RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. THIRD SEMESTER EXAMINATION, MARCH 2021
SECOND YEAR [BATCH 2019-22]
Date : 12/03/2021 CHEMISTRY [HONOURS]
Time : 11.00 am – 1.00 pm **Paper : V [CC 5]** Full Marks : 50

Attempt one question from each unit

Unit - I

1. a) Prove from the second law of thermodynamics two adiabats would never cross. [4]

[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]

b) If Helmholtz free energy is given by

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

find out the expression for pressure. [3]

c) (i) Draw a series of typical T-P isoenthalps obtained in a Joule Thompson experiment for a real gas.

(ii) Explain which region in the T-P space you expect the gas to cool down during the experiment.

(iii) Can you conclude anything on the relative magnitudes of attractive and repulsive potentials on the two regions? [2+2+2]

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

$$\frac{\overline{Cp}}{R} = 7.871 - \frac{1454.6K}{T} + \frac{160351K^2}{T^2}$$ [3]

2. a) If $\left(\frac{\partial U}{\partial V}\right)_T = 0$ for a certain gas, prove that P is proportional to T provided the temperature and pressure coefficients of the gas are constants. [3]

b) Entropy of a mixing is given by $\Delta S = -\sum_i x_i \ln x_i$. Calculate the composition at which this entropy of mixing maximizes and also calculate that maximum entropy, for a two component mixture. [3]

c) (i) Calculate the difference of slope of μ vs T curve between the two sides (before and after) of the normal boiling point of water. [Given: the latent heat of water 40 kJ/mol and normal boiling point 100˚C]

(ii) Calculate the difference of slope of μ vs P curve between the two sides (before and after) of the normal boiling point of water. [Given: the densities of water and water vapor at 100˚C are 0.958 g cm^{-3} and 0.598×10^3 $gm.cm^{-3}$, respectively.] [2+2]

d) 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 pressures 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 'open' with respect to the gas.

(i) Show that as a consequence there will be a net spontaneous flow of gas from A to B (if $P_A > P_B$).

(ii) Under what condition equilibrium would be reached?

(iii) Purely on a thermodynamic basis can you predict how much time the process will take to reach equilibrium?

(iv) Now imagine we radioactively mark a particular molecule in the chamber A before opening up the separating wall. Does the spontaneous flow of gas from A to B necessarily mean that once equilibrium is reached the marked molecule will be found in the chamber B? [3+1+1+1]

Unit - II

3. a) What is the method of initial rate and why is it used in chemical kinetics? [2]

b) For a reversible reaction

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} P$$

k_1 is 4.0×10^{-2} s−1 and k_2 is half of k_1. Initial concentration of A is 2.0 mol dm^{-3}. At what time the concentration of P will be 1.0 mol dm^{-3}. [3]

c) What is turnover number in enzyme catalysis? How would you determine turnover number of an enzyme experimentally? [1+3]

d) Predict the effect of increase in ionic strength on the rate constant for each of the following reactions. Explain your answer. [3]

$$\text{a) } Pt(NH_3)_3Cl^+ + NO_2^- ; \quad \text{b) } PtCl_4^{2-} + OH^- ; \quad \text{c) } Pt(NH_3)_2Cl_2 + OH^- .$$

e) For a second order reaction

$$A \xrightarrow{k} P$$

Plot (i) **[A]/[A]₀** vs **t** and (ii) **[A]₀ /[A]** vs **t,** both for three different rate constants, k_1, k_2 and k_3 where $k_1>k_2>k_3$. [2]

f) For the reaction scheme A → B → C where the concentrations of any intermediates are negligible, which of the following statements hold during the reaction? (i) $[A] = -[B]$; (ii) $\Delta[A] = -\Delta[B]$; (iii) $\Delta[A] + \Delta[B] + \Delta[C] = 0$. [2]

4. a) For the rate law $r = k[A]^n$, for what values of n does the reaction go to completion in a finite time? Explain your answer. [2]

b) The rate constant of a chemical reaction increases by 2 times when the temperature changes from TK to (T+10)K, whereas that of another reaction increases 3 times for the same change of temperature. Find the ratio of their activation energy if they have comparable pre-exponential factors. [3]

c) Explain the following: The steric factor involved in collision theory may be interpreted in terms of $\Delta S^{\neq}$. [2]

d) In gas-phase kinetics, pressures instead of concentrations are sometimes used in rate laws. Suppose that for aA → products, one finds that $(-1/a)dP_A/dt = k_P P_A^{\,n}$, where k_P is a constant and P_A is the partial pressure of A. Show that $k_P = k(RT)^{1-n}$. [2]

e) The reaction in aqueous solution involves the following two elementary steps:

Step 1: $Hg_2^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Hg^{2+} + Hg$ (rapid equilibrium)

Step 2: $Hg + Tl^{3+} \ \ k2 \ \ \rightarrow \ \ Hg^{2+} + Tl^{+1}$ (slow)

Show that the reaction is of negative order with respect to Hg^{2+}. [3]

f) In a parallel reaction where a reactant A is being converted to two products B and C with rate constant k_A and k_B respectively. Plot the concentration of A, B and C with respect to time when $k_A = 3\ k_B$. [2]

g) True or False? [1× 2]

(i) In homogeneous catalysis, the catalyst does not appear in any of the steps of the mechanism.

(ii) The pre-exponential factor A has the same units for all reactions.

Unit III

5. a) Butadiene contains 4 pi electrons, each of which moves freely from one end of the molecule to the other. Treat the molecule as a 1-D box whose length is equal to the length of the carbon chain plus half the C-C bond length on either side. The average C-C bond length is 0.14 nm. Calculate the positions of maximum and minimum electron density. [4]

b) Show that $[x^n, p_x] = -\frac{h}{2\pi i} n x^{n-1}$. [3]

c) A certain system is described by the operator $A = -d^2/dx^2 + x^2$.

(i) Show that $\Psi = cxe^{\frac{-x^2}{2}}$ is an eigenfunction of A. What is the eigenvalue?

(ii) What is the expectation value of x for the state described by the function, when x varies from -∞ to + ∞? [2+2]

d) Consider a system with n independent degenerate wave-functions ψ_1, ψ_2,…., ψ_n of energy W. Show that any linear combination of the n wavefunctions is an eigenfunction of the Hamiltonian with same eigenvalue, W. [3]

e) Consider an X-ray beam, with $\lambda = 1.00$ A° and also a γ ray beam with $\lambda = 1.88\text{x}10^{-2}$ A°. If the radiation scattered from free electrons is viewed at 90° to the incident beam.

(i) What is the Compton shift in each case?

(ii) What K.E. is given to the recoiling electron in each case? [2+2]

6. a) How do you define Hermitian operator? Show that eigenfunctions corresponding to different eigenvalues of a Hermitian operator are orthogonal. [4]

b) True or false? Justify.

(i) Commutator relation between two operators confirms the simultaneous measurement of the corresponding observables.

(ii) Laplacian is a linear operator. [2+2]

c) What is a node? Find out the node/s and sketch the function ψ_n and ψ_n^2 for n = 2 for particle in 1D box. Also point out the analogy with vibration of a string. [4]

d) Show that the set of eigenfunctions $\psi_n = sin\ \frac{n\pi x}{L}$ of the Schrowdinger equation are not the eigenfunctions of p_x operator but can be represented as linear combination of the eigenfunctions of latter. [3]

e) Explain, whether the following functions are acceptable or not (with reasons):

(i) $= e^{-x}$, (ii) $\psi = tanx$. [3]

———— × ————