

2019

## CHEMISTRY

( Major )

Paper : 4.1

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

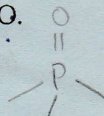
1. Answer the following :

1×7=7

(a) Why does elemental nitrogen exist as diatomic molecule whereas elemental phosphorus is a tetra-atomic molecule?

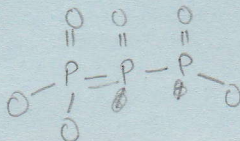
(b) How many P = O bonds are present in cyclotrimetaphosphoric acid  $(\text{HPO}_3)_3$ ?

✓ (c)  $\text{Ag}_2\text{S}$  is less soluble in water than  $\text{Ag}_2\text{O}$ . Give reason.



(d) Why is the bond angle in  $\text{PH}_4^+$  ion higher than that in  $\text{PH}_3$ ?

A9/961



( Turn Over )

( 2 )

(e) Explain why the first electron gain enthalpy of sulphur is -ve ( $-200 \text{ kJmol}^{-1}$ ) 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  $-141 \text{ kJmol}^{-1}$  and  $702 \text{ kJmol}^{-1}$  respectively, how can you account for the formation of large number of oxides having  $\text{O}^{2-}$  species and not  $\text{O}^-$ ?

(b) Why is white phosphorus more reactive than red phosphorus?

(c) Tetramethylammonium hydroxide is a stronger base than that of trimethylammonium hydroxide. Explain.

A9/961

( Continued )

( 3 )

(d) Bond dissociation energy of B—F bond in  $\text{BF}_3$  is  $646 \text{ kJmol}^{-1}$ , whereas that of C—F bond in  $\text{CF}_4$  is  $515 \text{ kJmol}^{-1}$ . Explain.

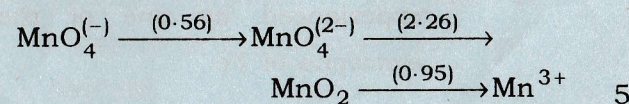
3. Answer the following (any three) : 5×3=15

(a) (i)  $(\text{SiH}_3)_3\text{N}$  is triangular planar with Si—N—Si bond angle of  $120^\circ$  and less basic than trigonal pyramidal  $(\text{CH}_3)_3\text{N}$  with bond angle of  $107^\circ$ . 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  $E^\circ$  for the skip-step couples  $\text{MnO}_4^-/\text{MnO}_2$



A9/961

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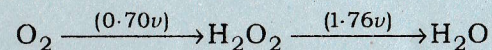
( 4 )

- (c) (i)  $\text{SO}_3$  can react with water to give  $\text{H}_2\text{SO}_4$ , but this acid is prepared by reacting  $\text{SO}_3$  first with  $\text{H}_2\text{SO}_4$  to give oleum and then oleum is hydrolysed to give  $\text{H}_2\text{SO}_4$ . 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— $\text{B}_5\text{H}_9$ ,  $\text{B}_6\text{H}_6^{2-}$ ,  $\text{B}_5\text{H}_{11}$ ,  $\text{B}_{10}\text{H}_{14}$  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

( 5 )

4. Answer the following (any three) : 10×3=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

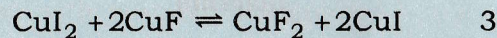
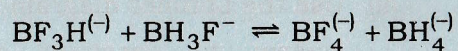
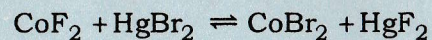


From the diagram, predict which species will undergo disproportionation. 4

- (iii) Discuss the clinical uses of oxides of nitrogen  $\text{N}_2\text{O}$  and  $\text{NO}$ . 3
- (b) (i) Discuss liquid  $\text{NH}_3$  as solvent in terms of acid-base neutralization and redox reactions. 5
- (ii) Graphite forms intercalation compounds but diamond does not. Explain. 2

( 6 )

- (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)  $\text{PbO}_2$  is stronger oxidising agent than  $\text{SnO}_2$ . Explain. 2

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