



## Lecture (2)

### 1. Reaction Rate (Rate Law, $r_A$ )

In **homogeneous reaction**, the reaction rate ( $r_A$ ) is defined as the change in moles of component A (reactant consumed) or mole of product formed with respect to time **per unit volume of reaction mixture**.

In **solid-catalyzed reactions**, the reaction rate ( $r_A'$ ) is defined as the change in moles of component A with respect to time **per unit reaction surface area or catalyst weight**.

- $r_A$  = rate of formation of A per unit volume
- $-r_A$  = rate of a disappearance of A per unit volume

#### Batch Reactor

$$-r_A = -\frac{dN_A}{V dt} = \frac{\text{mole of A disappear}}{\text{volume of fluid} \times \text{time}} \quad \text{homogeneous reaction ... 2a}$$

$$-r_{A''''} = -\frac{dN_A}{V_r dt} = \frac{\text{mole of A disappear}}{\text{volume of reactor} \times \text{time}} \quad \text{homogeneous reaction ... 2b}$$

$$-r_{\dot{A}} = -\frac{dN_A}{W dt} = \frac{\text{mole of A disappear}}{\text{mass of catalyst} \times \text{time}} \quad \text{heterogeneous reaction ... 2c}$$

$$-r_{A''} = -\frac{dN_A}{S dt} = \frac{\text{mole of A disappear}}{\text{surface} \times \text{time}} \quad \begin{array}{l} \text{heterogeneous or homogeneous reaction} \\ \text{...2d} \end{array}$$

$$-r_{A''''} = -\frac{dN_A}{V_s dt} = \frac{\text{mole of A disappear}}{\text{volume of Catalyst} \times \text{time}} \quad \text{heterogeneous reaction ... 2e}$$

$$Vr_A = Wr_{\dot{A}} = Sr_{A''} = V_s r_{A''''} = V_r r_{A''''} \dots \dots \dots 3$$

The rate of reaction per unit weight catalyst,  $-r_{\dot{A}}$  (e.g.,  $-r_A$ ), and the rate of reaction per unit volume,  $-r_A$ , are related through the **bulk density  $\rho_b$**  (mass of **solid / volume**) of the *catalyst* particles in the fluid media:

$$-r_A = \rho_b r_{\dot{A}}$$





### Tubular Flow Reactor

$$-r_A = -\frac{d\dot{N}_A}{dV} \dots\dots\dots 4$$

Where  $\dot{N}_A$  is the molal rate of flow component A into the volume element.

### Rate of reaction $r_A$ is:

- a function of concentration, temperature, pressure, and the type of catalyst (if any)
- independent of the type of reaction system (batch, plug flow, etc.) but on the reaction chemistry
- an algebraic equation, not a differential equation
- Rate of reaction per unit weight of catalyst and rate of reaction per unit volume is related through the bulk density of the catalyst particle in the fluid media

Rate of reaction  $r_A$  is an intensive quantity and depended on composition (Concentration), and the energy of the material (Temperature) . Energy of the material mean the temperature (random kinetic energy of the molecules), the light intensity within the system (this may affect the bond energy between atoms), the magnetic field intensity, etc. Ordinarily we only need to consider the temperature

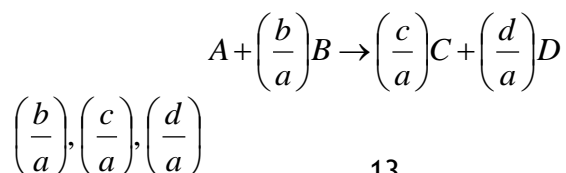
$$-r_A = f \{ \text{temperature dependent term, concentration dependent term} \}$$

$$= \text{mole/m}^3 \cdot \text{time}$$

## 2. Conceptes of Kinetics

### 1. Stoichiometry.

- Consider the general reaction;  $aA + bB \rightarrow cC + dD$
- on a “per mole of A basis” ...i.e assume A is the limiting reactant :-







- where the Stoichiometric Coefficients ,
- Molecules are lost and formed by reaction , and mass conservation requires that amounts of species are related by Stoichiometry as:-

