

2017

CHEMISTRY

(Major)

Paper : 4.1

Full Marks : 60

Time : 3 hours

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

1. Answer the following : 1×7=7

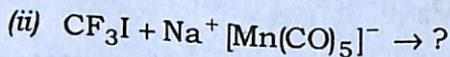
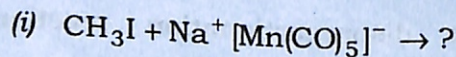
- (a) Why does carbon show greater tendency for catenation in comparison to silicon?
- (b) Give disproportionation reaction of H_3PO_3 .
- (c) Why does sulphur in vapour state show paramagnetic behaviour?
- (d) What will be the STYX topology for B_2H_6 ?
- (e) Why is the solution of sodium metal in liquid ammonia blue in colour?

- (f) Give the correct order of acidic strength for the oxyacids of phosphorus H_3PO_2 , H_3PO_3 and H_3PO_4 .
- (g) Why does $\text{R}_3\text{P}=\text{O}$ exist but $\text{R}_3\text{N}=\text{O}$ does not?

2. Answer the following : 2×4=8

(a) Knowing the electron gain enthalpy values of $\text{O} \rightarrow \text{O}^{(-)}$ and $\text{O} \rightarrow \text{O}^{(2-)}$ as -141 kJ mol^{-1} and 702 kJ mol^{-1} respectively, how can you account for the formation of a large number of oxides having O^{2-} species and not O^{-} species?

(b) Based on variation of electronegativity for iodine, write the products for the reaction between carbonylate anion and alkyl iodides :



(c) Based on Fajans' rules, give the correct order of the following :

(i) SiCl_4 , NaCl , MgCl_2 and AlCl_3
(melting point)

(ii) BeCO_3 , MgCO_3 and CaCO_3
(thermal stability)

(d) Discuss the clinical uses of NO and N_2O .

3. Answer the following (any three) : $5 \times 3 = 15$

(a) (i) BF_3 , BCl_3 and BI_3 are considered to be good Lewis acids. Give the correct Lewis acidic order and justify your answer. 3

(ii) $(\text{SiH}_3)_3\text{N}$ is triangular planar ($\text{Si}-\hat{\text{N}}-\text{Si}$, 120°) and less basic than trigonal pyramidal $(\text{CH}_3)_3\text{N}$ ($\text{C}-\hat{\text{N}}-\text{C}$, 107°). Explain. 2

(b) (i) The standard reduction electrode potential values for the couples $\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{MnO}_4^-/\text{Mn}^{2+}$ and Cl_2/Cl^- are 0.77 V, 1.52 V and 1.36 V respectively. Explain why HCl is not used for estimation of iron with KMnO_4 solution. 3

(ii) Despite acidic in nature, H_3PO_2 and H_3PO_3 show reducing character. Explain. 2

(c) (i) The accepted electronic configuration of K-atom is $[\text{Ar}]4s^1$ and not $[\text{Ar}]3d^1$. Calculate the effective nuclear charge for $4s^1$ and $3d^1$ electron of K-atom. Why does the valence electron occupy the $4s$ orbital and not the $3d$ orbital? 4

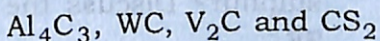
- (ii) Melting point of AgCl is only 445 °C while that of KCl is 776 °C though the crystal radii of Ag⁺ and K⁺ are almost the same. Give reason. 1
- (d) (i) Explain the term 'symbiosis' with suitable examples. 3
- (ii) Sketch the structures of P₄O₆ and P₄O₁₀. 2
- (e) (i) Use Wade's rule to classify the given borohydrides into *closo*, *nido* and *arachno* : 4
- B₆H₆²⁻, B₄H₁₀, B₈H₁₂ and C₂B₆H₈
- (ii) Draw the structures of peroxodisulphuric acid and peroxomonosulphuric acid. 1
4. Answer the following (any three) : 10×3=30
- (a) (i) Discuss liquid NH₃ as solvent in terms of acid-base reaction and redox reaction. 3
- (ii) Why does oxidising power of strong oxidising agent like permanganates get significantly reduced in liquid NH₃? 2

(iii) Draw the structures of white phosphorus and red phosphorus. Which one of these two types is more reactive and why? 3

(iv) Both diamond and graphite are allotropic forms of carbon but graphite is good conductor and diamond is bad conductor of electricity. Explain. 2

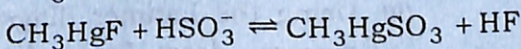
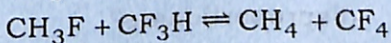
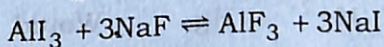
(b) (i) What are fullerenes? How are fullerenes prepared? Write about the structure and properties of C_{60} and C_{120} . 5

(ii) What are metal carbides? Classify the given carbides into their respective classes : 3



(iii) How is SO_2 an air pollutant? 2

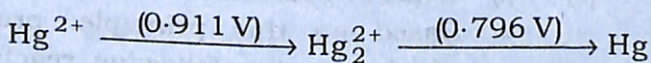
(c) (i) What is Pearson's HSAB principle? Based on this principle, predict which way the following reactions will go : 1+4=5



- (ii) Give the theoretical bases of hardness and softness of species that are used in hard and soft acid-base principle. 3
- (iii) Although boric acid is Lewis acid but it is monobasic in nature. Explain. 2
- (d) (i) What are superoxides? Give the method of preparation of superoxide. Why are superoxides generally coloured? What are the uses of potassium superoxides?

$$1+1+1+2=5$$

- (ii) Write the mechanism of formation and depletion of ozone layer in stratosphere. 3
- (iii) What are the allotropic forms of sulphur? Discuss the structure of SF_4 . 2
- (e) (i) The Latimer diagram for Hg in acidic medium is



Find the skip-step e.m.f. of $Hg^{2+} \rightarrow Hg$. Would Hg_2^{2+} disproportionate? 3

- (ii) Using the Latimer diagram for Hg system, draw Frost diagram and discuss its application. 4

- (iii) Discuss the thermodynamic conditions for dissolution in aqueous medium. 3
- (f) (i) Give the methods of preparation of hydrazine. Discuss the structure and uses of hydrazine. How does it react with Fehling's solution? 4
- (ii) Write about clathrate compounds with reference to stability, inert gas clathrates and clathrate hydrate. 4
- (iii) Discuss the structure of copper sulphate pentahydrate. 2
