

**CHEMISTRY  
Paper II**

Time Allowed : Three Hours

Maximum Marks : 200

**QUESTION PAPER SPECIFIC INSTRUCTIONS**

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

There are **FIFTEEN** questions divided under **THREE** Sections.

Candidate has to attempt **TEN** questions in all.

The **ONLY** question in Section ‘A’ is compulsory. In Section ‘B’, **SIX** out of **NINE** questions are to be attempted. In Section ‘C’, **THREE** out of **FIVE** questions are to be attempted.

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

Neat sketches are to be drawn to illustrate answers, wherever required. These shall be drawn in the space provided for answering the question itself.

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

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

Attempts of questions shall be counted in sequential 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 Question-cum-Answer Booklet must be clearly struck off.

Answers must be written in **ENGLISH** only.

## Some useful fundamental constants and conversion factors

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$\text{Rydberg constant} = 2.178 \times 10^{-18} \text{ J}$$

$$c = 2.998 \times 10^8 \text{ ms}^{-1}$$

$$k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$$

$$e = 1.602 \times 10^{-19} \text{ C}$$

$$m_e = 9.109 \times 10^{-31} \text{ kg}$$

$$F = 96485 \text{ C mol}^{-1}$$

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$

$$\pi = 3.142$$

$$1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg}$$

$$1 \text{ cal} = 4.184 \text{ J}$$

$$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$$

$$1 \text{ \AA} = 10^{-8} \text{ cm} = 10^{-10} \text{ m} = 0.1 \text{ nm} = 100 \text{ pm}$$

$$1 \text{ atm} = 760 \text{ torr} = 1.01325 \times 10^5 \text{ Pa}$$

$$1 \text{ bar} = 1 \times 10^5 \text{ Pa} = 0.9869 \text{ atm}$$

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

$$1 \text{ L atm} = 101.34 \text{ J}$$

$$1 \text{ eV} = 23060 \text{ cal}$$

## **SECTION 'A'**

- 1.(a) What are the postulates of kinetic theory of gases ? Out of these which ones are not valid for real gases ? 3+2

1.(b) What is Boyle temperature ( $T_B$ ). Assuming oxygen as a van der Waals gas, calculate the Boyle temperature of it. The values of van der Waals constants  $a$  and  $b$  for oxygen respectively are  $a = 1.36 \text{ dm}^6 \text{ atm mol}^{-2}$  and  $b = 0.0318 \text{ dm}^3 \text{ mol}^{-1}$ . Given :  $R = 0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$ . 5

1.(c) A temperature variation study of conductivity can distinguish between a metallic conductor and a semiconductor — Explain. 5

1.(d) Both NaCl and KCl crystallize in the same cubic pattern. However, X-ray diffraction study reveals that NaCl has FCC while KCl has SCC pattern — Explain. 5

1.(e)  $\text{HCl(g)} + \text{NH}_3\text{(g)} \rightleftharpoons \text{NH}_4\text{Cl(s)}$   
At lower temperatures the forward reaction is spontaneous while at higher temperatures the reverse reaction is spontaneous. Explain the reversal of the above reaction at different ranges of temperature in the light of thermodynamics (Given :  $\Delta H$  for the reverse reaction is positive). 5

1.(f) Calculate the Gibbs free energy change accompanying the compression of one mole of a gas at  $25^\circ\text{C}$  from 20 to 200 atm. The fugacities of the gas be taken as 18 and 120 atm respectively at pressure of 20 and 200 atm. 5

1.(g) Through derivation of the relevant relation, show whether  $t_{1/2}$  for a second order reaction depends on the initial concentration of the reactant or not. 5

1.(h) Why are Brownian movement and Tyndal effect shown by colloidal solutions only ? 5

1.(i) Derive Nernst equation for single electrode potential of an electrode of type, Pt/Cr<sup>6+</sup>, Cr<sup>3+</sup>. 5

1.(j) A given electrode can act as positive as well as negative — Justify or criticize. 5

1.(k) From the “uncertainty relation” how would you justify that the uncertainty in measuring the energy of a photoexcited state is greater than that of the ground state. 5

1.(l) Show that the eigenvalues of a Hermitian operator are real. 5

1.(m) If the rotational constants for  $^{14}\text{N}^{16}\text{O}$  and  $^{15}\text{N}^{16}\text{O}$  respectively are  $B$  and  $B'$ , then which of the following is correct and why ? 5

