LECTURE ONE: Overview of Reaction Engineering & challenges

This lecture covers: reaction stoichiometry, lumped stoichiometries in complex systems such as bioconversions and cell growth (yields), extent of reaction, independence of reactions, measures of concentrations, single reactions and reaction networks, and bioreaction pathways.

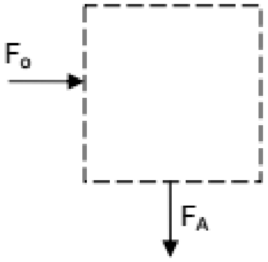


Figure 1. A schematic of a control volume with inflow of F_o and outflow of species A, F_A.

F = total molar flow rate (moles/sec)
F_o = total molar flow rate entering control volume
F_A = molar flow rate of species A
F_{Ao} = molar flow rate of species A entering control volume
N_A = Moles of species A

Mass balance: (change in "A" inside control volume)= (amount of "A" that entered)-(amount of "A" that exited) + (amount of "A" created inside the control volume) – (amount of "A" destroyed inside the control volume)

$$\frac{dN_A}{dt} = F_{Ao} - F_A + G_A$$

$$G_A [=] \frac{\text{moles}}{\text{sec}}$$

If homogeneous, $G_A = r_A V$

else, $G_A = \int r_A dV$

where V is volume and r_A is the rate of A created or destroyed (moles/sec/volume).

The mass balance can also be written as:

$$\frac{d\rho_A}{dt} = \overbrace{v\nabla\rho_A}^{\text{convection}} + \overbrace{D\nabla^2}^{\text{diffusion}}\rho_A + r_A$$

where v is velocity, D is the diffusion coefficient, and ρ_A is the molar density of A (moles/volume).

Example:

A+B→C+D

$$r_A = -k[A][B],\quad r_C = +k[A][B],\quad [A][=]\frac{\text{mole A}}{\text{liter}}$$

where k is a measurable rate constant that changes with respect to T and P but remains constant with respect to changing concentrations.

If $r_1 = k[A][B]$, then

$$r_A = \overbrace{\nu_{A,1}}^{=-1} r_1$$

where $\nu_{A,1}$ is the stoichiometric coefficient for species A in reaction 1. Likewise,

$$r_C = \overbrace{\nu_{C,1}}^{=+1} r_1$$

If there are n reactions involving species "A" then

$$r_A = \sum_{i=1}^{n} \nu_{A,i} r_i$$

$$G_A(t) = \iiint_{Vol.} \underbrace{r_A(x,y,z,t)}_{-k(T(x,y,z,t))[A(x,y,z,t)][B(x,y,z,t)]} dxdydz$$

$$\frac{d\overbrace{[A]}^{N_A/V}}{dt} = -k[A][B] \rightarrow \text{*only true if there are no flows!}$$

$$\frac{dN_A}{dt} = \int r_A dV \approx r_A V,\ \text{assume } r_A \text{ is true throughout volume}$$

If the system is homogeneous and there are no flows:

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

Therefore:

$$\frac{d}{dt}\left(\frac{N_A}{V}\right) = r_A \quad \text{iff homogeneous, no flow, constant V}$$

Extent of Reaction

$$\xi\,[=]\,\text{moles, extent of rxn.}$$

$$\dot{\xi}\,[=]\,\frac{\text{moles}}{\text{sec}},\ \text{rate of extent of rxn.}$$

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

$N_A = N_{A,\text{initially}} - \xi$, if there is one reaction involving A

$N_A = N_{A,\text{initially}} - \sum_n \nu_{A,n}\xi_n$, if there are several reactions

$\dot{\xi}_n = \int r_n dV$, n is the reaction number

$G_A = \int r_A dV$, A is the species

Conversion

$A + B \rightarrow C + D$

$X_A = \frac{N_{A,\text{initial}} - N_A}{N_{A,\text{initial}}}$ (dimensionless)

$X_C = \frac{N_C}{N_{A,\text{initial}}}$ (≈ 1 since rxn is 1:1)

$\begin{pmatrix} A + B \rightarrow C + D \\ A \rightarrow U \end{pmatrix}$ Selectivity is good if $A \rightarrow C$, bad if $A \rightarrow U$.

*May worsen as rxn. goes on ($A \rightarrow C$ slows, $A \rightarrow U$ keeps going)

The Reaction Rate & Reaction Mechanisms

The lecture covers: Definitions in terms of reacting compounds and reaction extent, rate laws, Arrhenius equation, elementary, reversible, non-elementary, catalytic reactions.

