

Chapter 4

Stoichiometry

Notes on
Elements of chemical reaction
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If the rate law depends on more than one species, we must relate the concentrations of the different species to each other.

⇒ Stoichiometric table.

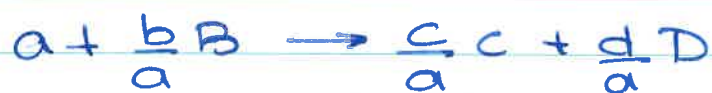
- Represents stoichiometric relationships between reacting molecules for a single reaction.
- How many molecules of one species will be formed during a chemical reaction given a number of molecules of another species disappear.

Lets consider general reaction
$$aA + bB \rightarrow cC + dD$$

relative rates

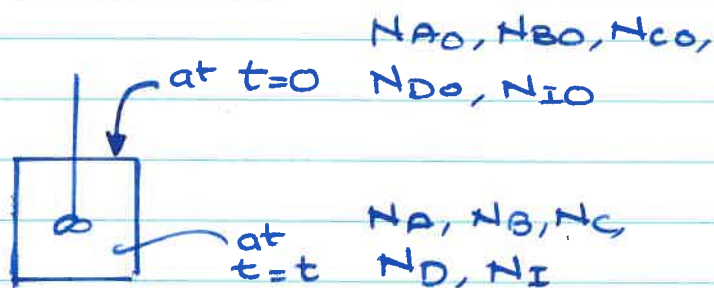
$$\frac{-r_A}{a} = -\frac{r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d}$$

Basis of calculation : species A



↳ everything on basis of per mole of A.

Batch systems



- primarily used for production of specialty chemicals
- to obtain rate data for determination of rate law and its parameters.

N_{A0} : No. of moles of A initially present

X : conversion at time t

$X \cdot N_{A0}$: moles of A consumed at time t

N_A : moles of A in system at time t
 $= N_{A0} - N_{A0}X = N_{A0}(1-X)$

stoichiometric table

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	N_{I0}	-	$N_I = N_{I0}$
Total	N_{T0}		$N_T = N_{T0} + \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1\right)N_{A0}X$

No. of mols of B remaining at t

$$\text{mol B reacted} = \frac{\text{mol B reacted}}{\text{mol A reacted}} \times \text{mol A reacted}$$

$$= \frac{b}{a} N_{A0} X$$

$$N_B = N_{B0} - \frac{b}{a} N_{A0} X$$

$$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$$

change in total number of moles
per mol A reacted.

Total number of moles

$$N_T = N_{T0} + \delta N_{A0} X$$

Now,

- reaction rate usually depends on the concentration of the reacting species raised to some power.
- To determine reaction rate as a function of X , concentration as a function of X ($c_j = h_j(X)$) is read.

Equations for batch concentrations

conc. = no. of moles / unit volume

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

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

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

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

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

Let $V = V_0$ (constant)

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

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

Let us define θ_i to factor out N_{A0} in each of the concentration equations

$$\boxed{\theta_i = \frac{N_{i0}}{N_{A0}} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{B0}}}$$

$$C_B = \frac{N_{A0} [N_{B0}/N_{A0} - (b/a)X]}{V_0}$$

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

$$\theta_B = \frac{C_{B0}}{C_{A0}}$$

For equimolar feed $\theta_B = 0$

For stoichiometric feed $\theta_B = \frac{b}{a}$

Similarly,

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

$$\theta_c = \frac{N_{c0}}{N_{A0}}$$

and

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

$$\theta_D = \frac{C_{D0}}{C_{A0}}$$

⇒ These give us equations for conc. for constant volume batch reactor.

↳ we can obtain $-r_A = f(x)$

→ For liquid phase reactions taking place in solution, the solvent dominates the situation.

↳ densities do not change during course of reaction

(except for polymerization processes)
↳ solution is concentrated / pure components are used.

