

ISC Class 12 Chemistry Specimen Paper 1

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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 point defect in which an equal number of cations and anions are missing from their lattice sites, so that the crystal stays electrically neutral but its density falls, is called:
(a) a Frenkel defect (b) a Schottky defect
(c) a metal excess defect (d) an interstitial defect
- (ii) State Henry's law as it applies to the solubility of a gas in a liquid.
- (iii) The quantity of electric charge carried by one mole of electrons is:
(a) 96500 C (b) 9650 C
(c) 1.6×10^{-19} C (d) 6.022×10^{23} C
- (iv) A first order reaction is half completed in 20 minutes. Calculate its rate constant. (Take $\ln 2 = 0.693$.)
- (v) When a gas is adsorbed on the surface of a solid, the change that always accompanies the process is:
(a) an increase in the entropy of the gas (b) no change in enthalpy
(c) a decrease in the entropy of the gas (d) an increase in the enthalpy of the system
- (vi) Name the method of refining used to obtain germanium of very high purity for the electronics industry.
- (vii) The oxoacid of phosphorus which is dibasic and acts as a reducing agent is:
(a) H_3PO_4 (b) H_3PO_3
(c) H_3PO_2 (d) $\text{H}_4\text{P}_2\text{O}_7$
- (viii) Give a reason why zinc, cadmium and mercury are not regarded as typical transition elements.
- (ix) The IUPAC name of the compound $\text{K}_3[\text{Fe}(\text{CN})_6]$ is:
(a) potassium hexacyanidoferrate(II) (b) potassium ferricyanide
(c) potassium hexacyanidoferrate(III) (d) potassium hexacyanidoiron(II)
- (x) In a nucleophilic substitution that follows the $\text{S}_{\text{N}}1$ route, the rate of the reaction depends upon the concentration of:

- (a) the substrate alone (b) the nucleophile alone
 (c) both the substrate and the nucleophile (d) neither of the two
- (xi) Name the organic product formed when phenol is shaken with bromine water at room temperature.
- (xii) Of the four acids named below, the strongest in aqueous solution is:
 (a) ethanoic acid (b) chloroethanoic acid
 (c) benzoic acid (d) trichloroethanoic acid
- (xiii) Name the reaction by which a primary aromatic amine is converted into its diazonium salt, and state the range of temperature at which it is carried out.
- (xiv) Nylon-6,6 is obtained by the condensation polymerisation of:
 (a) caprolactam alone (b) ethylene glycol and terephthalic acid
 (c) phenol and formaldehyde (d) hexamethylenediamine and adipic acid

SECTION B (26 Marks)

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

Question 2 [26]

