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B.Sc. Chemistry (FYUP) /Semester-IV
Paper Title: Phase Equilibria And Chemical Kinetics
Paper Code: BCH-DSC 402 TH

Time: 2 ½ hours **Maximum Marks: 60**

Abbreviations Used: CLO- Course Outcome, PLO- Program Outcome, BTL- Bloom Taxonomy Level: BT level 1-Remember; BT level 2-Understand; BT level 3-Apply; BT level 4-Analyse; BT level 5-Evaluate, BT level 6-Create.

Q. No.		BTL	CLO	PLO
SECTION A				
Very Short Type Questions (Attempt all):		**(1x15=15 marks)**		
A1	If solid ammonium chloride is allowed to dissociate in a vessel already containing some ammonia, calculate the value of F.	2	2	1-2
A2	Explain why food is cooked faster inside a pressure cooker than in an open vessel.	2	2	1-2
A3	State the phase rule.	1	2	2
A4	How are three-component systems studied with the help of the phase rule?	2	2	3
A5	Show that having more than three phases at equilibrium for a one-component system is impossible.	1	1-2	1-2
A6	State two conditions for the validity of the distribution law.	1	1	1
A7	Name the equation that relates the composition of the mixture in the liquid phase with the partial vapor pressures in the gas phase.	1	2	2
A8	What is an azeotropic mixture?	1	1	1
A9	Explain, with suitable example, zero-order reaction.	1	1-2	1-2
A10	In the decomposition of hydrogen iodide, what is the relationship between the rate of decomposition of HI and the rate of formation of H_2?	2	2-3	2-3
A11	What is the half-life period for the first-order decomposition of azomethane at 600 K if $k = 3.55 \times 10^{-4}$ sec^{-1}?	3	1-2	1-2
A12	Define parallel reactions.	1	2-3	3
A13	What do you understand by the term: 'rate determining step' of a complex reaction?	2	3	1-2
A14	Derive the mathematical expression for the rate constant of a reaction (A + B → Products) of the second order.	2	1-2	1-2
A15	Distinguish between reaction rate and rate constant of a reaction.	1	1-2	2
SECTION B				
Long Type Questions (Attempt any two out of four):		**(10x2=20 marks)**		
B1	(a) Derive the Clapeyron equation for the water ⇌ vapor equilibria. If the vapour pressures of water at 95°C and 100°C are 634 and 760 mm respectively, calculate the latent heat of vaporization per mole.	3	1-3	1-3

	(b) Prove that the expression of the phase rule remains unchanged even if one of the components is missing in some of the phases present at equilibrium.			
B2	(a) What do you understand by partially miscible liquids? Show that the formation of partially miscible liquids has sound theoretical background and can be explained qualitatively from Duhem-Margules equation. (b) Discuss the principle of fractional distillation of miscible liquid pairs and describe the use of fractionating column in this context. When two components 'A' and 'B' are mixed and the resulting solution formed is almost an ideal solution. Derive an expression for free energy change of mixing.	4-6	2-6	4-6
B3	(a) The following data was obtained on hydrolysis of methyl acetate at 25°C in 0.35N hydrochloric acid. Establish that it is a first-order reaction. t (secs) 0 4500 7140 ∞ ml alkali used 24.36 29.32 31.72 47.15 Discuss different methods employed for the determination of the order of the reaction. (b) For a certain reaction, it takes 5 minutes for the initial concentration of 0.5 mol lit^{-1} to become 0.25 mol lit^{-1} and another 5 minutes to become 0.125 mol lit^{-1}. What is the order and the rate constant of the reaction?	3-4	3-5	3-5
B4	(a) A ln k versus $1/T$ graph was plotted to calculate the activation energy of a reaction using the Arrhenius equation for the effect of temperature on reaction rate. The slope of the straight line was found to be -2.55×10^4. Calculate the activation energy of the reaction. (b) The rate of a particular reaction becomes three times when the temperature is increased from 298 K to 308 K. Calculate the energy of activation for the reaction.	4-5	3-6	3-6
	SECTION C			
Short Type Questions (Attempt all Questions):		**(5x5=25 marks)**		
C1	(a) Describe phenol-water system with respect to critical solution temperature. **OR** (b) Determine the number of components, number of phases and degrees of freedom for the following systems: (i) $H_2O(s) \rightleftharpoons H_2O(l) \rightleftharpoons H_2O(g)$ (ii) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$	3-4	4-5	4-5
C2	(a) Describe KI-H_2O system on the basis of phase rule. **OR**	2-3	2-4	3-4

	(b) Discuss the main features of the phase diagram of the water system, explaining especially why the slope of the solid-liquid line is negative for water.			
C3	(a) Apply Distribution law to the case when the solute forms a dimer in one of the solvents. **OR** (b) An organic acid was dissolved in two immiscible solvents (A) and (B). At equilibrium, the concentration of the acid in (A) and (B) was found to be 0.40 and 0.64 mole/liter respectively. Calculate the distribution coefficient of the organic acid, if it forms dimers in the solvent (B).	4-6	4	4-5
C4	(a) Hydrolysis of ethyl acetate by NaOH using equal concentration of the reactants, was studied by titrating 25ml of the reaction mixture at different time intervals against standard acid. From the data given below, establish that this is a second-order reaction. *t* (mins) 0 5 15 25 ml acid used 16.00 10.24 6.13 4.32 **OR** (b) The second-order rate constants of a reaction are given below at two temperatures: T (K) 298 308 10^5 x k ($M^{-1}s^{-1}$) 8.8 28 Calculate the activation energy of the reaction.	3-4	2-3	3-5
C5	(a) The relaxation methods are suitable for measuring the rates of fast reactions. The experimental techniques (such as titrimetry) are not useful for this purpose. Explain the reason. **OR** (b) The rate constants for the decomposition of SO_2Cl_2 are 1.01 x 10^{-6} s^{-1} at 552 K and 3.85 x 10^{-5} s^{-1} at 600 K. Calculate the activation energy and the frequency factor for the reaction, assuming them to be independent of temperature.	5-6	3-6	4-6