

Total number of printed pages-7

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.**

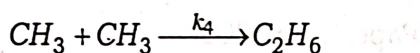
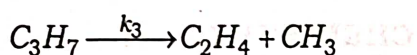
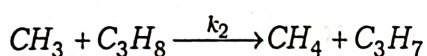
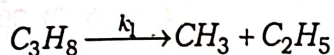
1. Why is the situation at equilibrium

$$-\frac{d[A]_{eq}}{dt} = 0, \text{ not a steady state?}$$

1

Contd.

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



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 ( $\gamma$ ). 5

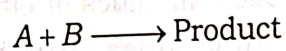
- (c) Discuss the chain branching explosion with the help of reaction between  $H_2$  and  $O_2$ .

A certain first order reaction has an activation energy of  $8.0 \times 10^4 \text{ J mol}^{-1}$  and a pre-exponential factor of  $3 \times 10^{12} \text{ s}^{-1}$ . 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  $r_A + r_B$ ,  $\mu$  and  $E_a$  constant. Given, initial temperature as 300K and  $E_a$  as  $25 \text{ kJ mol}^{-1}$ . 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



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  $1 \times 10^{-3} \text{ mol kg}^{-1} \text{ CaCl}_2 \text{ (aq)}$  at  $25^\circ\text{C}$ . 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 :



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?  $1\frac{1}{2}+1\frac{1}{2}$

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 quadrupole 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