Chemical Reactor Design

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第3章

Rate Laws and Stoichiometry

Chemical Reactor Design

化學反應裝置設計

Objectives

After completing Chapter 3, reader will be able to:

❶ Write a rate law and define reaction order and activation energy.

❷ Set up a stoichiometric table for both batch and flow systems and express concentration as a function of conversion.

❸ Calculate the equilibrium conversion for both gas and liquid phase reactions.

❹ Write the combined mole balance and rate law in measures other than conversion.

Reactor Size

Design Equations

Batch $$t = N_{A0}\int_0^X \frac{dX}{-r_A V}$$

CSTR $$V = \frac{F_{A0}X}{-r_A}$$

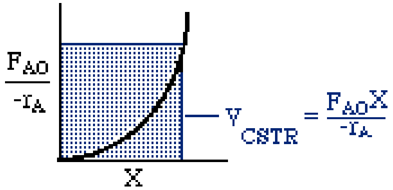
PFR $$V = F_{A0}\int_0^X \frac{dX}{-r_A}$$

PBR $$W = F_{A0}\int_0^X \frac{dX}{-r'_A}$$

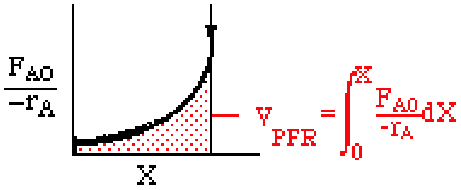
Graphical method

Levenspiel plot

CSTR



PFR



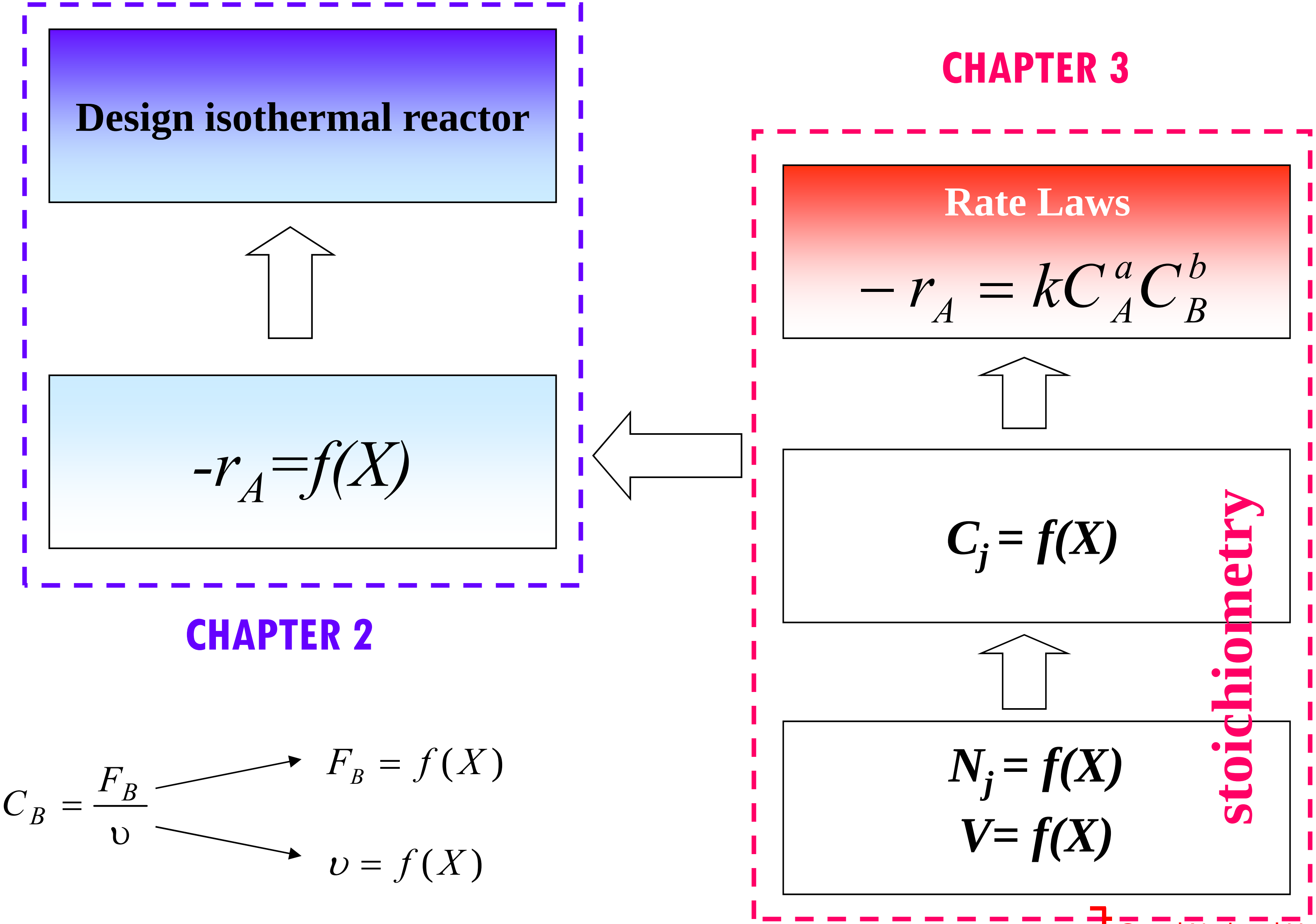
For $\frac{F_{A0}}{-r_A}$ vs. X, the volume of a CSTR and the volume of a PFR can be represented as the shaded areas in the Levenspiel plots.

PFR $$V = F_{A0}\int_0^X \frac{dX}{\boxed{-r_A}}$$

$$-r_A = f(X)$$

If we know the molar flow rate to the reactor and the reaction rate as a function of conversion, then we can calculate the reactor volume necessary to achieve a specific conversion.

Design Isothermal Reactor



CHAPTER 3

Design isothermal reactor

$-r_A = f(X)$

CHAPTER 2

Rate Laws

$$-r_A = kC_A^a C_B^b$$

$C_j = f(X)$

$N_j = f(X)$

$V = f(X)$

stoichiometry

$$C_B = \frac{F_B}{\upsilon} \rightarrow F_B = f(X), \quad \upsilon = f(X)$$

Part 1

Rate Laws

3.1.1 Relative Rates of Reactions

If the rate law depends on more than one species, we **MUST** relate the concentrations of different species to each other. A stoichiometric table presents the stoichiometric relationships between reacting molecules for a single reaction.

$$aA + bB \rightleftharpoons cC + dD \qquad (2\text{-}1)$$

In formulating our stoichiometric table, we shall take species A as our basis of calculation (i.e., limiting reactant) and then divide through by the stoichiometric coefficient of A. In order to put everything on a basis of "per mole of A."

$$A + \frac{b}{a}B \longrightarrow \frac{c}{a}C + \frac{d}{a}D \qquad (2\text{-}2)$$

The relationship can be expressed directly from the stoichiometry of the reaction.

$$\boxed{\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d}} \qquad (3\text{-}1)$$

3.2 Reaction Order and Rate Law

Let take A as the basis of calculation

a species A is one of the reactants that is disappearing as a result of the reaction. ***The limiting reactant is usually chosen as our basis for calculation.***

The rate of disappearance of A, $-r_A$, depends on temperature and concentration and it can be written as the product of the reaction constant k and

$$\boxed{-r_A(T,C) = k_A(T) \times f(C_A, C_B \ldots)}$$

Rate raw (Kinetic expression) : the algebraic equation that relates $-r_A$ to the species concentration

3.2.1 Power Law Models and Elementary Rate Laws

The dependence of the reaction rate $-r_A$ on the concentration of the species is almost without exception determined by experimental observation.

The **order of a reaction** refers to the powers to which the concentrations are raised in the kinetic rate law.

$$\boxed{-r_A = k_A C_A^{\alpha} C_B^{\beta}} \qquad (3\text{-}3)$$

α order with respect to reactant A
β order with respect to reactant B
n (=α+β) : the overall order of the reaction

Unit of Specific Reaction Rate

The unit of the specific reaction rate, k_A, ***vary*** with the order of the reaction.

