

2016

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) What significance results when stoichiometric mixture of O_2 and cyanogens burns?
- (b) Will Fe, Fe^{2+} or Fe^{3+} react more strongly with CO?
- (c) Give the correct order of aqua acid strengths of $[Fe(OH_2)_6]^{3+}$, $[Fe(OH_2)_6]^{2+}$ and $[Al(OH_2)_6]^{3+}$ complex ions.
- (d) What type of hydrate formation in brain tissue is responsible for the anesthetic effect of substances such as chloroform?

- (e) Why is KClO_3 insoluble in water at room temperature though it is ionic in behaviour?
- (f) Pure nitric acid is a colourless liquid, but why on exposure to light it turns slightly brown?
- (g) Why is phosphoric acid syrupy in nature?

2. Answer the following :

2×4=8

- (a) Despite the fact that Sn and Pb are same group members, SnCl_2 can be used as reducing agent but PbCl_2 doesn't. Explain.
- (b) What do you mean by effective nuclear charge? Calculate the effective nuclear charge experienced by one of the 4s electron of Zn.
- (c) Explain the following variation of bond lengths of silver halides with the help of Fajans' rule :

Compound	$r^+ + r^-$	$r_{\text{experimental}}$	Δ
AgF	248	246	-2
AgCl	296	277	-19
AgBr	311	289	-22
AgI	320	281	-39

- (d) Give reason why compounds of group 1 metals are typically white.

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

- (a) (i) Rationalize the following values for successive ionization energies of boron : 3

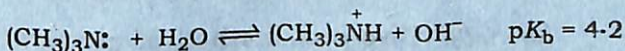
	IE_1	IE_2	IE_3	IE_4	IE_5
$\Delta_{\text{ion}} H(n) / (\text{kJ mol}^{-1})$	807	2433	3666	25033	32843

- (ii) MgSO_4 is soluble in water but BaSO_4 is insoluble in water. Explain. 2

(b) Explain the following :

- (i) Fluorine has low electron affinity than that of chlorine but acts as a stronger oxidizing agent than that of chlorine. 2

- (ii) The following nitrogen bases exhibit different basicities for the given reactions : 3



- (c) (i) Give the theoretical bases of hardness and softness of species that are used in hard and soft acid and base principles. 2

- (ii) Discuss liquid SO_2 as solvent in terms of acid-base and redox reactions. 3
- (d) What are *ortho*-hydrogen and *para*-hydrogen molecules? Discuss the effects of temperature on the relative proportions of the two forms in ordinary hydrogen. Give one method of preparation of pure *para*-hydrogen. 2+2+1
- (e) (i) Give the names and formulae of three important oxides of nitrogen. Discuss how one of the oxides of nitrogen is used in qualitative analysis of brown-ring test of nitrate radical. 3
- (ii) What is Frost diagram? How does it differ from Latimer diagram? 2
4. Answer the following (any three) : $10 \times 3 = 30$
- (a) (i) Give one method of preparation of diborane. Discuss the bonding and structure of diborane. What happens when diborane reacts with ammonia? 1+3+1
- (ii) Mention the advantages and disadvantages of using ammonia as a non-aqueous solvent. 3

- (iii) Discuss the structure of potassium-intercalated graphite compounds. 2
- (b) (i) Discuss the structures of oxoacids of sulphur. 3
- (ii) Give one method of preparation of each hydroxylamine and hydrogen azide. Explain the redox behaviour of both the two compounds. 3+4
- (c) (i) Discuss about different allotropic forms shown by phosphorus. 3
- (ii) Name the oxide of phosphorus which is also known as 'anhydride of phosphorus acid'. Give one method of preparation of that oxide. 2
- (iii) How many series of salts can be formed from orthophosphoric acid? Mention the salts with examples. 1+2
- (iv) Mention two oxoacids of nitrogen. 2
- (d) Discuss the following observations : 2×5=10
- (i) Acidic behaviours of methane, ethane and ethyne are in the order $\text{CH}_4 < \text{C}_2\text{H}_4 < \text{C}_2\text{H}_2$.
- (ii) Electron affinity goes on decreasing, as we move from top to bottom in a group of the periodic table.

(iii) The formation of F^{-} (g) from F (g) is exothermic while that of O^{2-} (g) from O (g) is endothermic.

(iv) Second ionization energy of sodium is higher than that of second ionization energy of magnesium.

(v) Despite the existence of phosphorus pentahalides, no hydride is known.

(e) (i) Catenation property of elements depends upon the bond energy of element (M-M). Explain. 3

(ii) The standard reduction potential values of the Fe^{3+}/Fe^{2+} and Fe^{2+}/Fe couples are +0.77 V and -0.47 V respectively. Calculate the standard potential (E°) for the conversion $Fe^{3+} \rightarrow Fe$. 3

(iii) Discuss how hydration energy and lattice energy values are related with each other to account for the solubility of salts in water. 4