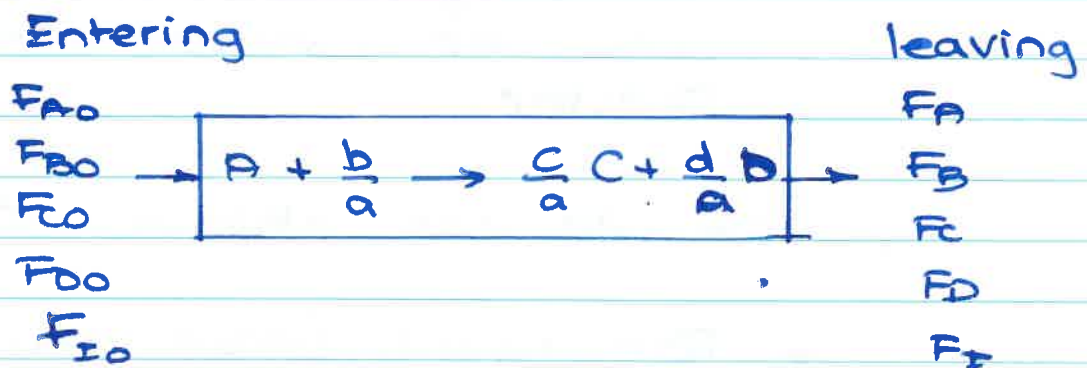
$$-r_A = k C_A C_B$$

$$-r_A = k \cdot C_{A0} (1-x) \cdot C_{A0} (\theta_B - \frac{b}{a} x)$$

$$-r_A = k C_{A0}^2 (1-x) (\theta_B - \frac{b}{a} x)$$

$$-r_A = f(x)$$

Flow systems



→ Form of stoichiometric table is virtually identical to batch systems

→ Replace N_{j0} by F_{j0} and N_j by F_j

Stoichiometric table for flow system

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}	$-\frac{b}{a}F_{A0}X$	$F_B = F_{A0}\left[\Theta_B - \frac{b}{a}X\right]$
C	F_{C0}	$+\frac{c}{a}F_{A0}X$	$F_C = F_{A0}\left[\Theta_C + \frac{c}{a}X\right]$
D	F_{D0}	$+\frac{d}{a}F_{A0}X$	$F_D = F_{A0}\left[\Theta_D + \frac{d}{a}X\right]$
I	F_{I0}	-	$F_I = F_{A0}\Theta_i$
Total	F_{T0}		$F_T = F_{T0} + \delta F_{A0}X$

$$F_{i0} = \Theta_i F_{A0}$$

$$\Theta_i = \frac{F_{i0}}{F_{A0}}$$

$$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$$

$$\Theta_i = \frac{F_{i0}}{F_{A0}} = \frac{C_{i0} V_0}{C_{A0} V_0}$$

Equations for concentration in flow system

$$C_A = \frac{F_A}{V} \quad \frac{\text{mol/time}}{\text{m}^3/\text{time}} = \frac{\text{mol}}{\text{time}}$$

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

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

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

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

Liquid phase concentration

for liquids $V = V_0$... no phase change.

↳ Negligible change in liq. volume

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

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

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

$$\Downarrow$$

$$-r_A = f(X)$$

} using these
rate can
be expressed in
terms of
X

For gas phase reactions

- Volumetric flow rate changes during the course of reaction
 - changes in total number of moles
 - changes in pressure and temp.

Gas phase concentrations

- Variable flow rate :-
gas phase reactions that do not have equal no. of product and reactant moles



- 4 mol. reactants give 2 mol. products
- equal no. of mols occupy equal volume at same p & T

stoichiometric tables

- No assumptions made re: volume
 - The tables are exactly same for constant volume (constant density) and variable volume (variable density systems)
- ⇒ Only for concentration expressed in terms of conversion - density / volume comes into play.

Flow reactors with variable volumetric flow rate

→ we will use relationships for total concentration.

$$C_T = \frac{F_T}{V} \quad \dots \frac{\text{total molar flow rate}}{\text{volumetric flow rate}}$$

for gases:

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

Z : compressibility factor

= 1 for ideal gas

at the entrance of the reactor

$$C_{T0} = \frac{P_0}{Z_0 R T_0}$$

($Z = Z_0$)
↑

assuming negligible change in Z

$$\boxed{V = V_0 \left(\frac{F_T}{F_{T0}} \right) \left(\frac{P_0}{P} \right) \left(\frac{T}{T_0} \right)}$$

We can now express C_j in terms of F , P , and T

$$C_j = \frac{F_j}{V} = \frac{F_j}{V_0 \left(\frac{F_T}{F_{T0}} \right) \left(\frac{P_0}{P} \right) \left(\frac{T}{T_0} \right)}$$
$$= \frac{F_{T0}}{V_0} \frac{F_j}{F_T} \frac{P_0}{P} \frac{T}{T_0}$$

$$\boxed{C_j = C_{T0} \frac{F_j}{F_T} \frac{P_0}{P} \frac{T}{T_0}} \quad \dots \quad \text{Use this for gas phase reactions}$$

$$F_T = \sum_{j=1}^N F_j = F_A + F_B + F_C + F_D + F_I$$

F_j : Found by solving mole balance equations.

