly in water, because the reaction $SO_3 + H_2O \rightarrow H_2SO_4$ is violently exothermic and throws up a dense fog of acid mist that will not condense and is very difficult to collect. The gas is instead absorbed in concentrated sulphuric acid to give oleum, $H_2S_2O_7$, and the oleum is diluted with the right amount of water afterwards to give acid of the strength required.

Catalyst named as vanadium pentoxide, with the purification of the gas 1. Temperature about 720 K and pressure about 2 atmospheres 1. Balanced equation for the catalysed step 1. Acid mist as the reason for absorbing in concentrated acid to give oleum 1.

Question 6 [10]

- (a) All three routes begin by diazotising the aniline. Aniline is dissolved in an excess of the dilute mineral acid and treated with sodium nitrite at 273 to 278 K, which gives benzenediazonium chloride, and that salt is the intermediate common to all three. For chlorobenzene the diazonium solution is warmed with cuprous chloride dissolved in hydrochloric acid, which is the Sandmeyer reaction, and nitrogen is given off. Gattermann's variation, using copper powder and hydrochloric acid, serves equally well. For phenol the diazonium solution is simply warmed with water to about 280 K and above, when the diazonium group is replaced by a hydroxyl group and nitrogen escapes. For iodobenzene the diazonium solution is shaken with potassium iodide in the cold, and no copper salt is needed because the iodide ion by itself displaces nitrogen.

Diazotisation with sodium nitrite and dilute acid at 273 to 278 K, and benzenediazonium chloride named as the common intermediate 1. Sandmeyer route to chlorobenzene with cuprous chloride, and warm water for phenol 1. Potassium iodide for iodobenzene 1.

- (b) An alpha amino acid is a single molecule carrying both a carboxyl group and an amino group on the same carbon atom, the alpha carbon, which stands next to the carboxyl group. A peptide is the product of joining two or more such molecules, the carboxyl group of one condensing with the amino group of the next and losing water to form the peptide bond, so a peptide is a chain of amino acid residues rather than a single amino acid. In the zwitterion form the carboxyl group has given its proton to the amino group of the same molecule, so the molecule holds a $-COO^-$ group and a $-NH_3^+$ group at the same time and carries no overall charge. This is why amino acids are crystalline solids of high melting point that behave as salts rather than as ordinary organic acids. The isoelectric point is the pH at which the amino acid exists very largely as this zwitterion, so that it carries no net charge and will not move towards either electrode in an electric field. The two kinds of secondary structure are the alpha helix and the beta pleated sheet, both held in shape by hydrogen bonding between the peptide linkages.

Alpha amino acid distinguished from a peptide through the peptide bond 1. Zwitterion described with both charged groups, and the isoelectric point defined 1. Alpha helix and beta pleated sheet named 1.

- (c) (1) Toluene is refluxed with alkaline potassium permanganate, and the solution is then acidified. The methyl group is oxidised right down to a carboxyl group, and the product is benzoic acid. Acidified potassium dichromate, or chromic acid, serves equally well. (2) Benzene is treated with ethanoyl chloride, or with ethanoic anhydride, in the presence of anhydrous aluminium chloride and in a dry solvent such as carbon disulphide. This is a Friedel-Crafts acylation, and the product is acetophenone, that is phenyl methyl ketone. (3) Propanoic acid is treated with bromine in the presence of a small quantity of red phosphorus, and the product is hydrolysed. This is the Hell-Volhard-Zelinsky reaction, which brominates the carbon next to the carboxyl group, and the product is 2-bromopropanoic acid. (4) Ethanenitrile is reduced with lithium aluminium hydride in dry ether, or by hydrogen over a nickel catalyst, or by sodium in ethanol, and the product is ethanamine.

Alkaline permanganate followed by acidification, giving benzoic acid 1. Friedel-Crafts acylation with ethanoyl chloride and anhydrous aluminium chloride, giving acetophenone 1. Hell-Volhard-Zelinsky reaction with bromine and red phosphorus, giving 2-bromopropanoic acid 1. Reduction of the nitrile with lithium aluminium hydride or an equivalent, giving ethanamine 1.