

B.Sc.(Honours) Examination, 2018
Semester-III (CBCS)
Chemistry (Honours)
Core Course: CC-7
(Physical Chemistry)

Time: Three Hours

Full Marks: 60

Questions are of value as indicated in the margin.

Group-A

Answer *any two* questions.

1. a) Using the relation, $Tds \geq \delta q$, prove that
i) $dS_{u,v} \geq 0$, ii) $dU_{S,V} \leq 0$, iii) $dS_{P,H} \geq 0$ and iv) $dH_{S,P} \leq 0$.
Comment on the entropy change in the surroundings and the universe for each case. 4+4
- b) Using the van der Waals equation with the thermodynamic equation of state, evaluate $\left(\frac{\partial U}{\partial V}\right)_T$ for the van der Waals gas, using this result and integrating the total differential dU for a van der Waals gas, show that if C_V is a constant, $U = U' + C_V T - \frac{na}{V}$, where U' is a constant of integration. 2.5+1.5
2. a) What are the possible observations in the Joule-Thomson (J-T) experiment? 1.5
b) Prove that at any stage of J-T experiment enthalpy is constant. Why does it happen? What is the basic difference between J-T experiment and the ordinary adiabatic process? 1.5+1+1
c) Account for the J-T effect based on the thermodynamics. 2
d) Show that for a real gas
$$\overline{C}_P \cdot \mu_{J-T} = \frac{RT^2}{P} \left(\frac{\partial z}{\partial T}\right)_P$$
where μ_{J-T} is the Joule-Thomson coefficient and $z = \frac{P\overline{V}}{RT}$ is the compressibility factor of the gas. 3
- e) From the purely mathematical properties of the exact differential $dU = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$, show that if $\left(\frac{\partial U}{\partial V}\right)_T$ is a function of only volume, then C_V is a function of only temperature. 2
3. a) Write the criteria for mixing (at constant temperature and pressure) of liquids and gases. 2
b) Find an expression for the equilibrium constant as a function of temperature for the cases:
i) ΔH_R is a constant.
ii) ΔH_R is a function of temperature. 5

P.T.O.

(2)

- c) Consider the equilibrium $2\text{NO} + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{NOCl}(\text{g})$. At 25°C for $\text{NOCl}(\text{g})$, $\Delta G_f^\circ = 66.07$ KJ/mole; for $\text{NO}(\text{g})$, $\Delta G_f^\circ = 86.57$ KJ/mole. If NO and Cl_2 mixed in the molar ratio 2:1, show that $x_{\text{NO}} = \left(\frac{2}{PK_p}\right)^{1/3}$ and $x_{\text{NOCl}} = 1 - \frac{3}{2}\left(\frac{2}{PK_p}\right)^{1/3}$ at equilibrium. 5

(Assume that $x_{\text{NOCl}} \approx 1$). (Note how each one of these quantities depends on pressure. Evaluate x_{NO} at 1 atm and at 10 atm.

Group-B

Answer *any three* questions

- Determine with citing reasons which of the following functions are acceptable wave functions:
 - $\sin x + \cos x$ (for $0 \leq x \leq \pi/2$)
 - e^{-ax} (for $x \leq 0$; a is constant). 2
 - Evaluate the commutator $[x, [x, P_x^2]]$; assume $[x, P_x] = i\hbar$. 2
 - Test whether the operator $i\frac{\partial}{\partial x}$ is hermitian or not. 3
 - Show that $e^{-\alpha x^2}$ (α is a constant) is an eigen function of the operator $\frac{1}{x} \frac{d}{dx}$ but not of $\frac{d^2}{dx^2}$.
What would be the eigen value in the former case? 3+1
 - The wave function ψ of a certain system is the linear combination $\psi = \sqrt{\frac{1}{4}}\psi_1 + \sqrt{\frac{3}{4}}\psi_2$; where ψ_1 and ψ_2 are energy eigen function with eigen values E_1 and E_2 ($E_1 \neq E_2$), respectively. What is the probability of finding that the system energy will be observed to be E_2 ? 1
- Show that if two operators have common complete set of eigen functions, then the two operators must commute. 2
 - The average momentum of the particle in 'particle in one dimensional box model' is zero – Justify it. Does this result imply that the particle is at rest? 3
 - What do you mean by degeneracy? Find the degree of degeneracy of a particle in a cubical box of length 'a' having energy $\frac{17h^2}{8ma^2}$. 3
 - Consider benzene molecule as a 4.0 \AA square box containing six electrons. Write down the expression for energy of the ground state of the system. Calculate the minimum energy required to promote an electron to the lowest unoccupied energy level. ($m_e = 9.31 \times 10^{-31} \text{ kg}$) 4

(3)

3. a) The L_S of 0.01 N KCl at 25 °C is $0.0014114 \text{ Ohm}^{-1} \text{ Cm}^{-1}$. The resistance of the solution in a given conductivity cell is found to be 85 Ohm. Calculate the cell constant. If the resistance of a 0.01(N) NaOH solution is found to be 50.63 Ohm, find out the value of equivalent conductance of 0.01(N) NaOH solution. 2+4

- b) Show that for a weak electrolyte one may write the following reaction:

$$\frac{1}{\Lambda_{\text{eq}}} = \frac{1}{\Lambda_{\text{eq}}^{\circ}} + \frac{1}{\Lambda_{\text{eq}}^{\circ 2} K_a} \cdot (\Lambda_{\text{eq}} C) \quad (\text{Symbols have usual meaning}). \quad 6$$

4. a) Write down the Debye-Hückel-Onsager (DHO) equation for a (1:1) strong electrolyte explaining the terms. Show that for cations with $t_+ > 0.5$, transport number increases with increase in concentration. 2+4

- b) Draw and explain the conductometric titration plot of oxalic acid against NaOH. Why the plot takes a different shape for H_2SO_4 ? 4+2

5. a) State the characteristic features of three model of liquid water. 3

- b) Explain why the viscosity of ethyl alcohol is greater than that of ether. 2

- c) Establish the following equation which shows the variation of viscosity of liquid with temperatures:

$$\eta = \frac{RT}{A'_{\text{vis}} V_m} \ell^{E_{\text{vis}}/RT} \quad (\text{Symbols have usual meaning}) \quad 4$$

- d) Discuss the general characteristics of liquids and compare with those of solids. 3
-