MANIPAL
ACADEMY of HIGHER EDUCATION
(Deemed to be University under Section 3 of the UGC Act, 1956)

DEPARTMENT OF SCIENCES
I SEMESTER M.Sc (CHEMISTRY)
END SEMESTER EXAMINATIONS, Feb 2021

Physical Chemistry-I [CHM 5153]
(Choice-Based Credit System, 2020)

Time: 3 Hours | Date: 12 Feb 2021 | MAX. MARKS: 50

- **Answer all questions. Show all the calculation steps wherever necessary.**
- **Draw a neat-labelled diagram and write equations wherever necessary.**

1 A **(i)** Explain the following with appropriate reasoning
(a) Collision theory is applicable only to simple gaseous reactions
(b) Thermal decomposition of acetaldehyde will not give the same product always
(c) For reactions in solutions, charges possessed by reactants affects the reaction rate considerably

(ii) A' follows parallel path 1st order reactions giving B and C. If initial concentration of A is 1M, determine the concentration of C after 10 hours of reactions. Given $e^{0.9} = 2.46$ and $(k_1 + k_2) = 25 \times 10^{-6}$ sec^{-1}; and $k_2 = 5 \times 10^{-5}$ sec^{-1}.

B. With relevant explanations and with suitable graphical representation, derive an expression for Lindemann-Christiansen hypothesis for elementary gas phase reaction. What are the limitations of this hypothesis? **[5+ 5]**

2 A **(i)** Explain the following with appropriate reasoning
(a) Nitrogen is preferred gas for adsorption, while determining the surface area of catalyst by B.E.T method
(b) Rate of enzyme catalysis will not uniformly vary with temperature
(c) Acid base catalysis is highly dependent on pH of the solution.

(ii) Calculate Arrhenius constant, if the rate constant of reaction is 1.5×10^7 s^{-1} at 50 °C and 4.5×10^7 s^{-1} at 100 °C. [R= 8.314 J K^{-1} mol^{-1}]

B. With reference to homogeneous catalysis, distinguish between specific and general acid catalysis. Derive an expression for rate of specific acid catalysis **[5+ 5]**

3 A. Write an explanatory note on the following
(i) Isothermal explosions during gas phase combustion of oxygen
(ii) Influence of dielectric constant on reactions in solutions

B. (i) Derive Gibb's-Helmholtz equation and write the applications of it.
(ii) Calculate the ionic strength of the following mixture having:60 mL of 0.1 M KCl, 20 mL of 0.2 M K_2SO_4 and 20 mL of H_2O

[5+5]

4 A.(i) Explain the determination of interfacial tension of mercury as a function of potential across the interface.

(ii)What is an electrocapillary curve? Give a schematic diagram of it.

(iii) Discuss the structure of electrified interfaces with reference to Helmholtz-Perin model.

B. (i) (a) Calculate the activity coefficients of K^+ and SO_4^{2-} ions in 1.0×10^{-3} M solution of K_2SO_4, (b) using the above data calculate the mean ionic activity coefficients.

(ii) Explain asymmetric effect and electrophoretic effect found in strong electrolytes

[5+5]

5 A. (i) Derive Clausius-Clapeyron equation. What are its applications?

(ii) Discuss the features of phase diagram of three components system one salt forms hydrate in two salts and water.

B. (i) State third law of thermodynamics. Derive the steps involved in the calculation of absolute entropies.

(ii) Calculate entropy change accompanying change of state of one mole of sulphur from rhombic to monoclinic state. Heat of transition of the process carried out reversibly is 322.17 joules per mole at the transition temperature 95.6 °C.

[5+5]

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