

2019

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 elemental nitrogen exist as diatomic molecule whereas elemental phosphorus is a tetra-atomic molecule?

(b) How many $P=O$ bonds are present in cyclotrimetaphosphoric acid $(HPO_3)_3$?

(c) Ag_2S is less soluble in water than Ag_2O .
Give reason.

(d) Why is the bond angle in PH_4^+ ion higher than that in PH_3 ?

- (e) Explain why the first electron gain enthalpy of sulphur is -ve (-200 kJmol^{-1}) whereas the second electron gain enthalpy is +ve ($+532 \text{ kJmol}^{-1}$).
- (f) Draw the structure of peroxydisulphuric acid (Marshall's acid).
- (g) Why is the solution of sodium metal in liquid ammonia blue in colour?

2. Answer the following :

2×4=8

- (a) Knowing the electron gain enthalpy values for $\text{O} \rightarrow \text{O}^-$ and $\text{O} \rightarrow \text{O}^{2-}$ as -141 kJmol^{-1} and 702 kJmol^{-1} respectively, how can you account for the formation of large number of oxides having O^{2-} species and not O^- ?
- (b) Why is white phosphorus more reactive than red phosphorus?
- (c) Tetramethylammonium hydroxide is a stronger base than that of trimethylammonium hydroxide. Explain.

- (d) Bond dissociation energy of B—F bond in BF_3 is 646 kJmol^{-1} , whereas that of C—F bond in CF_4 is 515 kJmol^{-1} . Explain.

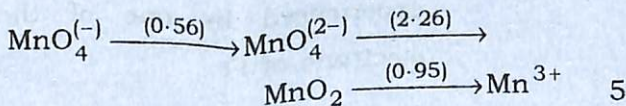
3. Answer the following (any three) : $5 \times 3 = 15$

- (a) (i) $(\text{SiH}_3)_3\text{N}$ is triangular planar with Si—N—Si bond angle of 120° and less basic than trigonal pyramidal $(\text{CH}_3)_3\text{N}$ with bond angle of 107° . Explain. 3

- (ii) Which of the following has the highest and lowest melting points and why? 2

NaCl , KCl , RbCl , CsCl

- (b) What do you mean by Latimer diagram? Use the Latimer diagram for Mn-system to find the E° for the skip-step couples $\text{MnO}_4^- / \text{MnO}_2$

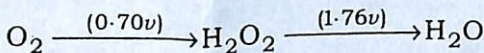


- (c) (i) SO_3 can react with water to give H_2SO_4 , but this acid is prepared by reacting SO_3 first with H_2SO_4 to give oleum and then oleum is hydrolysed to give H_2SO_4 . Explain. 2
- (ii) What do you mean by levelling effect and levelling solvents? Discuss with suitable examples. 3
- (d) Discuss the mechanism of ozone layer formation and its depletion in the stratosphere. 5
- (e) (i) Classify the higher boranes— B_5H_9 , $\text{B}_6\text{H}_6^{2-}$, B_5H_{11} , $\text{B}_{10}\text{H}_{14}$ and $\text{B}_{12}\text{H}_{12}^{2-}$ into *closo*-, *nido*- and *arachno*-boranes. 3
- (ii) Use Slater's rules to calculate the effective nuclear charge (Z^*) experienced by one of the 3d electrons of Fe. 2

4. Answer the following (any three) : $10 \times 3 = 30$

(a) (i) Define Frost diagram. Summarize the interpretations that can be obtained from this diagram. 3

(ii) Use the Latimer diagram for oxygen system to construct the Frost diagram



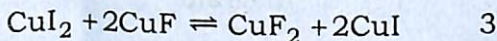
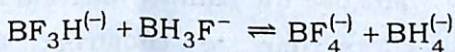
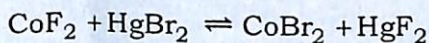
From the diagram, predict which species will undergo disproportionation. 4

(iii) Discuss the clinical uses of oxides of nitrogen N_2O and NO . 3

(b) (i) Discuss liquid NH_3 as solvent in terms of acid-base neutralization and redox reactions. 5

(ii) Graphite forms intercalation compounds but diamond does not. Explain. 2

- (iii) Based on Pearson's HSAB principle, predict the shift in direction of the equilibrium for the reactions given below :



- (c) (i) What are clathrate compounds? Discuss these clathrates with reference to gas hydrates. Why do He and Ne not form clathrates? 6
- (ii) What are carbides? How are these classified? Give one example in each type. 4
- (d) (i) Discuss the methods of preparation of hydrazine. Discuss its structure and uses. How does it react with Fehling's solution? 4

(7)

- (ii) Name and draw the structures of two oxyacids of nitrogen. Which oxyacid of nitrogen acts both as an oxidising agent as well as reducing agent and why? 4
- (iii) PbO_2 is stronger oxidising agent than SnO_2 . Explain. 2

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(Major)

Paper : 4.2

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1. Select the correct answer/Answer the following questions : 1×7=7

(a) The shape of the molecule XeO_2F_2 is

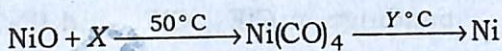
- (i) distorted tetrahedral
- (ii) tetrahedral
- (iii) trigonal bipyramidal
- (iv) square planar

(b) Which of the following species does not have a linear shape?