Concentration in terms of conversion

$$F_T = F_{T0} + F_{A0} \delta X$$

dividing by F_{T0}

$$\frac{F_T}{F_{T0}} = 1 + \frac{F_{A0}}{F_{T0}} \delta X$$

$$= 1 + \underbrace{y_{A0} \delta X}_\epsilon$$

y_{A0} : mol fr.
at inlet

$$\frac{F_T}{F_{T0}} = 1 + \epsilon X$$

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

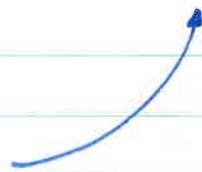
$$\boxed{\epsilon = y_{A0} \delta}$$

ϵ = change in total no. of moles
for complete conversion

$$\epsilon = \frac{\text{total moles fed}}{\text{total moles fed}}$$

at $X = 1$

$$\epsilon = \frac{F_T - F_{T0}}{F_{T0}}$$



Equation for vol. flow rate

$$V = V_0 (1 + \epsilon X) \frac{P_0}{P} \frac{T}{T_0}$$

Conc. of species j in flow system

$$C_j = \frac{F_j}{V}$$

Molar flow rate

$$\Rightarrow F_j = F_{j0} + \nu_j F_{A0} X$$

$$F_j = F_{A0} (\theta_j + \nu_j X)$$

$\nu_j \Rightarrow$ stoichiometric coefficient



$$\nu_A = -1$$

$$\nu_B = -\frac{b}{a}$$

$$\nu_C = \frac{c}{a} \dots \text{+ve for reactant}$$

$$\nu_D = \frac{d}{a}$$

+ve for product

$$\theta_j = \frac{F_{j0}}{F_{A0}}$$

$$C_j = \frac{F_{A0} (\theta_j - \nu_j X)}{v_0 (1 + \epsilon X) \left(\frac{P_0}{P} \right) \left(\frac{T}{T_0} \right)}$$

rearranging .

$$C_j = \frac{C_{A0} (\theta_j - \nu_j X)}{(1 + \epsilon X)} \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right)$$

$$C_j = h_j(X)$$

$$\Downarrow$$

$$-r_A = g(X)$$

Concentrations in a variable volume gas flow system

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

$$= \frac{F_{A0} (1 - X)}{v_0 (1 + \epsilon X)} \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right)$$

$$C_A = C_{A0} \frac{(1 - X)}{(1 + \epsilon X)} \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right)$$

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

$$= \frac{F_{A0} (\theta_B - \frac{b}{a} X)}{J_0 (1 + \epsilon X)} \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right)$$

$$C_B = C_{A0} \left(\frac{\theta_B - b/a X}{1 + \epsilon X} \right) \frac{P}{P_0} \frac{T_0}{T}$$

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

$$= \frac{F_{A0} (\theta_C + c/a X)}{J_0 (1 + \epsilon X)} \frac{P}{P_0} \frac{T_0}{T}$$

$$C_C = C_{A0} \left(\frac{\theta_C + c/a X}{1 + \epsilon X} \right) \frac{P}{P_0} \frac{T_0}{T}$$

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

$$= \frac{F_{A0} (\theta_D + d/a X)}{J_0 (1 + \epsilon X)} \frac{P}{P_0} \frac{T_0}{T}$$

$$C_D = C_{A0} \left(\frac{\theta_D + d/a X}{1 + \epsilon X} \right) \frac{P}{P_0} \frac{T_0}{T}$$

$$C_I = \frac{F_I}{J} = \frac{F_{A0} \Theta_I}{J}$$

$$= \frac{F_{A0} \Theta_I}{J_0 (1 + EX)} \frac{P}{P_0} \frac{T_0}{T}$$

$$C_I = C_{A0} \left(\frac{\Theta_I}{1 - EX} \right) \frac{P}{P_0} \frac{T_0}{T}$$