1 mole of A and  $\left(\frac{b}{a}\right)$  of B consumed , while  $\left(\frac{c}{a}\right)$  mole of C and  $\left(\frac{d}{a}\right)$  mole of D formed or appear

$$\text{Rate of reaction or disappearance of A} = -r_A \quad \frac{\text{mole}}{\text{m}^3 \cdot \text{time}}$$

$$\text{Rate of formation of C } (r_C) = \left(\frac{c}{a}\right) (-r_A) \quad \frac{\text{mole}}{\text{m}^3 \cdot \text{time}}$$

$$\text{Rate of formation of D } (r_D) = \left(\frac{d}{a}\right) (-r_A) \quad \frac{\text{mole}}{\text{m}^3 \cdot \text{time}}$$

$$\text{Also, Rate of formation of C } (r_C) = \left(\frac{c}{d}\right) (r_D)$$

$$\text{Rate of formation of D } (r_D) = \left(\frac{d}{c}\right) (r_C)$$

$$\text{Then the reaction Stoichiometry ; } \frac{-r_A}{a} = \frac{-r_B}{a} = \frac{r_C}{a} = \frac{r_D}{a}$$

### Examples (1),(2)

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## 2. Temperature – Dependent Term of a Reaction Rate Law.

 **Reaction Rate Contestant.**  $k_A(T)$

- Kinetic (reaction) Rate law  $(-r_A)$  gives relationship between reaction rate and concentration (is an algebraic equation that relates  $(-r_A)$  to species concentrations)

$$-r_A = f\{\text{temperature dependet term, concentration dependent term}\} \quad \frac{\text{mole}}{\text{m}^3 \cdot \text{time}}$$

$$-r_A = [k_A(T)] \cdot [f(C_A, C_B, \dots)] \dots\dots\dots 5$$





- $k_A(T)$  is the **reaction rate constant**
  - Strongly dependent on temperature
  - Depends on whether *or* not a catalyst is present
  - NOT really a constant, but  $\neq f(C_i)$
- The **rate constant** is described by Arrhenius equation :-

$$k_A(T) = Ae^{-E/RT} \dots\dots\dots 6$$

$$\ln(k) = \ln(A) - \frac{E}{R} \left( \frac{1}{T} \right) \dots\dots\dots 7$$

$A \equiv$  Pre-exponential factor (frequency factor)

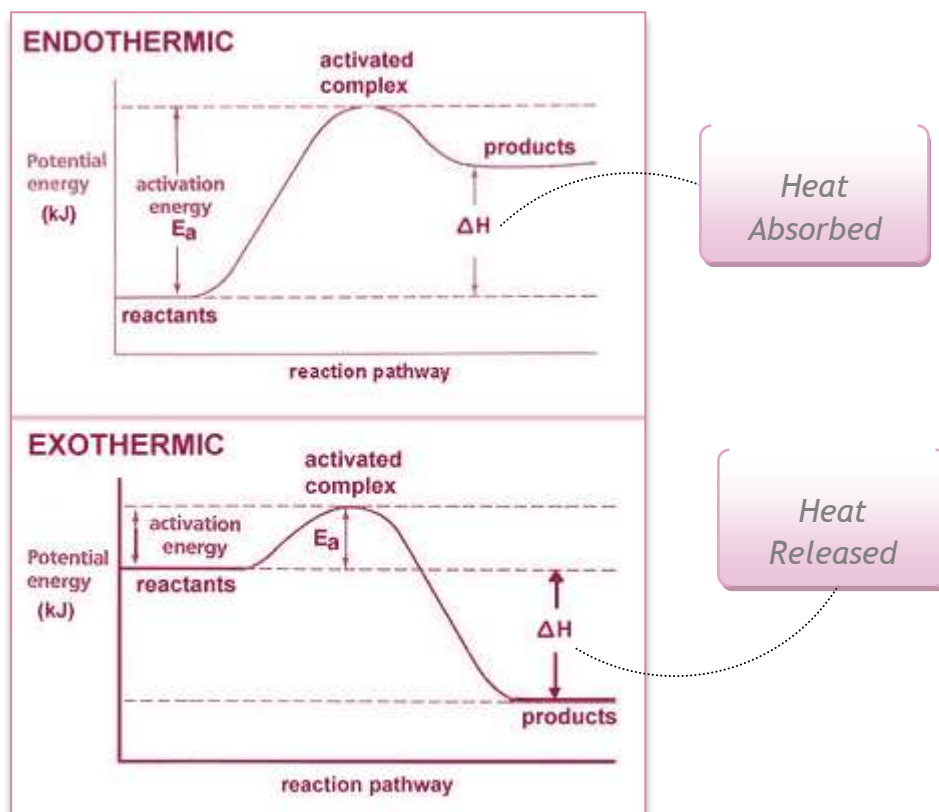
$E \equiv$  Activation energy (J/mol)