- (i) A metal crystallises in a body centred cubic lattice whose edge length is 288 pm, and the density of the metal is 7.23 g cm^{-3} . Calculate its molar mass. (Take Avogadro's number as $6.022 \times 10^{23} \text{ mol}^{-1}$.) [2]
- (ii) 9.0 g of glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, is dissolved in 250 g of water. Calculate the molality of the solution and the mole fraction of glucose in it. (C = 12, H = 1, O = 16.) [2]
- (iii) 1.80 g of a non volatile, non electrolyte solute is dissolved in 90 g of benzene, and the boiling point of the benzene rises from 80.10°C to 80.56°C . Calculate the molar mass of the solute. (K_b for benzene = $2.53 \text{ K kg mol}^{-1}$.) [2]
- (iv) Calculate the emf of the cell $\text{Zn} | \text{Zn}^{2+} (0.01 \text{ M}) || \text{Cu}^{2+} (0.1 \text{ M}) | \text{Cu}$ at 298 K. (E° for $\text{Zn}^{2+}/\text{Zn} = -0.76 \text{ V}$, E° for $\text{Cu}^{2+}/\text{Cu} = +0.34 \text{ V}$, and take $2.303RT/F$ as 0.0591 V .) [2]
- (v) The resistance of a 0.1 M solution of an electrolyte, measured in a conductivity cell whose cell constant is 1.25 cm^{-1} , is 85 ohm. Calculate the conductivity of the solution and its molar conductivity. [2]
- (vi) A first order reaction is found to be 25 per cent complete in 40 minutes. Calculate the rate constant of the reaction and its half life. (Take $\log 4 = 0.6021$ and $\log 3 = 0.4771$.) [2]
- (vii) Distinguish between the order and the molecularity of a reaction, and name one reaction in which the two are not equal. [2]
- (viii) In the froth flotation of an ore that contains both zinc sulphide and lead sulphide, sodium cyanide is added to the pulp. Explain the part played by the sodium cyanide, and state which of the two sulphides is carried up into the froth. [2]
- (ix) Explain why ammonia boils at a far higher temperature than phosphine. Draw the shape of the XeF_4 molecule and name that shape. [2]
- (x) Explain what is meant by the lanthanoid contraction, and state one consequence of it. [2]
- (xi) Account for the fact that $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic and square planar, while $[\text{NiCl}_4]^{2-}$ is paramagnetic and tetrahedral. [2]
- (xii) Give two separate reasons why chlorobenzene is far less reactive than chloroethane towards nucleophilic substitution. [2]
- (xiii) Write the equation for the preparation of ethoxyethane by Williamson's synthesis, and explain why the method fails when a tertiary alkyl halide is used. [2]

SECTION C (30 Marks)

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

Question 3 [10]

- (a) 6.0 g of urea, $\text{CO}(\text{NH}_2)_2$, is dissolved in water and the solution is made up to 500 cm^3 . Calculate the osmotic pressure of the solution at 300 K. (C = 12, O = 16, N = 14, H = 1, and $R = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$.) [3]
- (b) Define an azeotrope. Name the two kinds of azeotrope, give one example of each, and state the deviation from Raoult's law that each kind shows. [3]
- (c) The molar conductivity of a 0.05 M solution of ethanoic acid is $7.36 \text{ S cm}^2 \text{ mol}^{-1}$, and the molar conductivity of the acid at infinite dilution is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$. Calculate the degree of dissociation of the acid at this concentration and its dissociation constant. Name the law by which the value at infinite dilution must be arrived at for a weak electrolyte, and state it. [4]

Question 4 [10]

- (a) The rate constant of a first order reaction is $2.31 \times 10^{-3} \text{ s}^{-1}$. Calculate the time taken for the reaction to be 75 per cent complete and the half life of the reaction. (Take $\log 2 = 0.3010$.) [3]
- (b) State the Hardy-Schulze rule. Explain what is meant by the electrophoresis of a colloidal sol, and give a reason why a lyophilic sol is more stable than a lyophobic sol. [3]
- (c) Give a reason why most compounds of the transition metals are coloured. Explain why Cr^{2+} acts as a reducing agent while Mn^{3+} acts as an oxidising agent. Write the balanced equation for the fusion of manganese dioxide with potassium hydroxide in air, and the balanced ionic equation for the oxidation of oxalic acid by acidified potassium permanganate. [4]

Question 5 [10]

- (a) 2-bromo-2-methylpropane is warmed with aqueous potassium hydroxide. Name the mechanism by which the hydrolysis proceeds, draw the mechanism in full showing the intermediate formed, and name the organic product. [3]
- (b) Write the reagents, the conditions and the organic product for the Reimer-Tiemann reaction of phenol and for the Kolbe reaction of sodium phenoxide. Explain why phenol is a stronger acid than ethanol. [3]
- (c) Name the reaction, and give the organic product, in each of the following cases. (1) Ethanal is warmed with dilute sodium hydroxide solution. (2) Benzaldehyde is heated with concentrated sodium hydroxide solution. (3) Propanone is treated with hydrogen cyanide. (4) State a simple test, with the observation, by which benzoic acid may be distinguished from phenol. [4]

Question 6 [10]

