CHEMICAL REACTION ENGINEERING (SKF3223)

Chapter 3: Rate Laws and Stoichiometry

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TYPES OF REACTION

- Homogenous reaction – one phase reaction
- Heterogeneous reaction – more than one phase
- Irreversible reaction:

$$A + B \rightarrow C + D$$

$$(one\ direction)$$

- Reversible reaction:

$$A + B \leftrightarrow C + D$$

$$(foward\ or\ backward)$$

Relative rates of reaction

$$aA + bB \rightarrow cC + dD$$

$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$$

For every mole of A that is consumed/reacted, c/a moles of C appear

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

or

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

RATE LAWs

The rate law:

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

- Order with respect to A = α
- Order with respect to B = β
- Overall reaction order,
  n = α + β
- k = $\frac{(\text{Concentration})^{1-n}}{\text{Time}}$

$\text{Zero} - \text{order:}$

$-r_A = k_A : \{k\} = \text{mol}/(\text{dm})^3.\text{s}$

$\text{First} - \text{order}$

$-r_A = k_A C_A : \{k\} = \text{s}^{-1}$

$\mathit{Second} - \text{order}$

$-r_A = k_A C_A^2 : \{k\} = (\text{dm})^3 / mol.s$

$Third - order$

$-r_A = k_A C_A^3 : \{k\} = (\text{dm}^3 / mol)^2.s^{-1}$

Elementary rate laws

- The stoichiometry coefficients are the same as the individual reaction order of each species.
- For the reaction:

$$A + 2B \rightarrow C + D$$

- The rate law would be:

$$-r_A = k_A C_A C_B^2$$

NonElementary rate laws

- The stoichiometric coefficients are **not** the same as the individual reaction order of each species.

- For the reaction: $\mathrm{A + B \rightarrow C + D}$

- The rate law would be:

$$-r_A = k_A C_A^2 C_B$$

Then the reaction is said to be 2nd order in A, 1st order in B, and 3rd order overall.

REVERSIBLE REACTIONS

- For general reaction: $aA + bB \leftrightarrow cC + dD$
- The net rate of formation A

$$r_A \equiv r_{A,net} = r_{A,\,forward} + r_{A,reverse}$$

$$\boxed{r_{A,\,forward} = -k_A C_A^a C_B^b \text{ and } r_{A,reverse} = k_{-A} C_C^c C_D^d}$$

- At **equilibrium, r$_{net}$=0**. Thus,

$$k_A C_A^a C_B^b = k_{-A} C_C^c C_D^d$$

$$\boxed{\frac{k_A}{k_{-A}} = K_{equilibrium}}$$

K = thermodynamic equilibrium constant

$$r_A \equiv r_{A,net} = r_{A,forward} + r_{A,reverse}$$

$$r_A = -k_A C_A^a C_B^b + k_{-A} C_C^c C_D^d$$

- Multiplying both sides of equation by (-1), we obtain the rate law for the rate of disappearance of A:

$$-r_A = k_A C_A^a C_B^b - k_{-A} C_C^c C_D^d$$

- Replacing with K

$$\frac{k_A}{k_{-A}} = K_{equilibrium} \qquad \frac{k_{-A}}{k_A} = \frac{1}{K}$$

$$-r_A = k_A \left(C_A^a C_B^b - \frac{k_{-A}}{k_A} C_C^c C_D^d \right)$$

$$\boxed{-r_A = k_A \left(C_A^a C_B^b - \frac{C_C^c C_D^d}{K} \right)}$$

- At equilibrium, $-r_A = 0$:

$$k_A\left(C_A^a C_B^b - \frac{C_C^c C_D^d}{K}\right) = 0$$

$$C_A^a C_B^b - \frac{C_C^c C_D^d}{K} = 0$$

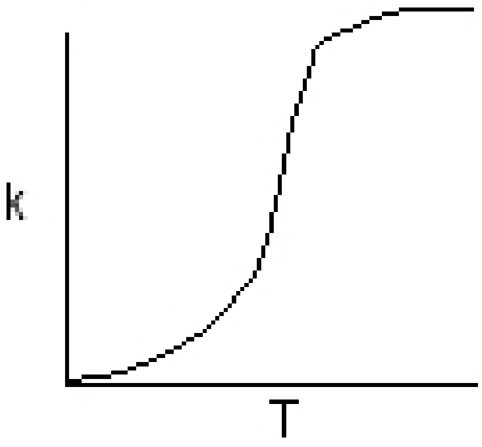
$$C_A^a C_B^b = \frac{C_C^c C_D^d}{K}$$

$$\boxed{K = \frac{C_C^c C_D^d}{C_A^a C_B^b}}$$

k

- Specific reaction rate or the rate constant
- *k* is temperature dependent, described by **Arrhenius equation**:

