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14 (CHM-2) CH 203

2019

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. (a) In a catalytic experiment involving the Haber process $N_2 + 3H_2 \longrightarrow 2NH_3$, the rate of reaction was measured as —

$$\text{Rate} = \frac{d[NH_3]}{dt} = 2.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}.$$

If there were no side reactions what is the rate of reaction expressed in terms of (a) N_2 (b) H_2 ? 2

Contd.

- (b) At 25°C the second order rate constant for the reaction

$I^- + ClO^- \longrightarrow IO^- + Cl^-$ is $0.060 \text{ M}^{-1}\text{s}^{-1}$. If a solution is initially $3.50 \times 10^{-3} \text{ M}$ w.r.t each reactant what will be the concentration of each species present after 300s ? 2

2. Answer **any two** from the following :

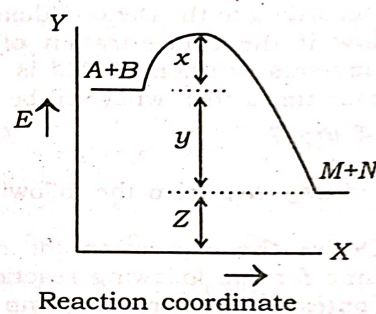
2×4=8.

- (a) What do you mean by chemical chaos ? Discuss briefly the key steps involved in the BZ-reaction. 2+2

- (b) What are competitive and non-competitive inhibitions ? For an enzyme catalysed reaction the turnover number is $3.7 \times 10^5 \text{ s}^{-1}$ at 310K. The molar mass of this enzyme is 52000 g mol^{-1} . What is the rate of the reaction if 0.050g of this enzyme is added to an excess of substrate ? 2+2

- (c) Discuss the Lotka-Volterra mechanism. How will you bring chemical oscillation ? 3+1

3. (a) What will be the enthalpy change of the reaction $A+B \rightarrow M+N$ as indicated by the following diagram ? In the context of the same diagram, predict the activation energy of the reaction $M+N \rightarrow A+B$. 2



- (b) What is the role of steric factor in reactions ? Show that ACT rate constant for the reaction of two atoms whose average diameter is $b_{\max}$ gives the same result as collision theory. Why is collision theory inferior to TST ? 1+3+1

Or

- (c) What do you mean by microscopic diffusion control? Deduce the expression of rate constant for partial microscopic diffusion controlled reaction. 1+4
- (d) Derive the Brönsted-Bjerrum equation and discuss its physical basis. 5
- (e) According to the Debye-Hückel limiting law if the concentration of a dilute aqueous solution of KCl is increased four times then what will be the value of $\ln \gamma_z$? 2
4. Answer **any two** from the following : 2×4=8
- (a) Derive the expression for relaxation time for the following reaction in the context of temperature-jump method—

$$2A \xrightleftharpoons[k_{-1}]{k_1} Z$$
 4
- (b) What are linearized rate equations? Why one could not employ conventional techniques to study very fast reactions? 3+1
- (c) How is Slater's treatment different from RRK treatment? What are the difficulties of Hinshelwood modification? 2+2

5. Answer **any two** from the following : 3×2=6
- (a) How are NMR studies helpful in the prediction of rate for fast reactions? 3
- (b) What are the assumptions of RRK treatment? State why Lindemann theory is not successful. 3
- (c) Discuss the principle of shock tube method. 3
6. (a) Explain the thermodynamic treatment of ion-solvent interactions. Illustrate ion-dipole and ion-multipole interactions in the structural model of ion-solvent interactions. 5+3
- (b) Derive the Debye-Hückel Onsager equation. What are the limitations of this theory? 4+3
7. (a) What are polarizable and non-polarizable interfaces? Derive the Lipmann equation. 3+5

Or

- (b) Derive Butler-Volmer equation. Explain the Tafel plots. 5+3

8. (a) Illustrate the following electrochemical techniques : 3+3+3

(i) Potential Step method

(ii) Potential Sweep method

(iii) Pulsed Voltametric method.

Or

(b) How are multistep reactions studied by electrochemical methods ? Give examples and illustrate. 6+3

9. (a) What are primary and secondary cells ? Give examples of these two types of cells. Write the cell reaction of Ni-Cd battery. 3+3+2

Or

(b) How are fuel cells different from electrochemical cells ? Explain the construction and cell reactions of lead-acid battery. 3+5