  - (i)  $B > B'$
  - (ii)  $B = B'$
  - (iii)  $B < B'$
  - (iv) none of these

- 1.(n) Citing the case of rotation of HCl molecule, explain how the photon-molecule interaction takes place. You may draw pictures or scheme to establish yourself. 5
- 1.(o) Radiative transitions (both absorption and emission) are displayed by vertical lines in Jablonski diagram. Explain why these lines are kept vertical. 5
- 1.(p) Calculate the relative energies of one einstein of photon of wavelength 600 nm to that of wavelength 300 nm. 5

## SECTION 'B'

- 2.(a) Derive the reduced equation of state from van der Waals equation. 5
- 2.(b) Show that the excluded volume is four times the actual volume of the gas molecule. 5
3. Establish the relative order of compactness between simple cubic, body centered cubic and face centered cubic crystals. Draw diagrams, if needed. 10
4. How does chemical potential vary with temperature and pressure ? Derive the relevant equations. 10
5. Derive an equation relating the effect of ionic strength on the rate constant of an ionic reaction. Discuss the effect of ionic product on rate constants. 6+4
- 6.(a) In lead acid storage cell write down the electrode reactions and the total cell reaction during discharging. 6
- 6.(b) Specific gravity of the sulfuric acid used in a lead acid storage cell gives an assessment about the performance of the cell — justify or criticise. 4
7. Solution of a two-dimensional box problem gives the following for wave function and energy :  

$$\psi_{n_1, n_2}(x, y) = \frac{2}{L} \sin\left(\frac{n_1\pi x}{L}\right) \sin\left(\frac{n_2\pi y}{L}\right) \text{ for } 0 \leq x \leq L \text{ and } 0 \leq y \leq L$$

$$\psi_{n_1, n_2}(x, y) = 0 \text{ outside the box and } E_{n_1, n_2} = (n_1^2 + n_2^2) \frac{\hbar^2}{8mL^2}.$$
- Show that if the 2D box becomes a square there arises the case of degeneracy. 10
- 8.(a) Homonuclear diatomic molecules like H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> are insensitive to microwave spectroscopy. Hence their bond lengths cannot be determined from microwave spectroscopy. How are their bond lengths determined ? — Logically explain your answer. 5

8.(b) We have the following spectral data for N<sub>2</sub>O molecule.

$\bar{v} \text{ (cm}^{-1}\text{)}$	<i>Infra-red</i>	<i>Raman</i>
589	Strong; PQR Contour	—
1285	Very strong; PR Contour	Very strong; polarized
2224	Very strong; PR Contour	Strong; depolarized

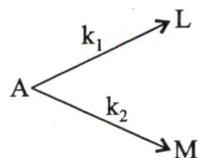
From this data logically comment on the structure of the linear N<sub>2</sub>O molecule. 5

- 9.(a) Using the relative method how can you determine the fluorescence quantum yield of a fluorophore in solution ? 5
- 9.(b) On which factors does fluorescence quantum yield of a fluorophore in a solution depend ? 5
10. CO<sub>2</sub> is a linear triatomic molecule. How many lines do you expect to have in its vibrational spectrum ? Compare this with the observed IR spectrum of CO<sub>2</sub>. 6+4

## SECTION 'C'

- 11.(a) From the concept of "particle in a box", how would you predict the relative positions of the absorption bands of linear conjugated alkenes as the chain length increases. 10
- 11.(b) A metallic element exists as a cubic lattice. Each edge of the unit cell is 2.88 Å. The density of the metal is 7.20 g cm<sup>-3</sup>. How many unit cells will be there in 100 g of the metal ? 10
- 12.(a) A buffer solution contains 0.2 mole of acetic acid and 0.25 mole of potassium acetate per litre. Calculate the change in pH of the solution if 0.5 mL of 1 M HCl is added to it. The dissociation constant of acetic acid at room temperature is  $1.75 \times 10^{-5}$ . (The volume change on the addition of HCl may be neglected). 10
- 12.(b) An aqueous solution at 25°C is 0.005 molal in sodium chloride and 0.001 molal in potassium sulphate. Calculate activities of Na<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> ions. At 25°C the Debye-Huckel constant *A* is equal to 0.509. 10

