# 2020

## CHEMISTRY — HONOURS

**Seventh Paper**

**(Group : A)**

**Full Marks : 75**

*Candidates are required to give their answers in their own words as far as practicable.*

Answer ***any six*** questions, taking ***one*** from each **Unit**.

*All questions carry equal marks.*

**(CHT - 33a)**

**Unit - I**

**1.** (a) Show that the distance of separation between the successive *hkl* planes in three dimensional cubic lattice is $a/(h^2 + k^2 + l^2)^{1/2}$, where $a$ is the unit distance along all three axes.

(b) Using X-rays of wavelength 179·0 pm, a metal produces a reflection at $2\theta = 47{\cdot}2^{\circ}$. If this is a first-order reflection from the [110] planes of a body-centred cubic lattice, what is the edge length of the cube?

**2.** (a) Derive Langmuir adsorption isotherm, clearly mentioning the assumptions involved.

(b) Find the c.g.s. unit of $\left(\mu^2 / k_B T\right)$, starting from the definition of $\mu$ (here $k_B$ is the Boltzmann constant).

**3.** (a) A gas ($X_2$) is adsorbed on a metal surface and then undergoes dissociation. Write down the appropriate form of the Langmuir adsorption equation.

(b) A stearic acid molecule [$C_{17}H_{35}COOH$, density = 0·85 g /cm$^3$] occupies an area of 0·205 (nm)$^2$ in a close packed surface film. Calculate the length of the molecule.

**4.** (a) What does 'peptization' refer to in the case of lyophobic colloids? Give an example.

(b) Explain the term 'Tyndall effect' using a labelled diagram. How does the wavelength of the scattered light depend on the size of the colloidal particle?

**5.** (a) Find the value of $C_{v,m}$ for a monatomic solid by using the classical equipartition theorem. Explain why the experimental value of $C_{v,m}$ for Diamond deviates largely from the classical value.

(b) The bond length of AB molecule is 150 pm and its dipole moment is 0·4 D. Calculate the percentage ionic character of the AB bond.

**Unit - II**

**6.** Show that for $n = 0$ state the average kinetic energy is equal to the average potential energy of a harmonic oscillator.

Given : $\psi_0(x) = \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\beta x^2}$

$$\int_{-\infty}^{+\infty} e^{-\beta x^2} dx = \left(\frac{\pi}{\beta}\right)^{1/2}$$

$$\int_{-\infty}^{+\infty} x^2 e^{-\beta x^2} dx = \frac{1}{2\beta}\left(\frac{\pi}{\beta}\right)^{1/2}$$

where $\beta$ is a constant.

**7.** For 1s state of the hydrogen atom $\psi_{1s} = b_0\, e^{-r/a_0}$.

(a) Find the normalization constant $b_0$.

(b) Evaluate the probability density for a 1s electron at the nucleus.

Given, $\int_0^{\infty} x^n e^{-qx} dx = \frac{n!}{q^{n+1}}, q > 0$ and $n$ is a positive integer.

**8.** (a) Explain the term 'tunneling effect' with respect to the S.H.O. (one-dimension). Use $\psi_0$ for demonstration, in graphical plots.

(b) Evaluate $\left\langle \frac{1}{r} \right\rangle$ for the 1s-orbital of H-atom and express the result in atomic units.

**(CHT - 33b)**

**Unit - I**

**9.** (a) Define the terms 'phase', 'component' and 'degrees of freedom' with a suitable example.

(b) Derive thermodynamically the 'phase rule' of Gibbs.

**10.** (a) Cyclopentane and cyclohexane form ideal mixtures of a large range of composition. Their vapour pressures in the pure state are 44·13 kPa and 20·0 kPa respectively, at 298 K. A certain mixture of both shows a total vapour pressure of 29·65 kPa and the composition of the vapour is such that $x$(cyclopentane) is 0·595. What is the composition of the original mixture?

(b) Explain why solid carbon-dioxide is called 'dry ice'.

**11.** Derive thermodynamically the relation between the elevation of boiling point of a solvent and the molal concentration of the solute in a binary mixture of the two. Mention the assumptions and approximations used. Draw the μ versus *T* plot for the solvent and solution to justify the elevation of boiling point.

**12.** (a) Derive Nernst distribution law using the concept of chemical potential.

(b) When 2g of a nonvolatile hydrocarbon containing 94.4% carbon is dissolved in 100g benzene, the vapour pressure of benzene at 293 K is lowered from 0.09954 atm to 0.09867 atm. Calculate the molecular formula of the hydrocarbon.