A → products

$$k = \frac{(\text{Concentration})^{1-n}}{\text{Time}}$$

$$Zero\text{-}order: \quad -r_A = k_A \qquad \{k\} = \frac{mol}{(dm)^3 \cdot s} \tag{3-4}$$

$$First\text{-}order: \quad -r_A = k_A C_A \qquad \{k\} = \frac{1}{s} \tag{3-5}$$

$$Second\text{-}order: \quad -r_A = k_A C_A^2 \qquad \{k\} = \frac{(dm)^3}{mol \cdot s} \tag{3-6}$$

$$Third\text{-}order: \quad -r_A = k_A C_A^3 \qquad \{k\} = \frac{(dm^3/mol)^2}{s} \tag{3-7}$$

Elementary and Non-elementary Reaction

Kinetic *rate raw*

“Elementary reaction”

$\text{O}\bullet + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O}\bullet + \text{OH}\bullet$

$$\boxed{-r_{\text{O}\bullet} = k\, C_{\text{O}\bullet}\, C_{\text{CH3OH}}}$$

1st order w.r.t. atomic oxygen

1st order w.r.t. methanol

overall is 2nd order reaction

Non-elementary reaction

$\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$

$$\boxed{-r_{CO} = kC_{CO}C_{Cl_2}^{3/2}}$$

1st order w.r.t. carbon monoxide

3/2 order w.r.t. chorine

overall is 5/2 order reaction

In general, first- and second-order reactions are more commonly observed.

Determination of Reaction Rate Law

It is important to remember that **the rate laws are determined by experimental observation!** They cannot be deduced from reaction stoichiometry.

They are function of the reaction chemistry and not the type of reactor in which the reactions occur.

Even though a number of reactions follow elementary rate laws, at least as many reactions do not. One must determine the reaction order from the experiments or from literature.

Literature

The activation energy, frequency factor, and reaction order

☑ Floppy disks and CDROMs by National Institute of Standards and Technology (NIST)

☑ Standard Reference Data 221/A320 Gaithersburg, MD 20899

☑ Tables of Chemical Kinetics: Homogeneous Reaction,
National Bureau of Standards Circular 510 (Sept. 1951)
Suppl. 1 (Nov. 14, 1956), Suppl. 2 (Aug. 5, 1960), Suppl. 3 (Sept. 15, 1961)
Washington, D.C., U.S. Government Printing Office

☑ Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling,
Evaluate No. 10, JPL Publication 92-20, Aug. 15, 1992, Jet Propulsion
Laboratories, Pasadena, CA, USA

☑ International Journal of Chemical Kinetics, Journal of Physical Chemistry

☑ Journal of Catalysis, Journal of Applied Catalysis

☑ AIChE Journal, Chemical Engineering Science, Korean Journal of Chemical Engineering

☑ Chemical Engineering Communications

☑ Industrial and Engineering Chemistry Research

Example of Rate Law

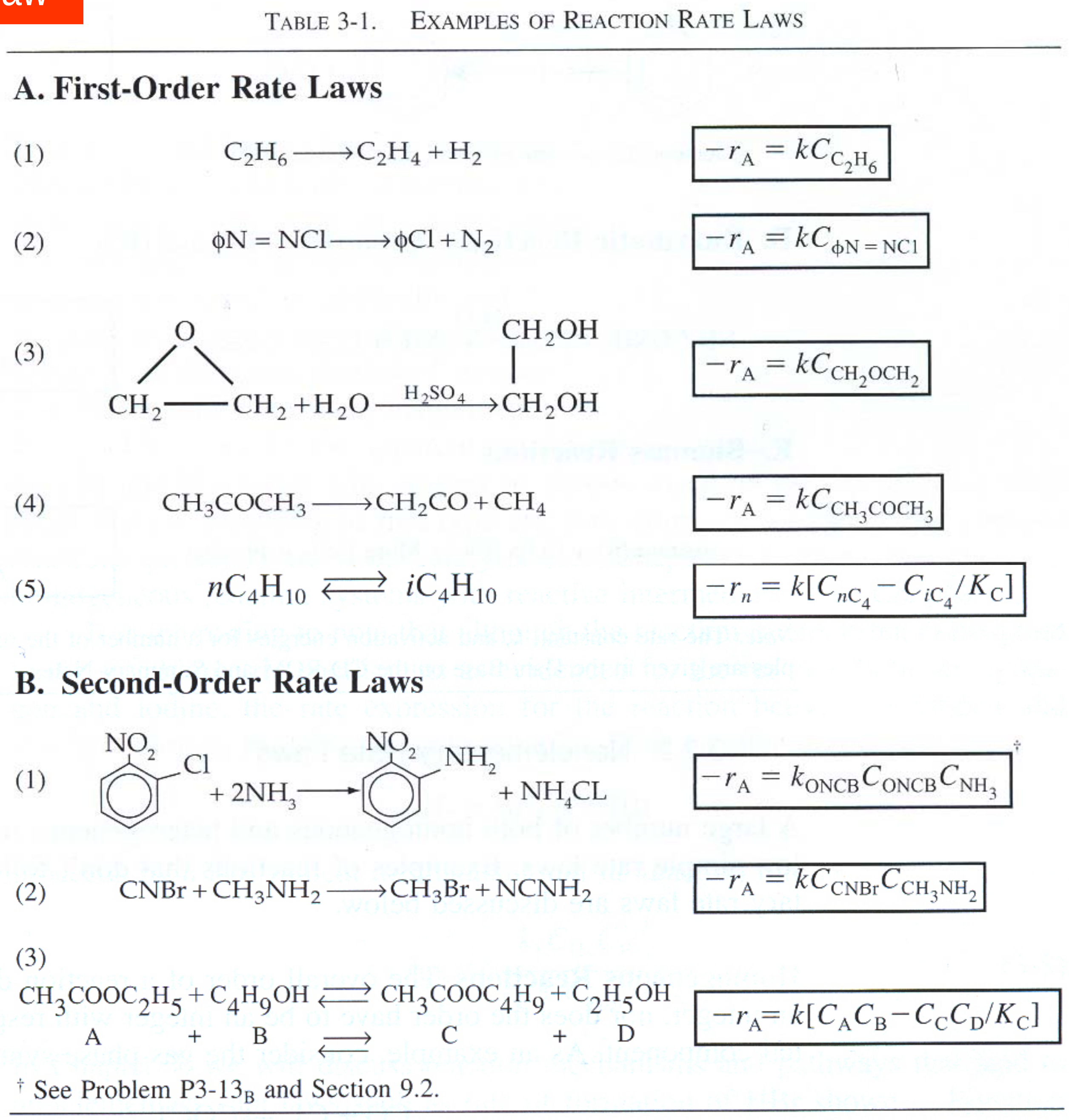


TABLE 3-1. EXAMPLES OF REACTION RATE LAWS

A. First-Order Rate Laws

(1)	$C_2H_6 \longrightarrow C_2H_4 + H_2$	$\boxed{-r_A = kC_{C_2H_6}}$
(2)	$\phi N = NCl \longrightarrow \phi Cl + N_2$	$\boxed{-r_A = kC_{\phi N = NCl}}$
(3)	$\overset{O}{CH_2 - CH_2} + H_2O \xrightarrow{H_2SO_4} \begin{matrix} CH_2OH \\ \vert \\ CH_2OH \end{matrix}$	$\boxed{-r_A = kC_{CH_2OCH_2}}$
(4)	$CH_3COCH_3 \longrightarrow CH_2CO + CH_4$	$\boxed{-r_A = kC_{CH_3COCH_3}}$
(5)	$nC_4H_{10} \rightleftarrows iC_4H_{10}$	$\boxed{-r_n = k[C_{nC_4} - C_{iC_4}/K_C]}$

B. Second-Order Rate Laws

(1)	NO_2, Cl + $2NH_3 \longrightarrow$ NO_2, NH_2 + NH_4CL	$\boxed{-r_A = k_{ONCB}C_{ONCB}C_{NH_3}}$[†]
(2)	$CNBr + CH_3NH_2 \longrightarrow CH_3Br + NCNH_2$	$\boxed{-r_A = kC_{CNBr}C_{CH_3NH_2}}$
(3)	$\underset{A}{CH_3COOC_2H_5} + \underset{B}{C_4H_9OH} \rightleftarrows \underset{C}{CH_3COOC_4H_9} + \underset{D}{C_2H_5OH}$	$\boxed{-r_A = k[C_AC_B - C_CC_D/K_C]}$

[†] See Problem P3-13$_B$ and Section 9.2.

