Sl. No. 0010610 A–IGQ–O–FGA

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) Carbon tetrachloride is inert towards water but boron trichloride hydrolyses in moist air. Suggest a reason. 5

(b) Francium has a smaller atomic radius than cesium and radium is smaller than barium. Explain why. 5

(c) Consider the complex ions dibromo-urate (I) and tetrabromourate (III). Which is more stable in aqueous solution and why? 5

(d) Although 18 valence electrons are found in $[Fe(H_2O)_6]^{2+}$, the effective atomic number rule is violated. Explain. 5

(e) Substitution reactions of polynuclear metal carbonyls with tertiary phosphines often induce the formation of bridging carbonyls. Provide an explanation. 5

(f) Draw the radial part of the wave functions for hydrogen atom with $n = 3,\ l = 2;\ n = 3,\ l = 0;\ n = 2,\ l = 1$. 5

(g) Draw the molecular orbital diagrams of O_2 and CO, and give the number of unpaired electrons and bond order in each case. 5

(h) Describe the structures of F_3ClO and XeF_6. What is the difference between the lone pairs present in the two compounds? 5

(i) Distinguish between nuclear fission and nuclear fusion reactions. 5

(j) Why is AgI_2^- complex stable but AgI_3^- complex is not? 5

Section—B

2. (a) What is meant by 'isoelectronic ions'? How does the size vary in the following series? Explain : 10

$$N^{3-},\quad O^{2-},\quad F^-$$

(b) Calculate the size of tetrahedral site in closed-packed structure. 10

(c) The second ionization energy of sodium is very high as compared to its first ionization energy. Give reason. 10

3. (a) Explain on the basis of MO theory as to why—

(i) oxygen molecule is paramagnetic while nitrogen molecule is diamagnetic;

(ii) hydrogen forms diatomic molecule while helium remains monatomic. 10

(b) What is lattice energy? Discuss Born-Haber cycle for experimental determination of lattice energy. 10

(c) What is polarization of molecules and ions? Discuss Fajans' rules regarding polarization. What are their effects? 10

Section—C

4. (a) What are meant by the terms labile and inert complexes? Explain, on the basis of crystal field theory, the cause of lability and inertness of octahedral complexes. 15

(b) Mention theories of *trans*-effect. Discuss any one of them in detail. Which theory explains better *trans*-effect of CO compared to pyridine? 15

5. (a) "All Arrhenius acids are also Brönsted acids but all Arrhenius bases are not Brönsted bases." Comment on the statement. 10

(b) Discuss briefly the solvent system concept of acids and bases. What are the limitations of this concept? 10

(c) What is a conjugate acid-base pair? Show that a strong acid has a weak conjugate base and a weak acid has a strong conjugate base. 10

Section—D

6. *(a)* Balance the following ionic reaction by ion-electron method in acid medium : 10

$$MnO_4^- \rightarrow Mn^{2+}$$

(b) Balance the above reaction by ion-electron method in basic medium. 10

(c) What is electrode potential? Explain why copper roofs get covered by a green layer of a mixture of $CuSO_4$ and $CuCO_3$ in damp environments. 10

7. *(a)* Define crystal field stabilization energy. Calculate its value for the following systems : 10

(i) d^5 low-spin complexes

(ii) d^6 tetrahedral complexes

(b) How does the valence bond theory account for the following facts? 10

(i) $[Ni(CN)_4]^{2-}$ is diamagnetic and square planar.

(ii) $[NiCl_4]^{2-}$ is paramagnetic and tetrahedral.

(iii) $Ni(CO)_4$ is paramagnetic and tetrahedral.

(c) Account on the basis of valence bond theory that the complex ion $[Co(NH_3)_6]^{3-}$ is octahedral and diamagnetic while the complex ion $[CoF_6]^{3-}$ is also octahedral but paramagnetic. 10

Section—E

8. (a) Explain why boron trichloride is monomeric while aluminium trichloride is dimeric. 10

(b) Discuss the structure of $(SiO_4)^{4-}$ ion. 10

(c) Discuss the variation of bond angles in hydrides of group 15 elements : 10

NH_3 (107·3°), PH_3 (93·6°),
AsH_3 (91·8°), SbH_3 (91·3°)

9. (a) Discuss the preparation and structure of ferrocene. 10

(b) Show how CO molecule functions as sigma-donor and π-acceptor ligand both. 10

(c) A living plant acquires a definite fraction of $^{14}_{6}C$ nuclei in its carbon content. If a freshly cut piece of wood gives 16·1 counts per minute per gram and an old wooden bowl gives 9·6 counts per minute per gram of carbon, calculate the age of the wooden bowl. The half-life of $^{14}_{6}C$ is 5770 years. 10

Section—F

10. *(a)* Compare the alkali metals with alkaline earth metals with respect to their *(i)* electronic configuration, *(ii)* size of atoms and ions, and *(iii)* ionization potential. 10

(b) "There occurs a progressive increase in metallic character in moving down a family of representative elements." Justify the above statement with reference to group 17. 10

(c) An electronegative element A has the electronic configuration $(n-2)s^2(n-1)s^2(n-1)p^6\ ns^2\ np^5$ and an electropositive element B has the electronic configuration $(n-2)s^2(n-1)s^2\ (n-1)p^6\ ns^1$.

(i) Name the two elements if $n = 3$.

(ii) To which block of elements in the periodic table, A and B belong to?

(iii) What would be the nature of the two elements—metallic or non-metallic?

(iv) What type of bond will be formed if the two elements combine together to form the compound AB and what properties are expected to be associated with the compound? 10

11. Comment on the following statements :

(a) Actinides have a greater tendency to form complexes than lanthanides. 10

(b) Lanthanides have little tendency to form complexes but their compounds are generally brilliantly coloured. 10

(c) Chemically actinides show a somewhat wider range of oxidation states. 10

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