

CHEMISTRY PAPER – 1 (THEORY)

PART I (20 Marks)

Answer *all* questions.

Question 1

- (a) Fill in the blanks by choosing the appropriate word/words from those given in the brackets: [5]

(Henry's, aldol condensation, absence, do not, ohm, Raoult's, increases, common ion effect, easily, three, solubility product, ohm^{-1} , two, four, $\text{ohm}^{-1}\text{cm}^2$, cannizzaro, $\text{ohm}^{-1}\text{cm}^{-1}$, zero, decreases, presence)

- Ideal solutions obey _____ law and they _____ form azeotropic mixtures.
- Benzaldehyde undergoes _____ reaction due to _____ of α -hydrogen atom.
- The solubility of silver chloride _____ in the presence of sodium chloride because of _____.
- The unit of conductance is _____ and that of specific conductance is _____.
- When the concentration of a reactant of first order reaction is doubled, the rate becomes _____ times, but for _____ order reaction, the rate remains same.

- (b) Complete the following statements by selecting the correct alternative from the choices given: [5]

(i) Electrochemical equivalent is the amount of substance which gets deposited from its solution on passing electrical charge equal to:

- 96,500 Coulombs
- 1 Coulomb
- 60 Coulombs
- 965 Coulombs

(ii) The complex ion $[\text{Ni}(\text{CN})_4]^{2-}$ is:

- Square planar and diamagnetic
- Tetrahedral and paramagnetic
- Square planar and paramagnetic
- Tetrahedral and diamagnetic

(iii) Wohler's synthesis is used for the preparation of:

- Glycine
- Amino acids
- Urea
- Proteins

(iv) When SO_2 gas is passed through acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution, the colour of the solution changes to:

- (1) Red
- (2) Black
- (3) Orange
- (4) Green

(v) In the equation $\text{CH}_3\text{COOH} + \text{Cl}_2 \xrightarrow[-\text{HCl}]{\text{Red P}} \text{A}$, the compound A is:

- (1) $\text{CH}_3\text{CH}_2\text{Cl}$
- (2) ClCH_2COOH
- (3) CH_3Cl
- (4) CH_3COCl

(c) Answer the following questions:

[5]

- (i) What is the order of reaction whose rate constant has the same unit as the rate of reaction?
- (ii) What is the pH value of a solution whose hydroxyl ion concentration is 1×10^{-2} M?
- (iii) Calculate the number of coulombs required to deposit 5.4g of Al when the electrode reaction is:



- (iv) Write the reaction to prepare acetaldehyde from hydrogen gas and an acid chloride.
- (v) The edge length of unit cell of a body centered cubic (bcc) crystal is 352 pm. Calculate the radius of the atom.

(d) Match the following:

[5]

- | | |
|------------------------------|--------------------------|
| (i) Weak electrolyte | (a) pH of a solution |
| (ii) Colour in crystals | (b) Iodoform |
| (iii) Acetone | (c) Tollen's reagent |
| (iv) Sorensen | (d) Ostwald dilution law |
| (v) Ammonical silver nitrate | (e) F - centre |

Comments of Examiners

- (a) (i) Some candidates wrote 'Henry's' instead of 'Raoult's' in the first blank. For the second blank, instead of 'do not' a few candidates wrote incorrect answers.
- (ii) Instead of 'Cannizzaro' some candidates wrote 'aldol condensation'. In place of 'absence' some wrote 'presence'.
- (iii) A number of candidates wrote 'increases' instead of 'decreases' in the first blank. Some candidates wrote 'solubility product' instead of 'common ion effect' in the second blank.
- (iv) Some candidates wrote wrong units for conductance and specific conductance.
- (v) Many candidates wrote 'four' instead of 'two' for the first blank. In the second blank also, instead of 'zero', some candidates wrote 'two'.
- (b) (i) Some candidates wrote '96,500 coulombs' instead of '1 coulomb'.
- (ii) Instead of 'square planer and diamagnetic' several candidates wrote wrong alternatives.
- (iii) A few candidates wrote 'protein' instead of 'urea'.
- (iv) Instead of 'green' some candidates gave wrong options.
- (v) A number of candidates attempted this part incorrectly.
- (c) (i) A number of candidates gave the answer as 'first and second order reaction' which was incorrect.
- (ii) Most candidates calculated the pH value = 2 instead of the correct value 12.
- (iii) Some candidates calculated the change in terms of Faraday whereas according to the question, the answer had to be written in Coulombs; incorrect responses were also given.
- (iv) Several candidates were not able to write the conditions for the reaction.
- (v) A number of candidates calculate the radius of bcc unit cell incorrectly as they used the wrong formula.
- (d) This part was attempted correctly by most of the candidates.

Suggestions for teachers

- Teach ideal and non-ideal solutions, Raoult's Law and azeotropic mixtures with examples.
- Explain the named organic reactions along with conditions.
- Ask students to learn common ion effect and its application on the solubility of weak electrolytes.
- Teach the terms 'conductance', 'specific conductance', etc. along with the units.
- Explain the relationship between the change in concentration and rate of reaction, for different order of reactions.
- The relationship between electrochemical equivalent and chemical equivalent should be explained to students.
- The geometry of hybridization and magnetic property of coordination compound must be explained with the help of valence bond theory.
- Sufficient practice should be given on the calculations of order of reaction.
- Give practice on numerical based on calculation of pH and pOH value.
- Stress must be laid on named reactions along with conditions. Ask students to write complete and balanced equations.
- The relationship between edge length (a) and radius (r) for various types of cubic unit cell must be explained to students.