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



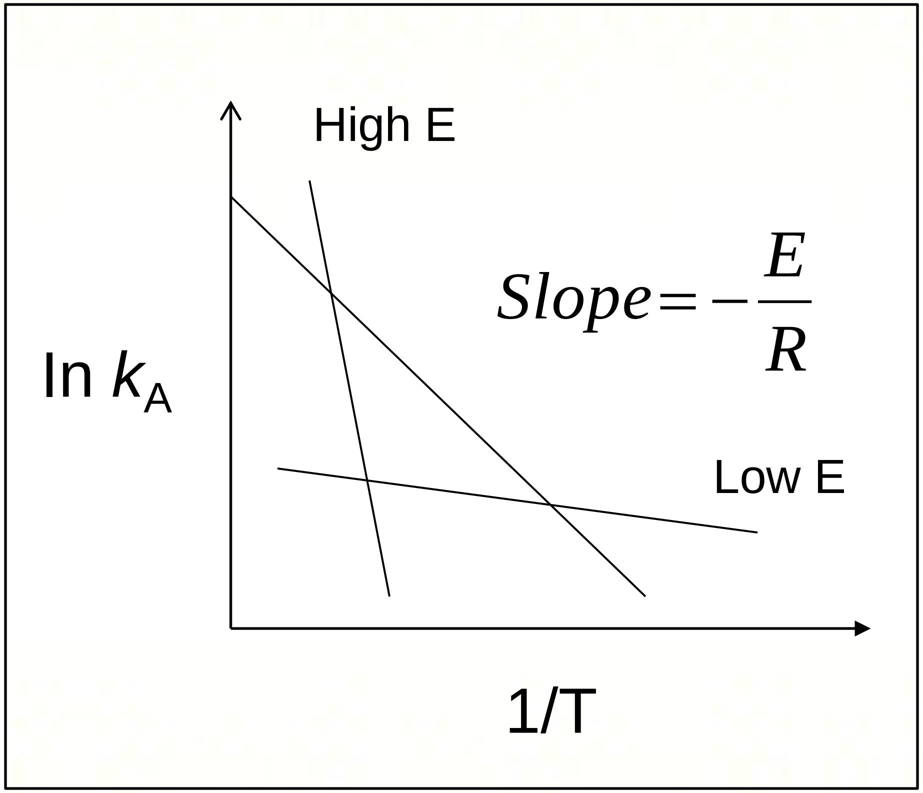
where
A = pre-exponential factor or frequency factor
E = activation energy, J/mol or cal/mol
R = gas constant= 8.314 J/mol.K
= 1.987 cal/mol.K
T = absolute temperature, K

❑ The activation energy is a measure of the minimum energy a that the reacting molecules must have in order for the reaction to occur.

- ❑ From Arrhenius equation: $k_A(T) = Ae^{-E/RT}$

- ❑ Activation energy is determined experimentally:

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



$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$$

STOICHIOMETRY TABLE - BATCH SYSTEMS

Species	Initially (mol)	Change (mol)	Remaining (mol)
A	N_{A0}	$-(N_{A0}X)$	$N_A = N_{A0} - N_{A0}X$
B	N_{B0}	$-\frac{b}{a}(N_{A0}X)$	$N_B = N_{B0} - \frac{b}{a}N_{A0}X$
C	N_{C0}	$\frac{c}{a}(N_{A0}X)$	$N_C = N_{C0} + \frac{c}{a}N_{A0}X$
D	N_{D0}	$\frac{d}{a}(N_{A0}X)$	$N_D = N_{D0} + \frac{d}{a}N_{A0}X$
I (inerts)	N_{I0}	-	$N_I = N_{I0}$
TOTALS	N_{T0}	$N_T = N_{T0} + \delta N_{A0}X$, $\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$	

