2 0 1 7

(April)

CHEMISTRY

(Elective/Honours)

(General Chemistry—II)

(Inorganic, Organic and Physical)

(Chem–EH–201)

Marks : 56

Time : 3 hours

The figures in the margin indicate full marks for the questions

SECTION—I

(Inorganic)

(*Marks* : 19)

1. *(a)* Define solubility product. The solubility of CaF_2 in water at 18 °C is $2 \cdot 05 \times 10^{-4}$ mol/l. Calculate its solubility product. $1 + 1\frac{1}{2} = 2\frac{1}{2}$

(Turn Over)

(b) How does iodometry differ from iodimetry?   1+1=2

(c) An aqueous solution is prepared by dissolving 4 g of NaOH to give 500 ml of it. Calculate the molarity of the solution.   1

(d) Define acids and bases on the basis of Arrhenius concept. Give an example for each. What is the limitation of this concept?   1+1+1=3

(e) Given the pK_a values for each, which is a strong acid, H_2SO_4 ($pK_a = -1$) or H_2SO_3 ($pK_a = 1·9$).   1

OR

2. (a) What are acid-base indicators? Discuss the action of phenolphthalein as an indicator.   1+2=3
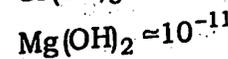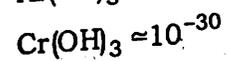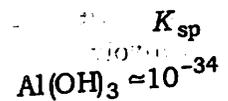
(b) In liquid NH_3, NH_4Cl and KNH_2 behave as an acid and base respectively. Explain using solvent system concept.   2

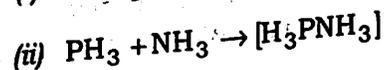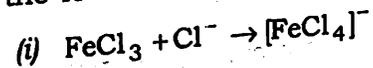(c) The solubility product of the hydroxides of Al, Cr and Mg are as follows :

$$K_{sp}$$
$$Al(OH)_3 \simeq 10^{-34}$$
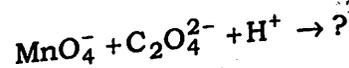$$Cr(OH)_3 \simeq 10^{-30}$$
$$Mg(OH)_2 \simeq 10^{-11}$$

In systematic group separation, explain how you would separate the hydroxides of Al and Cr from that of Mg.   2½

(d) Identify Lewis acid and Lewis bases in the following reactions :   1×2=2

(i) $FeCl_3 + Cl^- \rightarrow [FeCl_4]^-$

(ii) $PH_3 + NH_3 \rightarrow [H_3PNH_3]$

3. (a) Complete and balance the following equation by ion-electron method :   2

$$MnO_4^- + C_2O_4^{2-} + H^+ \rightarrow ?$$

(b) Write down the essential constituents of cement. What is the role of gypsum in the setting of cement?   1½+1=2½
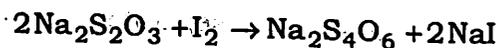
(c) Discuss in brief the process of extraction of aluminium from its bauxite ore. Write the relevant chemical equations involved. 3

(d) Identify the oxidant and reductant in the following reaction. Calculate the equivalent weight of the oxidant : 1+1=2
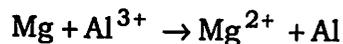
$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

Molecular weight of

$$Na_2S_2O_3 = 248 \cdot 2 \text{ g/mol}$$

Molecular weight of $I_2 = 253 \cdot 80$ g/mol

OR

4. (a) Describe how calcium superphosphate is manufactured. Why is it considered a good fertilizer? 2½

(b) What is electrochemical series? Predict whether the following reaction is feasible or not. Calculate the e.m.f. of the cell 1+2=3

$$Mg + Al^{3+} \rightarrow Mg^{2+} + Al$$

Given

$$E^{\circ}_{Mg^{2+}/Mg} = -2 \cdot 37 \text{ V}$$

$$E^{\circ}_{Al^{3+}/Al} = -1 \cdot 66 \text{ V}$$

(c) Write down the essential constituents of paints. What are the characteristics of good paints? 2

(d) Giving examples, differentiate the process of calcination from roasting. 2

SECTION—II

(Organic)

(Marks : 19)

5. (a) Generally S_N1 reactions of optically active substrates are said to be accompanied by racemization, but in actual practice it has been found that there is always some net inversion. Account for this observation. 3

(b) Why does isopropyl amine react faster than triethylamine with isopropyl iodide in an S_N2 reaction? 1½

(c) Predict the products in the following reaction. Which one is the major product and why? 2½

$$CH_3CH_2CHCH_3 \xrightarrow{EtO^{\ominus}} A + B$$
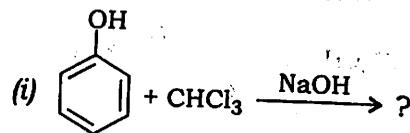$$\overset{|}{\underset{\overset{\oplus}{N}Me_3I^{\ominus}}{}}$$
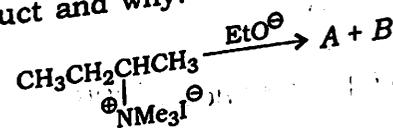
(6)

(d) Discuss the mechanistic pathway for the nucleophilic substitution of activated aryl halides. 2½

