

CHEMICAL REACTION ENGINEERING

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PART A: NOTES

INTRODUCTION

1.1 INTRODUCTION

Chemical Reaction Engineering is primarily knowledge of chemical kinetics and reactor design that distinguishes the chemical engineer from other engineers. The successful and economic design of chemical reactor is the aim of Chemical Reaction Engineering for that we require some basic knowledge of thermodynamics, fluid flow, Heat Transfer and Mass Transfer.

The Thermodynamics gives information about the

- Feasibility of a reaction
- Heat of reaction
- Maximum possible extent of reaction

Chemical Reaction Engineering gives information about the chemical kinetics; Chemical Kinetics is the study of chemical reaction rates (speed) and reaction mechanism (steps reaction occurs)

- Rate at which chemical reaction occurs
- Effect of parameters (Temperature, Pressure & Composition) on the reaction rates.
- Order of reaction / Type of reaction

1.2 TYPES OF CHEMICAL REACTIONS

Chemical reactions can be classified on the basis of various parameters as follows:

- i. On the basis of phase of reacting solution
 - Homogeneous / Heterogeneous Reactions
- ii. On the basis of catalyst presence
 - Catalytic / Non-catalytic Reactions
- iii. On the basis of number of molecules participating in reaction
 - Unimolecular / Poly molecular Reactions
- iv. On the basis of heat of reaction
 - Endothermic / Exothermic Reactions
- v. On the basis of order of reaction

- Zero / First / Second / Nth Order Reactions
- vi. On the basis of steps involving in reaction completion
 - Elementary / Non elementary Reactions
- vii. On the basis of reaction direction
 - Irreversible / Reversible Reactions

1.3 RATE OF CHEMICAL REACTION

The rate of reaction tells us how fast a number of moles of one component species are being consumed to form another chemical species. The term *chemical species* refers to any chemical component or element with a given identity.

We express the rate as the rate of disappearance of component A as $-\frac{dN_A}{dt}$

The rate of change of A (in no. of moles of A). The negative sign indicates that disappearance of reactant A during reaction.

The rate of reaction can be expressed in various forms as follows:

- i. Based on unit volume of reacting fluid

$$-r_A = -\frac{1}{V} \frac{dN_A}{dt}$$

- ii. Based on unit mass of solid in fluid solid system

$$-r'_A = -\frac{1}{W} \frac{dN_A}{dt}$$

- iii. Based on unit surface of solid in gas-solid system

$$-r''_A = -\frac{1}{S} \frac{dN_A}{dt}$$

The reaction rate is an intensive quantity & depends on concentration & temperature. From above rate equations, we've

$$(-r_A)V = (-r'_A)W = (-r''_A)S$$

1.4 RELATIVE RATE OF REACTION

The relative rate of reaction of various species involved in a reaction can be obtained from the ratio of stoichiometric coefficients. For reaction given below



We see that for every a mole of A reacted with b mole of B produces c mole of C and d mole of D. In other words

Rate of Formation of C = $\frac{c}{a}$ (Rate of disappearance of A)

$$r_C = \frac{c}{a} (-r_A)$$

$$r_C = \frac{c}{d} (r_D)$$

The relationship can be expressed directly from stoichiometric of reaction,

$$\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d}$$

1.5 FACTORS AFFECTING THE RATE OF REACTION

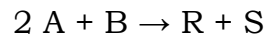
- i. Nature of reactant & product
- ii. Concentration of reactants
- iii. Temperature
- iv. Pressure
- v. Nature of catalyst
- vi. Surface area of reactant
- vii. Rates of heat & mass transfer

1.6 REACTION MECHANISM

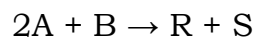
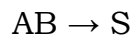
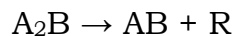
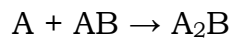
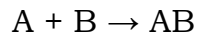
It refers to a step or series of steps by which the initial reactants interact in the process of forming products. A reaction usually does not take place in the single step rather takes place in a series of steps which when added

gives the overall stoichiometric equation, these steps are the mechanism of reaction

e.g.



Might take place as



The slowest step controls the rate of the chemical reaction & determines the form of overall rate equation.