- (a) Write the equation for the Hofmann bromamide degradation of propanamide and name the product. Describe the Gabriel phthalimide synthesis of a primary amine, and explain why it cannot be used to prepare aniline. [3]
- (b) Distinguish between a nucleoside and a nucleotide. Name the pentose sugar present in DNA and in RNA, and explain what is meant by the denaturation of a protein. [3]
- (c) Distinguish between an addition polymer and a condensation polymer, giving one example of each with its monomer or monomers. Name the monomers of Buna-S and the monomer of Teflon. Explain the difference between an antiseptic and a disinfectant, and name one substance that serves as both. [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) a Schottky defect. Cations and anions leave their sites in pairs, so the charge balance is kept while the same mass now occupies the same volume with fewer ions in it, and the measured density falls.
- (ii) Henry's law states that at a fixed temperature the mass of a gas dissolved in a given volume of a liquid is directly proportional to the partial pressure of the gas above the liquid. In its usual form $p = K_H x$, the partial pressure of the gas over the solution is proportional to the mole fraction of the gas in the solution.
- (iii) (a) 96500 C. This quantity of charge is one faraday, and it is the product of the Avogadro number and the charge on a single electron.
- (iv) For a first order reaction $k = 0.693/t_{1/2} = 0.693/20 = 0.0347 \text{ min}^{-1}$, that is $3.47 \times 10^{-2} \text{ min}^{-1}$.
- (v) (c) a decrease in the entropy of the gas. The gas molecules give up their freedom of movement when they are held on the surface, so the system becomes more ordered and ΔS is negative. Adsorption is also exothermic, so ΔH is negative.
- (vi) Zone refining, which depends on the impurities being more soluble in the molten metal than in the solid metal.
- (vii) (b) H_3PO_3 . Phosphorous acid holds two hydrogen atoms bonded to oxygen and one bonded directly to phosphorus. Only the two on oxygen are replaceable, so the acid is dibasic, and the P–H bond gives it its reducing character.
- (viii) In zinc, cadmium and mercury the d orbitals are completely filled, giving d^{10} configurations in the atom and in the common ion alike. A typical transition element must have an incompletely filled d subshell in at least one of its stable oxidation states, so these three fall outside the definition.
- (ix) (c) potassium hexacyanidoferrate(III). There are six cyanide ligands and three potassium ions, so the complex ion carries a charge of 3– and the oxidation state of iron is +3.
- (x) (a) the substrate alone. The slow step is the breaking of the carbon to halogen bond to give a carbocation, and the nucleophile takes no part in it, so the rate law is first order in the substrate only.
- (xi) 2,4,6-tribromophenol, which comes down as a white precipitate. The hydroxyl group activates the ring so strongly that substitution occurs at all three available positions even in the absence of a halogen carrier.
- (xii) (d) trichloroethanoic acid. Three chlorine atoms withdraw electrons strongly by the inductive effect, which spreads the negative charge of the anion and makes the anion the most stable of the four, so the acid is the strongest.
- (xiii) The reaction is diazotisation, carried out with sodium nitrite and an excess of dilute hydrochloric acid, and the temperature is held between 273 K and 278 K because the diazonium salt breaks down above that range.
- (xiv) (d) hexamethylenediamine and adipic acid. Each of the two monomers supplies six carbon atoms, which is what the two sixes in the name record.

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) For a body centred cubic lattice $Z = 2$. From $\rho = ZM/(a^3 N_A)$, $M = \rho a^3 N_A / Z$. Here $a = 288 \text{ pm} = 2.88 \times 10^{-8} \text{ cm}$, so $a^3 = 2.389 \times 10^{-23} \text{ cm}^3$. $M = (7.23 \times 2.389 \times 10^{-23} \times 6.022 \times 10^{23})/2 = 104.0/2 = 52.0 \text{ g mol}^{-1}$.
 $Z = 2$ with $a^3 = 2.389 \times 10^{-23} \text{ cm}^3$ 1. Molar mass 52.0 g mol^{-1} 1.
- (ii) Molar mass of glucose = $6 \times 12 + 12 \times 1 + 6 \times 16 = 180 \text{ g mol}^{-1}$, so moles of glucose = $9.0/180 = 0.0500 \text{ mol}$. Molality = $0.0500/0.250 \text{ kg} = 0.200 \text{ mol kg}^{-1}$. Moles of water = $250/18 = 13.89 \text{ mol}$, so mole fraction of glucose = $0.0500/(0.0500 + 13.89) = 0.0500/13.94 = 3.59 \times 10^{-3}$.
Molality 0.200 m 1. Mole fraction 3.59×10^{-3} 1.