Example of Rate Law

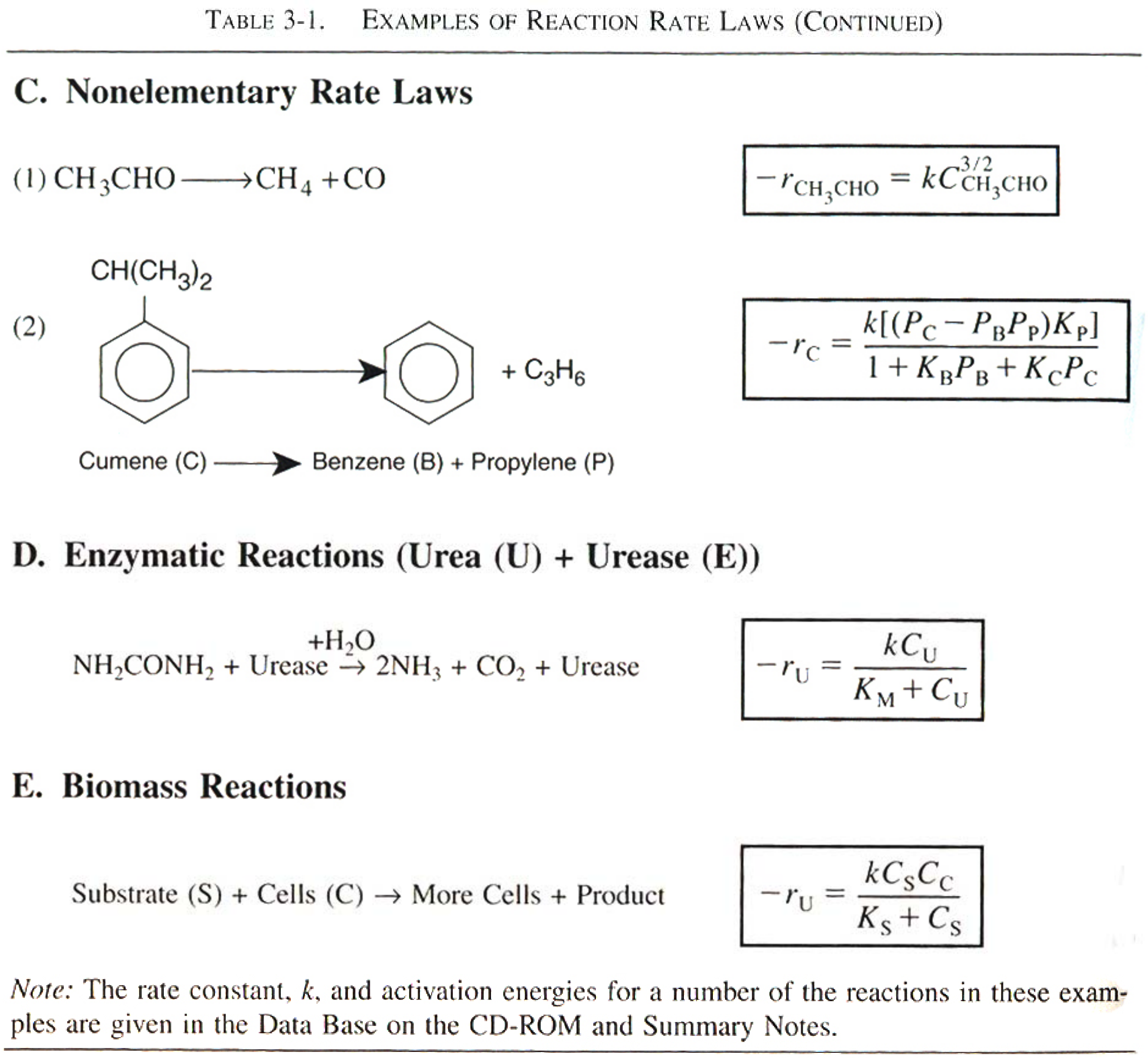


TABLE 3-1. EXAMPLES OF REACTION RATE LAWS (CONTINUED)

C. Nonelementary Rate Laws

(1) $CH_3CHO \longrightarrow CH_4 + CO$

$$\boxed{-r_{CH_3CHO} = kC_{CH_3CHO}^{3/2}}$$

(2) Cumene (C) ⟶ Benzene (B) + Propylene (P)

$$\boxed{-r_C = \frac{k[(P_C - P_B P_P)K_P]}{1 + K_B P_B + K_C P_C}}$$

D. Enzymatic Reactions (Urea (U) + Urease (E))

$NH_2CONH_2 + \text{Urease} \xrightarrow{+H_2O} 2NH_3 + CO_2 + \text{Urease}$

$$\boxed{-r_U = \frac{kC_U}{K_M + C_U}}$$

E. Biomass Reactions

Substrate (S) + Cells (C) → More Cells + Product

$$\boxed{-r_U = \frac{kC_S C_C}{K_S + C_S}}$$

Note: The rate constant, *k*, and activation energies for a number of the reactions in these examples are given in the Data Base on the CD-ROM and Summary Notes.

Example of Rate Law

A. First Order Reaction

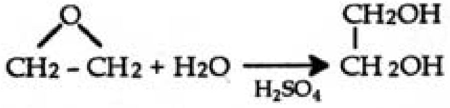
(1) $C_2H_6 \longrightarrow C_2H_4 + H_2$

$\boxed{-r_A = k\ C_{C_2H_6}}$ with $k = 0.072\ s^{-1}\ e^{\frac{82\,kcal}{mol}\left(\frac{1}{1000}-\frac{1}{T}\right)}$

(2) $\phi N = NCl \longrightarrow \phi Cl + N_2$

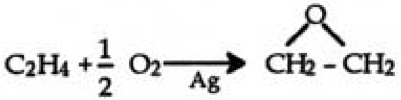
$\boxed{-r_A = k\ C_{\phi N=NCl}}$ with $k = 0.00717\ s^{-1}\ e^{-\frac{28.7\,kcal}{R\ mol}\left(\frac{1}{333}-\frac{1}{T}\right)}$

(3)



$\boxed{-r_A = k\ C_{CH_2OCH_2}}$

(4)



$\boxed{-r_A = k\ P_{C_2H_4}^{1/3}\ P_{O_2}^{2/3}}$ with $k = 0.014\ \frac{lbmol}{atm \cdot lb\ cat\ hr}$

While overall this reaction is first order, it is 1/3 order in ethylene and 2/3 order in oxygen.

(5) $\underbrace{(CH_3)_3COO(CH_3)_3}_{A} \longrightarrow C_2H_6 + 2CH_3COCH_3$

$\boxed{-r_A = kC_A}$ with $k_A = 10^{-4}\ min^{-1}$@$50°C$

and $E = 85 \frac{kJ}{mol}$

(6) $CH_3COCH_3 \longrightarrow CH_2CO + CH_4$

$\boxed{-r_A = k\ C_{CH_3COCH_3}}$ with $\ln k = 34.34 - \frac{34,322}{T}$

where k is in s^{-1} and T is in Kelvin

(7) $n-C_4H_{10} \rightleftarrows i-C_4H_{10}$

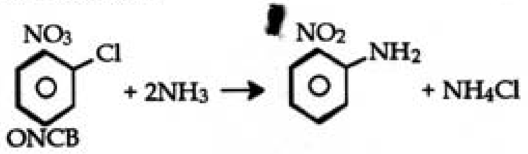
(n) (i)

$\boxed{-r_n = k\left[C_{nC_4} - C_{iC_4}/K_C\right]}$

where $\boxed{k = 31.1\ \exp\left[7906\left(\frac{T-360}{360T}\right)\right]}$ and $\boxed{K_C = 3.03\ \exp\left[-830.3\left(\frac{T-333}{333T}\right)\right]}$

B. Second Order Reaction

(1)



$\boxed{-r_A = k\ C_{ONCB}C_{NH_3}}$ with $k = 0.0017 \frac{m^3}{kmol \cdot min}$ at 188°C

and $E = 11,273 \frac{cal}{mol}$

This reaction is first order in ONCB, first order in ammonia and overall second order.

(2) $CNBr + CH_3NH_2 \longrightarrow CH_3Br + NCNH_2$

$\boxed{-r_A = k\ C_{CNBr}C_{CH_3NH_2}}$ with $k = \frac{2.2\ dm^3}{s\ mol}$

This reaction is first order in CNBr, first order in CH_3NH_2 and overall second order.

