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.

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 QCA Booklet must be clearly struck off.

Answers must be written in ENGLISH only.

Some useful fundamental constants and conversion factors

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

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

$c = 2{\cdot}998 \times 10^{8}$ m s^{-1}

$k_B = 1{\cdot}38 \times 10^{-23}$ J K^{-1}

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

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

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

$R = 8{\cdot}314$ J K^{-1} mol^{-1}

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

$\pi = 3{\cdot}142$

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

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

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

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

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

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

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

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

SECTION—A

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

(a) At what temperature will the average speed of oxygen molecules be equal to that of hydrogen molecules at 20 K?

(b) The fugacity (f) of a real gas will be greater than its observed pressure (P) when intermolecular repulsive interactions are dominant. Justify with reason.

(c) At room temperature, liquid water wets solid glass surface, but liquid mercury does not. Explain why.

(d) Estimate the number of particles per unit cell of an fcc crystal.

(e) In a Joule-Thomson experiment, the temperature of the gas decreases. What will be the sign of Joule-Thomson coefficient? Give reason.

(f) Show that $\Delta G = \Delta A$, for isothermal expansion of fixed amount of ideal gas.

(g) We know

$$K_p = \exp(-\Delta G^\circ / RT)$$

(Symbols have their usual meanings)

(i) What are the units (in SI system) of K_p and ΔG°?

(ii) Does the K_p value of a chemical reaction depend on temperature of reaction at equilibrium and mode of stoichiometric representation of the chemical reaction?

(h) At 25 °C, pH of 10^{-8} mol L^{-1} aqueous HCl solution is less than 7·0. Justify with reason.

(i) Boiling point of liquid depends on superincumbent pressure, not on external pressure. Justify with definition of boiling point of liquid.

(j) For the reaction

$$I^- (aq) + H_2O_2 (aq) \rightarrow IO^- (aq) + H_2O (l)$$

predict whether the reaction rate will be increased, decreased or unchanged with increase of ionic strength of the solution. Give reason(s) in support of your answer.

(k) The spontaneous adsorption of gas on a solid surface at constant pressure and temperature is an exothermic process. Give reasons with the help of principles of thermodynamics.

(l) Conductivity of an ionic solution does not depend on its mass, but depends on its temperature. Explain with reasons.

(m) The following photochemical reaction occurs when UV light is exposed to anthracene ($C_{14}H_{10}$) in benzene medium :

$$2\,C_{14}H_{10} + h\nu \rightarrow C_{28}H_{20}$$

What would be the expected quantum yield? The observed quantum yield is 0·5. How will you explain it?

(n) Show that the function $\psi_n = N \sin\left(\frac{n\pi x}{L}\right)$ satisfies the Schrödinger equation for a particle in a one-dimensional box with a potential function $V(x)$ equal to zero for $0 \leq x \leq L$ and infinity elsewhere. What is the eigenvalue?

(o) Which transition of the following corresponds to the second line of the Balmer spectrum?

(i) $4p \rightarrow 3s$

(ii) $2s \rightarrow 4p$

(iii) $3d \rightarrow 2p$

(iv) $4d \rightarrow 2p$

(v) $4d \rightarrow 3p$

Give reasons.

(p) Determine the number of normal modes for vibrational motion of each of the following molecules :

(i) Dinitrogen

(ii) Carbon dioxide

(iii) Water

(iv) Acetylene

(v) Ethylene

SECTION—B

Attempt *any* **six** questions : 10×6=60

2. *(a)* For fixed mass of an ideal gas, what would be the nature of the plot of $\ln(P/\text{bar})$ against $\ln(V/\text{L})$ at constant temperature? Give reason(s) in support of your answer.

(b) Find the Boyle temperature of He gas which obeys the van der Waals gas equation. Given $a = 0{\cdot}0341$ atm dm^6 mol^{-2} and $b = 2{\cdot}38\times10^{-2}$ dm^3 mol^{-1}.

5+5=10

3. The molar Gibbs free energy of a certain gas is given by $G_m = RT\ln\left(\frac{P}{\text{bar}}\right) + a + bP + cP^2$; where a, b and c are constants and is temperature dependent.

(a) Find the units of a, b and c in SI system.

(b) Obtain the equation of state for n mol of this gas. 5+5=10

4. 3·0 mol H_2 (g) and 1·0 mol N_2 (g) are in two compartments separated by a partition. The volume and temperature of both the compartments are the same. What will be the change in entropy (ΔS) of the system when the partition is removed and allowed to free mixing of gases? Assume that two gases behave ideally. 10

5. The vapour pressure of benzene is 53·3 kPa at 60·6 °C, but it lowers to 51·5 kPa when 19·0 g of a non-volatile organic compound is dissolved in 500·0 g benzene. Calculate the molar mass of the organic compound, taking the molar mass of benzene as 78·0 g. 10

6. The decomposition of HI (g) to H_2 (g) and I_2 (g) is a second-order reaction. The half-life of the reaction is found to be 13·5 min, when the initial pressure of HI (g) is 1·0 bar.

(a) Calculate the half-life when the initial pressure of HI (g) is 0·1 bar.

