14 (CHM-2) 203

2018

CHEMISTRY

Paper : CH-203

(Physical Chemistry 2)

Full Marks : 80

Time : Three hours

The figures in the margin indicate full marks for the questions.

1. Why is the situation at equilibrium $-\frac{d[A]_{eq}}{dt} = 0$, not a steady state ? 1

2. The following is a highly simplified mechanism for the decomposition of C_3H_8:

$$C_3H_8 \xrightarrow{k_1} CH_3 + C_2H_5$$

$$CH_3 + C_3H_8 \xrightarrow{k_2} CH_4 + C_3H_7$$

$$C_3H_7 \xrightarrow{k_3} C_2H_4 + CH_3$$

$$CH_3 + CH_3 \xrightarrow{k_4} C_2H_6$$

Pick out the intermediates and formulate SSA. Deduce the overall rate of reaction in terms of rate of production of CH_4 (using the conc. of intermediates). 3

3. *(a)* What are the features of oscillating reactions? Derive the Lineweaver-Burk equation for enzyme catalysed reaction. 1+4

Or

(b) Discuss the reaction kinetics of alkane pyrolysis on the basis of free radical mechanism considering decomposition of ethane and hence find the chain length (γ). 5

(c) Discuss the chain branching explosion with the help of reaction between H_2 and O_2.

A certain first order reaction has an activation energy of $8{\cdot}0 \times 10^4\ J\ mol^{-1}$ and a pre-exponential factor of $3 \times 10^{12}\ s^{-1}$. What temperature is necessary for the reaction to have a half life of 1·0 hour? 3+2

4. *(a)* How ACT is different from SCT? Calculate the effect on the rate constant if the temperature is increased by a factor of two by keeping $r_A + r_B$, μ and E_a constant. Given, initial temperature as $300K$ and E_a as $25\ kJ\,mol^{-1}$. 2+3

(b) Derive the relationship between the pre-exponential factor and steric factor by employing modified simple collision theory. 4

Or

(c) Derive the form of overall rate constant for the bimolecular reaction

$$A + B \longrightarrow \text{Product}$$

by taking into account the ACT. 4

(d) What is a diffusion controlled reaction? Derive the basic equation for full microscopic diffusion control. 1+3

(e) Calculate the ionic strength and the mean activity coefficient of 1×10^{-3} *mol* kg^{-1} $CaCl_2$ (aq) at 25°C. 2

5. What is a fast reaction? Discuss the principle of stopped flow technique. 1+2

6. (a) Derive the expression for relaxation time for the following reaction using relaxation method :

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Z$$ 5

Or

(b) What are the difficulties of Lindemann theory? How does Hinshelwood overcome those difficulties? 2+3

(c) How RRK treatment is different from the Hinshelwood treatment of unimolecular reaction? Why Marcus' extension of the RRK treatment is successful to describe the rate of unimolecular reactions? 1½+1½

7. Answer ***any three*** : 3×5

(a) Explain the Born model of ion solvation. Illustrate the thermodynamic interpretation of macroscopic solvation.

(b) How the structural concept of ion-solvent interaction is different from non-structural concept of ion solvation? Discuss.

(c) Describe the ion-dipole electrostatic interaction within primary solvation sheath.

(d) Explain the electrostatic interaction from the concept of ion/water quadruple and ion-induced dipole interaction.

8. Write the applications of potential step voltammetric techniques with proper example. Explain the working principle of this technique. 3+2

9. *(a)* Explain the working principle of normal pulse voltammetry technique and differential pulse voltammetry technique. 4

Or

(b) Write the applications and working principle of controlled current technique.

10. *(a)* Illustrate the thermodynamic treatment of electrical interface and derive Lippmann equation. 6

Or

(b) Derive the Butler-Volmer equation. What is Tafel plot?

11. *(a)* What is 'sulfation' in Lead storage cell? Discuss the functioning of Lead storage cell. 1+4

Or

(b) What are pseudocapacitors? Discuss the working principle of supercapacitors with suitable diagram.

12. Discuss the chemical reactions involved during charging and dis-charging of *Ni-Cd* battery. What are the advantages of *Li*-ion battery? 3+2
