

## CHEMISTRY—I

Time Allowed : Three Hours

Maximum Marks : 200

### INSTRUCTIONS

*Please read each of the following instructions carefully before attempting questions.*

There are ELEVEN questions divided under SIX Sections.

Candidate has to attempt SIX questions in all.

The ONLY question in Section—A is compulsory.

Attempt any ONE question from each of the other Sections B, C, D, E and F.

The number of marks carried by a question/part is indicated against it.

All parts and sub-parts of a question are to be attempted together in the answer-book.

Attempts of questions shall be counted in chronological order. Unless struck off, attempt of a question shall be counted even if attempted partly.

Any page or portion of the page left blank in the answer-book must be clearly struck off.

Neat sketches are to be drawn to illustrate answers, wherever required.

Unless otherwise mentioned, symbols and notations have their usual standard meanings.

Assume suitable data, if necessary and indicate the same clearly.

Answers must be written in ENGLISH only.

### Section—A

1. Answer *all* of the following : 5×10=50

(a) Discuss the radius ratio rule for predicting structure of ionic crystals. 5

(b) Discuss the effect of solvent on relative strengths of acids and bases. 5

(c) How do you account for the following disproportionation reaction? 5



(d) Explain why square planar Ni(II) organometallic complexes are stable though they do not obey the 18-electron rule. 5

(e) What do you mean by packing fraction? Explain how it indicates stability of elements. 5

(f) Lithium has the highest ionization potential among alkali metals, yet it is the most powerful reducing agent. Explain. 5

(g) Describe the structures of  $\text{ClO}_3^-$  and  $\text{ClO}_4^-$  ions on the basis of concept of hybridization. 5

(h) What are the important consequences of lanthanide contraction? 5

(i) Apply the concept of EAN rule on  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$  complexes, and find out its validity to these complexes. 5

(j) Explain the Hund's rule and determine the ground state terms for  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Ti}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{V}^{3+}$ .

(At. No. for Fe, Ni, Ti, Mn and V are 26, 28, 22, 25 and 23) 5

### Section—B

Attempt *any one* question

2. (a) The radius of a cation is invariably smaller and that of an anion is invariably larger than that of corresponding atom. Justify with examples. 10

(b) With the help of molecular orbital diagram, explain why—

(i) the bond order in  $\text{N}_2^+$  ion is less than that in  $\text{N}_2$  molecule, whereas the bond order in  $\text{O}_2^+$  ion is greater than that in  $\text{O}_2$  molecule;

(ii) the bond energy of  $\text{NO}^+$  is higher than that of  $\text{NO}$ . 10

- (c) Discuss electronegativity according to Pauling's approach and Mulliken's approach. 10
3. (a) Explain the cause of recurrence of properties of elements at regular interval of atomic numbers, with suitable examples. 10
- (b) Explain how atomic orbitals combine to form bonding and anti-bonding molecular orbitals. What are the limitations to such combinations? 10
- (c) Discuss the factors influencing electronegativity. 10

### Section—C

Attempt *any one* question

4. (a) Define hard and soft acids and bases. What is HSAB principle? Explain why—
- (i)  $\text{AgI}_2^-$  complex is stable, but  $\text{AgF}_2^-$  is not;
- (ii)  $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$  is stable, while  $[\text{Co}(\text{NH}_3)_5\text{I}]^{2+}$  is unstable;
- (iii)  $\text{CsF}$  reacts with  $\text{LiI}$  to give  $\text{LiF}$  and  $\text{CsI}$ . 15

- (b) (i) Explain briefly the term 'electrode potential'. Derive an expression for calculating  $E_{\text{cell}}$  for galvanic cell.
- (ii) Cr(II) is strongly reducing, but Mn(III) is strongly oxidizing. Explain why.

Given :

$$E_{\text{Mn}^{3+}/\text{Mn}}^{\circ} = +1.51 \text{ V}$$

$$E_{\text{Cr}^{2+}/\text{Cr}}^{\circ} = -0.41 \text{ V} \quad 15$$

5. (a) What is  $\text{p}K_{\text{a}}$  value of a weak acid? Derive its relationship with pH of the weak acid. 15
- (b) Explain the terms 'solubility product' and 'common ion effect', and their role in qualitative analysis of metal ions. 15

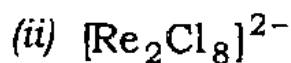
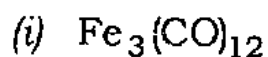
### Section—D

Attempt *any one* question

6. (a) Describe various reactions of ferrocene which establish its aromatic character. How is the aromaticity of ferrocene more than that of benzene? 15
- (b) Explain briefly the theory of nuclear fission reaction. Which of  $\text{U}^{235}$  or  $\text{U}^{238}$  is easily fissionable with thermal neutrons? Give reasons. 15

7. (a) Draw and discuss the structures of the following :

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- (b) Explain briefly the theory of neutron activation analysis. How is it used for the determination of an element in a sample?

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### Section—E

Attempt *any one* question

8. (a) Draw the complexes formed by  $\text{Li}^+$  and  $\text{Na}^+$  with salicylaldehyde and with acetylacetonone. Why do the coordination numbers differ?

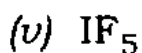
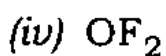
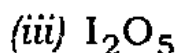
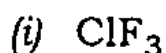
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- (b) What are metal carbonyls? Discuss the methods of preparation, properties and structures of some typical metal carbonyls.

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9. (a) Describe one method of preparation and structure of each of the following :

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- (b) (i) What are silicones? How are these synthesized? Discuss their structures, properties and uses.
- (ii)  $\text{CO}_2$  is a gas, but  $\text{SiO}_2$  is a highly stable solid. Explain. 15

### Section—F

Attempt *any one* question

10. (a) (i) What are the various oxidation states of vanadium? How would you account for them?
- (ii) The magnetic moment of  $[\text{Mn}(\text{CN})_6]^{3-}$  is 2.8 BM, while the magnetic moment of  $[\text{MnBr}_4]^{2-}$  is 5.9 BM. What are the geometries of the complex ions?
- (iii) Explain why Pt(II) and Pd(II) form square planar complexes almost exclusively but only a few Ni(II) complexes are known. 15
- (b) What is Jahn-Teller theorem? Describe symmetrical and unsymmetrical  $t_{2g}$  and  $e_g$  orbitals. Discuss the conditions for no distortion, slight distortion and strong distortion. 15

11. (a) Give the general electronic configuration of lanthanides. Explain—

(i) the filling of 4*f* sub-shell in the lanthanide series;

(ii) the anomalous oxidation states of +2 and +4 shown by some elements in the series;

(iii) the problems in the separation of lanthanides from one another. 15

(b) (i) Write the formula for the complex dichlorobis (ethylenediamine) cobalt(III) ion. Draw its geometrical and optical isomers.

(ii) Write the IUPAC names for



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