MARKING SCHEME		
Question 1		
(a)	(i)	Raoult's, do not
	(ii)	Cannizzaro, absence
	(iii)	decreases, common ion effect
	(iv)	ohm^{-1} , $\text{ohm}^{-1}\text{cm}^{-1}$
	(v)	two, zero
(b)	(i)	(2) or 1 Coulomb
	(ii)	(1) or Square planar and diamagnetic
	(iii)	(3) or Urea
	(iv)	(4) or Green
	(v)	(2) or ClCH_2COOH
(c)	(i)	Zero order reaction, $\text{rate} = k[\text{A}]^0$ $k = \frac{\text{rate}}{[\text{A}]^0} = \text{rate} = k$
	(ii)	$\text{pOH} = -\log_{10} [\text{OH}^-]$ $[\text{OH}^-] = 1 \times 10^{-2} \text{ M}$ $\text{pOH} = 2,$ $\text{pH} = 14 - 2 = 12$
	(iii)	$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$ 1 mole 3 mole 1 mole 27 g 3 Faraday 27 g $\therefore 27 \text{ g}$ if Al is deposited by 3 F $\therefore 5.4 \text{ g}$ Al is deposited by $\frac{3 \times 5.4}{27} = 0.6 \text{ F}$ Coulomb = Faraday $\times 96,500 = 0.6 \times 96,500$ $= 57,900 \text{ coulomb}$
	(iv)	$\text{CH}_3\text{COCl} + \text{H}_2 \xrightarrow{\text{Pd/BaSO}_4} \text{CH}_3\text{CHO} + \text{HCl}$
	(v)	For bcc structure radius of sphere $= r = \frac{\sqrt{3} a}{4}$ $a = 352 \text{ p m}$ (edge length of unit cell) Radius of atom $(r) = \frac{\sqrt{3}}{4} \times 352$ $= 152.42 \text{ p m}$

(d)	Match the following:			
	(i)	Weak electrolyte	(d)	Ostwald dilution law
	(ii)	Colour in crystals	(e)	F - centre
	(iii)	Acetone	(b)	Iodoform
	(iv)	Sorensen	(a)	pH of a solution
	(v)	Ammonical silver nitrate	(c)	Tollen's reagent

PART II (50 Marks)

Answer six questions choosing two from Section A, two from Section B and two from Section C.

SECTION A

Answer any two questions.

Question 2

- (a) (i) A 10% aqueous solution of cane sugar (mol. wt. 342) is isotonic with 1.754% aqueous solution of urea. Find the molecular mass of urea. [2]
- (ii) The molecular weight of an organic compound is 58 g mol^{-1} . What will be the boiling point of a solution containing 48 grams of the solute in 1200 grams of water? [2]
 [K_b for water = $0.513^\circ\text{C kg mole}^{-1}$; Boiling point of water = 100°C .]
- (iii) What will be the value of van't Hoff factor(i) of benzoic acid if it dimerises in aqueous solution? How will the experimental molecular weight vary as compared to the normal molecular weight? [1]
- (b) (i) Determine the pH value of 0.001 M acetic acid solution if it is 2% ionised at this concentration. How can the degree of dissociation of this acetic acid solution be increased? [2]
- (ii) The solubility product of PbCl_2 at 298K is 1.7×10^{-5} . Calculate the solubility of PbCl_2 in g/lit. at 298K. [2]
 Atomic Weights: [Pb = 207 and Cl = 35.5]
- (c) Graphite is anisotropic with respect to conduction of electric current. Explain. [1]

Comments of Examiners

- (a) (i) A number of candidates calculated the number of moles incorrectly. A few candidates calculated the molecular weight of urea directly.
- (ii) Calculation of elevation of boiling point (ΔT_b) was done correctly by many candidates but a few candidates subtracted this value from boiling point of water instead of adding ΔT_b to the boiling point of water to obtain the correct boiling point of solution.
- (iii) Several candidates wrote that $i < 1$ instead of $i = 0.5$ or $\frac{1}{2}$. Experimental molecular weight = $2 \times$ normal molecular weight was also not mentioned by a few candidates.
- (b) (i) The pH value was calculated correctly by most of the candidates. However, a number of candidates were not able to answer the second part of the question, i.e. 'How can the degree of dissociation of this acetic acid solution be increased?'
- (ii) Most of the candidates calculated the solubility of $PbCl_2$ in terms of moles per litre only but not in terms of g/litre, as asked in the question.
- (c) Many candidates were not able to explain clearly the term 'anisotropy' with reference to the electrical conductivity in graphite.

Suggestions for teachers

- Stress upon writing all the steps involved in solving the numerical problems i.e. the formula, substitution and calculation of answer with correct unit.
- Explain the difference between the boiling point of pure solvent and the solution.
- The abnormal molecular weights, Van't Hoff factor, degree of dissociation, degree of association must be explained clearly to students.
- Stress upon calculation of pH value by using correct formula. The concept of Ostwald dilution law and its application must be explained in detail to students.
- Use of the formula i.e. $K_{sp} = 4s^3$ for $BaCl_2$, conversion of solubility from moles/lit. to g/lit. and vice versa must be explained clearly to students.
- The concept of anisotropy and free electrons in graphite must be explained to students.