* -ve = disappearing from the system

1. To express the **concentration** of each component in terms of the **conversion X**:

$$\boxed{C_A = \frac{N_A}{V}}$$

2. Therefore,

$$C_A = \frac{N_A}{V} = \frac{N_{A0} - N_{A0}X}{V} = \frac{N_{A0}(1-X)}{V}$$

$$C_B = \frac{N_B}{V} = \frac{N_{B0} - (b/a)N_{A0}X}{V}$$

$$C_C = \frac{N_C}{V} = \frac{N_{C0} + (c/a)N_{A0}X}{V}$$

$$C_D = \frac{N_D}{V} = \frac{N_{D0} + (d/a)N_{A0}X}{V}$$

3. Simplify,

$$\boxed{\Theta_i = \frac{N_{i0}}{N_{A0}} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{A0}}}$$

$$C_B = \frac{N_{A0}\left(\frac{N_{B0}}{N_{A0}} - \frac{b}{a}X\right)}{V}$$

$$\boxed{\Theta_B = \frac{N_{B0}}{N_{A0}}}$$

$$C_C = \frac{N_{A0}\left(\frac{N_{C0}}{N_{A0}} + \frac{c}{a}X\right)}{V}$$

$$C_D = \frac{N_{A0}\left(\frac{N_{D0}}{N_{A0}} + \frac{d}{a}X\right)}{V}$$

CONSTANT-VOLUME BATCH SYSTEMS

$$\boxed{V = V_0}$$

$$C_A = \frac{N_A}{V} = \frac{N_{A0} - N_{A0}X}{V} = \frac{N_{A0}(1-X)}{V} = \frac{N_{A0}(1-X)}{V_0} = C_{A0}(1-X)$$

$$C_B = \frac{N_B}{V} = \frac{N_{B0} - (b/a)N_{A0}X}{V} = \frac{N_{A0}(\Theta_B - (b/a)X)}{V_0} = C_{A0}\left(\Theta_B - \frac{b}{a}X\right)$$

$$C_C = \frac{N_C}{V} = \frac{N_{C0} + (c/a)N_{A0}X}{V} = \frac{N_{A0}(\Theta_C + (c/a)X)}{V_0} = C_{A0}\left(\Theta_C + \frac{c}{a}X\right)$$

$$C_D = \frac{N_D}{V} = \frac{N_{D0} + (d/a)N_{A0}X}{V} = \frac{N_{A0}(\Theta_D + (d/a)X)}{V_0} = C_{A0}\left(\Theta_D + \frac{d}{a}X\right)$$

EXAMPLE

$$-r_A = kC_AC_B$$

$$C_A = C_{A0}(1-X)$$

$$C_B = C_{A0}\left(\Theta_B - \frac{b}{a}X\right)$$

$$-r_A = kC_{A0}(1-X)C_{A0}\left(\Theta_B - \frac{b}{a}X\right)$$

$$-r_A = kC_{A0}{}^2(1-X)\left(\Theta_B - \frac{b}{a}X\right)$$

$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$$

STOICHIOMETRY TABLE - FLOW SYSTEMS

Species	Feed rate to reactor (mol/time)	Change within reactor (mol/time)	Effluent rate from reactor (mol/time)
A	F_{A0}	$-(F_{A0}X)$	$F_A = F_{A0}(1 - X)$
B	$F_{B0} = \Theta_B F_{A0}$	$-\frac{b}{a}(F_{A0}X)$	$F_B = F_{A0}\left(\Theta_B - \frac{b}{a}X\right)$
C	$F_{C0} = \Theta_C F_{A0}$	$\frac{c}{a}(F_{A0}X)$	$F_C = F_{A0}\left(\Theta_C + \frac{c}{a}X\right)$
D	$F_{D0} = \Theta_D F_{A0}$	$\frac{d}{a}(F_{A0}X)$	$F_D = F_{A0}\left(\Theta_D + \frac{d}{a}X\right)$
I (inerts)	$F_{I0} = \Theta_I F_{A0}$	-	$F_I = F_{A0}\Theta_I$
TOTALS	F_{T0}	$F_T = F_{T0} + \delta F_{A0}X$,	$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$

To express the **concentration** of each component in terms of the entering molar flow rate, **F**, the conversion **X**, and the volumetric flow rate, ***v***:

$$C_A = \frac{F_A}{v} = \frac{F_{A0} - F_{A0}X}{v} = \frac{F_{A0}(1-X)}{v}$$

$$C_B = \frac{F_B}{v} = \frac{F_{B0} - (b/a)F_{A0}X}{v}$$

$$C_C = \frac{F_C}{v} = \frac{F_{C0} + (c/a)F_{A0}X}{v}$$

$$C_D = \frac{F_D}{v} = \frac{F_{D0} + (d/a)F_{A0}X}{v}$$

$$C_A = \frac{F_A}{v} = \frac{moles/time}{liters/time} = \frac{moles}{liter}$$

$$\Theta_B = \frac{F_{B0}}{F_{A0}} = \frac{C_{B0}v_0}{C_{A0}v_0} = \frac{C_{B0}}{C_{A0}} = \frac{y_{B0}}{y_{A0}}$$

