LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

THIRD SEMESTER – **NOVEMBER 2019**

18PCH3MC02 – THERMODYNAMICS AND CHEMICAL KINETICS

Date: 31-10-2019 Dept. No. Max. : 100 Marks

Time: 09:00-12:00

Part-A

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

1. Define fugacity. The fugacity of helium gas is always more than its pressure-Justify.
2. Draw the phase diagram for the formation of three pairs of partially miscible liquids.
3. Write the phenomenological equations for thermo mechanical effect.
4. Calculate the electronic partition function of the first excited fluorine atom ($^2P_{1/2}$) that lies at 0.05 eV above the ground state ($^2P_{3/2}$) at 1000 K.
5. What are Bosons? Give an example.
6. Find the number of vibrational degrees of freedom for the non-linear activated complex formed in the reaction, A + B → P. (Given: A and B have 4 and 6 atoms respectively)
7. For the reaction between unlike charges in aqueous solution, the pre-exponential factor is found to be high-Justify.
8. Define impact parameter. Mention its significance.
9. The conversion of cis-butene to trans-butene is first order in both directions. At 25^0C, the equilibrium constant is 0.406 and forward rate constant is $4.21 \times 10^{-4}\ s^{-1}$. Find the rate constant of the reverse reaction.
10. Distinguish between stationary and non-stationary chain reactions.

Part-B

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

11 Derive Gibbs-Duhem equation. Mention its physical significance.

12. How will you determine the activity of HCl using E.M.F method?
13. Write the phenomenological equations for electro kinetic effects and deduce their cross coefficients.
14. Explain: (i) Force and flux (ii) Prigogine's principle of minimum entropy production.
15. Maximizing the thermodynamic probability of a macrostate and invoking Lagrange's undetermined multipliers, derive the expressions for Fermi-Dirac statistics.
16. Obtain the expression of rotational partition function (q_{rot}). Calculate the q_{rot} for H_2 gas whose characteristic rotational temperature is found to be 87.49 K. (3+2)

17. Cyclohexane undergoes interconvertion between chair and boat structure. The activation parameters for the reaction are $\Delta^{\#}H^{o}$ = 31.38 kJ mol^{-1} and $\Delta^{\#}S^{o}$ = 16.74 J K^{-1} mol^{-1}at 400 K. Calculate the activation energy and Arrhenius pre-exponential factor for the interconversion.
18. Explain the primary salt effect on the kinetics of ionic reactions.
19. Explain any one mechanism of bimolecular surface reactions with an example.
20. Discuss the kinetics of polymerization reaction that follows molecular mechanism with a suitable example.
21. Describe any one flow technique for the study of kinetics of fast reactions.
22. Explain the kinetics of hydrogen-chlorine photochemical chain reaction.

Part-C

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

23a. Sketch the phase diagram and arrive at the degrees of freedom for all the regions of a ternary system leading to the formation of double salts.

b. Obtain an expression for the variation of chemical potential with respect to temperature and pressure. (6+4)

24. State and explain Onsager's reciprocal relationships and validate and verify the Onsager's equations for simple chemical reactions.

25a. Discuss the salient features of Einstein theory of the heat capacity of monoatomic crystals.

b. Obtain the following equation:

$(i)\ S = nR\left[\ln\frac{q}{N} + T\left(\frac{\partial lnq}{\partial N}\right)_N + 1\right]$ $(ii)\ q_{tr} = \left(\frac{2\pi mKT}{h^2}\right)^{\frac{3}{2}} \times V$ (5+5)

26a. Discuss the kinetics of a combination reaction following energy transfer mechanism.

b. Describe the equilibrium and steady state approach for the study of homogeneous catalytic reactions with the help of a potential energy diagram. (6+4)

27a. Derive Michaelis-Menten equation. Explain its verification.

b. The activation energy according to collision theory for the decomposition of HI at 450^{o} C is 181.2 kJ mol^{-1}. Evaluate the expected experimental energy of activation. (7+3)

28a. Derive the expressions to determine the concentrations of reactant and products at time,'t' for a first order parallel reaction.

b. Prove that the thermal decomposition of acetaldehyde follows fractional order kinetics. (6+4)

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