2 0 2 2

(February)

CHEMISTRY

(Elective/Honours)

(General Chemistry—III)

[Chem–EH–301]

Marks : 56

Time : 3 hours

The figures in the margin indicate full marks for the questions

SECTION—I

(Inorganic)

(*Marks* : 18)

1. *(a)* Arrange the alkali metal ions in increasing order of their conductivities in aqueous solution and give an appropriate reason for the arrangement made. 3

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

(i) Electron enthalpy of F is less than that of Cl.

(ii) SO_2 acts as both an oxidizing and reducing agent.

OR

2. *(a)* Beryllium, the first member of group-2 differs widely from the rest of the elements of the group. Explain the above fact on the basis of—

(i) the tendency of the metals to form covalent compounds;

(ii) the reactivity of metal with water. 1½+1½=3

(b) Give one method of preparation and use of the following : 1½+1½=3

(i) Sodium thiosulphate

(ii) Boric acid

3. *(a)* Explain the following, giving reasons for your answer : 1½+1½=3

(i) Transition metals have high tendency to form complexes.

(ii) The second and third rows of transition elements resemble each other more closely than they resemble the first row elements.

(b) Write one method of preparation of uranium hexafluoride and its reaction with water. Write one use of the compound. 1+1+1=3

OR

4. *(a)* Explain the following : 1½+1½=3

(i) Why do all lanthanide elements show a common oxidation of +3?

(ii) The post lanthanide transition metals have unusually high densities.

(b) What is actinide contraction? What are its consequences? 1

(c) Write down one method of preparation of potassium dichromate and one use of it in organic synthesis. 1+1=2

5. *(a)* Define effective atomic number (EAN) and calculate the EAN of Co in $Co_2(CO)_8$. 2

(b) Give the IUPAC nomenclature of the following : 1+1=2

(i) $[Co(NH_3)_5(ONO)]Cl_2$

(ii) $K_3[Fe(CN)_5(NO)]$

(c) Draw the optical isomers of *cis*-$[Co(en)_2Cl_2]$.

(en $H_2N—CH_2—CH_2—NH_2$) 2

OR

6. *(a)* Give examples of one paramagnetic and one diamagnetic complex of Co^{3} and calculate their spin-only magnetic moments ($_{s}$). 2

(b) Explain the following with suitable examples : 1+1=2

(i) Ionization isomerism

(ii) Hydrate isomerism

(c) On the basis of VBT, explain the bonding in $[Ni(CN)_4]^{2}$. 2

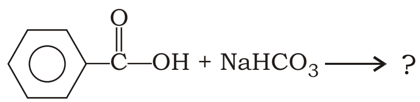
SECTION—II

(Organic)

(*Marks* : 19)

7. *(a)* Give proper justification to explain why CF_3COOH is a stronger acid than CCl_3COOH. 1½

(b) Complete the following reactions : 1×3=3

(i) 

(ii) $CH_3—\overset{O}{\overset{\|}{C}}—OH + NH_3 \text{ (excess)} \longrightarrow ?$

(iii) $CH_3—\overset{O}{\overset{\|}{C}}—O—\overset{O}{\overset{\|}{C}}—CH_3 \xrightarrow{H_2O/H} ?$

(c) Explain the term 'active methylene compounds' with a suitable example. 1½

(d) How can you convert ethyl acetoacetate to butanoic acid? 2

(e) Identify *A*, *B* and *C* in the following sequence of conversions : 1½

$$CH_3\text{—}COOH \xrightarrow{[A]} CH_3COCl \xrightarrow[\text{reduction}]{\text{Rosenmund}} [B] \xrightarrow{Zn/CH_3COOH} [C]$$

OR

8. *(a)* With a suitable example, illustrate Hell-Volhard-Zelinsky (HVZ) reaction. Why does benzoic acid not undergo HVZ reaction? 1½+½=2

(b) Complete the following reactions : (½+½)+1+1=3

(i) $CO_2 + CH_3\text{—}MgBr \xrightarrow[\text{ether}]{\text{Dry}} [A] \xrightarrow{H_2O/H} [B]$

(ii) $\begin{array}{l} COOH \\ | \\ COOH \end{array} + PCl_5 \text{ (excess)} \longrightarrow ?$

(iii) $\begin{array}{l} \quad\;\; CH_2\text{—}COOH \\ \quad\;\; | \\ HO\text{—}C\text{—}COOH \\ \quad\;\; | \\ \quad\;\; CH_2\text{—}COOH \end{array} \xrightarrow{150\ °C} ?$

