LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

THIRD SEMESTER – NOVEMBER 2016

CH 3814 - THERMODYNAMICS & CHEM. KINETICS

Date: 03-11-2016 Dept. No. Max. : 100 Marks

Time: 09:00-12:00

Part-A

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

1. What is Ellingham plot?
2. What is an isothermal saturation curve?
3. State Prigogine's principle of minimum entropy production.
4. Calculate the number of ways of distributing four molecules in four energy levels so that there are two molecules in the level E_0, 1 molecule in E_1, 1 molecule in E_2 and zero in level E_3.
5. Calculate the vibrational partition function of molecular hydrogen at 300 K, assuming it to be a harmonic oscillator. Given that $\omega = 4405\ cm^{-1}$.
6. What are contour diagrams?
7. At 300 K, the rate constants in $dm^3\ mol^{-1}s^{-1}$ for the alkaline hydrolysis of m-chloroethyl benzoate and p-methoxyethylbenzoate are 0.454 and 0.0114, respectively. Calculate the reaction constant. (Given: σ for m-Cl and p-OMe are +0.37 and -0.27, respectively.)
8. Compare the pre-exponential factors obtained for the reactions between molecules (A_m) and atoms (A_a).
9. 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 2.04×10^{-4} M s^{-1}.
10. Distinguish between stationary and non-stationary chain reactions.

Part-B

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

11. Discuss any two methods of determination of partial molar properties.
12. At 500º C, the EMF of the cell Ag(s) | AgBr(N_1) in fused LiBr | Br_2(g), is 0.7865 V when the electrolyte is pure AgBr; the E.M.F is 0.8085 V, when the mole fraction (N_1) is 0.5937. Calculate the activity coefficient in the latter case, the standard state being taken as pure liquid AgBr.
13. Explain: (a) Mechanocaloric effect (b) Relation between irreversible thermodynamics and biological systems.
14. Calculate the entropy change of one mole of helium when it is heated from 300 K to 600 K at constant pressure.
15. Obtain the relation between internal energy and partition function.
16. Calculate the translational partition function of a molecule of oxygen gas at 1 atm and 298 K moving in a vessel of volume 24.4 dm^3.
17. Derive Eyring equation relating thermodynamic parameters of a reaction.

18. Explain Langmuir-Hinshelwood mechanism for bimolecular surface reactions with an example.
19. Discuss any one flow technique to study the kinetics of fast reactions.
20. Explain the kinetics of reaction between hydrogen and bromine.
21. Describe the effect of substrate concentration on the kinetics of enzyme catalysis.
22. Consider the following reaction, $NH_4^+{}_{(aq)} + NO_2^-{}_{(aq)} \rightarrow N_{2(g)} + H_2O_{(l)}$, at 25°C. Determine the rate law and rate constant for the reaction using the following data.

$[NH_4^+]$, mol/L	$[NO_2^-]$, mol/L	Rate, mol/L/s
0.24	0.10	7.2×10^{-6}
0.12	0.10	3.6×10^{-6}
0.12	0.15	5.4×10^{-6}

Part-C

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

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

b. 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 salt formation.

24a. Explain Onsager theory in the light of phenomenological reciprocal relationship.

b. Write a note on thermoelectricity.

25a. Derive Bose – Einstein distribution law using its assumptions.

b. The first excited state of chlorine atom $^2P_{1/2}$ lies at 0.11 eV above the ground state $^2P_{3/2}$. Calculate the electronic partition function of chlorine at 500 °C.

26a. Derive an expression for the concentrations of A and B at time t for an opposing reaction, both forward and backward reactions following first order reaction kinetics.

b. State the principle of relaxation technique. **(8+2)**

27a. Discuss the kinetics of a combination reaction following energy transfer mechanism.

b. The molecular radius of nitrogen and oxygen are 1.58×10^{-8} cm and 1.46×10^{-8} cm respectively. When 2.45×10^{19} molecules of each are mixed in the reaction vessel at 27ºC, calculate the number collisions per second between nitrogen and oxygen molecules in one cm^3 (Given: molecular masses of N_2 and O_2 are 28 and 32 g mol^{-1} respectively). **(6+4)**

28 a. Explain the effect of added salt on the rates of ionic reactions.

b. The rate of a reaction catalyzed by carbonic anhydrase is 1.05×10^{-5} mol dm^{-3} s^{-1} when the substrate concentration is 2.0×10^{-3} mol dm^{-3}. Calculate Michaelis constant if the limiting rate of the reaction is 7.93×10^{-5} mol $dm^{-3}s^{-1}$. **(7+3)**

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