- 13.(a) Derive the rate equation for the overall reaction of type,



How can we evaluate individual rate constants k<sub>1</sub> and k<sub>2</sub> ? 10

- 13.(b)** The equilibrium constant of the reaction  $X \longrightarrow Y$  is doubled when temperature is raised from  $25^{\circ}\text{C}$  to  $35^{\circ}\text{C}$ . Calculate the enthalpy of the reaction. 10
- 14.(a)** Without derivation, write down the BET equation giving the meanings of the terms.  
Using BET equation how can one measure the total surface area of a solid catalyst in powder state. Given : cross sectional area of each adsorbed gas molecule is  $A$  and  $m$  g of solid adsorbent is present. 3+7
- 14.(b)** Using the law of corresponding state for a van der Waals gas, calculate pressure exerted by one mole of carbon dioxide at  $40^{\circ}\text{C}$  confined to a volume of  $0.107 \text{ dm}^3$ . (For carbon dioxide  $P_c = 73.0 \text{ atm}$ ;  $V_c = 0.0957 \text{ dm}^3$ ;  $T_c = 304 \text{ K}$ ) 10
- 15.(a)** On irradiation of propionaldehyde at  $30^{\circ}\text{C}$  with light of  $302 \text{ nm}$ , the quantum yield of formation of CO is found to be  $0.54$ . The intensity of incident light is  $15000 \text{ erg s}^{-1}$ . Find out the rate of formation of CO. 10
- 15.(b)** What are 1st overtone and hot band in IR spectroscopy ? How can these two be differentiated experimentally ? 6+4
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# CHEMISTRY

## Paper – I

Time Allowed : **Three Hours**

Maximum Marks : **200**

### Question Paper Specific 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**.*

*Out of the remaining **TEN** questions, the candidate has to attempt **FIVE**, choosing **ONE** 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.*

*Neat sketches are to be drawn to illustrate answers, wherever required. These shall be drawn in the space provided for answering the question itself.*

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

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

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

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*Answers must be written in **ENGLISH** only.*

**SECTION A**  
**(Compulsory Section)**

**Answer all of the following :**

**$5 \times 10 = 50$**

**Q1.** (a) Match the following : 5

- |  |                            |
|--|----------------------------|
| (i) $Mg_2SiO_4$                                  | (A) Spinel                 |
| (ii) $Be_3Al_2Si_6O_8$ (Beryl)                   | (B) Zeolite                |
| (iii) $M_q^{m+} [Si_{x-y} P_{1-x} Al_{1-y} O_4]$ | (C) Orthosilicate          |
| (iv) $MgAl_2O_4$                                 | (D) Aluminophosphate       |
| (v) $Ca(OH)(PO_4)_3$                             | (E) Cyclosilicate          |
|  | (F) Hydroxyapatite         |
|  | (G) Intercalation Compound |

(b) Determine the ground state terms for the following compounds using L-S coupling scheme : 5



(c) How many stereoisomers are possible for the square-planar complexes  
 (i)  $Ma_2bc$  and (ii)  $Mabcd$  (a, b, c and d are unidentate ligands) ? Draw the structures. 5

(d) Calculate the concentration of carbonate ions in 0.10 M  $H_2CO_3$  (aq).  
 (Given :  $K_{a_1} = 4.3 \times 10^{-7}$ ,  $K_{a_2} = 4.6 \times 10^{-11}$ ) 5

(e) A 25 mL solution containing  $Cl^-$  was treated with excess  $AgNO_3$  solution to precipitate 0.830 g of  $AgCl$ . What was the molarity of  $Cl^-$  in the unknown solution ? (At. wt. of Ag = 107.87, Cl = 35.453) 5

(f) A sample of 0.6128 g of iron ore is dissolved in HCl and all the iron is reduced to  $Fe^{2+}$  ions. This solution required 38.4 mL of 0.0198 M  $KMnO_4$  to titrate under acidic conditions. Calculate the mass percent of iron in the ore. (Given atomic weight of iron = 55.85) 5

(g) Explain the masking process and demasking process. How can the concentration of nickel(II) be determined in the presence of  $Cu^{2+}$ ? 5

(h) Consider the 18-electron rule and determine the value of n for the following compounds : 5