(3) $CH_3COOC_2H_2 + C_4H_9OH \rightleftarrows CH_3COOC_4H_9 + C_2H_5OH$

$A + B \rightleftarrows C + D$

$\boxed{-r_A = k\left[C_AC_B - C_CC_D/K_C\right]}$ with $K_C = 1.08$ and $k = 9 \times 10^{-5} \frac{dm^3}{mol \cdot s}$ at 300K

3.3 k_A: The specific reaction rate (the rate constant)

The reaction rate constant ***k*** is not truly a constant, but is merely independent of the concentrations of the species involved in the reaction.

The quantity ***k*** is also referred to as the specific reaction rate (constant). It is almost always strongly dependent on temperature. In gas-phase reactions, it depends on the catalyst and total pressure. In liquid systems, it depends on the total pressure, ionic strength and choice of solvent.

These other variables normally exhibit much less effect on the specific reaction rate than temperature does with the exception of supercritical solvents, such as supercritical water.

In this text, it will be assumed that k_A depends only on temperature.

Arrhenius equation

Activation energy, J/mol or cal/mol

Specific reaction rate (constant)

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

frequency factor

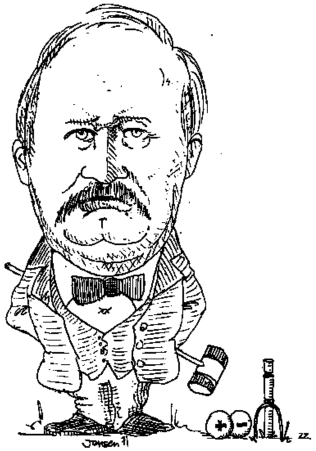
or

pre-exponential factor

mathematical number
e=2.71828…

Gas constant
8.314 J/mol · K
1.987 cal/mol · K
8.314 kPa · dm³/mol · K

Absolute Temperature, K



1903(44) :
Nobel Prize in chemistry for ionic theory

Activation energy

Activation energy *E* :

a minimum energy that must be possessed by reacting molecules before the reaction will occur.

$$\boxed{e^{-\frac{E}{RT}}}$$

The fraction of the collisions between molecules that together have this minimum energy *E* (the kinetic theory of gases)

Activation energy *E* is determined experimentally by carrying out the reaction at several different temperature.

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

Part 2

Stoichiometry

Reactor Size

Design Equations

Batch $$t = N_{A0}\int_0^X \frac{dX}{-r_A V}$$

CSTR $$V = \frac{F_{A0}X}{-r_A}$$

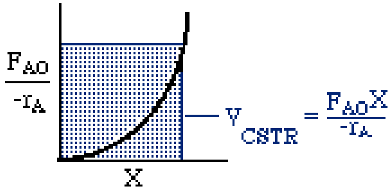
PFR $$V = F_{A0}\int_0^X \frac{dX}{-r_A}$$

PBR $$W = F_{A0}\int_0^X \frac{dX}{-r'_A}$$

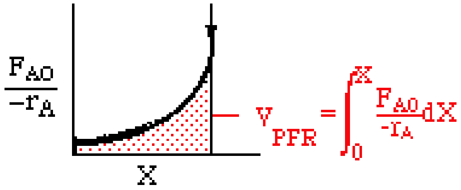
Graphical method

Levenspiel plot

CSTR



PFR



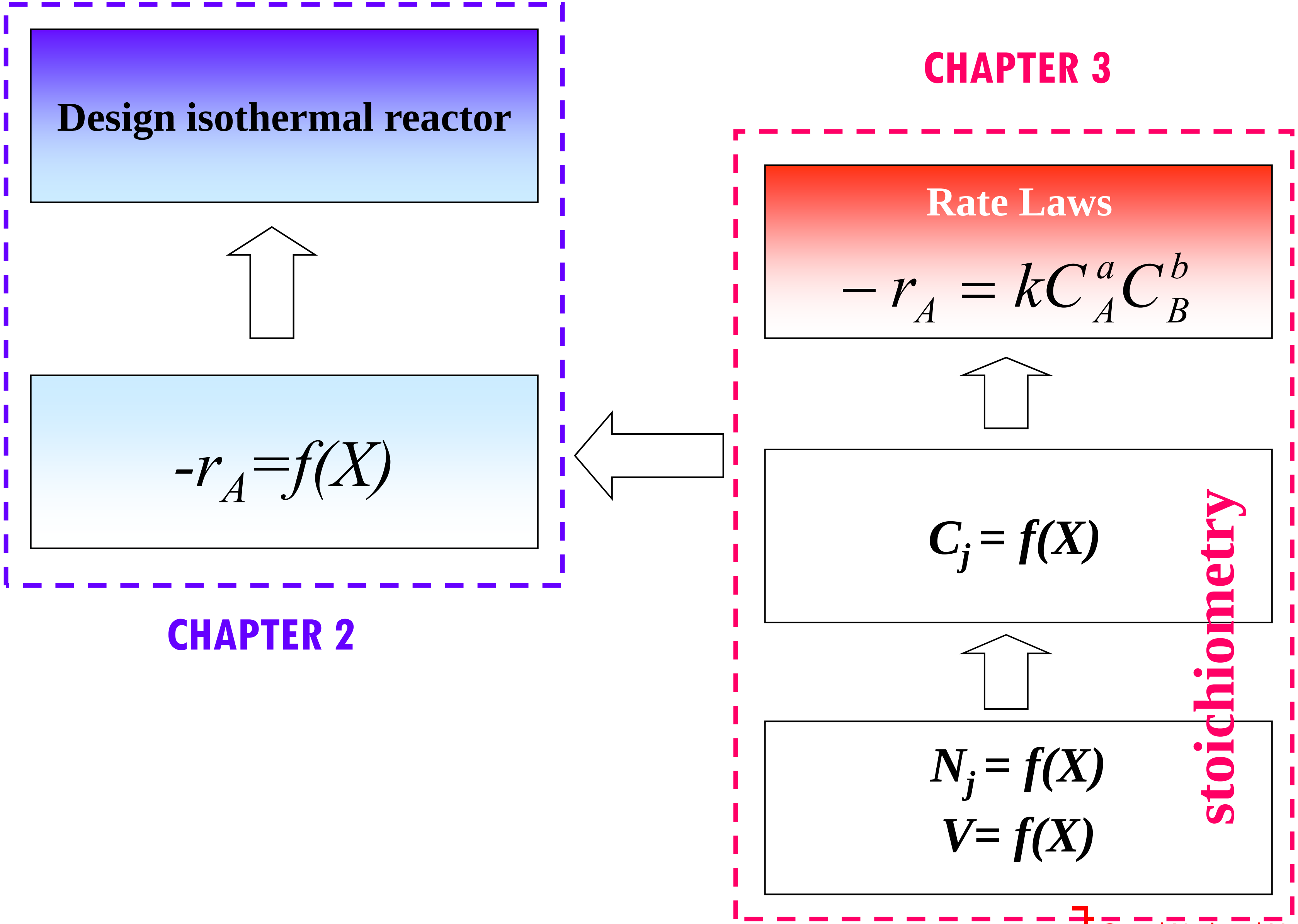
For $\frac{F_{A0}}{-r_A}$ vs. X, the volume of a CSTR and the volume of a PFR can be represented as the shaded areas in the Levenspiel plots.

PFR $$V = F_{A0}\int_0^X \frac{dX}{\boxed{-r_A}}$$

$$-r_A = f(X)$$

If we know the molar flow rate to the reactor and the reaction rate as a function of conversion, then we can calculate the reactor volume necessary to achieve a specific conversion.