MARKING SCHEME	
Question 2	
(a)	(i) No. of moles of cane sugar = $\frac{10}{342} = 0.0292$ No. of moles of urea = $\frac{1.754}{x}$ Π cane sugar = Π urea (isotonic solution) $n_1 RT/V = n_2 RT/V$ $0.0292 = 1.754/x$ $x = 60.06$
	(ii) 1200 g of water contains 48 g of solute 1000 g contains $48 \times 1000/1200 = 40$ g of solute Molality = $40/58 = 0.689$ mol / kg $\Delta T_b = k_b \text{ molality} = 0.513 \times 0.689 = 0.353^\circ\text{C}$

		B.P. = $100 + 0.353 = 100.353^{\circ}\text{C}$
	(iii)	Vant Hoff factor (i) = observed colligative property / normal colligative property Since benzoic acid dimerised, $i = \frac{1}{2}$ or 0.5 Experimental mol. wt. = twice the normal mol.wt.
(b)	(i)	$\alpha = \frac{2.0}{100} = 0.02$ $\text{pH} = -\log C \alpha$ $\text{pH} = -\log 0.001 \times 0.02 = -\log 2 \times 10^{-5}$ $\text{pH} = 4.69$ The degree of dissociation of this acetic acid can be increased by diluting the solution
	(ii)	Solubility product (k_{sp}) = $4S^3 = 1.7 \times 10^{-5}$ Solubility (S) = $0.01619 \text{ mol L}^{-1}$ Mol mass of $\text{PbCl}_2 = 278$ Solubility in g/lit. = $0.01619 \times 278 = 4.50 \text{ g/lit.}$
(c)		Graphite exists in the form of layer structure. The electrical conductivity is more parallel to the layer whereas the electrical conductivity is less perpendicular to the layer.

Question 3

- (a) (i) In a body centred and face centred arrangement of atoms of an element, what will be the number of atoms present in respective unit cells? Justify your answer with calculation. [2]
- (ii) A compound AB has a simple cubic structure and has molecular mass 99. Its density is 3.4 g cm^{-3} . What will be the edge length of the unit cell? [2]
- (b) (i) For the reaction: $2\text{NO}_{(g)} \rightleftharpoons \text{N}_{2(g)} + \text{O}_{2(g)}$; $\Delta H = -\text{heat}$ [2]
 $K_e = 2.5 \times 10^2$ at 298K
what will happen to the concentration of N_2 if:
(1) Temperature is decreased to 273K.
(2) Pressure is reduced.
- (ii) In a first order reaction, 10% of the reactant is consumed in 25 minutes. Calculate: [2]
(1) The half-life period of the reaction.
(2) The time required for completing 87.5% of the reaction.
- (c) Water acts as Bronsted acid as well as a Bronsted base. Give one example each to illustrate this statement. [2]

Comments of Examiners

- (a) (i) Most of the candidates wrote the answer directly without showing the calculation.
- (ii) While many candidates were able to calculate the value of a^3 , the value of edge length was not calculated correctly in many cases. Some candidates substituted the value of $z = 4$ instead of $z = 1$.
- (b) (i) A few candidates were confused regarding whether the given reaction is exothermic or endothermic, hence gave wrong answers. The second part was not attempted correctly by many candidates.
- (ii) While a number of candidates were able to calculate $t_{1/2}$ correctly, the time required for completing 87.5% of the reaction was not calculated correctly by many candidates.
- (c) Concept of Bronsted acid and Bronsted base was not clear to many candidates. Most of the candidates could not give proper examples of water acting as Bronsted acid and as Bronsted base.

Suggestions for teachers

- Explain the calculations to find out the number of atoms in various types of cubic unit cells i.e. simple cubic, body centered cubic and face centered cubic.
- Give more practice in solving numerical problems based on density, edge length, etc.
- Factors affecting chemical equilibrium using Le Chatelier's principle should be explained to students.
- Sufficient practice in numericals based on half-life period ($t_{1/2}$) should be given.
- Bronsted Lowry's concept and acid-base conjugate pairs should be explained clearly with examples.

MARKING SCHEME

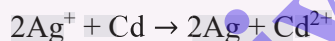
Question 3

(a)	(i)	BCC corner atoms = $8 \times \frac{1}{8} = 1$ Body centred atom = $1 \times 1 = 1$ Total number of atoms $1 + 1 = 2$ FCC corner atoms = $8 \times \frac{1}{8} = 1$ Face centred atoms = $6 \times \frac{1}{2} = 3$ Total number of atoms $1 + 3 = 4$
	(ii)	$\rho = \frac{Z \times M}{a^3 \times N_A}$ <p>Simple cubic structure $Z = 1$</p> <p>$M = 99$, $N_A = 6.023 \times 10^{23}$, density = 3.4 g/cm^3</p> $a^3 = \frac{Z \times M}{\rho \times N_A} = \frac{1 \times 99}{3.4 \times 6.023 \times 10^{23}}$ $a^3 = 4.834 \times 10^{-23} \text{ cm}^3$ $a = 3.64 \times 10^{-8} \text{ cm}$

(b)	(i)	(1)	The reaction is exothermic hence decrease in temperature will favour the forward reaction, i.e. concentration of N_2 will increase.
		(2)	Pressure has no effect on equilibrium.
	(ii)	(1)	$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$ $k = \frac{2.303}{25} \log_{10} \frac{100}{90}$ $k = 0.0042 \text{ min}^{-1}$ $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0042} = 165 \text{ min}$
		(2)	$t = \frac{2.303}{0.0042} \log_{10} \frac{100}{12.5}$ $t = 495.14 \text{ min}$
(c)	$HCl_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + Cl^-_{(aq)}$ acid-1 base-2 acid-2 base-1 $H_2O_{(l)} + NH_3_{(l)} \rightleftharpoons NH_4^+_{(aq)} + OH^-_{(aq)}$ acid-1 base-2 acid-2 base-1		

Question 4

- (a) (i) Consider the following cell reaction at 298 K: [3]



The standard reduction potentials (E°) for Ag^+/Ag and Cd^{2+}/Cd are 0.80V and -0.40V respectively:

- (1) Write the cell representation.
- (2) What will be the emf of the cell if the concentration of Cd^{2+} is 0.1 M and that of Ag^+ is 0.2 M?
- (3) Will the cell work spontaneously for the condition given in (2) above?

