RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. THIRD SEMESTER EXAMINATION, MARCH 2022
SECOND YEAR [BATCH 2020-23]
CHEMISTRY (HONOURS)
Paper : V [CC5]

Date : 02/03/2022
Time : 11 am – 1 pm
Full Marks : 50

[Attempt **one question** from **each unit**]

Unit I [16 marks]

1. a) Prove from the second law of thermodynamics two adiabats would never cross. [Hint : Consider two adiabats in a P-V space, allow them to cross at one end, now connect the other ends by an isotherm to complete the cycle. Now calculate the W, Q, ΔU for the cycle and see if this feasible] [4]

   b) If Helmholtz free energy is given by

   $$A = f(T) - RT(\bar{V} - b) - \frac{a}{\bar{V}}$$

   find out the expression for pressure. [4]

   c) Draw a series of typical T-P isoenthalps obtained in a Joule Thompson experiment for a real gas. Explain which region in the T-P space you expect the gas to cool down during the experiment. [3+3]

   d) Calculate the change of entropy when one mole of SO_2(g) at 300 K and 1.00 bar is heated to 100 K, 0.01 bar. The molar heat capacity of SO_2(g) is given as

   $$\frac{\overline{C_P}}{R} = 7.871 - \frac{1454.6K}{T} + \frac{160351K^2}{T^2}$$ [2]

2. a) A fixed amount of pure ideal gas is confined in a chamber that has two sub-units (A and B) separated by a closed, immovable wall. All outside walls are non-adiabatic, immovable and closed so that the temperature, number density of gas and total volume are constants. The pressure of the gas in the two subunits are different (P_A and P_B respectively in sub-units A and B). The separating wall is now made movable.

   (i) Show that as a consequence the wall will start moving towards B (if $P_A > P_B$).

   (ii) Purely on a thermodynamic basis can you predict how much time the process will take to reach equilibrium? [4+2]

   b) A 23600 BTU/hr air-conditioning unit has an energy efficiency rating (EER) of 7.5. The EER is defined as the number of BTU/hr extracted from the room divided by the power consumption in Watts (1 BTU=1.055kJ).

   (i) What is the actual coefficient of performance of this refrigerator ?

(ii) If the outside temperature is 305 K and the inside temperature is 295 K, what percent of the theoretical maximum value is the coefficient of performance? [3+3]

c) Consider the thermodynamic equation of state $\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$. Show that for a van-der-Waals gas $\left(\frac{\partial H}{\partial P}\right)_T = b - \frac{2a}{RT}$

[As a first approximation take the compressibility factor for a van-der-Waals gas as $\frac{PV}{RT} = 1 + \left(b - \frac{a}{RT}\right)\frac{P}{RT}$] [4]

Unit II [16 marks]

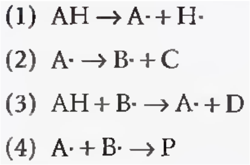
3. a) Nitrous oxide, $N_2O(g)$ decomposes into $N_2(g)$ and $O_2(g)$. If the reaction is first order, develop expression for the rate constant as a function of time and initial pressure and total pressure of the system. [2]

b) Show that the ratio $t_{1/2}/t_{3/4}$ of a nth order reaction is a function of n alone. [2]

c) Can activation energy of a reaction be negative? [1]

d) Derive rate of a unimolecular reaction from Lindeman-Hinshelwood theory. Under what conditions the reaction becomes 2nd order? [4]

e) Depict potential energy diagram of michaelis-menten mechanism of enzyme kinetics. [2]



(1) $AH \rightarrow A\cdot + H\cdot$

(2) $A\cdot \rightarrow B\cdot + C$

(3) $AH + B\cdot \rightarrow A\cdot + D$

(4) $A\cdot + B\cdot \rightarrow P$

f) Consider the following chain reaction. Use steady state approximation to deduce that decomposition of AH is first order in AH. [3]

g) Deduce expression of rate constant from collision theory based on simple hard sphere theory. [2]

4. a) Draw (ln[A] vs time) and (1/[A] vs time) graphs for a second order reaction. [A] is the concentration of reactant. [2]

b) The half life of the homogeneous gaseous reaction $SO_2Cl_2 \rightarrow SO_2 + Cl_2$, which obeys first order kinetics, is 8.0 sec. How long will it take for the concentration of SO_2Cl_2 to be reduced to 1% the initial value. [2]

c) The rate constant of decomposition of a certain substance is 1.7×10^{-2} $dm^3mol^{-1}sec^{-1}$ at 24°C and 2.01×10^{-2} $dm^3mol^{-1}sec^{-1}$ at 37°C. Evaluate activation energy and pre-exponential factor for the reaction. [2]

d) The following reaction mechanism involves an intermediate A. Deduce the rate law for the reaction. [2]

$$\begin{array}{ll} A_2 \rightleftharpoons A + A & \text{(fast)} \\ A + B \rightarrow P & \text{(slow)} \end{array}$$

e) The enzyme catalyzed conversion of a substrate at 25°C has a Michaelis menten constant of 0.035 mol dm^{-3}. The rate of the reaction is 1.15 □ 10^{-3} mol dm^{-3} sec^{-1} when the substrate concentration is 0.110 mol dm^{-3}. What is the maximum velocity of the enzymolysis. [2]

f) For a competitive adsorption reaction (A and B being two gases adsorbed on the same surface following Langmuir adsorption isotherm), find out surface coverage by A and B individually. [2]

g) Briefly state the assumptions of CTST (transition state theory). [2]

h) Draw potential energy diagram of a catalysis reaction to clearly explain vant hoff intermediate and Arrhenius intermediate. [2]

Unit III [18 marks]

5\. a) Evaluate $[x^n, p_x]$, with n being a positive number, as a function of n and x. [3]

b) Show that $(T + V)^2 = (V + T)^2$, where T and V are the one-dimensional kinetic and potential energy operators, respectively. Also establish a condition for $(T + V)^2 = T^2 + 2TV + V^2$. [3+2]

c) The quantum number, n, for the particle in a 1D box is the outcome of the boundary condition. Using the same boundary conditions, justify that n = 0 can't be the ground state for the above model system. [No need to do the detailed calculations. Start from the intermediate stage] [3]

d) A system is represented by function Ψ, with

$$\Psi = \frac{1}{\sqrt{5}}\phi_1 + \frac{2}{\sqrt{5}}\phi_2$$

where Φ_1 and Φ_2 are orthonormal. What is the expression for the weighted average of energy? What is the probability of getting the energy E_1 as the eigenvalue of Φ_1, if a single measurement is made? [3+2]

e) Estimate the minimum uncertainty in the x-component of velocity of an electron whose position is measured to an uncertainty of $1\text{x}10^{-10}$ m. [2]

6\. a) Prove that if a normalized function is expanded in terms of an orthonormal set of functions, the sum of squares of coefficients is unity. [3]

b) Eigenfunctions corresponding to different eigenvalues of a Hermitian operator are orthogonal. Justify. [3]

c) What are the different energy levels and states possible for a particle in a cubic system, with E < ($9h^2/8ml^2$)? Write the form of functions for a set of degenerate energy states with the above energy condition. [2+3]

d) Find the de Broglie wavelengths of (i) a 46 gm golf ball with a velocity of 30 m/s and (ii) electron with a velocity of 10^7 m/s. Comment on the nature of particles, by comparing. [3+1]

e) Show that the set of eigenfunctions $\Psi_n = sin\left(\frac{n\pi x}{L}\right)$ of the Schrowdinger equation are not the eigenfunctions of p_x operator but can be represented as linear combination of the eigenfunctions of the later. [3]

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