(c) How can you convert diethylmalonate to succinic acid? 2

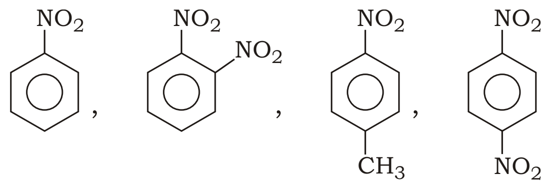
(d) Show how the phenomenon of 'tautomerism' stabilizes an active methylene compound. 1

(e) Why should the ester formed be removed from the reaction vessel periodically in the reaction between carboxylic acid and alcohols? 1½

9. *(a)* Give a method to distinguish between primary, secondary and tertiary alcohols. 3

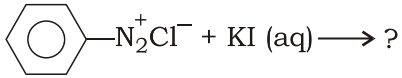
(b) Giving proper equation, show what happens when nitrobenzene is reduced with stannous chloride in alkaline medium. 1½

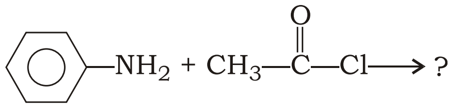
(c) Arrange the following compounds in order of increasing acid strength with proper justification : 2



(d) What happens when a primary aliphatic amine is treated with nitrous acid? Give correct equation. 1

(e) Complete the following reactions : 1×2=2

(i) 

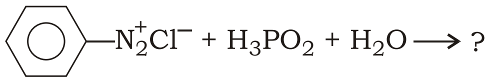
(ii) 

OR

10. (a) Write the mechanism for the formation of benzene diazonium chloride from aniline. 2

(b) Complete the following reactions : 1×3=3

(i) $$(CH_3)_2N\text{—}H + HNO_2 \xrightarrow[(0\text{–}5)\ ^\circ C]{(NaNO_2\ +\ HCl)} ?$$

(ii) 

(iii) $C_2H_5\text{—}NH_2 + CS_2 \longrightarrow ?$

(c) Write the mechanism of carbylamine reaction. 2

(d) Give the correct equation to show what happens when acetic acid reacts with diazomethane. 1

(e) Why are aromatic diazonium chlorides more stable than aliphatic diazonium chlorides? 1½

SECTION—III

(Physical)

(*Marks* : 19)

11. (a) Derive an expression for entropy change of a gas when temperature changes from T_1 to T_2 and volume changes from V_1 to V_2. 3

(b) Calculate the efficiency of a steam engine that operates between temperatures of 100 °C and 35 °C. 2

(c) Derive a relationship between K_p and K_c. 2½

(d) The value of equilibrium constant for the reaction $H_2 \quad I_2 \rightleftharpoons 2HI$ at 720 K is 48. What is the value of the equilibrium constant for the reaction $2HI \rightleftharpoons H_2 \quad I_2$? 2

OR

12. (a) Derive the Gibbs-Helmholtz equation. 3

(b) Calculate the entropy change involved in the isothermal reversible expansion of 5 moles of an ideal gas from a volume of 10 litres to a volume of 100 litres at 300 K. 2

(c) State and explain the Le Chatelier's principle and explain the effect of temperature on the following reaction : 1½+1½=3

$$N_2(g) \quad 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$H \quad 92{\cdot}38 \text{ kJ}$$

(d) The value of K_p for the water gas reaction

$$CO \quad H_2O \rightleftharpoons CO_2 \quad H_2$$

is $1{\cdot}06 \quad 10^5$ at 25 °C. Calculate the standard state free energy change ($G°$) of the reaction at 25 °C ($R \quad 8{\cdot}314 \text{ JK}^{\ 1} \text{ mol}^{\ 1}$). 1½

13. *(a)* Derive an expression for the rate constant of a first-order reaction of the type $A \quad$ products. 3

(b) Discuss the effect of catalyst on the rate of a reaction. 2

(c) State Henry's law. What are the limitations of Henry's law? 1½+1=2½

(d) 50% of a first-order reaction is completed in 23 minutes. Calculate the time required to complete 90% of the reaction. 2

OR

14. *(a)* Show that the lowering of vapour pressure is directly related to osmotic pressure. 2½

(b) Define order of a reaction. What is meant by zero-order reaction? Give one example of a zero-order reaction. 1+1+1=3

(c) What is the cause of abnormal molar mass of solutes in solutions? 1½

(d) For a particular reaction, the rate constant k is $2{\cdot}8 \quad 10^{\ 5}$ lit mol$^{\ 1}$ sec$^{\ 1}$ at 300 K and $7{\cdot}0 \quad 10^{\ 1}$ lit mol$^{\ 1}$ sec$^{\ 1}$ at 400 K. Calculate the energy of activation for the reaction. (Given $R \quad 1{\cdot}38$ cal mol$^{\ 1}$ deg$^{\ 1}$) 2½

★ ★ ★