- (ii) What is a buffer solution? How is it prepared? Explain the buffer action of a basic buffer with a suitable example. [2]

- (b) Explain the following: [2]

- (i) When NaCl is added to $AgNO_3$ solution, a white precipitate is formed.
- (ii) An aqueous solution of ammonium chloride is acidic in nature.

- (c) A 0.05 M NH_4OH solution offers the resistance of 50 ohms to a conductivity cell at 298K. If the cell constant is 0.50 cm^{-1} and molar conductance of NH_4OH at infinite dilution is $471.4 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, calculate: [3]

- (i) Specific conductance
- (ii) Molar conductance
- (iii) Degree of dissociation

Comments of Examiners

- (a) (i) The cell representation was not given correctly by many candidates; the calculation of emf of the cell by using Nernst equation was also not correct, in some cases. The third part of the question was generally answered correctly by most candidates.
- (ii) Many candidates explained acidic buffer and its action instead of basic buffer
- (b) (i) Some of the candidates did not mention that the white precipitate is due to the formation of AgCl.
- (ii) Several candidates mentioned 'anionic hydrolysis' instead of 'cationic hydrolysis'.
- (c) (i) Specific conductance (k) was calculated correctly in most cases.
- (ii) While most candidates calculated molar conductance correctly, the unit was not mentioned in several cases.
- (iii) The degree of dissociation (α) was not calculated correctly by many candidates.

Suggestions for teachers

- Give more practice in cell representation; Numericals based on Nernst equation should be taught with examples. The relationship between Gibbs free energy (G) and emf of the cell (E) must be explained clearly.
- Theory of precipitation that I.P. > ksp should be explained to students.
- Explain cationic and anionic hydrolysis to students by giving suitable examples.
- Explain clearly the calculations of specific conductance and degree of dissociation.

MARKING SCHEME			
Question 4			
(a)	(i)	(1)	$\text{Cd}_{(s)} / \text{Cd}^{2+}_{(aq)} // \text{Ag}^{+}_{(aq)} / \text{Ag}$
		(2)	$E_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$ $= 0.80 - (-0.40)$ $= 1.2\text{V}$ $E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n} \log_{10} \frac{[\text{cd}^{2+}][\text{Ag}]^2}{[\text{Ag}^+]^2 [\text{cd}]}$ $= 1.2 - \frac{0.0591}{n} \log \frac{[0.1]}{[0.2]^2}$ $= 1.18\text{V}$
		(3)	$\Delta G = -nFE^{\circ}$ <p>Since E° is positive, ΔG will be negative so the cell will work spontaneously.</p>
	(ii)	<p>Buffer solutions are those solutions which resist the change in their pH value when small quantity of acid or alkali is added to it.</p> <p>Preparation of buffer</p> <ul style="list-style-type: none"> • By taking aqueous solution of a weak acid and its salt with a strong base. or • By taking aqueous solution of a weak base and its salt with a strong acid. 	

		<p>Buffer action of basic buffer</p> $\text{NH}_4\text{OH}(\text{aq}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$ $\text{NH}_4\text{Cl}(\text{aq}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{Cl}^-(\text{aq})$ <p>On adding NaOH</p> $\text{NH}_4^+ + \text{OH}^- \longrightarrow \text{NH}_4\text{OH}(\text{aq})$ <p>From buffer from NaOH</p> <p>On adding HCl</p> $\text{OH}^-(\text{aq}) + \text{H}_3\text{O}^+ \longrightarrow 2\text{H}_2\text{O}(\text{l})$ <p>From buffer from HCl</p> <p>Hence, there is no change in pH of buffer solution.</p> <p><i>Buffer action of any basic buffer solution may be given.</i></p>
(b)	(i)	$\text{NaCl}_{\text{aq}} \longrightarrow \text{Na}^+ + \text{Cl}^-$ $\text{AgNO}_3_{\text{aq}} \longrightarrow \text{Ag}^+ + \text{NO}_3^-$ $\text{NaCl} + \text{AgNO}_3 \rightarrow \text{AgCl} + \text{NaNO}_3$ <p style="text-align: center;">white ppt</p>
	(ii)	Ammonium chloride is a salt of strong acid and weak base, hence due to cationic hydrolysis, the <i>aq</i> solution of ammonium chloride is acidic in nature.
(c)	(i)	<p>Specific conductance $\kappa = \frac{1}{R} \times \text{cell constant}$</p> $= \frac{1}{50} \times 0.50$ $= 0.01 \text{ ohm}^{-1} \text{ cm}^{-1}$
	(ii)	<p>Molar conductance (\wedge_m) = $\frac{1000 \times \kappa}{c} = \frac{1000 \times 0.01}{0.05}$</p> $= 200 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$
	(iii)	<p>Degree of dissociation (α) = $\frac{\wedge_m}{\wedge_{m^\infty}} = \frac{200}{471.4} = 0.4242$</p>

SECTION B

Answer any two questions

Question 5

- (a) Write the IUPAC names of the following: [2]
- (i) $[\text{Co}(\text{NH}_3)_4\text{SO}_4]\text{NO}_3$
- (ii) $\text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_3]$
- (b) What type of isomerism is exhibited by the following pairs of compounds: [1]
- (i) $[\text{PtCl}_2(\text{NH}_3)_4]\text{Br}_2$ and $[\text{PtBr}_2(\text{NH}_3)_4]\text{Cl}_2$
- (ii) $[\text{Cr}(\text{SCN})(\text{H}_2\text{O})_5]^{2+}$ and $[\text{Cr}(\text{NCS})(\text{H}_2\text{O})_5]^{2+}$

- (c) How does $K_2[PtCl_4]$ get ionised when dissolved in water? Will it form precipitate [2]
when $AgNO_3$ solution is added to it? Give a reason for your answer.

