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## DEPARTMENT OF SCIENCES, I SEMESTER M.Sc., (Chemistry) END SEMESTER EXAMINATIONS, (Makeup) March 2022

Physical Chemistry-I [CHM 5103] (CBCS Scheme)

Time: 2 Hours

Date: 16 March 2022

MAX. MARKS: 40

Note: (i) Answer any four full questions.

- (ii) Draw diagrams, and write equations wherever necessary
- 1 A Explain the following with appropriate reasoning
  - (a) During thermal oxidation of hydrogen, first two explosion limits are isothermal limits whereas third limit is thermal explosion limit
  - (b) Arrhenius equation is useful tool to evaluate energy of activation of a chemical reaction.
  - (c) Order and molecularity of reaction need not be same
- Temperature of the reaction was increased from  $T_1$  to  $T_2$ . If the product of  $T_1$  and  $T_2$  is equal to  $\frac{Ea}{0.0693R}$  and the difference  $(T_2 T_1)$  is 10, what is the value of ratio of rate constants?
- 1 C Explain the assumption of CTST. Based on CTST, derive an equation to relate rate constant and thermodynamic parameters of a gas phase reaction [3+2+5]
- 2 A Explain the following with appropriate reasoning
  - (a) In gas phase reaction, not all collisions lead to the formation of products
  - (b) In solution phase reaction, variation of rate constant with ionic strength helps to understand the mechanism of reaction
  - (c) Activated complex and energized molecules are not same
- **2 B** Write assumptions of B.E.T adsorption isotherm and write mathematical form of it. Explain how it is useful in explaining Type II to Type V adsorption isotherms.
- 2 C Explain characteristic features of enzyme catalysis. Derive Michaelis-Menten equation, and explain the determination of Km by graphical methods [3+2+5]
- **3 A** Deduce any two Maxwell's relations.
- Calculate the thickness of ionic atmosphere for 0.01 M 1:2 electrolytes in water at 298 K (Dielectric constant = 78.54)

**3 C** Write an explanatory note on the following

4 C

- (i) Influence of pH on reaction rate of acid base catalysis. (Draw suitable graph)
- (ii) Mechanism of uni-molecular and bi molecular surface reactions.

[3+2+5]

- **4 A** (i) The latent heat of vaporization of benzene at its boiling point (80 °C) is 743 cal mol<sup>-1</sup>. What is the vapour pressure of benzene at 27 °C?
  - (ii) Calculate the standard free energy of formation of NH $_3$  (g) , NO(g) and H $_2$ O(l) are  $-16.8,\,86.7$  and -237.2kJmol $^{-1}$  respectively
- **4 B** Justify: a) Fugacity of a gas can both be less or more than the pressure. b) Eutectic is a mixture and not a compound.
  - Mention any two merits and limitations of phase rule. Explain in detail the phase diagram of Na<sub>2</sub>SO<sub>4</sub> NaCl H<sub>2</sub>O [3+ 2+5]
- **5 A** Deduce Gibbs Duhem equation. Give its significance.
- 5 B (i) Calculate the mean ionic activity coefficient of K<sub>2</sub>SO<sub>4</sub> at a molality of 0.001 in aqueous solution at 25 °C
  - (ii) Justify: Work is not a state function while entropy change is a state function.
- **5** C Discuss the structure of electrified interfaces with reference to the Stern model.

[3+2+5]

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