OR

6. (a) What happens when alcohol is treated with thionyl chloride in the presence of pyridine? Explain with appropriate mechanism. 3

(b) Explain the stereospecific nature of E2 reactions by giving suitable examples. 2½

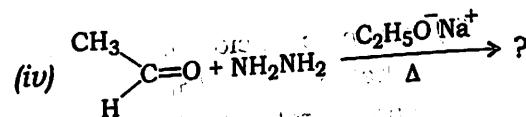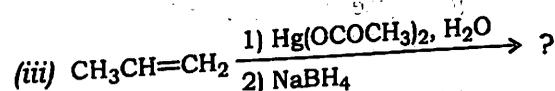(c) Complete the following reactions with mechanism : 2+2=4

(i)

$$\overset{\overset{+}{N_2}\bar{Cl}}{C_6H_5} \xrightarrow[\text{HCl}]{\text{Cu}_2\text{Cl}_2} ?$$

(ii) $CH_3CH_2I + AgNO_2 \longrightarrow ?$
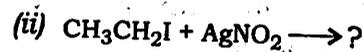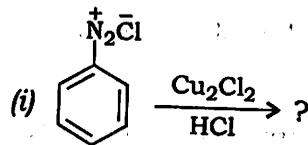
7. (a) Write the product(s) of the following reactions with mechanism (any *three*) : 3×3=9

(i)

$$\text{C}_6\text{H}_5\text{OH} + CHCl_3 \xrightarrow{\text{NaOH}} ?$$

(7)

(ii) $2C_6H_5CHO \xrightarrow{\text{NaOH}} ?$

(iii) $CH_3CH=CH_2 \xrightarrow[\text{2) NaBH}_4]{\text{1) Hg(OCOCH}_3)_2,\ H_2O} ?$

(iv)

$$\overset{CH_3}{\underset{H}{\diagdown}}C=O + NH_2NH_2 \xrightarrow[\Delta]{C_2H_5\bar{O}\ Na^+} ?$$
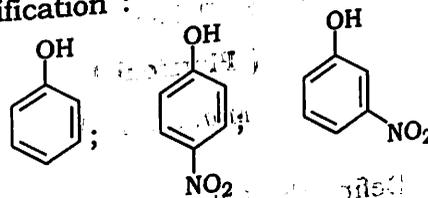
(b) Which one is more reactive towards nucleophiles, aldehydes or ketones? ½

OR

8. (a) Arrange the following in increasing order of acidity with proper justification : 2

$$\text{OH} \qquad \overset{\text{OH}}{\underset{NO_2}{\bigcirc}} \qquad \overset{\text{OH}}{\underset{NO_2}{\bigcirc}}$$

(b) Starting from an alkene, how is a *trans*-diol prepared? Explain with mechanism. 2½

(8)

(c) Explain with chemical equations, what happens when—

(i) glycerol is treated with oxalic acid at 230 °C;

(ii) ethanal is treated with sodium bisulphite;

(iii) ethanoic acid is treated with ethanol in the presence of concentrated H_2SO_4;

(iv) glycol is treated with lead-tetra-acetate;

(v) phenol is treated with benzene diazonium chloride in alkaline medium. 1×5=5

SECTION—III

(Physical)

(Marks : 18)

9. (a) Define the following terms : 1×3=3

(i) Closed system

(ii) Isolated system

(iii) Isobaric process

(9)

(b) Calculate the pressure-volume work performed by the system during reversible isothermal expansion of two moles of an ideal gas from 2 litres to 10 litres at 20 °C.

[$R = 8\cdot314$ joule degree^{-1} mol^{-1}] 2

(c) Describe the viscometric method used to determine the molecular mass of macromolecules. 4

OR

10. (a) State the first law of thermodynamics and give its mathematical formulation. 1+2=3

(b) Explain the following terms : 1½×2=3

(i) Joule-Thomson coefficient

(ii) Inversion temperature

(c) Equal numbers of molecules with $M_1 = 10000$ and $M_2 = 100000$ are mixed. Calculate number average molecular mass ($\overline{M}_N$) and weight average molecular mass ($\overline{M}_M$). 1½+1½=3

11. *(a)* Derive Kirchhoff's equation showing the influence of temperature on ΔH and ΔU of a reaction.   4

(b) The enthalpy of neutralization of a strong acid with a strong base is always the same. Explain why.   2

(c) Enthalpies of formation of $C_2H_5OH(l)$, $CO_2(g)$ and $H_2O(l)$ are $-277 \cdot 0$ kJ mol^{-1}, $-393 \cdot 5$ kJ mol^{-1} and $-285 \cdot 8$ kJ mol^{-1} respectively. Calculate enthalpy change for the reaction at 25 °C and 1 atm pressure.

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \quad 3$$

OR

12. *(a)* Define the following :   1×3=3

    (i) Enthalpy of combustion

    (ii) Enthalpy of formation

    (iii) Enthalpy of solution

(b) Distinguish between absorption and adsorption.   2

(Continued)

(c) Discuss the behaviour of Langmuir isotherm at very high and very low pressure and hence show that at intermediate pressure it reduces to Freundlich isotherm.   4

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