Comments of Examiners

- (a) (i) Some candidates wrote 'amine' instead of 'ammine'. A few candidates wrote the wrong oxidation state.
(ii) Several candidates wrote 'platinumate' or 'platinum' instead of 'platinate'.
- (b) (i) While most candidates wrote the correct type of isomerism some wrote ionic and structural isomerism instead of 'ionization isomerism'.
(ii) Some candidates wrote 'ligand isomerism' instead of 'linkage isomerism'.
- (c) The ionization of $K_2[PtCl_4]$, was not correctly mentioned by a number of candidates. A few candidates wrote that precipitate will be formed when $AgNO_3$ solution is added.

Suggestions for teachers

- Given sufficient practice in writing IUPAC names.
- Calculation of oxidation state of central metal atom should be given more emphasis.
- Isomerism of coordination compounds should be explained to students with examples.

MARKING SCHEME		
Question 5		
(a)	(i)	Tetraamminesulphato cobalt(III) nitrate
	(ii)	Potassium ammine trichloridoplatinate(II)
(b)	(i)	Ionisation isomerism
	(ii)	Linkage isomerism
(c)	$K_2[PtCl_4] \rightarrow 2K^+ + [PtCl_4]^{2-}$ It will not form white precipitate with $AgNO_3$ solution because Cl^- ion is not free to form white precipitate of $AgCl$.	

Question 6

- (a) Give balanced equations for the following reactions: [3]
- (i) Silver nitrate is added to dilute solution of sodium thiosulphate.
- (ii) Potassium dichromate is treated with acidified ferrous sulphate solution.
- (iii) Phosphorous reacts with conc. sulphuric acid.
- (b) How will you obtain pure potassium permanganate ($KMnO_4$) crystals from its ore, pyrolusite? Give the steps involved and the reactions. [2]

Comments of Examiners

- (a) Most of the candidates wrote either incorrect or incomplete equations. In many cases, the equations were unbalanced.
- (b) The conversion of pyrolusite (MnO_2) to pure potassium permanganate was not answered correctly by the candidates. Candidates were not able to write the steps correctly.

Suggestions for teachers

- More practice should be given in writing complete and balanced equations.
- Emphasis should be given on writing complete and correct equations of preparation of KMnO_4 from MnO_2 (pyrolusite ore)

MARKING SCHEME		
Question 6		
(a)	(i)	$2\text{AgNO}_3 + \text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Ag}_2\text{S}_2\text{O}_3 + 2\text{NaNO}_3$ white ppt $\text{Ag}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{Ag}_2\text{S} + \text{H}_2\text{SO}_4$ black
	(ii)	$\text{K}_2\text{Cr}_2\text{O}_7 + 7\text{H}_2\text{SO}_4 + 6\text{FeSO}_4 \rightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + 3\text{Fe}_2(\text{SO}_4)_3 + 7\text{H}_2\text{O}$
	(iii)	$\text{P}_4 + 10\text{H}_2\text{SO}_4 \rightarrow 4\text{H}_3\text{PO}_4 + 10\text{SO}_2 + 4\text{H}_2\text{O}$
(b)		Conversion of pyrolusite (MnO_2) to potassium manganate $2\text{MnO}_2 + 4\text{KOH} + \text{O}_2 \xrightarrow{\Delta} 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}$ Or $2\text{MnO}_2 + 2\text{K}_2\text{CO}_3 + \text{O}_2 \xrightarrow{\Delta} 2\text{K}_2\text{MnO}_4 + 2\text{CO}_2$ Oxidation of potassium manganate to potassium permanganate. $3\text{K}_2\text{MnO}_4 + 2\text{CO}_2 \rightarrow 2\text{KMnO}_4 + \text{MnO}_2 + 2\text{K}_2\text{CO}_3$ Or $2\text{K}_2\text{MnO}_4 + \text{Cl}_2 \rightarrow 2\text{KMnO}_4 + 2\text{KCl}$ <i>(or any other correct method)</i>

Question 7

- (a) (i) Sulphur dioxide acts as an oxidizing agent as well as a reducing agent. Give one reaction each to show its oxidizing nature and its reducing nature. [3]
- (ii) Explain why an aqueous solution of potassium hexacyanoferrate (II) does not give the test for ferrous ion.
- (b) What is meant by Lanthanide contraction? Write the general electronic configuration of inner transition elements. [2]

Comments of Examiners

- (a) (i) Most of the candidates were not able to write this answer correctly. The examples given were also not correct.
- (ii) The ionisation of complex compounds was shown correctly by many candidates but some gave invalid reasons.
- (b) Incorrect meaning of lanthanide contraction was given by several candidates. The general electronic configuration of inner-transition element was not written correctly in many cases.

Suggestions for teachers

- Explain the properties of oxidising and reducing agents with correct examples.
- Explain ionisation of co-ordination compounds clearly. Basic idea of complex compound should be given.
- Explain the general electronic configuration of block elements.

