10.37 Chemical and Biological Reaction Engineering, Spring 2007
Prof. William H. Green

# Lecture 2: 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 -> $r_A = 0$

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

↖ 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

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

$$A \rightarrow B + C$$

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

$$\rightarrow K_C$$

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

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

$P^o$ 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.

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

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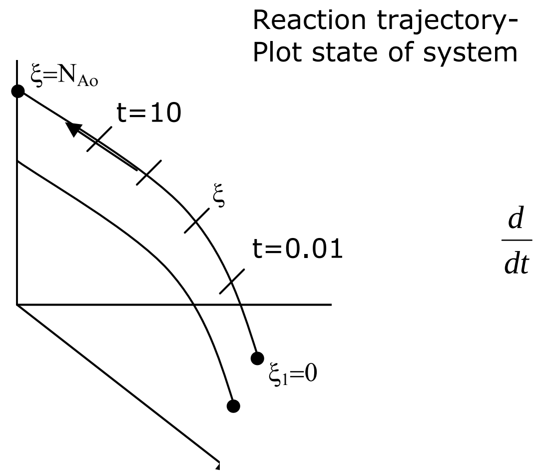
$$\overbrace{\underline{N}}^{\text{column vector}} = \overbrace{\underline{N}_o}^{\text{column vector}} + \overbrace{\underline{\underline{\nu}}}^{\text{matrix}} \bullet \overbrace{\underline{\xi}}^{\text{vector}}$$

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



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

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

## *Conservation Laws*

Conserve atoms

$$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O$$

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

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

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

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