- (iii) $\Delta T_b = 80.56 - 80.10 = 0.46$ K. From $\Delta T_b = K_b w_2 \times 1000 / (M_2 w_1)$, $M_2 = K_b w_2 \times 1000 / (\Delta T_b w_1) = (2.53 \times 1.80 \times 1000) / (0.46 \times 90) = 4554 / 41.4 = 110 \text{ g mol}^{-1}$.

Elevation 0.46 K 1. Molar mass 110 g mol⁻¹ 1.

- (iv) Zinc is the anode and copper the cathode, so $E^\circ_{\text{cell}} = 0.34 - (-0.76) = 1.10$ V. The cell reaction $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$ has $n = 2$ and $Q = [\text{Zn}^{2+}] / [\text{Cu}^{2+}] = 0.01 / 0.1 = 0.1$. By the Nernst equation $E = E^\circ - (0.0591/2) \log Q = 1.10 - 0.02955 \times (-1) = 1.10 + 0.0296 = 1.13$ V.

$E^\circ_{\text{cell}} = 1.10$ V with $Q = 0.1$ 1. $E_{\text{cell}} = 1.13$ V 1.

- (v) Conductivity $\kappa = \text{cell constant} / \text{resistance} = 1.25 / 85 = 0.0147 \text{ S cm}^{-1}$. Molar conductivity $\Lambda_m = 1000\kappa / c = (1000 \times 0.0147) / 0.1 = 147 \text{ S cm}^2 \text{ mol}^{-1}$.

Conductivity 0.0147 S cm⁻¹ 1. Molar conductivity 147 S cm² mol⁻¹ 1.

- (vi) If 25 per cent has gone, 75 per cent remains. $k = (2.303/t) \log (a/(a-x)) = (2.303/40) \log (100/75) = (2.303/40) \times (\log 4 - \log 3) = (2.303/40) \times (0.6021 - 0.4771) = (2.303/40) \times 0.1250 = 7.19 \times 10^{-3} \text{ min}^{-1}$. Half life $t_{1/2} = 0.693/k = 0.693 / 7.19 \times 10^{-3} = 96.3$ min.

Rate constant $7.19 \times 10^{-3} \text{ min}^{-1}$ 1. Half life 96.3 min 1.

- (vii) Order is the sum of the powers to which the concentration terms are raised in the experimentally determined rate law. It is found by experiment, it may be zero, fractional or negative, and it belongs to the overall reaction. Molecularity is the number of reacting species that take part in an elementary step as written in the balanced equation. It is a theoretical count, it is always a small whole number, and it has meaning only for an elementary step. The acid catalysed hydrolysis of ethyl ethanoate is bimolecular yet first order, because water is present in such excess that its concentration does not change appreciably, so it is a pseudo first order reaction.

Order defined and contrasted with molecularity 1. A reaction in which the two differ, with the reason 1.

- (viii) Sodium cyanide acts as a depressant. It reacts with the zinc sulphide at the surface of the particles to form the soluble complex $\text{Na}_2[\text{Zn}(\text{CN})_4]$, which leaves the zinc sulphide wetted by water instead of by the oil, so it is not picked up by the air bubbles and sinks with the gangue. Lead sulphide is unaffected, stays oil wetted and is carried up into the froth.

