LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – CHEMISTRY

THIRD SEMESTER – APRIL 2017

CH 3814- THERMODYNAMICS & CHEM. KINETICS

Date: 24-04-2017   Dept. No.   Max. : 100 Marks
Time: 09:00-12:00

Part-A

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

1. How does fugacity vary with pressure?
2. Mention the significance of reduced phase rule for three component systems.
3. Write the phenomenological equation for streaming potential.
4. Define De Donder's affinity of chemical reactions.
5. Calculate the rotational partition function for CO gas at 27° C, if the moment of inertia is 14.5×10^{47} kg m^2.
6. Define true order of a reaction.
7. The slope and y-intercept of LineWeaver –Burk plot for an enzymatic reaction are 94.88 min and 8.0 $\times 10^4$ mol^{-1} dm^3 min respectively. Calculate Michaelis constant.
8. What is volume of activation? Mention its significance.
9. Draw the potential energy diagram for Arrhenius intermediate formed in homogeneous catalytic reaction.
10. Write the Rice-Herzfeld mechanism for thermal decomposition of acetaldehyde.

Part-B

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

11. How will you explain the reduction of metal oxides using Ellingham diagram?
12. Explain entropy production in chemical reactions.
13. Benzene and Toluene form two ideal solutions. In one of the solutions, the mole fraction of benzene is 0.6 and in the other solution, it is 0.4 at 298 K and 1 atm. Calculate the difference in chemical potential of benzene between these solutions.
14. Calculate the total standard entropy of nitrogen gas at 25° C. Given that: vibrational frequency = 2360 cm^{-1}; Moment of inertia = 13.9×10^{-40} g cm^2.
15. Derive Maxwell-Boltzmann distribution law using its assumptions.
16. Calculate the translational partition function for argon atom in a cubical box of side 1 cm^3 at 25 ° C.

17. Show that the energy of activation calculated by collision theory is less than that calculated by Arrhenius equation.

18. Explain any one mechanism of bimolecular surface reactions with an example.

19. Discuss the effect of pressure on reaction rate of branched chain reactions.

20a. Predict the influence of ionic strength of the medium for the following reaction,

$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$

  b. The rate constant for the above reaction is 1.6×10^{-5} mol^{-1}dm^{3}s^{-1}. Calculate the rate constant of the same reaction in the presence of 10^{-2} mol dm^{-3} of KCl.

21. Derive Michaelis – Menten equation.

22. Explain T-jump method to study the kinetics of fast reactions.

Part-C

Answer any FOUR questions. $(4 \times 10 = 40)$

23a. How are the activity and activity coefficient determined by the vapour pressure and Randall-White method?   (8)

  b. Calculate the ionic strength of 0.25m CaSO$_4$ solution.   (2)

24a. Explain Seebeck and Peltier effects.

  b. Prove that $L_{ik} = L_{ki}$ using reciprocal relationship.

25a. Derive the Einstein equation for specific heat capacity of solids.

  b. The rotational constant of gaseous HCl determined from microwave is 10.59 cm^{-1}. Calculate the rotational partition function of HCl at 100 K.

26a. Derive the expressions for the concentrations of A, B and C at time 't' for the simplest consecutive reaction, $A \rightarrow B \rightarrow C$.   (6)

  b. Discuss the kinetics of first order parallel reaction.   (4)

27a. Discuss the role of potential energy surfaces in reaction kinetics with relevant diagrams.

  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 activation energy, $E_a = 110$ kJ mol^{-1})   (5+5)

28a. Explain the influence of dielectric constant on the rate of reactions in solution.   (7)

  b. Differentiate competitive and non-competitive enzyme inhibition reactions.   (3)

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