LIQUID-PHASE REACTIONS

$$\boxed{v = v_0}$$

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v} = \frac{F_{A0}(1-X)}{v_0} = C_{A0}(1-X)$$

$$C_B = C_{A0}\left(\Theta_B - \frac{b}{a}X\right)$$

$$C_C = C_{A0}\left(\Theta_C + \frac{c}{a}X\right)$$

$$C_D = C_{A0}\left(\Theta_D + \frac{d}{a}X\right)$$

*similar with constant-volume batch systems

BATCH REACTORS with VARIABLE VOLUME

- Equation of state:

$$PV = ZN_T RT$$

P=total pressure (atm)
V=volume
Z=compressibility factor
N_T=total number of moles
R=gas constant=0.08206 dm^3.atm/mol.K
T=temperature (K)

- At t=0:

$$P_0 V_0 = Z_0 N_{T0} R T_0$$

$$\boxed{\frac{N_T}{N_{T0}} = 1 + \varepsilon X}$$

$$\boxed{\varepsilon = \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1\right)\frac{N_{A0}}{N_{T0}} = y_{A0}\delta}$$

- At any time t, the volume of gas (Z_0=Z):

$$V = V_0\left(\frac{P_0}{P}\right)\frac{T}{T_0}\left(\frac{Z}{Z_0}\right)\frac{N_T}{N_{T0}}$$

$$\boxed{V = V_0\left(\frac{P_0}{P}\right)(1+\varepsilon X)\frac{T}{T_0}}$$

FLOW REACTORS with VARIABLE VOLUMETRIC FLOW RATE

- ☐ Total concentration found from the gas law:

$$C_T = \frac{F_T}{v} = \frac{P}{ZRT}$$

- ☐ At t=0:

$$C_{T0} = \frac{F_{T0}}{v_0} = \frac{P_0}{Z_0RT_0}$$

- ☐ At any time t, the volume of gas (Z_0=Z):

$$v = v_0\left(\frac{F_T}{F_{T0}}\right)\frac{P_0}{P}\left(\frac{T}{T_0}\right)$$

$$\boxed{v = v_0(1+\varepsilon X)\frac{P_0}{P}\left(\frac{T}{T_0}\right)}$$

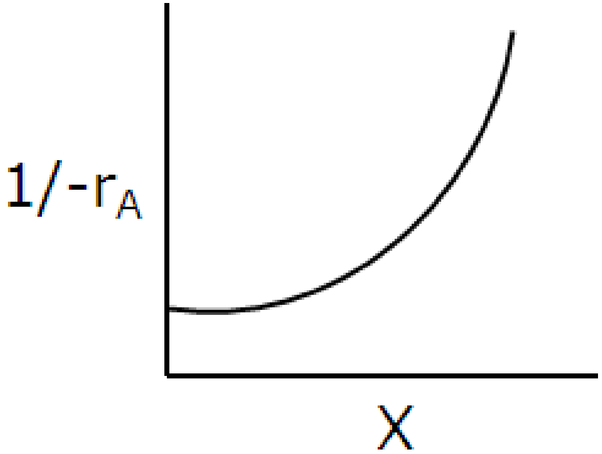
CONCENTRATION IN TERMS OF THE CONVERSION X

$$C_j = \frac{F_j}{v} \quad , \quad F_j = F_{A0}(\Theta_j + v_j X) \quad , \quad v = v_0(1+\varepsilon X)\frac{P_0}{P}\left(\frac{T}{T_0}\right)$$

$$C_j = \frac{F_{A0}(\Theta_j + v_j X)}{v_0\left[(1+\varepsilon X)\frac{P_0}{P}\frac{T}{T_0}\right]}$$

$$\boxed{C_j = \frac{C_{A0}(\Theta_j + v_j X)}{(1+\varepsilon X)}\left(\frac{P}{P_0}\right)\frac{T_0}{T}}$$

We now have **$-r_A$ as a function of X** and can use the methods in Chapter 2 to design reactors.



Expressing concentration in terms other than conversion

- Membrane reactors and gas-multiple reaction:

$$\boxed{C_j = C_{T0}\left(\frac{F_j}{F_T}\right)\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right)}$$

For j = A,B,C,D,I

$$F_T = F_A + F_B + F_C + F_D + F_I$$

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