Depressant forming the soluble cyanido complex of zinc 1. Lead sulphide named as the sulphide that floats 1.

- (ix) In ammonia the nitrogen atom is small and strongly electronegative, so each molecule is held to its neighbours by intermolecular hydrogen bonding, and a good deal of extra energy is needed to pull the molecules apart. Phosphorus is much larger and far less electronegative, so phosphine forms no hydrogen bonds and its molecules are held only by weak van der Waals forces, which gives it the lower boiling point. XeF_4 should be drawn with xenon at the centre of a square, one fluorine atom at each corner, and the two lone pairs placed one above and one below the plane of the square. The shape is square planar, the hybridisation being sp^3d^2 .

Hydrogen bonding in ammonia against van der Waals forces in phosphine 1. Correct square planar drawing with the two lone pairs, and the shape named 1.

- (x) The lanthanoid contraction is the steady fall in atomic and ionic radius met on passing from lanthanum to lutetium. Each added electron enters a 4f orbital, and because the 4f orbitals shield one another very poorly, the effective nuclear charge felt by the outer electrons rises at every step and draws them inwards. One consequence is that the members of the series differ so little in size that their separation by ordinary chemical means is extremely difficult. A second is that the elements that follow the series, hafnium among them, are almost the same size as the corresponding members of the second transition series, so that zirconium and hafnium behave nearly alike.

Contraction described with poor shielding by the 4f electrons 1. One correct consequence 1.

- (xi) In both complexes nickel is in the +2 state with the configuration 3d^8 . Cyanide is a strong field ligand, so the splitting it produces is large enough to drive the two unpaired 3d electrons into the same orbital. One 3d orbital is thereby freed, the metal hybridises as dsp^2 , the shape is square planar and there is no unpaired electron left, so the ion is diamagnetic. Chloride is a weak field ligand and the splitting it produces is too small to force pairing, so the two unpaired electrons remain, the metal hybridises as sp^3 , the shape is tetrahedral and the ion is paramagnetic.

Cyanide as a strong field ligand giving dsp^2 , square planar and diamagnetic 1. Chloride as a weak field ligand giving sp^3 , tetrahedral and paramagnetic with two unpaired electrons 1.

- (xii) First, the lone pair of the chlorine atom overlaps the π system of the ring, so the carbon to chlorine bond acquires partial double bond character. It is therefore shorter and stronger than the bond in chloroethane and much harder to break. Second, the carbon carrying the chlorine in chlorobenzene is sp^2 hybridised, while in chloroethane it is sp^3 . The sp^2 carbon is smaller and more electronegative, so it holds the shared pair more tightly. A third acceptable reason is that the π electron cloud of the ring repels the approaching nucleophile, and a fourth is that the phenyl cation needed for an S_N1 route is very unstable.

Resonance giving partial double bond character 1. Any one further correct reason, such as the sp^2 carbon, the repulsion of the nucleophile or the instability of the phenyl cation 1.

- (xiii) Sodium ethoxide is heated with bromoethane: $C_2H_5ONa + C_2H_5Br \rightarrow C_2H_5OC_2H_5 + NaBr$. The alkoxide ion attacks the carbon from the side opposite the bromine in an S_N2 step. With a tertiary alkyl halide the carbon is too crowded for the alkoxide to reach it, and the alkoxide, being a strong base, instead removes a hydrogen atom from the carbon next door. Elimination therefore takes over from substitution and the main product is an alkene, not an ether.

Correct equation for the synthesis 1. Elimination by the alkoxide acting as a base, giving an alkene with a tertiary halide 1.

Question 3 [10]

- (a) Molar mass of urea = $12 + 16 + 2 \times (14 + 2) = 60 \text{ g mol}^{-1}$, so moles of urea = $6.0/60 = 0.100 \text{ mol}$. Volume = $500 \text{ cm}^3 = 0.500 \text{ dm}^3$. From $\pi V = nRT$, $\pi = nRT/V = (0.100 \times 0.0821 \times 300)/0.500 = 2.463/0.500 = 4.93 \text{ atm}$.