MARKING SCHEME	
Question 7	
(a)	(i) The oxidation state of S in SO ₂ is + 4 Which is an intermediate state and may increase or decrease. Hence, SO ₂ can act both as an oxidizing and reducing agent. Example of oxidizing agent → 3Fe + SO ₂ → 2FeO + FeS Example of reducing agent → SO ₂ + I ₂ + 2H ₂ O → H ₂ SO ₄ + 2HI
	(ii) Aqueous solution of K ₄ [Fe(CN) ₆] ionizes as K ₄ [Fe(CN) ₆] ⇌ 4K ⁺ + [Fe(CN) ₆] ⁴⁻ Fe ²⁺ ion is not in free state, hence it does not give the test of Fe ²⁺ ion.
(b)	On moving from La ³⁺ (At. No. 57) to Lu ³⁺ (At. No. 71) the size of the atoms and ions decreases regularly due to increase in nuclear charge. This decrease in size is called Lanthanide contraction. The general electronic configuration of inner transitional elements is ns ² (n-1) d ⁰⁻¹ (n- 2)f ¹⁻¹⁴

SECTION C

Answer any two questions.

Question 8

- (a) How can the following conversions be brought about:
- (i) Acetaldehyde to acetaldehyde phenyl hydrazone. [1]
 - (ii) Benzoic acid to aniline. [1]
 - (iii) Methyl chloride to acetone. [2]
 - (iv) Benzene to benzene diazonium chloride. [1]
- (b) (i) Glycerol (propane 1, 2, 3 triol) is more viscous than ethylene glycol (ethane 1, 2, diol). Explain. [1]
- (ii) How can urea be detected by Biuret test? [1]
- (c) Identify the compounds **A**, **B** and **C**: [3]
- (i) $C_2H_5OH \xrightarrow{PCl_5} A \xrightarrow{KCN} B \xrightarrow{H_3O^+} C_2H_5COOH \xrightarrow[\Delta]{NH_3} C$
- (ii) $C_6H_5COOH \xrightarrow{SOCl_2} A \xrightarrow{NH_3} B \xrightarrow{Br_2/KOH} C$

Comments of Examiners

- (a) Most of the candidates answered this part correctly. Some common errors made by them were:
- (i) The product formed was correct but the equation given was not balanced.
 - (ii) The conversion of benzoic acid to aniline was answered correctly. However, some candidates failed to write the conditions for the reaction.
 - (iii) Many candidates could not complete the reaction after reaching up to acetic acid.
 - (iv) Incomplete or incorrect equation was given by the candidates, temperature $0^\circ - 5^\circ$ was not mentioned.
- (b) (i) The explanation given by a few candidates were not correct. Some failed to mention that the extent of hydrogen bonding is more in glycerol, hence it is more viscous than ethylene glycol.
- (ii) Some candidates did not mention heating of urea at above $132^\circ C$ to form biuret. Instead of violet colour, some candidates wrote pink or blue colour.
- (c) (i) Most of the candidates identified compounds A, B and C correctly, but some identified compound C as CH_3COONH_4 instead of CH_3CONH_2
- (ii) Compound 'A' was not identified correctly by some of the candidates.

Suggestions for teachers

- Stress upon writing complete and balanced equations along with proper conditions while giving the chemical equations.
- Properties of alcohols should be taught in much more detail.
- Named organic reactions such as biuret test must be explained to the students.
- Give more practice to students in identifying organic compounds.
- More practice should be given to solve such problems.

MARKING SCHEME		
Question 8		
(a)	(i)	$\text{CH}_3 \underset{\text{H}}{\text{C}} = \text{O} + \text{H}_2 \text{NHN} \cdot \text{C}_6\text{H}_5 \rightarrow \text{CH}_3 \underset{\text{H}}{\text{C}} = \text{NHN} \text{C}_6\text{H}_5 + \text{H}_2\text{O}$
	(ii)	$\text{C}_6\text{H}_5\text{COOH} \xrightarrow[\Delta]{\text{NaOH/CaO}} \text{C}_6\text{H}_5\text{COO}^- \text{Ca}^+ \xrightarrow[\text{conc}]{\text{HNO}_3/\text{H}_2\text{SO}_4} \text{C}_6\text{H}_5\text{NO}_2 \xrightarrow{\text{Sn/HCl}} \text{C}_6\text{H}_5\text{NH}_2$
	(iii)	$\text{CH}_3\text{Cl} \xrightarrow{\text{KCN}} \text{CH}_3\text{CN} \xrightarrow{\text{HOH/H}^+} \text{CH}_3\text{COOH}$ $\xrightarrow{\text{Ca(OH)}_2} (\text{CH}_3\text{COO})_2\text{Ca} \xrightarrow{\text{distil.}} \text{CH}_3\text{COCH}_3$
	(iv)	$\text{C}_6\text{H}_6 \xrightarrow[\text{6[H]}]{\text{conc HNO}_3/\text{conc H}_2\text{SO}_4} \text{C}_6\text{H}_5\text{NO}_2 \xrightarrow{\text{Sn/HCl}} \text{C}_6\text{H}_5\text{NH}_2$ $\text{C}_6\text{H}_5\text{NH}_2 \xrightarrow[0^\circ - 5^\circ\text{C}]{\text{NaNO}_2/\text{HCl}} \text{C}_6\text{H}_5\text{N}_2\text{Cl}$
b)	(i)	Glycerol is more viscous than ethane 1, 2 diol because, in glycerol, there are three OH groups as compared to two OH groups in ethane 1, 2 diol. Therefore, the extent of hydrogen bonding is more, hence glycerol is more viscous.
	(ii)	<p>Biuret test:</p> <p>2 moles of urea when heated above 132°C</p> $2 \text{H}_2\text{NCO} \boxed{\text{NH}_2 + \text{H}} \text{NH} \cdot \text{CONH}_2 \xrightarrow[\text{above}]{132^\circ\text{C}} \text{H}_2\text{NCO} \text{NHCONH}_2 + \text{H}_2\text{O}$ <p style="text-align: center;">Biuret</p> <p>When alkaline solution of biuret is treated with copper sulphate solution, a violet colour is produced.</p>
(c)	(i)	<p>A = C₂H₅Cl</p> <p>B = C₂H₅CN</p> <p>C = C₂H₅CONH₂</p>
	(ii)	<p>A = C₆H₅COCl</p> <p>B = C₆H₅CONH₂</p> <p>C = C₆H₅NH₂</p>

