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.

Diagrams/Figures, wherever required, shall be drawn in the space provided for answering the question itself.

Wherever any assumptions are made for answering a question, they must be clearly indicated.

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

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

$N_A = 6{\cdot}022 \times 10^{23}\ \text{mol}^{-1}$

Rydberg constant $= 2{\cdot}178 \times 10^{-18}$ J

$c = 2{\cdot}998 \times 10^{8}\ \text{ms}^{-1}$

$k_B = 1{\cdot}38 \times 10^{-23}\ \text{JK}^{-1}$

$e = 1{\cdot}602 \times 10^{-19}$ C

$m_e = 9{\cdot}109 \times 10^{-31}$ kg

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

$R = 8{\cdot}314\ \text{JK}^{-1}\ \text{mol}^{-1}$

$h = 6{\cdot}626 \times 10^{-34}$ Js

$\pi = 3{\cdot}142$

1 amu $= 1{\cdot}66 \times 10^{-27}$ kg

1 cal $= 4{\cdot}184$ J

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

$1\ \text{Å} = 10^{-8}\ \text{cm} = 10^{-10}\ \text{m} = 0{\cdot}1\ \text{nm} = 100\ \text{pm}$

$1\ \text{atm} = 760\ \text{torr} = 1{\cdot}01325 \times 10^{5}\ \text{Pa}$

$1\ \text{bar} = 1 \times 10^{5}\ \text{Pa} = 0{\cdot}9869\ \text{atm}$

$1\ \text{eV} = 1{\cdot}602 \times 10^{-19}\ \text{J}$

1 L atm $= 101{\cdot}34$ J

1 L bar $= 100$ J

SECTION A

Q1. Answer all of the following questions : *5×16=80*

(a) The ratio of estimated molar heat capacities at constant volume (using Principle of Equipartition of Energy) of linear N-atomic molecules to its non-linear one is $\frac{13}{12}$. Find the value of N. *5*

(b) In the van der Waals gas equation, the pressure correction term is $\frac{n^2a}{V^2}$.

Find the SI unit of van der Waals constant, 'a'. *5*

(c) Show that surface energy of a cube-shaped liquid is 1·24 times of its sphere shape. *5*

(d) An element exists in the bcc structure where cell edge is 2·88 Å. The density of this element is 7·20 g cm^{-3}. How many atoms does 104 g of the element contain ? *5*

(e) Show that $\left(\frac{\partial C_V}{\partial V}\right)_{T,n} = 0$; for any ideal gas. *5*

(f) What will be the change in molar entropy (in SI) when volume of any ideal gas is doubled at constant temperature ? *5*

(g) Calculate the activity coefficient of Zn^{++} ions and Cl^- ions in 1·0 mM $ZnCl_2$ (aq) solution at 25°C. Given : A of water at 25°C = 0·51 $M^{-1/2}$. *5*

(h) What is buffer solution ? Explain the buffer action in a buffer solution of (NH_4OH + NH_4Cl). *5*

(i) Liquids A and B form an ideal solution. At 50°C the total vapour pressure of solution containing 1 mol of A and 2 mol of B is 300 torr. When 1 mol more of A is added to the solution, total vapour pressure increases to 400 torr. Calculate the vapour pressures of pure liquids A and B at 50°C. *5*

(j) Define zero order reaction. Show that its half-life period is proportional to initial concentration of reactant. *5*

(k) Distinguish between Physisorption and Chemisorption. Which of these is responsible for the phenomenon of heterogeneous catalysis ? 5

(l) Deduce Nernst equation for single electrode potential of electrode represented by (Pt) | Fe^{3+}, Fe^{2+} at T K. 5

(m) Define one 'Einstein' of energy. Calculate its value for 350 nm of light. 5

(n) Derive Bohr's quantum postulate, angular momentum ($L \equiv m_e vr$) of rotating electron around the nucleus of H-atom in circular path is $n\hbar$ (where n = 1, 2, 3, ...), using wave property of electron. (Symbols have their usual meanings) 5

(o) Explain the terms 'bathochromic shift' and 'hypsochromic shift' with a suitable example of each. 5

(p) The ^{1}H-NMR spectrum of C_4H_9Br consists of single line. What could be its structure ? 5

SECTION B

Attempt any *six* questions :

Q2. (a) The number of gas molecules of mass 'm' at T K within the speed range 'c' to 'c + dc' is given by

$$dN = Ac^2 e^{-mc^2/2k_BT}\, dc.$$

Find the expression of A.

Given : $\int_0^\infty x^2 e^{-\beta x^2}\, dx = \frac{1}{4}\left(\frac{\pi}{\beta^3}\right)^{\frac{1}{2}}$ *5*

(b) Dimethyl ether is more volatile than ethanol though both are of same molar masses. Explain with reason(s). *5*

Q3. (a) Silver crystallizes in a fcc structure with a unit cell length of 408·6 pm. Use Bragg's equation to calculate first two diffraction angles from the 111 planes using X-ray radiation with wavelength of 154·43 pm. *5*

(b) At 37°C, the osmotic pressure of blood is 7·65 atm. How much glucose ($M = 180\ g\ mol^{-1}$) should be used per L for an intravenous injection that is to be isotonic with osmotic pressure of blood ? *5*

Q4. Define compressibility factor (Z) of a gaseous state. Find the numerical value of a gas obeying equation of state : $P(V - nb) = nRT$, when its molar volume is 10 b at pressure P and temperature T K. *10*

Q5. Define Carnot efficiency. You have to increase it either by increasing 10 K source temperature or decreasing same value of sink temperature. What will you do ? Give reason(s). *10*

Q6. (a) For a gas phase reaction, pressure does not affect the value of equilibrium constant at constant temperature. Explain with reason. *5*

(b) Which of the function(s) is/are eigenfunction(s) of the operator $\frac{d^2}{dx^2}$?