Moles of urea 0.100 mol 1. Correct substitution in $\pi = nRT/V$ 1. Osmotic pressure 4.93 atm 1.

- (b) An azeotrope is a binary liquid mixture of a particular composition which boils at a constant temperature and distils over unchanged, so that its two components cannot be separated by fractional distillation. A minimum boiling azeotrope boils below either pure component, and the mixture of ethanol and water containing about 95 per cent ethanol by mass is the standard example. Such mixtures show a positive deviation from Raoult's law. A maximum boiling azeotrope boils above either pure component, and the mixture of nitric acid and water containing about 68 per cent acid by mass is the standard example. Such mixtures show a negative deviation from Raoult's law.

Azeotrope defined as a constant boiling mixture that cannot be separated by fractional distillation 1. Minimum boiling kind with its example and positive deviation 1. Maximum boiling kind with its example and negative deviation 1.

- (c) The degree of dissociation is $\alpha = \Lambda_m/\Lambda_m^\circ = 7.36/390.5 = 0.0188$, that is about 1.88 per cent. For a weak acid HA of concentration c , $K_a = c\alpha^2/(1 - \alpha) = (0.05 \times 0.0188^2)/(1 - 0.0188) = (0.05 \times 3.554 \times 10^{-4})/0.9812 = 1.777 \times 10^{-5}/0.9812 = 1.81 \times 10^{-5}$. The value of Λ_m° for a weak electrolyte cannot be found by extrapolation, and is obtained instead from Kohlrausch's law of the independent migration of ions, by which the limiting molar conductivity of an electrolyte is the sum of the limiting molar conductivities of the ions it furnishes.

Degree of dissociation 0.0188 1. Correct expression $K_a = c\alpha^2/(1 - \alpha)$ 1. Dissociation constant 1.81×10^{-5} 1. Kohlrausch's law named and stated 1.

Question 4 [10]

- (a) For a first order reaction $k = (2.303/t) \log (a/(a - x))$. When the reaction is 75 per cent complete, $a/(a - x) = 100/25 = 4$, so $t = (2.303/k) \log 4 = (2.303/2.31 \times 10^{-3}) \times 2 \times 0.3010 = 997.0 \times 0.6020 = 600 \text{ s}$, that is 10.0 minutes. Half life $t_{1/2} = 0.693/k = 0.693/2.31 \times 10^{-3} = 300 \text{ s}$, that is 5.00 minutes. The figures agree, since 75 per cent completion takes exactly two half lives.

Correct first order expression with $a/(a - x) = 4$ 1. Time for 75 per cent completion 600 s 1. Half life 300 s 1.

- (b) Hardy-Schulze rule: the coagulation of a sol is brought about by the ion whose charge is opposite in sign to that on the colloidal particles, and the greater the magnitude of the charge on that ion the greater its coagulating power. A negatively charged sol is therefore thrown down far more readily by Al^{3+} than by Na^+ . Electrophoresis is the movement of the colloidal particles themselves towards one or other electrode when a direct potential difference is applied across the sol. Since all the particles of a given sol carry the same sign of charge, they all travel the same way, which is how the sign of that charge is found. A lyophilic sol is the more

stable of the two because its particles have a strong attraction for the dispersion medium and carry a thick solvated sheath around them. That sheath keeps the particles apart quite apart from any charge they bear, so the sol is not easily coagulated and can be reformed simply by adding the medium again. A lyophobic sol is held up by its charge alone, and loses its stability as soon as that charge is neutralised.

Hardy-Schulze rule stated 1. Electrophoresis explained 1. Greater stability of the lyophilic sol traced to solvation of the particles 1.

