

PHEN 612

SPRING 2008

WEEK 3

LAURENT SIMON

Chapter 6*

Types of reactions: series, parallel, complex, and independent

1) Parallel (or competing) reactions: $A \begin{matrix} \xrightarrow{k_1} B \\ \xrightarrow{k_2} C \end{matrix}$

2) Series (or consecutive reactions): $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

3) Complex reactions: parallel + series reactions

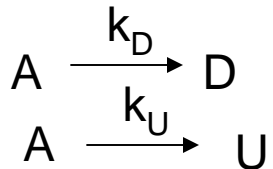
4) Independent reactions: $A \rightarrow B+C$



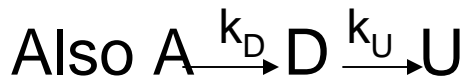
*Elements of Chemical Reaction Engineering – Fourth Edition
by H. Scott Fogler, Prentice Hall, 2006

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5) Desired or undesired reactions



D is the desired product; U is undesired.



Instantaneous selectivity of D with respect to U

$$S_{D/U} = r_D/r_U = (\text{rate of formation of D})/(\text{rate of formation of U})$$

Overall selectivity = F_D/F_U = (exit molar flow rate of desired product)/(exit molar flow rate of undesired product)

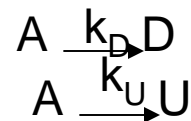
For batch systems: Overall selectivity = N_D/N_U

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- 6) Instantaneous reaction yield: $Y_D = r_D / -r_A$
Overall reaction yield (batch) = $N_D / (N_{A0} - N_A)$
Overall reaction yield (flow) = $F_D / (F_{A0} - F_A)$

6.2 Parallel Reactions

Undesired products (U) can be minimized through selection of the reactor types and conditions.



The rate laws: $r_D = k_D C_A^{\alpha 1}$; $r_U = k_U C_A^{\alpha 2}$ $-r_A = r_D + r_U = k_D C_A^{\alpha 1} + k_U C_A^{\alpha 2}$

$\alpha 1$ and $\alpha 2$ are positive reaction orders

Goal: we want r_D to be high with respect to r_U

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- Selectivity parameter: $S_{D/U} = r_D / r_U = (k_D / k_U) C_A^{\alpha_1 - \alpha_2}$

6.2.1 Maximizing the desired product for one reactant

Maximize $S_{D/U}$

Case 1: $\alpha_1 > \alpha_2$ $S_{D/U} = (k_D / k_U) C_A^a$

Let $a = \alpha_1 - \alpha_2$,

For gas phase: high pressure; for liquid phase: minimum diluent

-- A batch or plug flow reactor should be used

--- In a CSTR, the concentration of the reactant is at its lowest value

Case 2: $\alpha_2 > \alpha_1$ $S_{D/U} = (k_D / k_U) C_A^b$

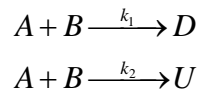
Let $b = \alpha_2 - \alpha_1$,

$S_{D/U}$ is large if A is kept as low as possible

--- A CSTR should be used; dilution of feed

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6.2.2 Reactor Selection and Operating Conditions



$$r_D = k_1 C_A^{\alpha_1} C_B^{\beta_1}; \quad r_U = k_2 C_A^{\alpha_2} C_B^{\beta_2}$$

$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_1}{k_2} C_A^{\alpha_1 - \alpha_2} C_B^{\beta_1 - \beta_2}$$

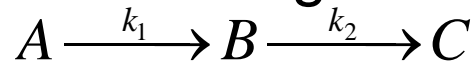
Rate selectivity parameter:

- Different reactors and schemes are shown in Fig. 6.3
- Tubular or batch if we need to keep conc. high. CSTR if we need to keep conc. Low.

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6.3 Maximizing the desired product in series reactions

To optimize B, one need to pay attention to how fast both B and C are being formed.