Design Isothermal Reactor



Design isothermal reactor

$-r_A = f(X)$

CHAPTER 2

CHAPTER 3

Rate Laws

$$-r_A = kC_A^a C_B^b$$

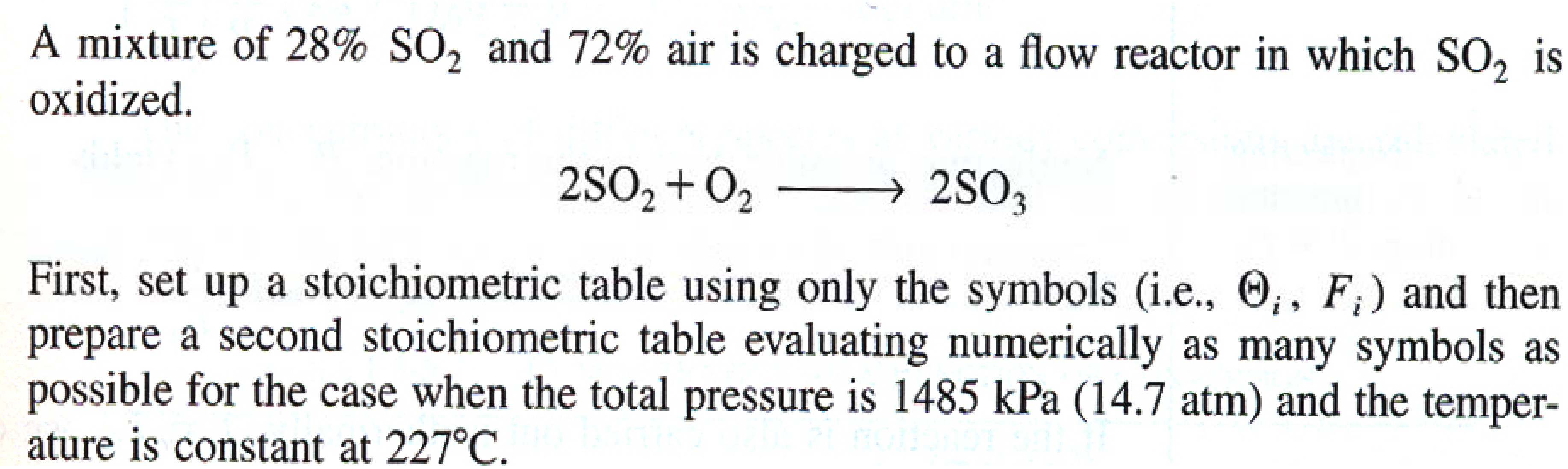
$C_j = f(X)$

$N_j = f(X)$

$V = f(X)$

stoichiometry

Example 3-5: Determination of $C_j=h_j(X)$ for a Gas-Phase Reaction



A mixture of 28% SO_2 and 72% air is charged to a flow reactor in which SO_2 is oxidized.

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

First, set up a stoichiometric table using only the symbols (i.e., Θ_i, F_i) and then prepare a second stoichiometric table evaluating numerically as many symbols as possible for the case when the total pressure is 1485 kPa (14.7 atm) and the temperature is constant at 227°C.

Isothermal

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

Stoichiometric Table

If the rate law depends on more than one species, we MUST relate the concentrations of different species to each other. A stoichiometric table presents the stoichiometric relationships between reacting molecules for a single reaction.

$$\mathbf{aA + bB \rightleftharpoons cC + dD} \qquad (2\text{-}1)$$

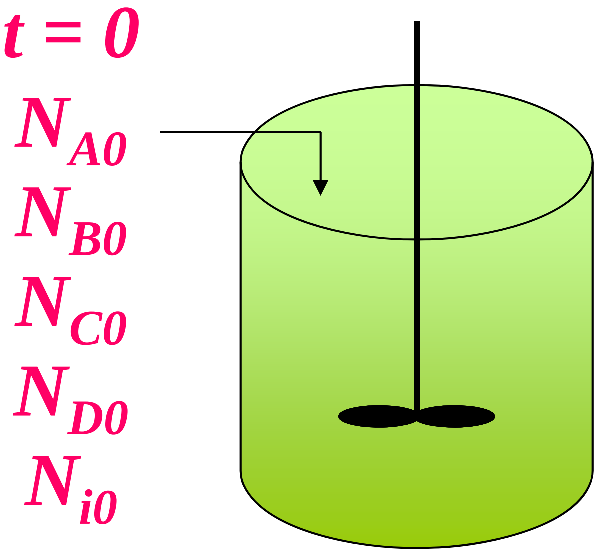
$$\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d} \qquad (3\text{-}1)$$

In formulating our stoichiometric table, we shall take species A as our basis of calculation (i.e., limiting reactant) and then divide through by the stoichiometric coefficient of A

$$A + \frac{b}{a}B \longrightarrow \frac{c}{a}C + \frac{d}{a}D \qquad (2\text{-}2)$$

In order to put everything on a basis of "per mole of A."

3.5 Batch System



$t = 0$

N_{A0}

N_{B0}

N_{C0}

N_{D0}

N_{i0}

$t = t$

N_A

N_B

N_C

N_D

N_i

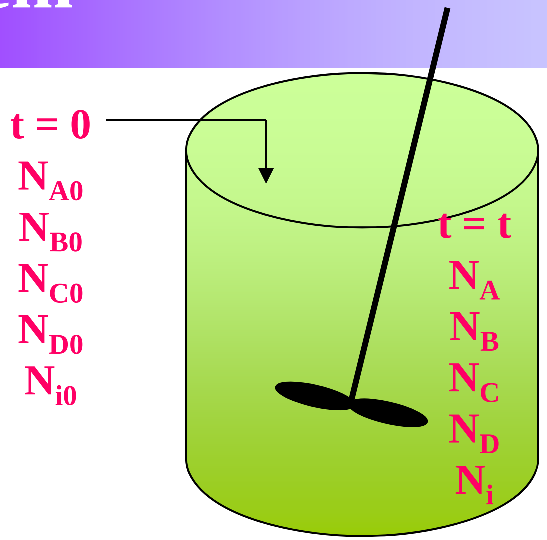
$$A + \frac{b}{a}B \longrightarrow \frac{c}{a}C + \frac{d}{a}D$$

Batch reactors are primarily used for the production of specialty chemicals and to obtain reaction rate data in order to determine reaction rate laws and rate law parameters such as k, the specific reaction rate.

3.5 Batch System

At time t=0, we will open the reactor and place a number of moles of species A, B, C, D, and I (N_{A0}, N_{B0}, N_{C0}, N_{D0}, and N_{I0}, respectively)

Species A is our basis of calculation.



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

N_{A0} is the number of moles of A initially present in the reactor.

$N_{A0}X$ moles of A are consumed as a result of the chemical reaction.

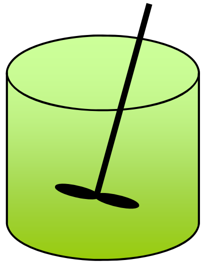
$N_{A0}-N_{A0}X$ moles of A leave in the system.

The number of moles of A remaining in the reactor after conversion X

$$N_A = N_{A0} - N_{A0}X = N_{A0}(1-X)$$

Determination of the number of moles of B

To determine the number of moles of species B remaining at time t (after $N_{A0}X$ moles of A have reacted). For every mole of A that reacts, b/a moles of B must reacted;



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

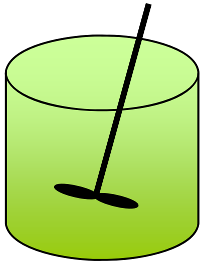
The number of moles of B remaining in the system, N_B

$$N_B = N_{B0} - \underbrace{\frac{b}{a}\overbrace{N_{A0}X}^{\textit{moles of A reacted}}}_{\textit{moles of B disappeared}}$$

moles of B initially

Stoichiometric table

To determine the number of moles of each species remaining after $N_{A0}X$ moles of **A** have reacted, we form the **stoichiometric table** (Table 3-3).



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

This stoichiometric table presents the following information.

Column 1: the particular species

Column 2: the number of moles of each species initially present

Column 3: the change the number of moles brought about by reaction

Column 4: the number of moles remaining in the system at time *t*.

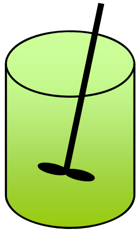
Stoichiometric Table for a Batch System

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}	$+\frac{d}{a}(N_{A0}X)$	$N_D = N_{D0} + \frac{d}{a}N_{A0}X$
$I(inert)$	N_{I0}		$N_I = N_{I0}$
Total	N_{T0}		$N_T = N_{T0} + \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1\right)N_{A0}X$