- (c) Most transition metal compounds are coloured because the metal ion has a partly filled d subshell. The ligands split the five d orbitals into two sets of different energy, and the energy gap between them corresponds to a wavelength in the visible region, so an electron can be lifted from the lower set to the upper set by absorbing visible light. The colour seen is the complement of the colour absorbed. Cr^{2+} is a reducing agent because on losing one more electron it becomes Cr^{3+} , which has the stable half filled t_{2g}^3 arrangement of a d^3 ion, so the change is readily made. Mn^{3+} is an oxidising agent because on gaining one electron it becomes Mn^{2+} , which has the extra stable half filled d^5 configuration, so it takes an electron readily. Fusion of manganese dioxide with alkali in air gives the green manganate: $2\text{MnO}_2 + 4\text{KOH} + \text{O}_2 \rightarrow 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}$. Oxidation of oxalic acid by acidified permanganate: $2\text{MnO}_4^- + 5\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O}$.

Colour traced to d-d transitions in a partly filled d subshell 1. Cr^{2+} reducing and Mn^{3+} oxidising, each explained by the stability of the product configuration 1. Equation for the fusion of manganese dioxide 1. Ionic equation for the oxidation of oxalic acid 1.

Question 5 [10]

- (a) The mechanism is $\text{S}_{\text{N}}1$, and it goes in two steps. In the slow step the carbon to bromine bond breaks on its own, the bromide ion leaving with the shared pair, and a tertiary carbocation $(\text{CH}_3)_3\text{C}^+$ is formed. This intermediate is planar at the central carbon, which is sp^2 hybridised, and it is stabilised by the electron releasing inductive effect and the hyperconjugation of the nine hydrogen atoms on the three methyl groups. In the fast step a water molecule or a hydroxide ion attacks the carbocation at either face and, after the loss of a proton where water is the attacking species, gives the alcohol. The mechanism should be drawn with curved arrows, the first arrow running from the C–Br bond to the bromine and the second from the lone pair of the attacking oxygen to the positive carbon. The product is 2-methylpropan-2-ol. The reaction takes this route rather than $\text{S}_{\text{N}}2$ because the central carbon carries three methyl groups, which block the back side approach of the nucleophile, and because the carbocation that must form is tertiary and therefore the most stable of its kind.

Mechanism named as $\text{S}_{\text{N}}1$ and the slow ionisation step drawn with the tertiary carbocation 1. Fast attack by the nucleophile drawn with curved arrows 1. Product named as 2-methylpropan-2-ol 1.

- (b) Reimer-Tiemann reaction: phenol is treated with chloroform and aqueous sodium hydroxide, and the product is then acidified. The reagent that attacks the ring is dichlorocarbene, and the product is salicylaldehyde, that is 2-hydroxybenzaldehyde. Kolbe reaction: sodium phenoxide is heated with carbon dioxide under a pressure of a few atmospheres at about 400 K, and the product on acidification is salicylic acid, that is 2-hydroxybenzoic acid. Phenol is the stronger acid because the phenoxide ion left after the loss of the proton is stabilised by resonance, the negative charge being spread from the oxygen over the ortho and para carbon atoms of the ring. No such delocalisation is open to the ethoxide ion, where the whole charge stays on one oxygen atom. The carbon joined to oxygen in phenol is also sp^2 hybridised and so more electronegative than the sp^3 carbon in ethanol, which further helps the proton to leave.

Reimer-Tiemann with its reagents, conditions and salicylaldehyde 1. Kolbe reaction with its conditions and salicylic acid 1. Greater acidity of phenol traced to resonance stabilisation of the phenoxide ion 1.

- (c) (1) Aldol condensation. Two molecules of ethanal join, the carbanion formed by the removal of an alpha hydrogen from one of them attacking the carbonyl carbon of the other, and the product is 3-hydroxybutanal. On warming it loses water to give but-2-enal. (2) Cannizzaro reaction. Benzaldehyde has no alpha hydrogen, so it cannot give an aldol and instead disproportionates, one molecule being reduced and another oxidised. The products are benzyl alcohol and sodium benzoate. (3) Nucleophilic addition of hydrogen cyanide across the carbonyl group gives the cyanohydrin, 2-hydroxy-2-methylpropanenitrile. (4) Add a little sodium hydrogen carbonate solution to each. Benzoic acid, being stronger than carbonic acid, gives a brisk effervescence of carbon dioxide, while phenol is too weak an acid to set the gas free and gives no effervescence. Phenol may

be confirmed separately by the violet colour it gives with neutral ferric chloride solution.