Question 9

- (a) Give balanced equations for the following name reactions: [3]
- Benzoin condensation
 - Wurtz-Fittig reaction
 - Carbylamine reaction
- (b) Give chemical test to distinguish: [3]
- Formaldehyde and acetaldehyde
 - Dimethyl ether and ethyl alcohol.

- (c) (i) Write the structure of three ethers with molecular formula C₄H₁₀O. [4]
 (ii) Starting with Grignard's reagent, how will you prepare propanoic acid?

Comments of Examiners

- (a) (i) Many candidates wrote the structure of Benzoin incorrectly. Some failed to mention alcoholic KCN.
 (ii) Some candidates missed the condition 'dry ether', while some gave the example of Fittig reaction.
 (iii) A number of candidates did not mention alcoholic KOH. Some gave incomplete equations - they did not mention by-products.
 (b) (i) Correct observations were not written in some cases although the tests given were correct.
 (ii) Some candidates wrote the positive test for ethyl alcohol but did not write anything about dimethyl ether.
 (c) (i) Most of the candidates were able to write the structure of at least two ethers. However, a number of candidates were not able to write the structure of branched chain ether.

Suggestions for teachers

- To distinguish between compounds by chemical test, the experiment, condition and observation must be given. Students must be asked to write the positive test for one compound and negative test for the other.
- Insist that the students must learn the structural formula of organic compounds.
- Teach preparation of different organic compounds by starting with Grignard's reagent.

- (ii) Instead of 'propanoic acid' many candidates wrote the preparation of 'ethanoic acid'.

MARKING SCHEME	
Question 9	
(a)	(i) Benzoin condensation: $\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{C}_6\text{H}_5\text{C} + \text{H} - \text{C} - \text{C}_6\text{H}_5 \xrightarrow[\Delta]{\text{KCN(alc)}} \text{C}_6\text{H}_5 - \text{C} - \text{C} - \text{C}_6\text{H}_5 \\ \qquad \qquad \qquad \\ \text{H} \qquad \qquad \qquad \text{H} \\ \text{Benzoin} \end{array}$
	(ii) Wurtz-Fittig reaction: $\text{C}_6\text{H}_5\text{Cl} + 2\text{Na} + \text{ClCH}_3 \xrightarrow{\text{dry ether}} \text{C}_6\text{H}_5. \text{CH}_3 + 2\text{NaCl}$
	(iii) Carbylamine reaction: $\text{RNH}_2 + \text{CHCl}_3 + 3\text{KOH}_{(\text{alc})} \xrightarrow{\Delta} \text{R} - \text{N} \equiv \text{C} + 3\text{KCl} + 3\text{H}_2\text{O}$
(b)	(i) Formaldehyde and acetaldehyde: Acetaldehyde on reaction with iodine and alkali gives yellow precipitate of iodoform which has a characteristic odour. Formaldehyde does not give this test. <i>(or any other suitable test.)</i>
	Dimethyl ether and ethyl alcohol: Ethyl alcohol when reacts with iodine and alkali gives yellow precipitate of iodoform

		which has characteristic odour. Diethyl ether does not give this test. (or any other suitable test)
(c)	(i)	$\text{CH}_3 - \text{O} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$ $\text{CH}_3 \text{CH}_2 - \text{O} - \text{CH}_2 - \text{CH}_3$ $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{O} - \text{CH} - \text{CH}_3 \end{array}$
	(ii)	$\text{C}_2\text{H}_5\text{MgBr} + \text{O} = \text{C} = \text{O} \rightarrow \begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{O} = \text{C} - \text{O} \text{MgBr} \end{array} \xrightarrow{+\text{HOH}} \begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{O} = \text{C} - \text{OH} \end{array} + \text{Mg} \begin{array}{c} \text{Br} \\ / \\ \backslash \\ \text{OH} \end{array}$

Question 10

- (a) An organic compound A has the molecular formula $\text{C}_7\text{H}_6\text{O}$. When A is treated with NaOH followed by acid hydrolysis, it gives two products B and C. When B is oxidized, it gives A, when A and C are each treated separately with PCl_5 , they give two different products D and E. [3]
- (i) Identify A, B, C, D and E.
- (ii) Give the chemical reaction when A is treated with NaOH and name the reaction.
- (b) Answer the following: [4]
- (i) What do you observe when glucose solution is heated with Tollen's reagent?
- (ii) Name the monomers and the type of polymerisation in each of the following polymers:
- (1) Terylene
 - (2) Polyvinyl chloride
- (c) Give balanced equations for the following reactions: [3]
- (i) Ethylamine with nitrous acid.
- (ii) Diethyl ether with phosphorous pentachloride.
- (iii) Aniline with acetyl chloride.