**13.** (a) Draw temperature-composition diagrams of phenol-water system showing the effect of addition of NaCl and indicate the number of degrees of freedom in its different regions.

(b) The vapour pressures of solid and liquid white phosphorus are given by the expressions

$$\log\left(P_s/atm\right) = -\frac{(2875\,\mathrm{K})}{T} + 5.36 \quad \text{and} \quad \log\left(P_e/atm\right) = -\frac{(2740\,\mathrm{K})}{T} + 4.95$$

**Unit - II**

**14.** (a) Obtain the barometric formula from the Boltzmann distribution mentioning the assumptions involved.

(b) What is the temperature of a two level system of energy separation equivalent to 300 $cm^{-1}$ when the population of the upper state is one-third that of the lower state?

**15.** (a) State and explain the Nernst Heat Theorem, with suitable diagrams. Mention the important conclusions regarding entropy and heat capacity changes in reactions carried out under very low temperature conditions.

(b) State Planck's formulation of the Third Law of thermodynamics. What is 'residual entropy'?

**16.** (a) Three identical but distinguishable particles are distributed among three energy levels having energies 0, ε and 2ε. Write down the different possible distributions of the particles for total energy (i) ε and (ii) 2ε. Also obtain the thermodynamic probability of each distribution and hence the change in entropy for increasing the total energy from (i) to (ii).

(b) What is the physical significance of the term 'partition function'?

**(CHT - 33c)**

**Unit - I**

**17.** (a) Describe the salient features of the Transition state theory of chemical kinetics.

(b) What will be the effect of increasing ionic strength of the medium on the value of the rate constant of the reaction $S_2O_8^{2-} + I^- \rightarrow$ products? Use a graphical plot for explanation.

**18.** (a) State the Stark-Einstein law of photochemical equivalence. Is this law violated for very high quantum yields obtained in chain reactions. Explain carefully.

(b) An aqueous solution of a dye of concentration $1{\cdot}0\times10^{-4}$(M) has 20% transmission in a cell of path length 1.0 cm at 450 nm wavelength. Calculate molar absorption coefficient ($\epsilon$). If the concentration is halved and path length doubled, calculate % transmittance.

**19.** (a) The photochemical decomposition of HI proceeds by the following mechanism :

$$HI + h\nu \longrightarrow H + I$$
$$H + HI \xrightarrow{k_2} H_2 + I$$
$$I + I \xrightarrow{k_3} I_2$$

Derive an expression for –d[HI]/dt and hence calculate the quantum yield ($\phi$).

(b) Show that the following experimental observations follow the above Kinetic features of the photochemical decomposition of gaseous HI : Absorption of $3{\cdot}07\times10^{9}$ ergs of energy, (wavelength of light is 2537 $\mathring{A}$ ) decomposes $1{\cdot}30\times10^{-3}$ moles of HI. [One Einstein = $1{\cdot}196\times10^{8}/\lambda$ ergs/mole]

**20.** (a) 'Phosphorescence' of aromatic hydrocarbons is usually observed at low temperature in a rigid matrix.— Explain.

(b) In a certain reaction A + B = 2D the forward reaction proceeds photochemically with a rate given by.

**21.** (a) 'Unimolecular reactions are not always first-order'. Justify the statement using Lindemann's mechanism.

(b) Average bond energies of C – H, C – C and C = O are 414, 347 and 732 kJ $mol^{-1}$ respectively. Predict the possible products of photodecomposition of acetone with radiation of wavelength 3000 $\mathring{A}$ .

## Unit - II

**22.** (a) The bond length of $^{12}C^{16}O$ is 112·8 pm. At what wave numbers do the first three rotational transitions appear? [Assume CO is a rigid molecule, at wt. of $^{16}O$ = 15·9994]

(b) What is the essential condition for a molecule to be Raman active?

**23.** (a) The vibrational energy levels of the fluorine molecule is given by expression for $\epsilon_v(cm^{-1})$ :

$$\epsilon_v = 215(v + 0{\cdot}5)\{1 - 0{\cdot}003(v + 0{\cdot}5)\}.$$

Find the anharmonicity constant, equilibrium oscillation frequency and zero-point energy.

(b) Of the four modes of vibration of the $CO_2$ molecules identify them as either IR active or Raman active. Use diagrams to justify your answer.

**24.** (a) How will you determine the bond length of $H_2$ molecule using rotational spectroscopy?

(b) What are meant by overtone and hot bands in vibrational spectroscopy?