Aldol condensation named with 3-hydroxybutanal 1. Cannizzaro reaction named with benzyl alcohol and sodium benzoate 1. Cyanohydrin named as 2-hydroxy-2-methylpropanenitrile 1. Sodium hydrogen carbonate test with the observation for each 1.

Question 6 [10]

- (a) Hofmann bromamide degradation of propanamide: $\text{CH}_3\text{CH}_2\text{CONH}_2 + \text{Br}_2 + 4\text{NaOH} \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2 + \text{Na}_2\text{CO}_3 + 2\text{NaBr} + 2\text{H}_2\text{O}$. The product is ethanamine, a primary amine holding one carbon atom fewer than the amide it came from. Gabriel phthalimide synthesis: phthalimide is treated with alcoholic potassium hydroxide to give potassium phthalimide, this is heated with an alkyl halide so that the nitrogen is alkylated, and the N-alkylphthalimide formed is then hydrolysed with alkali, or treated with hydrazine, to set the primary amine free. The method gives a pure primary amine with no secondary or tertiary amine mixed in. It cannot be used to make aniline, because the step that joins the nitrogen to the carbon is a nucleophilic substitution on the halide, and an aryl halide such as chlorobenzene does not undergo that substitution under these conditions.

Correct balanced equation with ethanamine named 1. Gabriel synthesis described through the three stages 1. Failure with aniline traced to the unreactivity of aryl halides towards nucleophilic substitution 1.

- (b) A nucleoside is formed when a nitrogen containing base is joined to the C-1 of a pentose sugar through a glycosidic linkage, so it has two parts, a base and a sugar. A nucleotide has a third part, a phosphate group esterified to the C-5 hydroxyl of the sugar of a nucleoside, so a nucleotide is a phosphorylated nucleoside and it is the nucleotides that are strung together to build a nucleic acid. The sugar in DNA is 2-deoxy-D-ribose and the sugar in RNA is D-ribose. Denaturation is the loss of the secondary and tertiary structure of a protein brought about by heat, by a change of pH or by certain reagents. The hydrogen bonds and other weak forces that held the chain coiled are broken while the peptide bonds of the primary structure survive, the globular protein uncoils into something more like a fibrous one, and the protein loses its biological activity. The coagulation of egg white on boiling is the familiar example.

Nucleoside and nucleotide distinguished by the phosphate group 1. Both sugars named correctly 1. Denaturation explained with the primary structure left intact and activity lost 1.

- (c) In an addition polymer the monomer units simply add to one another, usually across a carbon to carbon double bond, and nothing is eliminated, so the polymer has the same percentage composition as its monomer. Polyethene, made from ethene, is an example. In a condensation polymer each joining step throws out a small molecule, most often water, and the monomers must each carry two reactive functional groups. Nylon-6,6, made from hexamethylenediamine and adipic acid with the loss of water at every link, is an example. Buna-S is a copolymer of buta-1,3-diene and styrene. The monomer of Teflon is tetrafluoroethene. An antiseptic and a disinfectant both stop microorganisms from growing or kill them outright, but an antiseptic is mild enough to be applied to living tissue, as on a wound or in a mouthwash, while a disinfectant is used on floors, drains and instruments and would damage living tissue. Phenol serves as both, a solution of about 0.2 per cent acting as an antiseptic and one of about 1 per cent as a disinfectant.

Addition and condensation polymers distinguished with one example and its monomers for each 1. Monomers of Buna-S 1. Monomer of Teflon 1. Antiseptic distinguished from disinfectant, with phenol named as serving both purposes 1.