Comments of Examiners

- (a) (i) A number of candidates were able to identify compounds A, B, C, D, & E correctly. Some candidates identified compound 'C' as 'C₆H₅COONa' instead of 'C₆H₅COOH'. A few candidates were not able to identify compound D correctly.
- (ii) The Cannizzaro's reaction was given correctly by most of the candidates.
- (b) (i) Most of the candidates wrote that silver mirror is formed. Some wrote that a white precipitate is formed.
- (ii) Many candidates were unable to write the correct monomers of Terylene. Some wrote incorrect polymerization.
- (c) (i) Incomplete equations was given by some candidates. A few candidates could not write C₂H₃OH as product.
- (ii) A number of candidates wrote wrong products such as C₂H₅COCl or C₂Cl₅-O-C₂Cl₅ although correct answer was C₂H₅Cl and POCl₃.
- (iii) In some cases, wrong formula of the product was written - instead of C₆H₅NHCOCH₃, several candidates wrote C₆H₅NHCH₃CO.

Suggestions for teachers

- Give more practice for questions in which identification of compounds is based on different chemical reactions.
- Give more emphasis on named reactions.
- Insist that the students read the observations for different organic reactions. They should mention colour or ppt. properly.
- Teach the polymers and their monomers in detail. The types of polymerisation should also be explained in detail.
- Ask students to write balanced equations with correct reactants and products.

MARKING SCHEME		
Question 10		
(a)	(i)	(A) = C ₆ H ₅ CHO (B) = C ₆ H ₅ CH ₂ OH (C) = C ₆ H ₅ COOH (D) = C ₆ H ₅ CHCl ₂ (E) = C ₆ H ₅ COCl
	(ii)	2 C ₆ H ₅ CHO + NaOH → C ₆ H ₅ COONa + C ₆ H ₅ CH ₂ OH OR Cannizzaro reaction

(b)	(i)	$\begin{array}{ccc} \text{CHO} & & \text{COONH}_4 \\ & & \\ (\text{CHOH})_4 + 2[\text{Ag}(\text{NH}_3)_2]^+ \text{OH}^- \xrightarrow{\Delta} & & (\text{CHOH})_4 + 2\text{Ag} + 3\text{NH}_3 + \text{H}_2\text{O} \\ & \text{Tollen's reagent} & \\ \text{CH}_2\text{OH} & & \text{CH}_2\text{OH} \\ \text{glucose} & & \text{Silver mirror} \end{array}$	
		<p style="text-align: center;">OR</p> $\begin{array}{ccc} \text{CHO} & & \text{COOH} \\ & & \\ (\text{CHOH})_4 + \text{Ag}_2\text{O} \xrightarrow{\Delta} & & (\text{CHOH})_4 + 2\text{Ag} \\ & \text{Tollen's reagent} & \\ \text{CH}_2\text{OH} & & \text{CH}_2\text{OH} \\ \text{glucose} & & \text{Silver mirror} \end{array}$	
	(ii)	(1)	Terylene: Ethylene glycol + terephthalic acid Condensation polymerisation
		(2)	Polyvinyl chloride: Vinyl chloride Addition polymerisation
(c)	(i)	$\text{C}_2\text{H}_5\text{NH}_2 + \text{HONO} \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{N}_2 + \text{H}_2\text{O}$	
	(ii)	$\text{C}_2\text{H}_5 - \text{O} - \text{C}_2\text{H}_5 + \text{PCl}_5 \rightarrow 2\text{C}_2\text{H}_5\text{Cl} + \text{POCl}_3$	
	(iii)	CH_3CO	$\text{Cl} + \text{H} \quad \text{NHC}_6\text{H}_5 \rightarrow \text{CH}_3\text{CONHC}_6\text{H}_5 + \text{HCl}$

GENERAL COMMENTS:

(a) Topics found difficult by candidates:

- Numerical problems of relative molecular mass and mole, Van't Hoff factor and its relation with molecular weight, calculation of degree of dissociation
- Anisotropic nature of graphite, calculation of edge length (a) and radius (r) of unit cell
- Chemical equilibrium, Le Chatelier's principle
- Electrolytic conductance, calculation of emf of the cell and cell representation, Nernst equation
- Ionic equilibria, calculation of pH value, solubility and solubility product
- Bronsted-Lowry's concept for acid and base. Buffer action of basic buffer
- Preparation of inorganic compounds
- General electronic configuration of inner transition elements
- Conversion of organic compounds, balancing of equations and named organic reactions
- Chemical tests to distinguish between organic compounds

(b) Concepts between which candidates got confused:

- Van't Hoff factor and molecular weight
- Anisotropic and isotropic
- Common ion effect and solubility product
- Total number of particles in bcc and fcc unit cell and their relationship
- Paramagnetic and diamagnetic
- Edge length (a) and radius (r) of various types of cubic unit cell and their relationship
- Buffer action of acidic and basic buffer
- Concept of oxidation and reduction of SO_2
- Gibb's free energy and emf of cell in terms of spontaneity
- Types of polymerization and polymer

(c) Suggestions for candidates:

- Read questions carefully and understand what is required before attempting the question.
- Practice numerical problems regularly, solve the numerical stepwise with correct formula and write the answer with correct unit.
 - Learn complete and balanced equations along with the conditions, in inorganic and organic compounds
 - Avoid selective study.
 - Practice writing the IUPAC names for coordination compounds as well as organic compounds.
 - Learn both positive and negative chemical tests in organic reactions.
 - Learn the shapes and hybridization of molecules with diagram.
 - While solving numerical problems, proper steps should be followed, i.e. formula, substitution and correct answer with units.