1.7 MOLECULARITY

The *Molecularity* of a reaction is the number of atoms, ions or molecules involved (colliding) in a reaction step. It is the number of molecules, ions or atoms interacting or colliding in any one reaction step.

Molecularity of a reaction must be a whole no. & never be zero or a fraction.

1.8 ORDER OF REACTION

The *order of a reaction* refers to the powers to which the concentrations are raised in the kinetics rate law. This is experimental quantity. The algebraic equation that relates $-r_A$ to the species concentrations is called the kinetic expression or *rate law*.

For above reaction 1.1, the rate law can be expressed as

$$-r_A = [k_A(T)] [f(C_A, C_B, \dots)]$$

The dependence of the reaction rate, $-r_A$, on the concentration of the species present, $f(C_j)$, is almost without exception determined by experimental observations. One of the most acceptable and general form to relate this theory is power law model. Here the rate law is the product of

concentrations of the individual reacting species, each of which is raised to a power, e.g.

$$-r_A = k_A C_A^\alpha C_B^\beta$$

The exponents of the concentration n above equation lead to the concept of *reaction order*.

Here, the overall order of reaction, n , is

$$\mathbf{n = \alpha + \beta}$$

Example 1.1 For the gaseous reaction, the rate expression is $-\frac{dC_A}{dt} = kC_A^n$. Find the rate equation in terms of partial pressure (p_A)

Solution:

For gases

$$PV = nRT$$

$$P = \frac{n}{V} RT$$

$$P = CRT$$

where $C = \frac{n}{V}$, write this equation for component A as

$$\Rightarrow p_A = C_A RT \text{ and } dC_A = \frac{dp_A}{RT} \text{ and put in given rate equation}$$

hence

$$-\frac{dp_A}{RT \cdot dt} = k \left(\frac{p_A}{RT} \right)^n$$

$$\Rightarrow \boxed{-\frac{dp_A}{dt} = k (p_A)^n \cdot (RT)^{1-n}}$$

Example 1.2 For a reaction $A + 3B \longrightarrow 5C + 7D$. Which is correct:

$$(a) -r_A = -\frac{1}{3}r_B = \frac{1}{5}r_C = \frac{1}{7}r_D \text{ (Direct solution from article 1.4)}$$

$$(b) -r_A = -3r_B = 5r_C = 7r_D$$

$$(c) -r_A = -\frac{1}{3}r_B = -5r_C = -7r_D$$

$$(d) -r_A = \frac{1}{3}r_B = -\frac{1}{5}r_C = -\frac{1}{7}r_D$$

Example 1.3 For a rate expression, $-r_A = kC_A^{0.7}C_B^{0.3}$, overall order of reaction is:

(a) 0.7 (b) 0.3 (c) 0.4 **(d) 1**

(Direct solution from article 1.8)

1.9 RATE CONSTANT (k)

The term k referred to as either *specific reaction rate* or *the rate constant*. It is almost strongly dependent on temperature. In gas phase reactions, it may be a function of total pressure. In liquid systems it can also be a function of other parameters, such as ionic strength and choice of solvent. There are various theories giving the relation for dependency of k_A on Temperature. These theories are as follows:

1.9.1 ARRHENIUS THEORY

For a reaction to occur it is first necessary to break or weaken the bonds between atoms & molecules of the reactant which require a definite amount of energy. If colliding molecules do not pass this energy a collision between them does not result in the formation of new molecules. The minimum amount of energy which the colliding molecules must have in order to bring about the reaction is known as activation energy.

$$k = k_0 e^{-E/RT}$$

Where, k_0 = Pre Frequency Factor and it has dimension as rate constant k but it is independent of temperature