(i) What is Carbon-14 dating ? Why is this method used to determine the age of the ancient articles made of wood ? 5

(j) Arrange the following metal ions in the increasing order of their oxidising power. Give reasons. 5



## SECTION B

**Attempt any one question :**

- Q2.** (a) Perovskite mineral contains calcium, titanium and oxygen. 10  
(i) Draw the unit cell of perovskite with titanium at the centre of the unit cell.  
(ii) Draw the unit cell of perovskite with calcium at the centre of the unit cell.  
(iii) Find the formula of perovskite in both the unit cell representations.  
(iv) What is the coordination number of titanium in each representation of the unit cell ?
- (b) The conductivity of silicon semiconductor is small compared to metals. Propose two methods to increase the conductivity of silicon, with examples. Draw the energy level diagrams illustrating the two methods. 10
- (c) (i) The crystalline form of fullerene has a face-centred cubic array of  $C_{60}$  molecules. What is the basis of this unit cell ?  
(ii) What are the products likely to form when  $Ta_2O_5$  is heated at  $700^{\circ}C$  in the flow of  $NH_3$  gas ? 4
- (d) Match the following : 6
- |                                    |                    |
|------------------------------------|--------------------|
| (i) Schottky defects               | (A) $ReO_3$        |
| (ii) Frenkel defects               | (B) $Ti_{1-x}O$    |
| (iii) Non-Stoichiometric compound  | (C) Silver halides |
| (iv) Semiconductor                 | (D) $CaF_2$        |
| (v) Corundum structure             | (E) GaAs           |
| (vi) Conductor at room temperature | (F) $Ti_2O_3$      |
- Q3.** (a) Identify the electron configurations which cause strong distortions and weak distortions for  $d^1$  to  $d^9$  metals in the case of strong and weak field octahedral complexes. Give reasons. 10  
(b) Discuss the factors which affect the crystal field splitting energy values. 10  
(c) Calculate the magnetic moment values for the following complexes based on the unpaired electrons present : 10  
(i)  $[Fe(NH_3)_6]^{3+}$   
(ii)  $[CoBr_6]^{3-}$  and  $[CuCl_4]^{2-}$

## SECTION C

**Attempt any one question :**

- Q4.** (a) How does the VBT account for the following facts ? 10
- (i)  $[\text{NiCl}_4]^{2-}$  is paramagnetic and tetrahedral.
  - (ii)  $[\text{Ni}(\text{CO})_4]$  is diamagnetic and tetrahedral.
- (b) Identify the type of selection rules observed for the following compounds in their electronic absorption spectra. Justify your answer. 10
- (i)  $[\text{Co}(\text{NH}_3)_6]^{2+}$
  - (ii)  $[\text{NiBr}_4]^{2-}$
  - (iii)  $[\text{MnBr}_4]^{2-}$
  - (iv)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
  - (v)  $\text{KMnO}_4$
- (c) Draw and explain the crystal field splitting energy diagram of  $[\text{Ni}(\text{CN})_4]^{2-}$  complex. 10
- Q5.** (a) 50 mL of 0.1 M HCl was titrated against 0.1 M NaOH. Calculate the pH at the start of titration and after addition of 10 mL, 50 mL and 60 mL of NaOH. 10
- (b) The phenolphthalein indicator gives pink colour in presence of dilute alkali, while in presence of excess of concentrated alcoholic alkali, the pink colour disappears. Explain by drawing the structures. 10
- (c) Write the reactions involved in the volumetric titration of weak base with strong acid. Explain using titration curve. 10

## SECTION D

**Attempt any one question :**

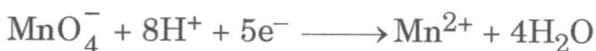
- Q6.** (a) A 2.000 gm of a rock sample contains lead, iron and copper. This sample is dissolved to form a solution containing the three metals. Gravimetric estimation of the metals yielded 0.3188 gm of  $\text{PbSO}_4$ , 0.7282 gm of  $\text{Fe}_2\text{O}_3$  and 0.4787 gm of  $\text{CuCNS}$ . Calculate the percentages of the three metals in the rock sample. 10

(Given atomic weights : Pb = 207.19, S = 32.07, O = 16.01, Fe = 55.85, Cu = 63.54, N = 14.01, C = 12.01)

- (b) Explain nucleation and particle growth. What are the techniques that promote particle growth ? 10

- (c) Give the principles involved in gravimetric volatilization methods. How are the carbonate content of dolomite, and carbon and hydrogen content of organic compounds determined using this method ? 10

- Q7.** (a) Calculate the reduction potential of the following half-cell reaction at 25°C. 10



The concentrations are  $[\text{MnO}_4^-] = 0.1 \text{ M}$ ,  $[\text{Mn}^{2+}] = 0.010$  and  $\text{pH} = 3.0$ .