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

The total number of moles per mole of A reacted

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



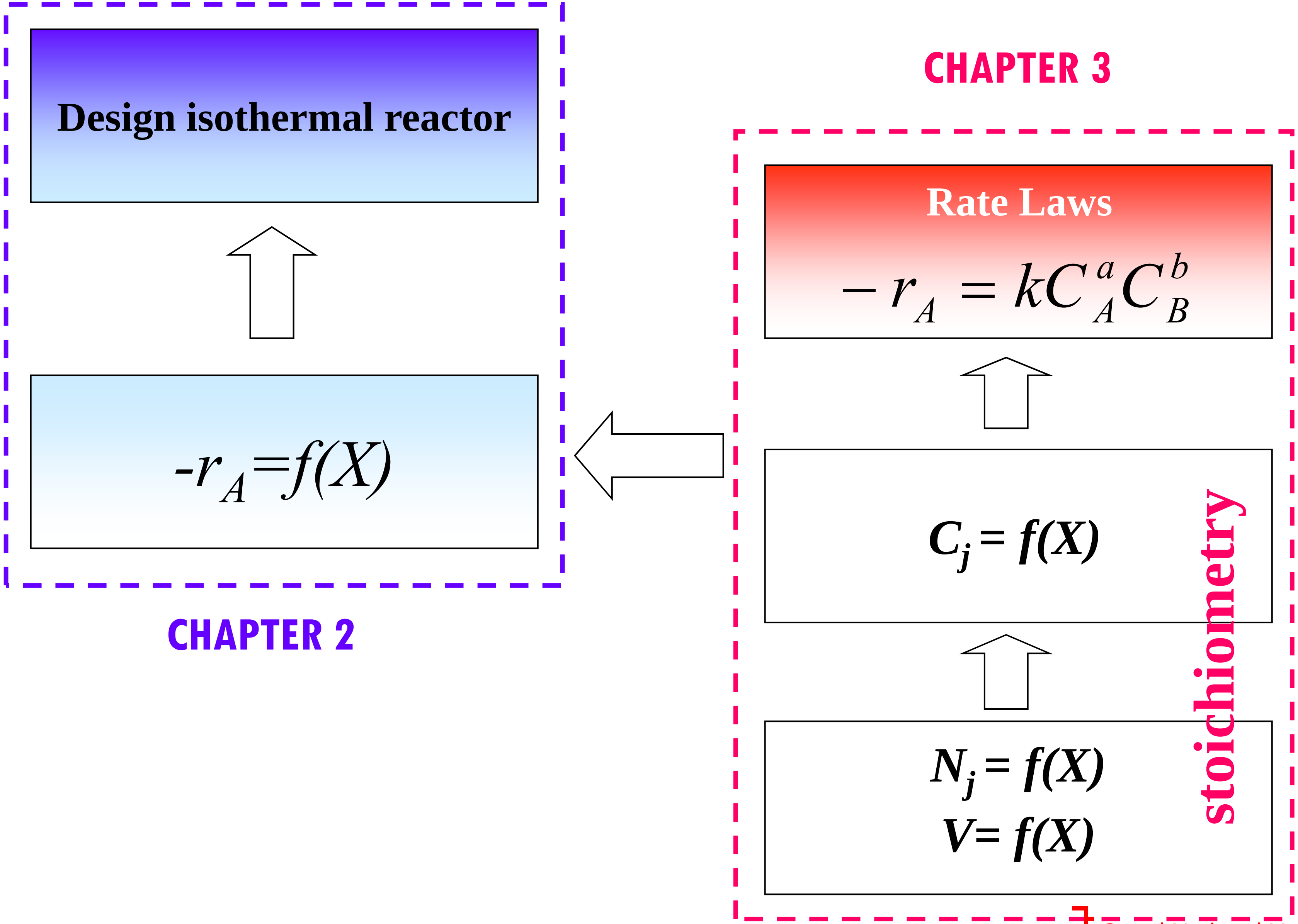
The total number of moles in the system, $\boldsymbol{N_T}$

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

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

$$\boxed{\delta \equiv \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1} \longleftarrow \frac{\text{Change in the total number of moles}}{\text{mole of A reacted}}$$

Design Isothermal Reactor



CHAPTER 3

Rate Laws

$$-r_A = kC_A^a C_B^b$$

$$C_j = f(X)$$

$$N_j = f(X)$$
$$V = f(X)$$

stoichiometry

Design isothermal reactor

$$-r_A = f(X)$$

CHAPTER 2

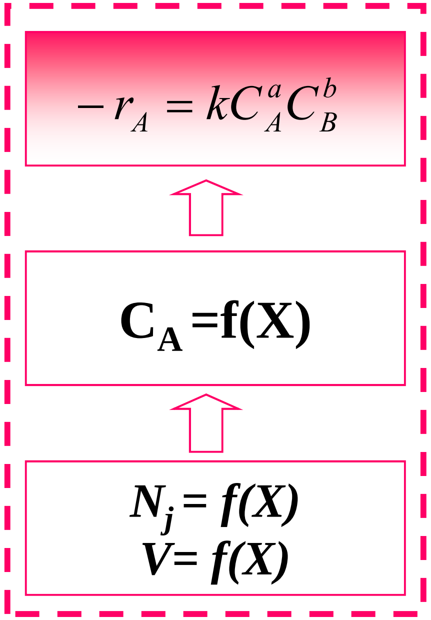
3.5.1. Concentration of each species

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

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

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

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



$-r_A = kC_A^aC_B^b$

$\Uparrow$

$C_A = f(X)$

$\Uparrow$

$N_j = f(X)$
$V = f(X)$

3.5.1. Concentration of each species

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

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

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

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

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

3.5.2 Volume as a function of conversion

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

We need ***V(X)*** to obtain $C_B = f(X)$

- For liquids, **volume** change with reaction is negligible when no phase changes are taking place. ($V=V_0$)

- For gas-phase reactions, the **volumetric flow rate** most often changes during the course of the reaction due to a change in the total number of moles or in temp. or pressure.

3.5.2 Constant-Volume Batch Reaction Systems

Constant volume system (=constant density system):

(1) The lab bomb calorimeter reactor: the volume within the vessel is fixed and will not change. $\mathbf{V=V_0}$

(2) A constant-volume gas-phase isothermal reaction occurs when the number of moles of products equals the number of moles of reactants. (Ex: water-gas shift reaction, $CO+H_2O \leftrightarrows CO_2+H_2$)

(3) For liquid-phase reactions taking place in solution, the solvent usually dominates the situation. As a result, changes in the density of the solute do not affect the overall density of the solution significantly and therefore it is essentially a constant-volume reaction process: Most liquid-phase organic reactions, except polymerization.

Constant Volume Batch Reactor

$V = V_0$

$$\left.\begin{aligned}
C_A &= \frac{N_{A0}(1-X)}{V_0} = C_{A0}(1-X) \\
C_B &= N_{A0}\frac{[(N_{B0}/N_{A0})-(b/a)X]}{V_0} = \frac{N_{A0}[\Theta_B-(b/a)X]}{V_0} = C_{A0}\left(\Theta_B-\frac{b}{a}X\right) \\
C_C &= N_{A0}\frac{[(N_{C0}/N_{A0})+(c/a)X]}{V_0} = C_{A0}\left(\Theta_C+\frac{c}{a}X\right) \\
C_D &= N_{A0}\frac{[(N_{D0}/N_{A0})+(d/a)X]}{V_0} = C_{A0}\left(\Theta_D+\frac{d}{a}X\right)
\end{aligned}\right\} \quad (3-26)$$

Constant Volume System

For Liquid phase reactions (or isothermal and isobaric gas-phase reactions with no change in the total number of moles)

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

$-r_A = f(C)$

$$-r_A = k_A C_A C_B$$

$-r_A = f(X)$

Eq. (3-26)

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

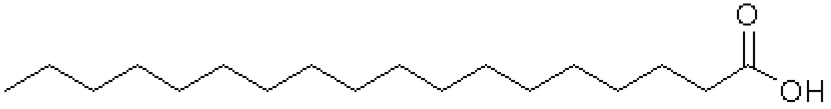
Levenspiel plot

Example 3-2: Liquid-Phase Reaction

Soap consists of the sodium and potassium salts of various fatty acids as oleic(C18=), stearic(C18), palmitic(C16), lauric(C12), and myristic(C14) acids. The saponification for the formation of soap from aqueous caustic soda and glyceryl stearate is as follow.

$$3NaOH + (C_{17}H_{35}COO)_3C_3H_5 \rightarrow 3C_{17}H_{35}COONa + C_3H_5(OH)_3$$

