

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  $\text{H}_3\text{PO}_3$ .
- (c) Why does sulphur in vapour state show paramagnetic behaviour?
- (d) What will be the STYX topology for  $\text{B}_2\text{H}_6$ ?
- (e) Why is the solution of sodium metal in liquid ammonia blue in colour?



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- (f) Give the correct order of acidic strength for the oxyacids of phosphorus  $\text{H}_3\text{PO}_2$ ,  $\text{H}_3\text{PO}_3$  and  $\text{H}_3\text{PO}_4$ .
- (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  $-141 \text{ kJ mol}^{-1}$  and  $702 \text{ kJ mol}^{-1}$  respectively, how can you account for the formation of a large number of oxides having  $\text{O}^{2-}$  species and not  $\text{O}^-$  species?
- (b) Based on variation of electronegativity for iodine, write the products for the reaction between carbonylate anion and alkyl iodides :
- (i)  $\text{CH}_3\text{I} + \text{Na}^+ [\text{Mn}(\text{CO})_5]^- \rightarrow ?$
- (ii)  $\text{CF}_3\text{I} + \text{Na}^+ [\text{Mn}(\text{CO})_5]^- \rightarrow ?$
- (c) Based on Fajans' rules, give the correct order of the following :
- (i)  $\text{SiCl}_4$ ,  $\text{NaCl}$ ,  $\text{MgCl}_2$  and  $\text{AlCl}_3$  (melting point)
- (ii)  $\text{BeCO}_3$ ,  $\text{MgCO}_3$  and  $\text{CaCO}_3$  (thermal stability)
- (d) Discuss the clinical uses of  $\text{NO}$  and  $\text{N}_2\text{O}$ .

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3. Answer the following (any three) :

5×3=15

- (a) (i)  $\text{BF}_3$ ,  $\text{BCl}_3$  and  $\text{BI}_3$  are considered to be good Lewis acids. Give the correct Lewis acidic order and justify your answer.

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

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- (b) (i) The standard reduction electrode potential values for the couples  $\text{Fe}^{3+}/\text{Fe}^{2+}$ ,  $\text{MnO}_4^-/\text{Mn}^{2+}$  and  $\text{Cl}_2/\text{Cl}^-$  are 0.77 V, 1.52 V and 1.36 V respectively. Explain why  $\text{HCl}$  is not used for estimation of iron with  $\text{KMnO}_4$  solution.

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- (ii) Despite acidic in nature,  $\text{H}_3\text{PO}_2$  and  $\text{H}_3\text{PO}_3$  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?

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- (ii) Melting point of AgCl is only 445 °C while that of KCl is 776 °C though the crystal radii of  $\text{Ag}^+$  and  $\text{K}^+$  are almost the same. Give reason. 1
- (d) (i) Explain the term 'symbiosis' with suitable examples. 3
- (ii) Sketch the structures of  $\text{P}_4\text{O}_6$  and  $\text{P}_4\text{O}_{10}$ . 2
- (e) (i) Use Wade's rule to classify the given borohydrides into *closo*, *nido* and *arachno* : 4
- $\text{B}_6\text{H}_6^{2-}$ ,  $\text{B}_4\text{H}_{10}$ ,  $\text{B}_8\text{H}_{12}$  and  $\text{C}_2\text{B}_6\text{H}_8$
- (ii) Draw the structures of per-oxodisulphuric acid and peroxomonosulphuric acid. 1
4. Answer the following (any three) :  $10 \times 3 = 30$
- (a) (i) Discuss liquid  $\text{NH}_3$  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  $\text{NH}_3$ ? 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  $\text{C}_{60}$  and  $\text{C}_{120}$ . 5
- (ii) What are metal carbides? Classify the given carbides into their respective classes : 3
- $\text{Al}_4\text{C}_3$ ,  $\text{WC}$ ,  $\text{V}_2\text{C}$  and  $\text{CS}_2$
- (iii) How is  $\text{SO}_2$  an air pollutant? 2
- (c) (i) What is Pearson's HSAB principle? Based on this principle, predict which way the following reactions will go :  $1+4=5$
- $\text{AlI}_3 + 3\text{NaF} \rightleftharpoons \text{AlF}_3 + 3\text{NaI}$
- $\text{CH}_3\text{F} + \text{CF}_3\text{H} \rightleftharpoons \text{CH}_4 + \text{CF}_4$
- $\text{CH}_3\text{HgF} + \text{HSO}_3^- \rightleftharpoons \text{CH}_3\text{HgSO}_3 + \text{HF}$



