2025

CHEMISTRY

(Major)

Paper : CHE4300104 MJ

(Chemistry–III)

Full Marks : 45

Time : 2 hours

The figures in the margin indicate full marks for the questions.

1. Choose the correct option from the following questions : 1×5=5

   (a) The species responsible for the superacidity of $SbF_5 - HSO_3F$ system is

   (i) HSO_3F

   (ii) SbF_5

   (iii) HF

   (iv) $H_2SO_3F^+$

(b) The complexes $[Pt(CN)_4]^{2-}$ and $[NiCl_4]^{2-}$ respectively are

(i) Paramagnetic, Paramagnetic

(ii) Diamagnetic, Diamagnetic

(iii) Paramagnetic, Diamagnetic

(iv) Diamagnetic, Paramagnetic

(c) Which of the following species is aromatic according to Hückel's rule?

(i) Cyclobutadiene

(ii) Cyclopentadienyl anion

(iii) Cyclooctatetraene

(iv) Cyclopentadienyl cation

(d) According to Raoult's law, the partial vapour pressure of a component in an ideal solution is directly proportional to :

(i) Its mole fraction in the vapour phase

(ii) Its mole fraction in the liquid phase

(iii) Total pressure of the solution

(iv) Temperature of the system

(e) Consider this assertion-reason statement :

Assertion (A) : Aniline does not undergo Friedel-Craft alkylation easily.

Reason (R) : The diazonium salts of aromatic amines are more stable than those of aliphatic amines.

Which one of the following is correct ?

(i) Both (A) and (R) are true and (R) is the correct explanation of (A).

(ii) Both (A) and (R) are true and (R) is not the correct explanation of (A).

(iii) (A) is true, but (R) is false.

(iv) Both (A) and (R) are false.

2. Answer ***any five*** from the following questions : 2×5=10

(a) Predict which compound is more acidic, H_2SO_4 or H_2SeO_4 and justify your answer.

(b) Taking overpotential into account show that iron (Fe) is likely to be oxidized rapidly to Fe^{2+} by water at 25°C. (Given $Fe^{2+}/Fe = 0{\cdot}44\,V$ $[H_2(P) = 1\,bar$ $[Fe^{2+}] = 1\,mol.)$

(c) State Raoult's law and Henry's law.

(d) How alcohols can be prepared from alkene ? Give equations only.

(e) Explain the physical significance of fugacity.

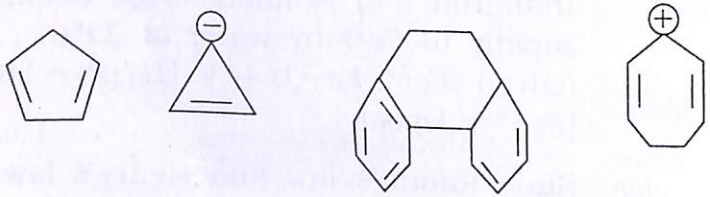
(f) Why is cyclopentadiene ($K_a = 10^{-15}$) much more acidic than 1,3-cyclohexadiene ?

(g) What are the limitations of Valence Bond theory of co-ordination compounds ?

(h) How can you distinguish between aldehydes and ketones by oxidation reactions ?

(i) How the nature of solvent affects the rate of nucleophilic substitution reaction ?

(j) Classify the following compounds as aromatic, antiaromatic or non-aromatic : ½×4=2



3. Answer ***any four*** from the following questions : 5×4=20

(a) In aqueous solution, arrange the basicities of the following amines and justify your answer : 2+3=5

Me_3N, Me_2NH, $MeNH_2$, NH_3

(b) Discuss the principle of redox titration. Why *HCl* is not used in redox titration ? 4+1=5

(c) Explain why vapour pressure of a solvent decreases when a non-volatile solute is added. The vapour pressure of pure benzene at 25°*C* is 100*mm Hg*. When 2·0*g* of a non-volatile solute (molar mass = 120*g mol*$^{-1}$) is dissolved in 78·0*g* benzene, calculate the vapour pressure of the solution. 2+3=5

(d) (i) Find the *A*, *B*, *C* and *D* : ½×4=2

$$CH_3OH \xrightarrow{P+I_2} A \xrightarrow[\text{dry ether}]{Mg} B \xrightarrow{HCHO} C \xrightarrow{H_2O} \underset{\text{major}}{D}$$

(ii) Find out the major products of following reactions : 2

$$B \xleftarrow[NaBH_4]{Hg(OAc)_2,\ H_2O} = \xrightarrow[H_2O_2/OH^-]{BH_3,\ THF} A$$

(iii) A molecule with 10π electrons in a conjugated, cyclic and flat system will be aromatic. 1

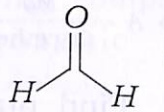
(State True ***or*** *False)*

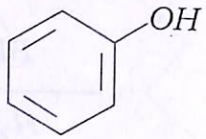
(e) Explain hybridization, geometry and magnetic properties of $[Co(CN)_6]^{3-}$ on the basis of Valence Bond theory.

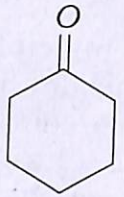
(f) Write *one* preparation reaction of PCC. How PDC is advantageous over PCC ? 3+2=5

(g) Discuss the dependence of partial molar Gibbs free energy on mole fraction in a binary mixture. Draw the μ-x diagram for ideal and non-ideal mixtures. 3+2=5

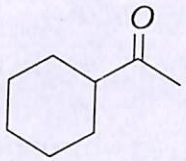
(h) Write the products of the following reaction : 1×5=5

(i) $R - MgCl +$  $\xrightarrow{H_3O^+}$?

(ii)  $\xrightarrow[3KOH]{CHCl_3}$?

(iii)  $\xrightarrow[(ii)\ NaOEt,\ \Delta]{(i)\ H_2NNH_2}$?

(iv)  $\xrightarrow[\text{Isopropyl alcohol}]{Al\,(i\,Pr\,O)_3}$?

(v)  $\xrightarrow[CH_2Cl_2]{PbCOOOH}$?

4. Answer ***any one*** from the following questions : 10×1=10

(a) (i) What is symbiosis ? Explain the following reactions in terms of symbiosis : 1+2=3

$R_2SBF_3 + R_2O \rightarrow R_2OBF_3 + R_2S$

$R_2OBH_3 + R_2S \rightarrow R_2SBH_3 + R_2O$

(ii) What is proton sponge ? Give *one* example. 2

(iii) Write the postulates of Valence Bond theory of coordination complexes. What are inner orbital and outer orbital complexes ? Give *one* example each. 3+2=5

(b) (i) Establish Rault's law for a completely miscible liquid pair. Show graphically how the vapour pressure of a completely miscible liquid pair changes with the composition of the mixture. 3+2=5

(ii) What do you mean by activity of a substance? Show that

$G + G^{\circ} + RT \ln a$. 2+3=5

(c) (i) Derive Gibbs-Duhem Equation. 3

(ii) What are abnormal colligative properties? 2

(iii) How do you differentiate 1°, 2°, 3° alcohols? Give chemical reactions. 5

(d) (i) What are magic acids? Give *one* example. 1+1=2

(ii) Define levelling effect. How it helps in discrimination of strength of various acids? 1+2=3

(iii) Write short notes on the following topics : ***(any two)*** 2½×2=5

(i) Hückel's rule

(ii) Benzyne mechanism

(iii) Oppenauer oxidation

(iv) Concept of chemical potential