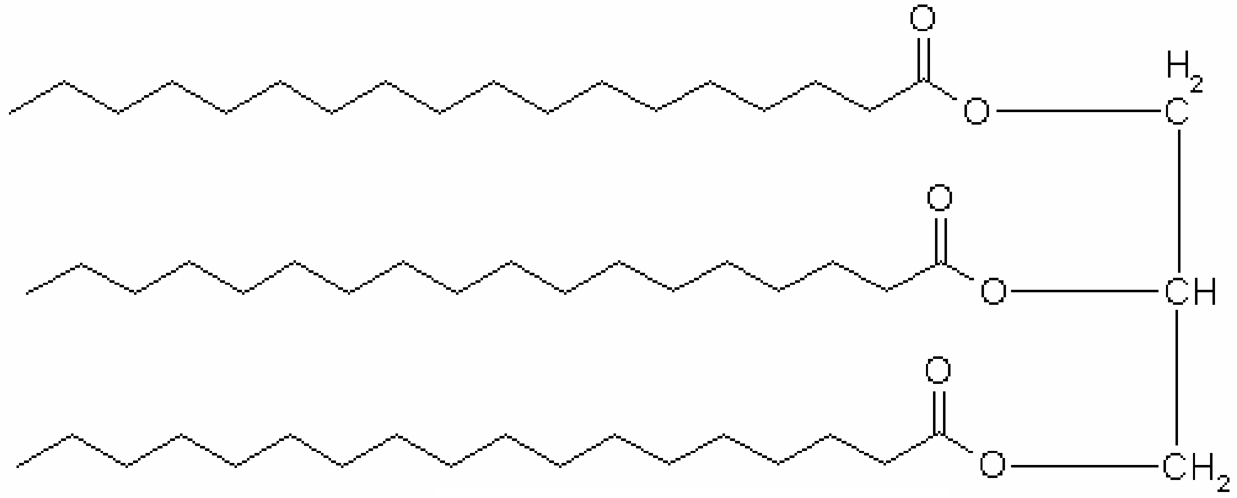
Letting X represent the conversion of sodium hydroxide (the mole of sodium hydroxide reacted per mole of sodium hydroxide initially present), set up a stoichiometric table expressing the concentration of each species in terms of its initial concentration and the conversion of X.



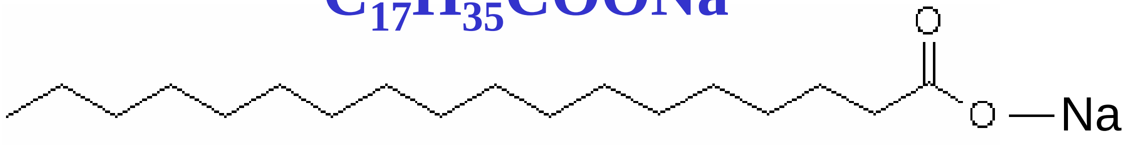
Stearic acid

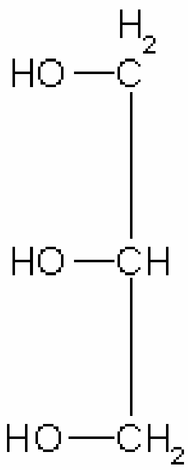
Example 3-2: Liquid-Phase Reaction

$(C_{17}H_{35}COO)_3C_3H_5$ Glyceryl stearate



$C_{17}H_{35}COONa$





$C_3H_5(OH)_3$

Glycerine=Glycerol

Example 3-2: Liquid-Phase Reaction

Because we are taking sodium hydroxide as our basis, we divide through by the stoichiometric coefficient of sodium hydroxide to put the reaction expression in the form

$$\mathrm{NaOH} + \tfrac{1}{3}(\mathrm{C_{17}H_{35}COO})_3\mathrm{C_3H_5} \longrightarrow \mathrm{C_{17}H_{35}COONa} + \tfrac{1}{3}\mathrm{C_3H_5(OH)_3}$$

$$\mathrm{A} + \tfrac{1}{3}\mathrm{B} \longrightarrow \mathrm{C} + \tfrac{1}{3}\mathrm{D}$$

We may then perform the calculations shown in Table E3-2.1. Because this is a liquid-phase reaction, the density ρ is considered to be constant; therefore, $V = V_0$.

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

$$\Theta_B = \frac{C_{B0}}{C_{A0}} \qquad \Theta_C = \frac{C_{C0}}{C_{A0}} \qquad \Theta_D = \frac{C_{D0}}{C_{A0}}$$

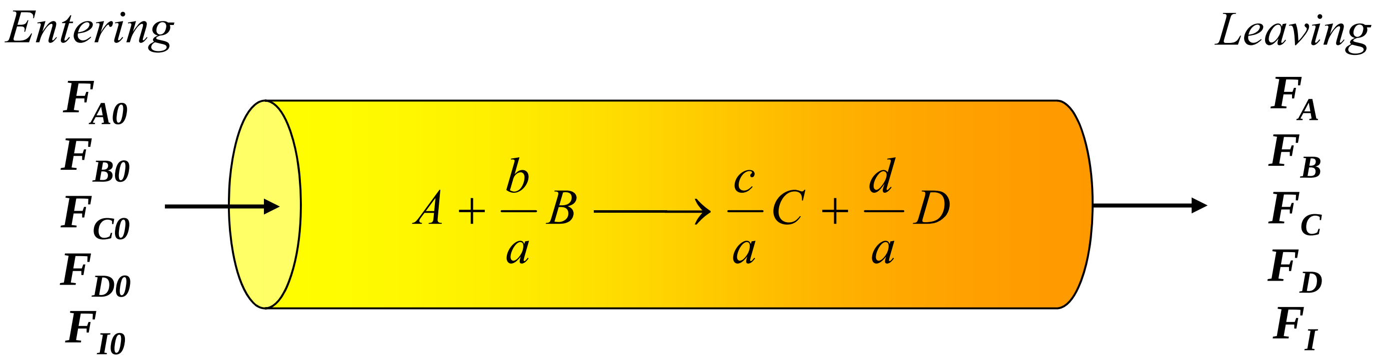
Example 3-2 Stoichiometric Table

$$3NaOH + (C_{17}H_{35}COO)_3C_3H_5 \rightarrow 3C_{17}H_{35}COONa + C_3H_5(OH)_3$$

$$A + \frac{1}{3}B \longrightarrow C + \frac{1}{3}D$$

Species	Initially (mol)	Change (mol)	Remaining (mol)	Concentration (mol/m^3)
A	N_{A0}	$-(N_{A0}X)$	$N_{A0}(1-X)$	$C_{A0}(1-X)$
B	N_{B0}	$-\frac{1}{3}(N_{A0}X)$	$N_{A0}\left(\Theta_B - \frac{X}{3}\right)$	$C_{A0}\left(\Theta_B - \frac{X}{3}\right)$
C	N_{C0}	$(N_{A0}X)$	$N_{A0}(\Theta_C + X)$	$C_{A0}(\Theta_C + X)$
D	N_{D0}	$\frac{1}{3}(N_{A0}X)$	$N_{A0}\left(\Theta_B + \frac{X}{3}\right)$	$C_{A0}\left(\Theta_B + \frac{X}{3}\right)$
$I(inert)$	N_{I0}		N_{I0}	C_{I0}
$Total$	N_{T0}	0	$N_T = N_{T0}$	

3.6 Flow Systems



Entering

F_{A0}
F_{B0}
F_{C0}
F_{D0}
F_{I0}

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

Leaving

F_A
F_B
F_C
F_D
F_I

Definition of concentration for flow system

Molar flow rate

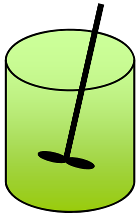
$$\boxed{C_A = \frac{F_A}{\upsilon} = \frac{\text{moles/time}}{\text{liters/time}} = \frac{\text{moles}}{\text{liter}}} \qquad \textbf{(3-27)}$$

volumetric flow rate

$$\boxed{\Theta_i = \frac{F_{i0}}{F_{A0}} = \frac{C_{i0}v_0}{C_{A0}v_0} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{A0}}}$$