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- (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  $\text{SF}_4$ . 2
- (e) (i) The Latimer diagram for Hg in acidic medium is
- $$\text{Hg}^{2+} \xrightarrow{(0.911 \text{ V})} \text{Hg}_2^{2+} \xrightarrow{(0.796 \text{ V})} \text{Hg}$$
- Find the skip-step e.m.f. of  $\text{Hg}^{2+} \rightarrow \text{Hg}$ . Would  $\text{Hg}_2^{2+}$  disproportionate? 3
- (ii) Using the Latimer diagram for Hg system, draw Frost diagram and discuss its application. 4

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- (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

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- (b) Taking nickel as a typical example, discuss the general characteristics of transition elements with special reference to complex formation and catalytic activity. 10
- (c) (i) What is the composition (formulae) of zeolites? How would you prepare a zeolite such as ZSM-5? Describe the structure of zeolites. 2+2+3=7
- (ii) Iodine is usually insoluble in water, but soluble in solution of KI. Discuss the structure of the product formed in solution. 3
- (d) (i) Explain the importance of alloys and intermetallic compounds. What make alloys different from intermetallic compounds? 6
- (ii) Explain why unlike other elements in group 14, Sn and Pb are more stable in the bivalent state than the tetravalent state. 4
- (e) Describe the trends in physical and chemical properties of second and third transition series in comparison to the first series. 10

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## CHEMISTRY

( Major )

Paper : 4.2

Full Marks : 60

Time : 3 hours

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

1. Select the correct answer/Answer the following questions : 1×7=7
- (a) Pyrolusite is an ore of
- (i) iron  
(ii) chromium  
(iii) vanadium  
(iv) manganese
- (b) Which of the following compounds is aromatic?
- (i)  $P_4S_4$  (ii)  $S_4N_4$   
(iii)  $S_2N_2$  (iv)  $P_4S_7$
- (c) Mica is made up of
- (i)  $(Si_2O_7)^{6-}$  (ii)  $(SiO_4)^{4-}$   
(iii)  $(Si_2O_5)^{2-}$  (iv)  $(SiO_3)^{2-}$



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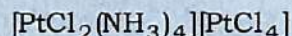
(d) The chemical properties of Ru is most similar to those of

- (i) Rh                      (ii) Os  
(iii) Fe                    (iv) Re

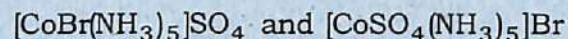
(e) The origin of the yellow colour of an aqueous solution of  $K_2CrO_4$  is due to

- (i)  $d-d$  transition  
(ii)  $H_2O$  to  $Cr^{6+}$  charge transfer  
(iii)  $O^{2-}$  to  $K^+$  charge transfer  
(iv)  $O^{2-}$  to  $Cr^{6+}$  charge transfer

(f) Name the compound according to IUPAC



(g) Following are two coordination compounds :



What type of isomerism are they exhibiting?

2. Answer the following questions :  $2 \times 4 = 8$

- (a) Sketch the three isomers of dicarbocloso-dodecaborane.  
(b) Show with example the amphoteric behaviour of  $SnO_2$ .  
(c) Why are the coinage metals Cu, Ag, Au considered as transition metals although they have filled  $d$ -shells in the elemental state?

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(d) Write a note on the coordination complexes of divalent Zn.

3. Answer any three from the following questions :  $5 \times 3 = 15$

- (a) Compare and contrast the properties and reactivity of borazine and benzene.  
(b) What are phosphazines? Suggest synthesis and give balance equations for the preparation of  $[NP(OCH_3)_2]_4$ .  
(c) Discuss the principle of extraction of vanadium from its ore.  
(d) Although  $H_2$  is a reducing agent yet it is not widely used as a reducing agent in metallurgical operations. Why?  
(e) Suggest a method for the preparation of the complex cation  $[Cr(en)_3]^{3+}$ . Comment on its tendency to react with  $NH_3$  in aqueous solution.

4. Answer any three from the following questions :  $10 \times 3 = 30$

- (a) Discuss the synthesis, structures and bonding in  $Fe(CO)_5$ ,  $Fe_2(CO)_9$  and  $Fe_3(CO)_{12}$ . Explain why CO is called  $\pi$ -acid ligand. Compare the  $\sigma$ - and  $\pi$ -bonding ability of CO and  $NO^+$  as ligands.  $6 + 1 + 3 = 10$