From previous lecture:

$$\frac{dN_A}{dt} = F_{Ao} - F_A + G_A,\ G_A = \int r_A dV$$

Example:

$A + B \rightarrow 2C$

*Reactions are reversible (often will neglect reverse)

$$X_A = \frac{N_{Ao} - N_A}{N_{Ao}} \qquad X_A = \frac{F_{Ao} - F_A}{F_{Ao}} \qquad X_C = \frac{F_C}{2F_{Ao}}$$

Figure 1. A reactor with reactants A and B constantly flowing in and product C and unused reactants A and B flowing out.

$$F_{Ao} = \frac{\text{moles A flowing in}}{\text{sec}} = [A]_{input} \underbrace{v_{in}}_{\frac{\text{liters}}{\text{sec}}} = [A]_o v_o$$

$$F_A = \frac{\text{moles A flowing out}}{\text{sec}} = [A]_{output} v_{out}$$

$$X = 1 - \frac{[A]_{output} v_{out}}{[A]_{in} v_{in}}$$

Closed reactor, const. V

Detailed balance- all steps in equilibrium, total system

$$\frac{d[A]}{dt} = r_A = -k[A][B]$$

$$K_{eq} = \frac{[C]^2}{[A][B]}$$

when $[A][B] = \frac{[C]^2}{K_{eq}}$ the rxn. stops -> $r_A=0$

$$r_A = -k\left([A][B] - \frac{[C]^2}{K_{eq}}\right), \quad k_{rev} = \frac{k_{for}}{K_{eq}}, \quad \text{forward-reverse in one expression}$$

↖ same! ↗

Catalysis

$$r_{A,forward} = k_{cat}\left[\text{catalyst}\right]\left[A\right]\ \underbrace{f\left(\left[B\right]\right)}_{\substack{\text{may be included}\\ \text{i.e. when B is}\\ \text{very small}}}$$

Rate limiting step determines the kinetics (slow step). The kinetics are insensitive to [B] because B is not part of this slow step.

$$r_{A,reverse} = r_{A,forward}\frac{\left[C\right]^2}{K_{eq}\left[A\right]\left[B\right]}$$

$$r_{A,net} = -k_{cat}\left[\text{catalyst}\right]\left(\left[A\right]-\frac{\left[C\right]^2}{K_{eq}\left[A\right]\left[B\right]}\right)$$

Standard state

$$K_{eq} = e^{-\Delta G/RT} \qquad \Delta G = \Delta G^{o}_{f,products} - \Delta G^{o}_{f,reactants}$$

$$A \rightarrow B + C$$

$$K_{\cancel{eq}} = \frac{\left[B\right]\left[C\right]}{\left[A\right]}\left[=\right]\frac{\text{moles}}{\text{liter}}$$

$$\rightarrow K_C$$

$$\frac{\overbrace{p_B p_C}^{\text{Partial Pressures}}}{p_A P^o} = K_{eq} = \frac{\left[B\right]\left[C\right]}{\left[A\right]\frac{P^o}{RT}}$$

$$\text{Ideal Gas: } pV = nRT \Rightarrow \frac{n}{V} = \frac{P}{RT}$$

P^o is the standard state pressure (1 atm), this makes the units cancel. Using partial pressures is accurate within 10%, more error with liquids.

Stoichiometric coefficient

$$N_A = N_{A,initial} + \sum \nu_{A,i}\xi_i$$

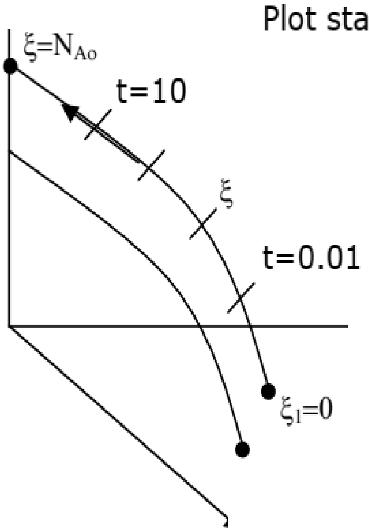
Extent of rxn.

$$N_C = N_{C,initial} + \sum_{i=1}^{N_{rxn}} \nu_{C,i}\xi_i$$

$$\overbrace{\underline{N}}^{\text{column vector}} = \overbrace{\underline{N}_o}^{\text{column vector}} + \overbrace{\underline{\underline{\nu}}}^{\text{matrix}} \cdot \overbrace{\underline{\xi}}^{\text{vector}}$$

→ Do columns span space? Often no, limits on what is achievable.

Reaction trajectory-
Plot state of system



$$\frac{d}{dt}\left(\underline{N}\right) = \underline{F}\left(\underline{N}\right)$$

Figure 2. A plot of the reaction trajectory. ξ is the extent of reaction.

Conservation Laws

Conserve atoms

$$2\mathrm{CH_4} + \mathrm{O_2} \rightarrow \mathrm{C_2H_4} + 2\mathrm{H_2O}$$

$$\underbrace{C_A}_{\text{constant}}\ \underbrace{N_A}_{\text{moles}} + C_B N_B + C_C N_C = \text{const.}$$

$$\underline{C}: 1 \times N_{CH_4} + 2 \times N_{C_2H_4} = N_{C,initial}$$

$$\underline{H}: 4 \times N_{CH_4} + 4 \times N_{C_2H_4} + 2N_{H_2O} = N_{H,initial}$$