E = Activation Energy

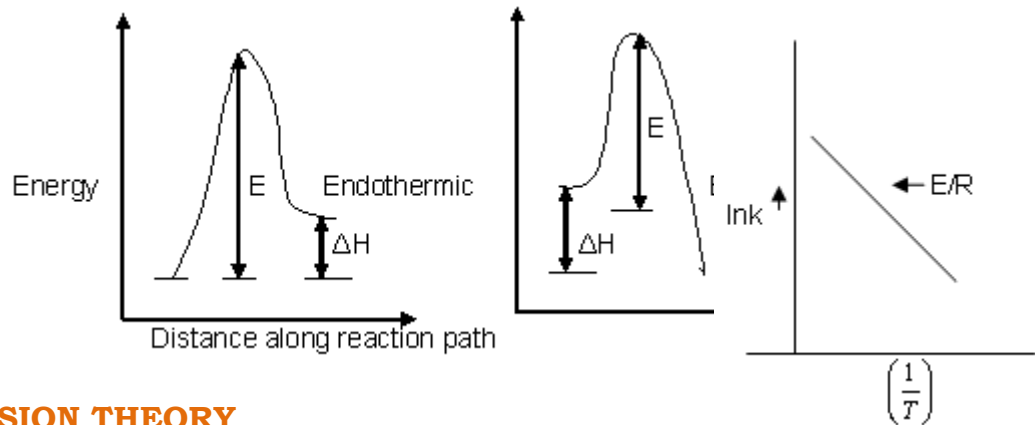
Let log on both side of equation, we get

$$\ln k = \ln k_0 - \frac{E}{R} \left(\frac{1}{T} \right)$$

If the rate is known at two different Temperature T_1 & T_2 , we can evaluate E.

$$\ln \frac{r_2}{r_1} = \frac{E}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\ln(k_2 / k_1) = \frac{E}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$



1.9.1 COLLISION THEORY

For bimolecular reactions,

$$k = T^{1/2} e^{-E/RT}$$

It fails with uni-molecular reactions.

1.9.2 TRANSITION STATE THEORY

It is based on statistical mechanics collision based on kinetic theory of gases.

Transition state theory views that formation of activated complex is very rapid whereas collision theory view that decomposition of activated complex is very rapid.

$$k = T \cdot e^{-E/RT}$$

Example 1.4 For a reaction $\frac{1}{2} A + B \rightarrow R + \frac{1}{2} S$ has the rate equation $-r_A = 2C_A^{0.5} C_B$, what is rate equation for given reaction $A + 2B \rightarrow 2R + S$

Solution: Since, order of reaction does not depend on stoichiometric coefficient for non- elementary reaction. Hence, Reaction rate will be same as $-r_A = 2C_A^{0.5}C_B$.

Example 1.5 On doubling the concentration of reactant the rate of reaction triples find the reaction order:

- (a) 1 (b) 2 **(c) 1.6** (d) 0.6

Solution:

$$\frac{-r_{A2}}{-r_{A1}} = \frac{kC_{A2}^n}{kC_{A1}^n}$$

$$\Rightarrow \frac{3(-r_{A1})}{-r_{A1}} = \frac{k(2C_{A1})^n}{kC_{A1}^n}$$

$$\Rightarrow 3 = 2^n$$

$$\Rightarrow \ln 3 = n \ln 2$$

$$\Rightarrow n = 1.589$$

$$\boxed{\Rightarrow n \approx 1.6}$$

Example 1.6 The activation energy of a bimolecular reaction is about 9150 cal / mol, how much faster this reaction will take place at 500 K then at 400 K.

- (a) 9 times (b) 16 times **(c) 10 times** (d) 6 times

Solution: from Arrhenius law, $k = k_0 e^{-E/RT}$

$$\text{Or } \ln \left(\frac{-r_2}{-r_1} \right) = \frac{E}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\ln \left(\frac{-r_2}{-r_1} \right) = \frac{9150}{1.98624} \left[\frac{1}{400} - \frac{1}{500} \right]$$

$$\ln \left(\frac{-r_2}{-r_1} \right) = 2.303 \Rightarrow \frac{-r_2}{-r_1} = e^{2.303} = 10$$

$$\boxed{-r_2 = 10(-r_1)}$$

Example 1.7 At 500 K, reaction is 10 times faster than that of at 400 K, find the activation energy (E), by Collision theory,

(a) 9150 cal / mol (b) 10,150 cal / mol

(c) 8707 cal / mol (d) 7808 cal / mol

Solution: from Collision theory, $k = T^{1/2} \cdot e^{-E/RT}$

Or

$$\ln\left(\frac{k_2}{k_1}\right) = \ln\left(\frac{T_2}{T_1}\right) + \frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\ln\left(\frac{k_2}{k_1}\right) = \ln\left(\frac{500}{400}\right) + \frac{E}{1.98624}\left[\frac{1}{400} - \frac{1}{500}\right]$$

$$E = 8707 \frac{\text{cal}}{\text{mol}}$$