$R \equiv$  Gas constant (8.314 J/mol·K, 1.987 cal/mol ·K)

$T \equiv$  Absolute temperature (K)

### **Activation Energy**

Activation energy has been equated with minimum energy that must be possessed by reacting molecules before the reaction will occur.







Figure(2.1)Activation energy for exothermic and endothermic reaction.

At the same concentration but different two temperature **Activation Energy** can be estimated as :

$$\frac{\ln(r_2)}{\ln(r_1)} = \frac{\ln(k_2)}{\ln(k_1)} = \frac{E}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \dots\dots\dots 8$$

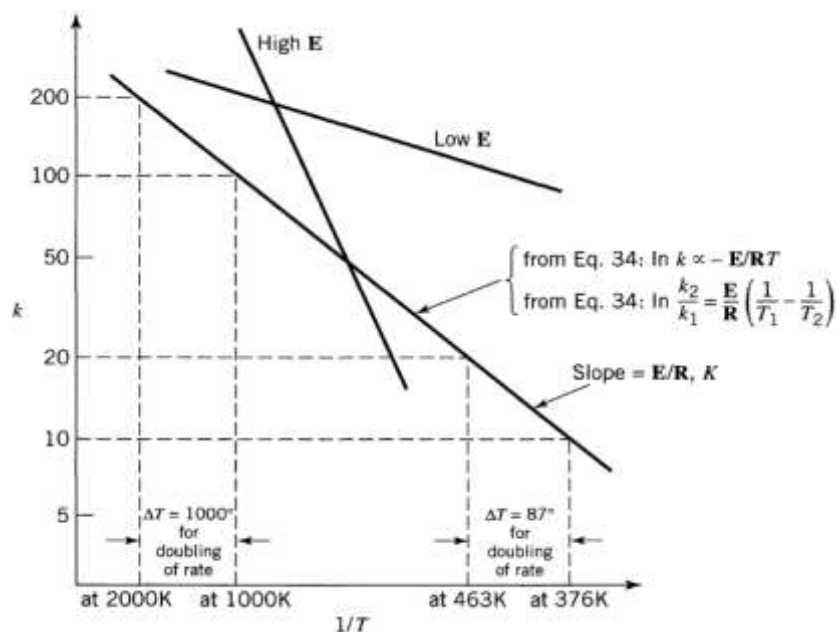


Figure (2.2) shows temperature dependency of the reaction rate

Example (4)

Example (5) =example 3.1 from elemental of chemical reaction engineering , 4ed pag 95

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### 3. Concentration – Dependent Term of a Reaction Rate Law.

$$-r_A = [k_A(T)] \cdot [f(C_A, C_B, \dots)] \dots\dots\dots 5$$

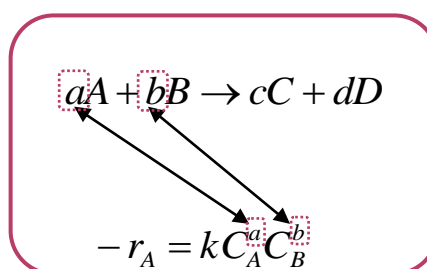
$$f(C_A, C_B, \dots)$$

One of the most common general forms of this dependence is the product of concentrations of the individual reacting species, **each** of which is raised to a power .

