



‘সমানো মন্ত্র: সমিতি: সমানী’

UNIVERSITY OF NORTH BENGAL

B.Sc. Honours 3rd Semester Examination, 2022

CC7-CHEMISTRY

PHYSICAL CHEMISTRY-III

Time Allotted: 2 Hours

Full Marks: 40

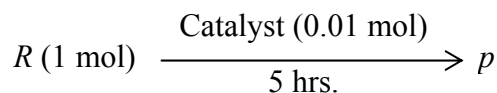
The figures in the margin indicate full marks.

All symbols are of usual significance.

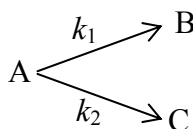
1. Answer any **five** questions from the following: 1×5 = 5
 - (a) What do you mean by order of a reaction?
 - (b) Reactions of order greater than two are rare – Explain.
 - (c) What is dry ice?
 - (d) Write down the thermodynamic criteria for an ideal solution.
 - (e) Zero order reaction will be completed within the finite time. — Justify.
 - (f) What do you mean by turn-over frequency?
 - (g) Why transition state theory is better than Collision theory of a reaction?
 - (h) Ethyl alcohol cannot be purified beyond 96% by weight from its aqueous solution – Explain.

2. Answer any **three** questions from the following: 5×3 = 15
 - (a) (i) Derive the Duhem-Margule’s equation for a binary solution of *A* and *B*. Hence show that if *A* shows positive deviation from ideality then *B* will also show positive deviation from ideality. 3
 - (ii) For a given reaction rate is independent of concentration; will it go to completion? 2
 - (b) (i) Draw the labelled phase diagram of carbon-dioxide system and explain the important points, lines and areas. 3
 - (ii) Explain why the slope of fusion curve is positive in case of CO₂ but negative in case of H₂O. 2
 - (c) (i) Four phases of sulphur cannot exist simultaneously at equilibrium. – Justify. 2
 - (ii) The rate of reaction becomes doubled on raising the temperature from 25°C to 35°C. Calculate the activation energy. 3
 - (d) (i) Discuss the “differential method” for determination of order of a reaction. 3
 - (ii) For inhibition reaction $n_i > n_c$ where as for autocatalytic reaction $n_c > n_i$ – Explain. 2
 - (e) (i) Discuss the transition state theory of reaction rate. 3
 - (ii) Distinguish between adsorption and absorption. 2

3. Answer any **two** questions from the following: 10×2 = 20
- (a) (i) Derive using classical thermodynamics, the expression for the rate constant in terms of activated complex in a bimolecular gas phase reaction. 3
- (ii) The plot of $[R]^{-1}$ vs. time is a straight line with positive intercept for an elementary reaction $R \rightarrow \text{Product}$. What will be the order of the reaction? 2
- (iii) Calculate turnover frequency (TOF) when the yield of the product is 80% for the following catalytic reaction 2



- (iv) Consider a parallel reaction 3

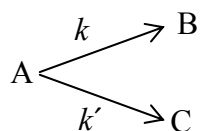


Show that activation energy (E_a)

$$E_a = \frac{k_1 E_1 + k_2 E_2}{k_1 + k_2}, \text{ where } E_1 \text{ and } E_2 \text{ are the activation energies for paths}$$

with rate constants k_1 and k_2 respectively.

- (b) (i) Derive Nernst distribution law from thermodynamic consideration. Write down the limitations of this distribution law. 3+2
- (ii) Find out the number of degrees of freedom in the following system: 3
- (A) $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{Na}_2\text{SO}_4(\text{s}) + 10\text{H}_2\text{O}(\text{g})$
- (B) $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
- (iii) Distinguish between eutectic and peritectic points. 2
- (c) (i) What is Michaelis-Menten's constant? Write down its S.I unit. 2
- (ii) Photochemical reaction between H_2 and Cl_2 to produce HCl is a zero order reaction. Why? 2
- (iii) Define phase rule. Find out the number of components in PCl_5 decomposition. 2+1
- (iv) For a parallel reaction k_1 and k' equal to $3.42 \times 10^{-2} \text{ min}^{-1}$ and $1.14 \times 10^{-2} \text{ min}^{-1}$ respectively. Find out the % of 'A' converted into B and C after 20 min 3



- (d) (i) Surfaces of the catalysts in heterogeneous catalysis are crucial. — Explain. 2
- (ii) What are the basic differences between physical and chemical adsorptions? 3
- (iii) Write down the postulates of Lindemann's Time-Lag theory. 3
- (iv) A eutectic has a definite composition and a sharp melting points yet it is not a compound. — Explain. 2

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