The standard reduction potential of the reaction at 25°C,  $E^\circ = 1.51 \text{ V}$ . 10

- (b) Answer the following : 10

- What is the difference between iodimetry and iodometry ?
- Why is iodine used in a solution containing excess  $\text{I}^-$  ?
- Why is starch used as an indicator in titrations involving iodine ?
- Is starch a redox indicator ?
- In iodometric titrations, the contents of the reaction mixture are usually kept in dark after adding KI solution. Why ?

- (c) A piece of 1.06 g of copper metal is dropped in 250 mL of 0.20 M  $\text{AgNO}_3$  solution. Will all the copper dissolve in this solution ? Write the net reaction equation. 10

(Given atomic weight of Cu = 63.54 and atomic weight of Ag = 107.87)

## SECTION E

**Attempt any one question :**

- Q8.** (a) Write the formation constant ( $K_f$ ) and conditional formation constant ( $K'_f$ ) for metal – EDTA complex. Calculate the conditional (effective) formation constant for  $\text{Fe}^{3+}$  in a solution of 0.10 M  $\text{FeY}^-$  at pH 4.00 and at pH = 1.00. 10

(Given :  $K_f$  for  $\text{FeY}^-$  is  $1.3 \times 10^{25}$

$$\alpha_{\text{Y}^{4-}} \rightarrow \text{at } 4.00 \text{ pH is } 3.8 \times 10^{-9}$$

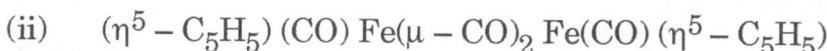
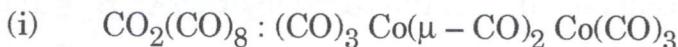
$$\alpha_{\text{Y}^{4-}} \rightarrow \text{at } 1.00 \text{ pH is } 1.9 \times 10^{-18})$$

- (b) Give the stepwise chemical equations and calculate the overall stability constant  $\beta_2$  for the formation of  $[\text{Ag}(\text{NH}_3)_2]^+$  from  $[\text{Ag}(\text{H}_2\text{O})_4]^+$ . 10

(Given :  $K_1 = 2.1 \times 10^3$ ,  $K_2 = 8.2 \times 10^3$ )

- (c) Explain the metal ion – indicator – EDTA reactions. What are the important criteria to be satisfied by metal ion indicator for visual detection of end points ? 10

- Q9.** (a) Determine the total valency electrons of metal and number of metal-metal bonds present in the following compounds, which obey the 18-electron rule. Draw structures. 10



- (b) Draw the structures of  $\text{Fe}_2(\text{CO})_9$  and  $\text{Fe}_3(\text{CO})_{12}$ . Explain hybridization and bonding present in them. 15

- (c) Which one of the given complexes will undergo ligand substitution faster with  $\text{PPh}_3$ ? Why? 5



## SECTION F

**Attempt any one question :**

- Q10.** (a) Calculate the rate of disintegrations that occur in the first second(s) from 1·0 mol of a radioactive material with  $t_{1/2} = 12000$  years,  $t_{1/2} = 12$  hours and  $t_{1/2} = 12$  seconds.

15

Avogadro number =  $6\cdot022 \times 10^{23}$  mole<sup>-1</sup>

- (b) Complete the following nuclear reactions :

5



- (c) What is the principle involved in Geiger–Müller counter which is used to measure the radioactivity levels ?

10

- Q11.** (a) The atomic size increases from 3d to 4d metals. However, the atomic size is similar between 4d and 5d metals. Give reasons.

10

- (b) How is magnetic data useful to distinguish between strong field and weak field octahedral complexes of d<sup>1</sup> to d<sup>9</sup> metals ?

10

- (c) How are lanthanides separated by ion-exchange method ? Explain.

10