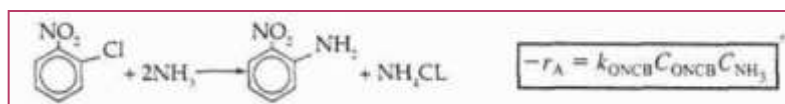
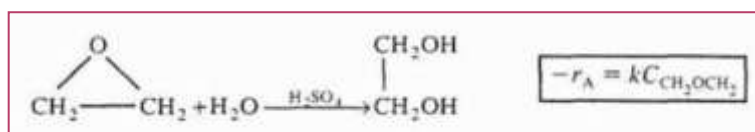
#### Reaction Order.

##### – Elementary Reaction

A reaction order for which each specie is identical to its Stoichiometric coefficient as shown :-



- a and b represent the reaction order with respect to the reactant A and B respectively ,  
over all reaction order( n ) = a + b



- Reaction rate constant, **k** will **vary** with the order of the reaction as shown :-

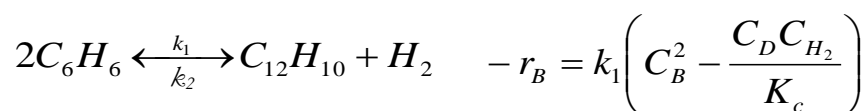
**A → products**





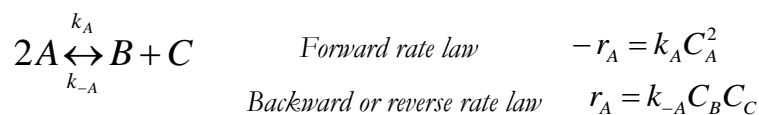
Order	Rate Equation	Units
Zero	$-r_A = k$	$\text{mol.V}^{-1}.\text{s}^{-1}$
First	$-r_A = kC_A$	$\text{s}^{-1}$
Second	$-r_A = kC_A^2$	$\text{V.mol}^{-1}.\text{s}^{-1}$
Third	$-r_A = kC_A^3$	$(\text{V.mol}^{-1})^2.\text{s}^{-1}$
nth order	$-r_A = kC_A^n$	$(\text{concentration})^{1-n}.\text{s}^{-1}$

- Another example of elementary reaction ; reversible second order :-



where  $K_c$  equilibrium constant

- All reversible reaction rate laws must reduce to the thermodynamic relationship relating reacting species concentrations at equilibrium.
- At equilibrium, the *net* rate of reaction is zero for all species involved in the reaction-  $r_{ie} = 0$



*net rate law*

$$r_{A,net} = r_A + r_{-A} = -k_A C_A^2 + k_{-A} C_B C_C$$

$$r_{A,net} = 0 = -k_A C_A^2 + k_{-A} C_B C_C$$

$$\text{Equilibrium condition} \quad k_A C_A^2 = k_{-A} C_B C_C$$

$$\text{Equilibrium relationship} \quad \frac{k_A}{k_{-A}} = \frac{C_B C_C}{C_A^2} = K_C$$

$$\text{Rate law in term Equilibrium relationship} \quad -r_A = k_A \left( C_A^2 - \frac{C_B C_C}{K_C} \right)$$

### Example (6)

#### - Non-Elementary Reaction

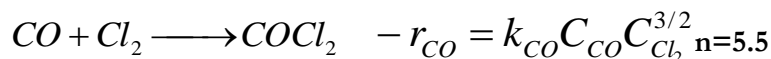




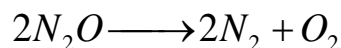
Do not follow the Stoichiometric coefficients for the overall reaction

#### ✚ Homogeneous Reactions :

Gas-phase synthesis of phosgene,



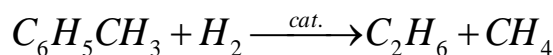
Decomposition of nitrous oxide



$$-r_{N_2O} = \frac{k_{N_2O} C_{N_2O}}{1 + k' C_{O_2}} \quad \text{n depended on } CO_2 \text{ concentration}$$