(b) Calculate the reaction time required for the pressure of HI (g) to fall from 1·0 bar to 0·1 bar. 5+5=10

7. The Heisenberg Uncertainty Principle (HUP) can be given mathematically as

$$\Delta x \, \Delta p_x \geq \frac{h}{4\pi}$$

For a particle trapped in a one-dimensional box of length L, the maximum value of Δx is L. Calculate the minimum value of Δp_x for an electron trapped in a linear molecule of length $L = 3{\cdot}0$ nm and clearly state the units. 10

8. *(a)* Find the inter-planar distance between two successive 110-planes of a bcc crystal having unit cell edge length as 100·0 pm.

(b) Write down the expression of the 'Langmuir adsorption isotherm' in terms of the fraction of surface sites covered (θ) and equilibrium pressure (P) of the adsorbed gas at constant temperature. How would you determine the constant involved in this equation? 5+5=10

9. *(a)* With increase of temperature of HCl (aq) solution, the transport number of the H^+ ion decreases, though its velocity increases. Explain with reason(s).

(b) The conductivity of $KClO_4$ (aq) solution at 25 °C is 13·78 mS m^{-1} when its concentration is 1·0 mmol dm^{-3}. Calculate its molar conductivity. 5+5=10

10. *(a)* The anti-Stokes lines of the pure rotational Raman spectrum of a molecule are roughly of the same intensity as the Stokes lines, but anti-Stokes lines of the vibrational Raman spectrum are generally much weaker than the Stokes lines. Account for the observation.

(b) In the pure rotational Raman spectrum of a diatomic molecule, the first three transitions are observed at 26·52 cm^{-1}, 44·20 cm^{-1} and 61·88 cm^{-1}.

(i) Calculate the rotational constant $\tilde{B}$ of the molecule.

(ii) What other information would you need to calculate the equilibrium bond length of the molecule? Explain your answer. 5+(3+2)=10

SECTION—C

Attempt *any* **three** questions : 20×3=60

11. *(a)* For chemical equilibrium, which of the following thermodynamic conditions are correct?

(i) $\left(\frac{\partial G}{\partial \xi}\right)_{P,T} = 0$

(ii) $\sum_i \nu_i \mu_i = 0$ (at constant P and T)

(iii) $\sum_i \nu_i \mu_i^\circ = 0$ (at constant T)

(iv) $\Delta S_{sys} = 0$

(v) $\Delta S_{univ} = 0$

[ξ = advancement of reaction]

(b) Obtain the expression of e.m.f. (E) of the following galvanic cell in terms of its standard e.m.f. ($E°$), molality of aqueous solution (m) and its mean ionic activity coefficient ($\gamma_\pm$) :

$$Zn \mid ZnCl_2 \text{ (aq, } m) \mid AgCl, Ag$$

(c) The electronic spectrum of a diatomic molecule A_2 shows a series of bands converging to a continuum at 200 nm. One of the atoms formed at 200 nm is in an excited state, which lies 8000 cm^{-1} above its ground state. Calculate the bond dissociation energy of A_2. 5+5+10=20

12. *(a)* Which of the following molecules may show an infrared vibrational absorption spectrum?

(i) Cl_2

(ii) HCl

(iii) NH_3

(iv) CO_2

(v) CH_4

(b) If the two methyl proton resonances in the proton NMR spectrum of methyl acetate (CH_3COOCH_3) are 320 Hz apart in an instrument operating at 200 MHz, calculate the difference in frequency (Hz) for the two signals in the spectrum of an instrument operating at 500 MHz.

(c) By predicting the appearance of their proton NMR spectra, show how 1,3,5-trinitrobenzene can be distinguished from 1,2,4-trinitrobenzene. Sketch the low resolution NMR spectrum of each molecule.

(d) How would you distinguish between $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in a carbonyl compound? Give the differences, including effect of increasing solvent polarity. 5+5+5+5=20

13. (a) Calculate the average internal energy per molecule of oxygen gas at 300 K, using 'principle of equipartition of energy'.

(b) Deduce the reduced equation of state for the van der Waals gas. Mention its significance. 10+10=20

14. (a) Why is glycerol more viscous than water?

(b) Arrange the following molecules in order of their increasing acid strength, giving reason :

(i) H_3PO_4, H_3PO_3 and H_3PO_2

(ii) CH_3COOH and CF_3COOH

(c) Using the integrated rate law for the second-order reaction

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$$

show that the half-life period of a second-order reaction is given by

$$t_{½} = \frac{1}{k[A]_0}$$

(d) Evaluate the commutator $[\hat{x}, \hat{p}_x]$. 5+5+5+5=20

15. (a) If we mix 70·0 mL of ethanol with 30·0 mL of water at normal pressure and temperature, then the total volume will be less than 100·0 mL. Explain why.

(b) An ideal gas follows two different routes to change its state from X to Z :

Route—A

$$X(P_1, V_1, T_1) \xrightarrow{\text{I}} Z(P_2, V_2, T_1)$$

Route—B

$$X(P_1, V_1, T_1) \xrightarrow{\text{II}} Y(P_3, V_2, T_2) \xrightarrow{\text{III}} Z(P_2, V_2, T_1)$$

Process I : Isothermal reversible expansion

Process II : Adiabatic reversible expansion

Process III : Reversible heating

(i) Calculate ΔS for each process, Route—A and Route—B.

(ii) Compare ΔS values for the two different routes and comment on your answer. 5+15=20

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