Find its eigenvalue(s) also. *5*

(i) $6 \cos (4x)$

(ii) $5x^2$

(iii) $3e^{-5x}$

(iv) $ln(2x)$

(v) $\sin (3x)$

Q7. The activity product ($\equiv a_{H^+} \times a_{-OH}$) of pure water is 1×10^{-14} at 25°C. What will be the minimum and maximum possible values of pH for an aqueous solution at that temperature ? Give reasons in support of your answer. Finally give the pH-scale of aqueous solution at 25°C. *10*

Q8. (a) Define adsorption isotherm. Write down the expression of Langmuir adsorption isotherm in terms of fraction of surface sites covered (θ) and equilibrium pressure (P). How can this expression be converted in terms of volume of gas adsorbed ? *5*

(b) Write down cell reaction and calculate emf of the following cell at 25°C.

$$Fe \,|\, Fe^{2+} (0{\cdot}01 \text{ M}) \,\|\, Ag^{+} (0{\cdot}1 \text{ M}) \,|\, Ag$$

Given : $E^0_{Ag^+/Ag} = 0{\cdot}8$ V and $E^0_{Fe^{2+}/Fe} = -0{\cdot}44$ V at 25°C. *5*

Q9. (a) For the reaction

$$H_2 (g) + Cl_2 (g) \rightarrow 2 HCl (g),$$

the quantum yield was found to be $1{\cdot}0 \times 10^6$ with wavelength of 480 nm. What amount of HCl (g) would be produced under these conditions per calorie of radiant energy absorbed ? *5*

(b) How can we distinguish between p-xylene and ethyl benzene by using NMR spectra ? *5*

Q10. (a) $^1H\,^{35}Cl$ has a force constant value of 480 Nm^{-1}. Calculate the fundamental frequency and wave number. *5*

(b) 'Electronic spectrum of molecules is more complex.' Justify this statement. *5*

SECTION C

Attempt any *three* questions :

Q11. (a) Suppose initially all the gas molecules (in a rigid and adiabatic container) have the same translational kinetic energy of $6{\cdot}0 \times 10^{-21}$ J. As time passes, the motion becomes random, chaotic and energies get finally distributed in a Maxwellian way. Compute the final temperature and average translational kinetic energy per mol. *10*

(b) With the help of Jablonski diagram, explain the possible decay routes for an electronically excited molecule. *5*

(c) Find the number of degeneracy of the energy level $\frac{14\,h^2}{8\,mL^2}$ for a free particle of mass 'm' in a cubical box of edge length L. *5*

Q12. (a) The working substance used in an engine is 1 mol diatomic ideal gas ($\gamma = 1{\cdot}4$). The engine completes its cycle with the following three steps :

(i) An adiabatic expansion against a constant pressure of 1 bar from volume 10 to 20 L.

(ii) Cooling and contraction at constant pressure of 1 bar to its initial volume of 10 L.

(iii) Heating at constant volume to its initial pressure.

Calculate the work involved in each step in SI system and efficiency of the engine. Mention the redundant data also. *15*

(b) Symmetric stretching vibration of CO_2 molecule is IR inactive but Raman active. Explain why. *5*

Q13. (a) For the reaction : $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$; change of pressure does not affect the K_p-value but affects the K_x-value at constant temperature. Explain, by deriving a relation between K_p and K_x. Assume all component gases in the reaction mixture behave ideally. *15*

(b) A dilute solution of KCl was placed between two Pt electrodes 10 cm apart, across which a potential difference of 6·0 V was applied. What will be the velocity of K^+ ion ? Given : Molar ionic conductivity of K^+ ion at this dilution and at experimental temperature is $73{\cdot}52 \times 10^{-4}$ S m^2 mol^{-1}. *5*

Q14. For the reaction : $A \xrightarrow{k_1} B \xrightarrow{k_2} C$; (both steps are elementary)

when t = 0;	C_0	0	0
at any time,	C_1	C_2	C_3

Derive the expressions of C_1, C_2 and C_3 in terms of rate constants and time of reaction and draw the plot of concentration of each A, B and C against time. *20*

Q15. (a) KCl but not NaCl has been used in construction of salt-bridge. Justify. *5*

(b) In connection to the ^{1}H-NMR spectrum, arrange the following compounds in increasing order of chemical shift, with reason. *5*

(i) CH_2Cl_2

(ii) Cyclohexane

(iii) CH_4

(iv) CH_3COCH_3

(v) $CH_2 = CH_2$

(vi) C_6H_6

(c) (i) Define rotational constant of a rigid rotor molecule. Does it depend on temperature ?

(ii) Spacing between two spectral lines in MW spectra of $^1H\,^{127}I$ is $13{\cdot}2$ cm^{-1}. Calculate its equilibrium bond length in pm. *4+6=10*