LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

THIRD SEMESTER – **NOVEMBER 2019**

CH 3814 – THERMODYNAMICS & CHEM. KINETICS

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

Time: 09:00-12:00

Part-A

Answer ALL questions **(10 x 2 = 20)**

1. Define Fugacity and mention its unit.
2. Calculate the ionic strength of 0.01M KCl.
3. What are coupled and non-coupled reactions?
4. Calculate translational partition function (q_{tr}) for hydrogen molecule in a box of volume 3 dm^3 at 300 K.
5. Obtain the expression for relationship between internal energy and partition function.
6. Differentiate time and true order of a reaction.
7. Mention the factors that determine the effectiveness of collisions.
8. Compare competitive and non-competitive enzyme inhibitions.
9. State the principle of relaxation techniques for studying the kinetics of fast reactions.
10. What are stationary and non-stationary chain reactions?

Part-B

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

11. Sketch the phase diagram and arrive at the degrees of freedom for all the regions of a ternary system leading to the hydrate formation.
12. Discuss the two methods of determining the activity and activity coefficient of non-electrolytes.
13. Write the phenomenological equations for electrokinetic phenomenon and deduce their corresponding cross-coefficients.
14. Show that the rate of entropy production in chemical reactions $\frac{d_i S}{dt} = \frac{A}{T}\left(\frac{d\epsilon}{dt}\right) > 0.$
15. Write the expression for rotational partition function. Calculate the molecular rotational partition function (q_{rot}) of N_2 gas at 300 K whose moment of inertia (I) = 13.9 $x10^{-47}$ Kg m^2.
16. Discuss the salient features of Debye theory of heat capacity of monoatomic crystals.
17. Calculate the number of collisions per second occurring between equvimolar mixture of H_2 and I_2 molecules in one cm^3 at a pressure of 101.3 kPa and a temperature of 700 K. (Given: d_{H2} = 2.2Å and d_{I2} = 4.6Å)

18. Derive the general equation for the rate of unimolecular gas reactions using steady state hypothesis proposed by Hinshelwood.

19. Describe any one mechanism of bimolecular surface reactions with an example.

20. Explain the primary salt effect on the kinetics of ionic reactions.

21. Distinguish between Arrhenius and van't Hoff intermediates in homogeneous catalytic reactions.

22. Explain the kinetics of thermal H_2 -Br_2 reaction.

Part-C

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

23a. Obtain an expression for the variation of chemical potential with respect to temperature.

b. Explain the relative ease of reducing a given metallic oxide to metal using Ellingham's diagram. (3+7)

24a. State and explain phenomenological laws leading to the Onsager's reciprocal relations.

b. State Peltier effect and deduce their cross coefficients. (6+4)

25a. What are fermions? Obtain the most probable distribution of distinguishable particles using Fermi-Dirac statistics.

b. Derive Sackur-Tetrode equation. (5+5)

26a. Derive Eyring equation which relates the thermodynamic parameters with the rate constant of a reaction.

b. Explain the double sphere model for the influence of dielectric constant on the rate of an ion-ion reaction in solution. (5+5)

27a. Derive Michaelis-Menten equation for single substrate enzymatic reaction and explain its verification.

b. Calculate the activation energy of a reaction whose rate constant increases twice by a rise of 15^0C from a temperature of 27^0C. (8+2)

28 a. Derive the expressions for the concentrations of A, B and C at time 't' for the simplest consecutive reaction, $A \rightarrow B \rightarrow C$

b. Explain flash photolysis technique for the study of kinetics of fast reactions. (5+5)

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