6.4 Algorithm for solution of complex reactions

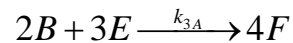
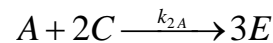
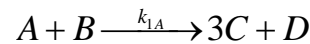
Mathematical software should be used to solve most of these problems

6.4.1 Mole balances: Mole balances for multiple reactions are summarized in Table 6-1, page 327.

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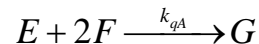
6.4.2 Net Rates of Reaction

We need to write the net rate of formation for each species. We have q reactions:



..

...



$$r_A = r_{1A} + r_{2A} + r_{3A} + \dots + r_{qA} = \sum_{i=1}^q r_{iA}$$

$$r_B = r_{1B} + r_{2B} + r_{3B} + \dots + r_{qB} = \sum_{i=1}^q r_{iB}$$

$$r_j = \sum_{i=1}^q r_{ij}$$

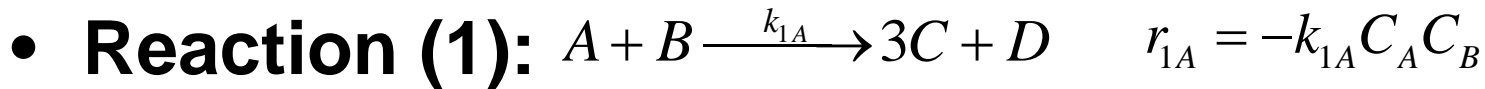
6.4.2-B Rate laws $r_{ij} = k_{ij} f_i(C_A, C_B, \dots, C_j, \dots, C_n)$

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6.4.2-C Stoichiometry: Relative Rates of Reaction



$$(-r_A/a) = (-r_B/b) = (r_C/c) = (r_D/d)$$



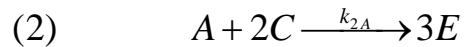
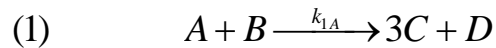
$$(-r_{1A}/1) = (-r_{1B}/1) = (r_{1C}/3) = (r_{1D}/1)$$

As a result: $r_{1B} = -k_{1A} C_A C_B$

The same calculations can be done for reactions 2 and 3.

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6.4.2-D Combine individual rate laws to find the net rate



$$r_A = r_{1A} + r_{2A} = -k_{1A} C_A C_B - k_{2A} C_A C_C^2$$

$$r_B = r_{1B} = -k_{1A} C_A C_B$$

$$r_C = r_{1C} + r_{2C} = 3k_{1A} C_A C_B - 2k_{2A} C_A C_C^2$$

$$r_D = r_{1D} = k_{1A} C_A C_B$$

$$r_E = r_{2E} = 3k_{2A} C_A C_C^2$$

6.4.3 For gas phase, we have to take changes in volumetric flow rate (v) into account and use appropriate equations.

Chapter 7*

Reaction mechanisms, pathways, bioreactions, and bioreactors

- An active intermediate (A^*) is a high-energy molecule that reacts virtually as fast as it is formed: $A+M \rightarrow A^*+M$

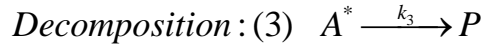
7.1.1. Pseudo-steady state hypothesis:

$r_{A^*}=0$: Net rate of formation is zero

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Ex:



Rate of product formation: $r_p = k_3 C_{A^*}$

$$r_{1A^*} = k_1 C_A C_M; \quad r_{2A^*} = -k_2 C_{A^*} C_M; \quad r_{3A^*} = -k_3 C_{A^*}$$

$$r_{A^*} = r_{1A^*} + r_{2A^*} + r_{3A^*};$$

$$r_{A^*} = k_1 C_A C_M - k_2 C_{A^*} C_M - k_3 C_{A^*} = 0;$$

$$C_{A^*} = \frac{k_1 C_A C_M}{k_2 C_M + k_3};$$

$$r_p = \frac{k_1 k_3 C_A C_M}{k_2 C_M + k_3} = -r_A$$

Since C_M is constant (i.e., inert)

$$r_p = k C_A$$

with

$$k = \frac{k_1 k_3 C_M}{k_2 C_M + k_3}$$

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Chain reactions

- 1) Initiation: formation of an active intermediate
- 2) Propagation or chain transfer: interaction of an active intermediate with the reactant or product to produce another active intermediate
- 3) Termination: deactivation of the active intermediate to form products

