LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – **CHEMISTRY**

THIRD SEMESTER – **APRIL 2022**

PCH 3502 – THERMODYNAMICS AND CHEMICAL KINETICS

Date: 15-06-2022 Dept. No. Max. : 100 Marks

Time: 09:00 AM - 12:00 NOON

Part-A

Answer ALL Questions. **(10 × 2= 20)**

1. Define activity and activity coefficient.
2. Calculate the ionic strength of 0.05m K_2SO_4.
3. What is Peltier effect? Mention its importance.
4. Define the term flux. Mention the cause for the flux.
5. Calculate the electronic partition function for an atom at its ground electronic state $^2P_{3/2}$.
6. Define impact parameter. Mention its significance.
7. The experimentally determined energy of activation for the decomposition of a diatomic molecule is 220.0 kJ mol^{-1}. Calculate the energy of activation at 400ºC according to collision theory.
8. For the reaction between unlike charges in aqueous solution, the pre-exponential factor is found to be high. Justify.
9. Sketch the block diagram of flash photolysis for studying the kinetics of fast reactions.
10. Mention the factors that affect the first explosion limit of branched chain reactions.

Part-B

Answer any EIGHT Questions. **(8 × 5= 40)**

11 What is Ellingham's plot? How does it prove that carbon is a good reducing agent for the oxides of several metals?

12. Draw and explain the phase diagram of a ternary system consisting of two solids and water with the formation of a double salt.
13. What is a coupled phenomenon? Discuss the entropy production in a coupled phenomenon.
14. Calculate the relative Boltzmann population of two vibrational energy levels that are separated by 2000 cm^{-1} at 27°C.
15. Derive an expression for the translational entropy of a monoatomic gas.
16. Describe the application of Bose-Einstein statistics to the theory of paramagnetism.
17. Calculate the rate constant for the decomposition of hydrogen iodide at 700 K, using collision theory formula. (Given: Ea =198.4 kJ mol^{-1} and Collision diameter of HI = 3.5 A^0).
18. Explain the equilibrium and steady state approach for the study of homogeneous catalytic reactions with the help of potential energy diagram.
19. Illustrate with an example, any one mechanism of bimolecular surface reactions.
20. Discuss the different types of reversible inhibition reaction mechanisms.
21. Describe any one flow technique for the study of kinetics of fast reactions.
22. Obtain the expressions for the concentrations of A, B and C at time't' for the simplest consecutive reaction, A → B→ C.

Part-C

Answer any FOUR Questions. **(4 × 10 = 40)**

23a. Derive Gibbs-Duhem equation and mention its significance.

b. Calculate the reduction in the chemical potential of toluene at 25°C when a solute is added at a mole fraction of 0.25. (6+4)

24. What is Onsager reciprocal relation? How is it verified by the principle of microscopic reversibility?

25a. Obtain an expression to show the relation between partition function and equilibrium constant.

b. The translational heat capacity at constant volume is 12.47 $JK^{-1}mol^{-1}$. Calculate its translational energy at 500 K.

(6+4)

26a. Explain the primary salt effect on the kinetics of ionic reactions.

b. Calculate the change in enthalpy, entropy and free energy of activation for the bimolecular reaction, $2NO_{2(g)} \rightarrow 3NO_{(g)} + O_{2(g)}$ at 500 K. (Given: Arrhenius parameter, $A = 2 \times 10^9\ s^{-1}$ and $E_a = 110\ kJ\ mol^{-1}$)

(5+5)

27a. Discuss the effect of substrate concentration on the rate of enzymatic reaction. How can it be verified?

b. The presence of 1.0 mM L^{-1} of a competitive inhibitor decreases the initial rate of a reaction catalyzed by a factor of 2.5. Calculate the degree of inhibition if the initial rate is $2.04 \times 10^{-4}\ M\ s^{-1}$.

(7+3)

28a. Prove that the thermal decomposition of acetaldehyde follows fractional order kinetics.

b. Explain the kinetics of hydrogen-bromine thermal chain reaction. (4+6)

@@@@@@@