#### ✚ Heterogeneous Reactions :

Heterogeneous reaction and corresponding rate law is the hydrodemethylation of toluene (T) to form benzene (B) and methane (M) carried out over a solid catalyst.



$$-r'_T = \frac{k P_{H_2} P_T}{1 + K_B P_P + K_T P_T}$$

$$k = \frac{\text{mol toluene}}{\text{kg}_{cat} \cdot \text{s} \cdot \text{kPa}^2}$$

$$-r_A = \rho_b r'_A$$

#### 4. Molecularly Reaction.

The term molecularity refers to number of atoms, ions, or molecules involved in the rate-limiting step of the reaction.

- Unimolecular – one reactant involved in reaction
- Bimolecular – two reactants must collide to react
- Termolecular – three reactants must interact for reaction to occur

#### 5. Conversion , yield and selectivity





**conversion, X**, is defined as the fraction (or percentage) of the more important or limiting reactant that is consumed. With two reactants A and B and a nearly Stoichiometric feed, conversions based on each reactant could be calculated.

$$X = \frac{\text{mole A reacted}}{\text{mole A fed}} \dots\dots\dots 8$$

**yield, Y**, is the amount of desired product produced relative to the amount that would have been formed if there were no byproducts and the main reaction went to completion

$$Y = \frac{\text{moles of product formed}}{\text{maximum moles of product, } x = 1.0} \dots\dots 9$$

## 6. Van't Hoff Equation.

Van't Hoff equation relates equilibrium composition to temperature:

$$\frac{d(-\Delta G_R^o / RT)}{dT} = \frac{\Delta H_r^o}{RT^2} = \frac{d \ln K_{eq}}{dT} \dots\dots\dots 10$$

Van't Hoff equation can be integrated from 298K to any temperature T to yield :

$$\ln K_{eq} = \ln K_{298} + \int_{298}^T \frac{\Delta H_r}{RT^2} dT \dots\dots\dots 11$$

Enthalpy change of reaction varies with temperature as:

$$\Delta H_r(T) = \Delta H_r^o(T_{298}) + \int_{T_{298}}^T \Delta C_p dT \dots\dots\dots 12$$

An approximate estimate of equilibrium constant at any time , ignore the second term in equation 12, then equation 11 became :

$$\ln K_{eq} = \ln K_{298} - \frac{\Delta H_{r298}}{R} \left( \frac{1}{T} - \frac{1}{298} \right) \dots\dots\dots 13$$

For endothermic reactions, the equilibrium constant,  $K_{eq}$ , increases with increasing temperature. While for exothermic reactions,  $K_{eq}$  and  $X_{eq}$  decreases with increasing temperature.



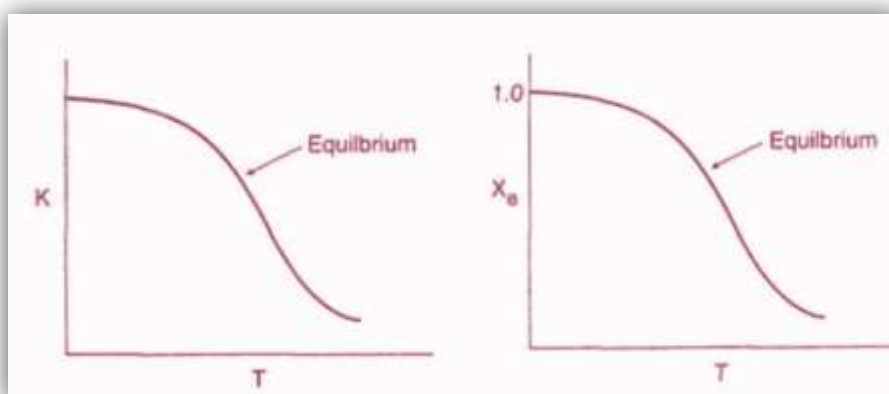


Figure (2.3) show the variation of the concentration equilibrium constant and equilibrium conversion as a function of temperature for an exothermic reaction.