- (i) I_3^+
- (ii) I_3^-
- (iii) ICl_2^-
- (iv) IBrF^-

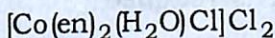
- (c) The existence of two different coloured complexes of $\text{Co}(\text{NH}_3)_4\text{Cl}_2$ is due to
- (i) optical isomerism
 - (ii) geometrical isomerism
 - (iii) linkage isomerism
 - (iv) coordination isomerism
- (d) The transition element having least enthalpy of atomization is
- (i) Fe
 - (ii) V
 - (iii) Cu
 - (iv) Zn
- (e) The carborane $\text{B}_{10}\text{C}_2\text{H}_{12}$ is isoelectronic with which one of the following?
- (i) $\text{B}_{12}\text{H}_{12}^{2-}$
 - (ii) $\text{B}_{12}\text{H}_{12}^{2+}$
 - (iii) $\text{B}_{12}\text{H}_{12}^+$
 - (iv) $\text{B}_{12}\text{H}_{12}$

- (f) In the extraction of pure Ni, the following reaction is utilized



In the above reaction, what are X and temperature Y respectively?

- (g) Give the IUPAC name of the following compound :



2. Answer the following questions : 2×4=8

- (a) Write the syntheses of the following compounds :



- (b) $\text{N}(\text{CH}_3)_3$ is pyramidal but $\text{N}(\text{SiH}_3)_3$ is planar. Explain.

- (c) Define the term 'ligand'. What feature(s) would be necessary for a molecule or ion to act as a bidentate ligand?

- (d) Copper and iron have several oxidation states, whereas zinc exists in only one. Justify.

3. (a) How is it possible to form interhalogen compounds? Explain the structures and bondings in ClF_3 , ClF_5 and IF_7 . $2+3=5$

(b) For S_4N_4 , answer the following : $1+1+1+2=5$

- (i) One method of preparation of it
- (ii) One reaction where the heterocyclic ring is retained
- (iii) One reaction where the smaller ring is formed
- (iv) At least four resonance structures of the molecule

Or

What are pseudohalogens? Why are they so called? Write the similarities between the reactions of halogens and pseudohalogens. $1+2+2=5$

(c) Name one important ore of manganese. Describe the extraction of chromium from its ore. $1+4=5$

Or

- (i) Give reasons why a solution of Fe^{3+} is slightly acidic in nature. 2
- (ii) Mention two important alloys of copper and write their uses. 3

4. (a) (i) What are silicones? Give a brief account of synthesis, structure and important applications of silicones. What is silly putty? 5+1=6

(ii) The hydration energy of group 2 metals is much greater than group 1 metals and among group 2 metals beryllium has the maximum. Give reasons to justify this statement. 4

Or

(i) How does SiH_4 chemically differ from CH_4 ? Give the structural representations of $\text{Si}_3\text{O}_9^{6-}$ and $\text{Si}_6\text{O}_{18}^{12-}$. 2+3=5

(ii) How are alkali metals generally characterized? What are different oxides formed by alkali metals? Write a brief account of their stability. 5

(b) (i) How can you explain the following properties of metals? 5

Brightness, malleability, catalytic activity, semiconductor property and ability to form coordination compounds

- (ii) What is inert pair effect? Explain why, unlike other elements in group 14, Sn and Pb are more stable in their bivalent state than the tetravalent state.

5

Or

Give a comparative study of the following properties of first row transition elements : 4+3+3=10

- (i) Oxidation state
- (ii) Magnetic properties
- (iii) Catalytic behaviour
- (c) (i) Discuss the preparations and structures of $\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$ and $\text{Fe}_3(\text{CO})_{12}$. 3+3=6
- (ii) Draw the structure of trisoxalato chromate (III) anion. Would you expect this complex to show any isomerism? Suggest a preparative method for $\text{K}_3[\text{Cr}(\text{ox})_3] \cdot 3\text{H}_2\text{O}$. 2+2=4

Or

- (i) A compound $\text{Co}(\text{en})_2(\text{NO}_2)_2\text{Cl}$ has been prepared in three isomeric forms A, B and C. A undergoes no reaction with AgNO_3 or en and

is optically active, *B* reacts with AgNO_3 , but not with en and is optically inactive. *C* is optically active and reacts with both AgNO_3 and en. Identify *A*, *B* and *C*.

[en = ethylenediamine] 6

- (ii) Give an account of occurrence and the principle of extraction of nickel. 4

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