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Enzyme: high-molecular-weight protein that accelerates a biological reaction:



7.2.1 Enzyme-substrate complex

Two models for enzyme-substrate interactions:

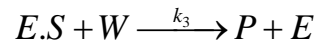
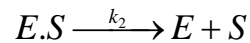
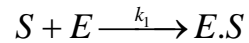
- 1) Lock and key model: topographical, structural compatibility between enzyme and substrate
- 2) Induced model: enzyme and substrate molecules are distorted

7.2.2 Mechanisms

- 1) Complex formation
- 2) Decomposition of complex
- 3) Product formation

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Ex:



$$r_{1S} = -k_1(E)(S); \quad r_{2S} = -k_2(E.S); \quad r_{3P} = k_3(E.S)(W);$$

$$-r_s = k_1(E)(S) - k_2(E.S);$$

$$r_{E.S} = k_1(E)(S) - k_2(E.S) - k_3(E.S)(W);$$

$$PSSH: \quad r_{E.S} = 0$$

$$-r_s = \frac{k_1 k_3 (E)(S)(W)}{k_2 + k_3 W}$$

but $E_t = E + E.S$

As a result:

$$-r_s = \frac{k_1 k_3 (W)(E_t)(S)}{k_1 (S) + k_2 + k_3 W}$$

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7.2.3 Michaelis-Menten Equation

$$k_{cat} = k_3 (W)$$

Since water is in excess and $K_M = \frac{k_{cat} + k_2}{k_1}$

$$-r_S = \frac{k_{cat} (E_t)(S)}{(S) + k_M}$$

called Michaelis-Menten equation

K_{cat} (1/time) is the Turnover number = number of substrate molecules converted to product in a given time on a single-enzyme molecule when the enzyme is saturated with the substrate

K_M (mole/volume): Michaelis constant = affinity constant = measure of the attraction of the enzyme for the substrate.

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- $V_{\max} = k_{\text{cat}} [E_t]$

Maximum rate of reaction for a given total enzyme concentration

$$-r_s = \frac{V_{\max} (S)}{k_M + S}$$

- Evaluation of Michaelis-Menten parameters:

V_{\max} and K_M : *Lineweaver – Burk plot* : $\frac{1}{-r_s} = \frac{1}{V_{\max}} + \frac{K_M}{V_{\max}} \left(\frac{1}{(S)} \right)$;

Hanes – Woolf plot : $\frac{(S)}{-r_s} = \frac{K_M}{V_{\max}} + \frac{1}{V_{\max}} (S)$;

Eadie – Hofstee plot : $-r_s = V_{\max} - K_M \left(\frac{-r_s}{(S)} \right)$

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- The product-enzyme complex:



- Briggs-Haldane rate law:
$$-r_s = \frac{V_{\max} \left(C_S - \frac{C_P}{K_C} \right)}{C_S + K_{\max} + K_P C_P}$$

- **7.2.4 Batch reactor calculations for enzyme reactions**

$$- \frac{dN_S}{dt} = -r_s V; \quad - \frac{dC_S}{dt} = -r_s; \quad -r_s = \frac{V_{\max} C_S}{K_M + C_S}$$

$$t = \int_{C_S}^{C_{S0}} \frac{dC_S}{-r_s}; \quad t = \frac{K_M}{V_{\max}} \ln \left(\frac{C_{S0}}{C_S} \right) + \frac{C_{S0} - C_S}{V_{\max}};$$

$$t = \frac{K_M}{V_{\max}} \ln \left(\frac{1}{1-X} \right) + \frac{C_{S0} X}{V_{\max}};$$

$$\frac{1}{t} \ln \left(\frac{1}{1-X} \right) = \frac{V_{\max}}{K_M} - \frac{C_{S0} X}{K_M t}$$

- Effect of temperature is the result of arrhenius equation and enzyme de-activation