3.6.1 Equations for Concentrations in Flow Systems

Batch System



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

Flow System

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

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

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

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

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

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

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

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

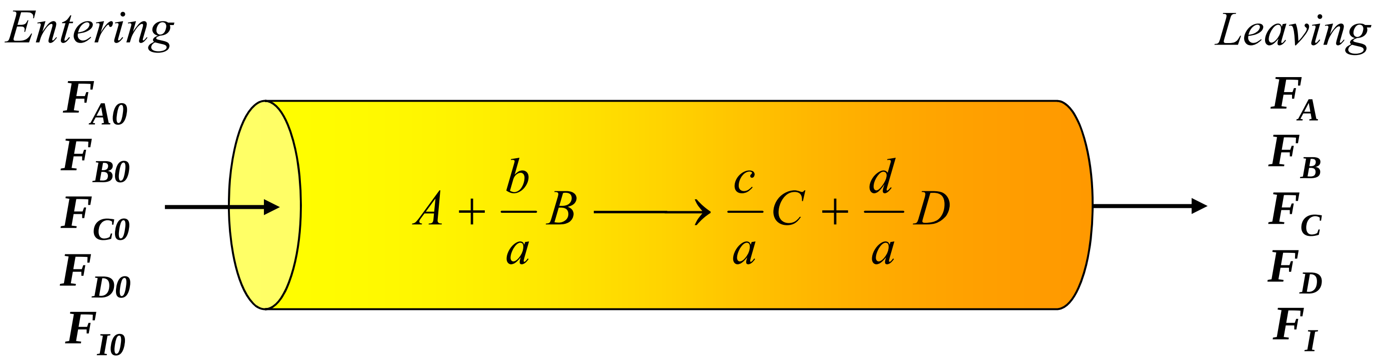
Stoichiometric Table for a Flow System

Species	Feed rate to reactor (mol/time)	Change in 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(inert)	$F_{I0} = \Theta_I F_{A0}$		$F_I = F_{A0}\Theta_I$
Total	F_{T0}		$F_T = F_{T0} + \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1\right)F_{A0}X$

Table 3-4

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

3.6.2 Liquid-Phase Concentrations



Entering

F_{A0}
F_{B0}
F_{C0}
F_{D0}
F_{I0}

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

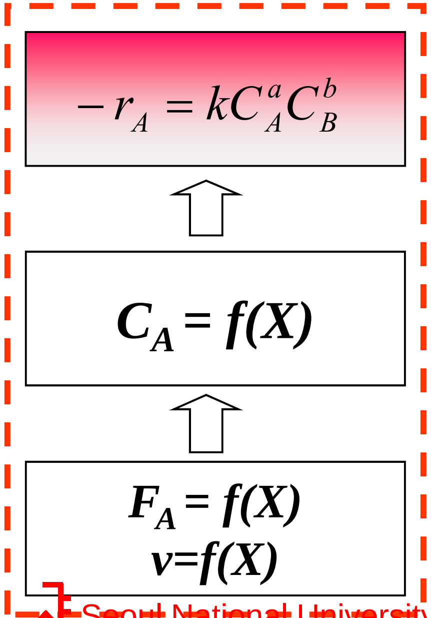
Leaving

F_A
F_B
F_C
F_D
F_I

$$C_A = \frac{F_A}{\upsilon} = \frac{F_{A0}}{\upsilon_0}(1 - X) = C_{A0}(1 - X)$$

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

(3-29)



$$-r_A = kC_A^a C_B^b$$

$C_A = f(X)$

$F_A = f(X)$
$v=f(X)$

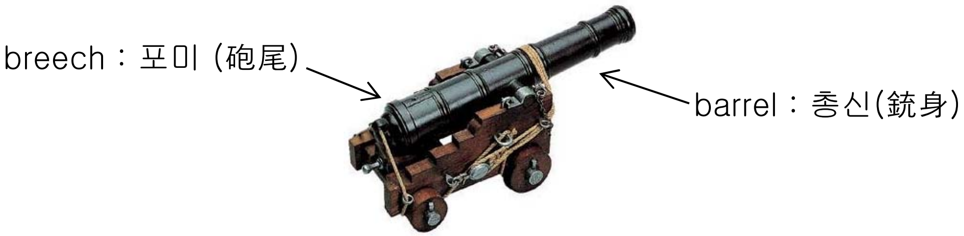
3.6.3 Change in the Total Number of Moles with Reaction in the Gas Phase

(1) Gas-phase reactions that do not have an equal number of product and reactant moles. In flow systems where this type of reaction occurs, the molar flow rate will be changing as the reaction progress. The volumetric flow rate will also change due to molar flow change.

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

(2) The combustion chamber of the internal-combustion engine

(3) The expanding gases within the breech and barrel of a firearm as it is fired.



Batch Reactor with Variable Volume

$$C_B = \frac{N_B(X)}{V(X)}$$

Individual concentrations can be determined by expressing the volume V for batch system (or volumetric flow rate v for a flow system) as a function of conversion using the following equation of state.

$$PV = ZN_T RT \qquad (3\text{-}30)$$

T = temperature, K
P = total pressure, atm (kPa; 1 atm=101.3 kPa)
Z = compressibility factor
R = gas constant = 0.08206 dm^3·atm/gmol · K

This equation is valid at any point in the system at any time. At time t=0,

$$P_0 V_0 = Z_0 N_{T0} RT_0 \qquad (3\text{-}31)$$

Dividing (3-30) by (3-31) and rearranging yields

$$V = V_0 \left(\frac{P_0}{P}\right)\frac{T}{T_0}\left(\frac{Z}{Z_0}\right)\boxed{\frac{N_T}{N_{T0}}} \longleftarrow \text{We need this!} \qquad (3\text{-}32)$$

Stoichiometric Table for a Batch System

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}	$-\frac{d}{a}(N_{A0}X)$	$N_D = N_{D0} + \frac{d}{a}N_{A0}X$
$I(inert)$	N_{I0}		$N_I = N_{I0}$
$Total$	N_{T0}		$N_T = N_{T0} + \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1\right)N_{A0}X$

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

Volume as a function of conversion

variable-volume batch reactor

The total number of moles in the system, $\boldsymbol{N_T}$

$$N_T = N_{T0} + \delta N_{A0} X \qquad (3\text{-}33)$$

We divide through by $\boldsymbol{N_{T0}}$

$$\frac{N_T}{N_{T0}} = 1 + \frac{N_{A0}}{N_{T0}} \delta X = 1 + \delta y_{A0} X = 1 + \varepsilon X \qquad (3\text{-}34)$$

where y_{A0} is mole fraction of A initially present. If all the species in the generalized reaction are in the gas phase, then

$$\varepsilon = \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \right) \frac{N_{A0}}{N_{T0}} = y_{A0} \delta \qquad (3\text{-}35)$$

Eq (3-32) now becomes

$$V = V_0 \left(\frac{P_0}{P} \right) \frac{T}{T_0} \left(\frac{Z}{Z_0} \right) \boxed{\frac{N_T}{N_{T0}}} = V_0 \left(\frac{P_0}{P} \right) \frac{T}{T_0} \left(\frac{Z}{Z_0} \right) \boxed{(1 + \varepsilon X)} \qquad (3\text{-}37)$$

Volume as a function of conversion

variable-volume batch reactor

In gas-phase systems that we shall be studying, the temperature and pressure are such that the compressibility factor will not change significantly during the course of the reaction; hence $Z_0 \sim Z$. For a batch system the volume of the gas at any time t is

$$\boxed{V = V_0 \left(\frac{P_0}{P} \right) (1 + \varepsilon X) \frac{T}{T_0}} \qquad (3\text{-}38)$$

Eq (3-38) applies only to a *variable-volume* batch reactor. If the reactor is a rigid steel container of constant volume, then of course $V = V_0$. For a constant-volume container, $V = V_0$, and Eq. (3-38) can be used to calculate the pressure inside the reactor as a function of temperature and conversion.

Volume as a function of conversion

variable-volume flow system

To derive the concentration of the species in terms of conversion for a variable-volume flow system, we shall use the relationships for the total concentration. The total concentration at any point in the reactor is

$$C_T = \frac{F_T}{\upsilon} = \frac{P}{ZRT} \qquad (3\text{-}39)$$

At the entrance to the reactor

$$C_{T0} = \frac{F_{T0}}{\upsilon_0} = \frac{P_0}{Z_0 R T_0} \qquad (3\text{-}40)$$

Taking Eq (3-40)/Eq(3-39) and assuming $Z \sim Z_0$,

$$\boxed{\upsilon = \upsilon_0 \left(\frac{F_T}{F_{T0}}\right) \frac{P_0}{P} \left(\frac{T}{T_0}\right)} \qquad (3\text{-}41)$$

Concentration as a function of conversion

variable-volume flow system

We can express the concentration equation of species j for a flow system in terms of conversion:

$$C_j = \frac{F_j}{\upsilon} = \frac{F_j}{\upsilon_0 \left(\frac{F_T}{F_{T0}} \frac{P_0}{P} \frac{T}{T_0} \right)} = \left(\frac{F_{T0}}{\upsilon_0} \right) \left(\frac{F_j}{F_T} \right) \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right)$$

$$\boxed{C_j = C_{T0} \left(\frac{F_j}{F_T} \right) \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right)} \qquad (3\text{-}42)$$

The total molar flow rate is just the sum of the molar flow rates of each of the species in the system and is

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

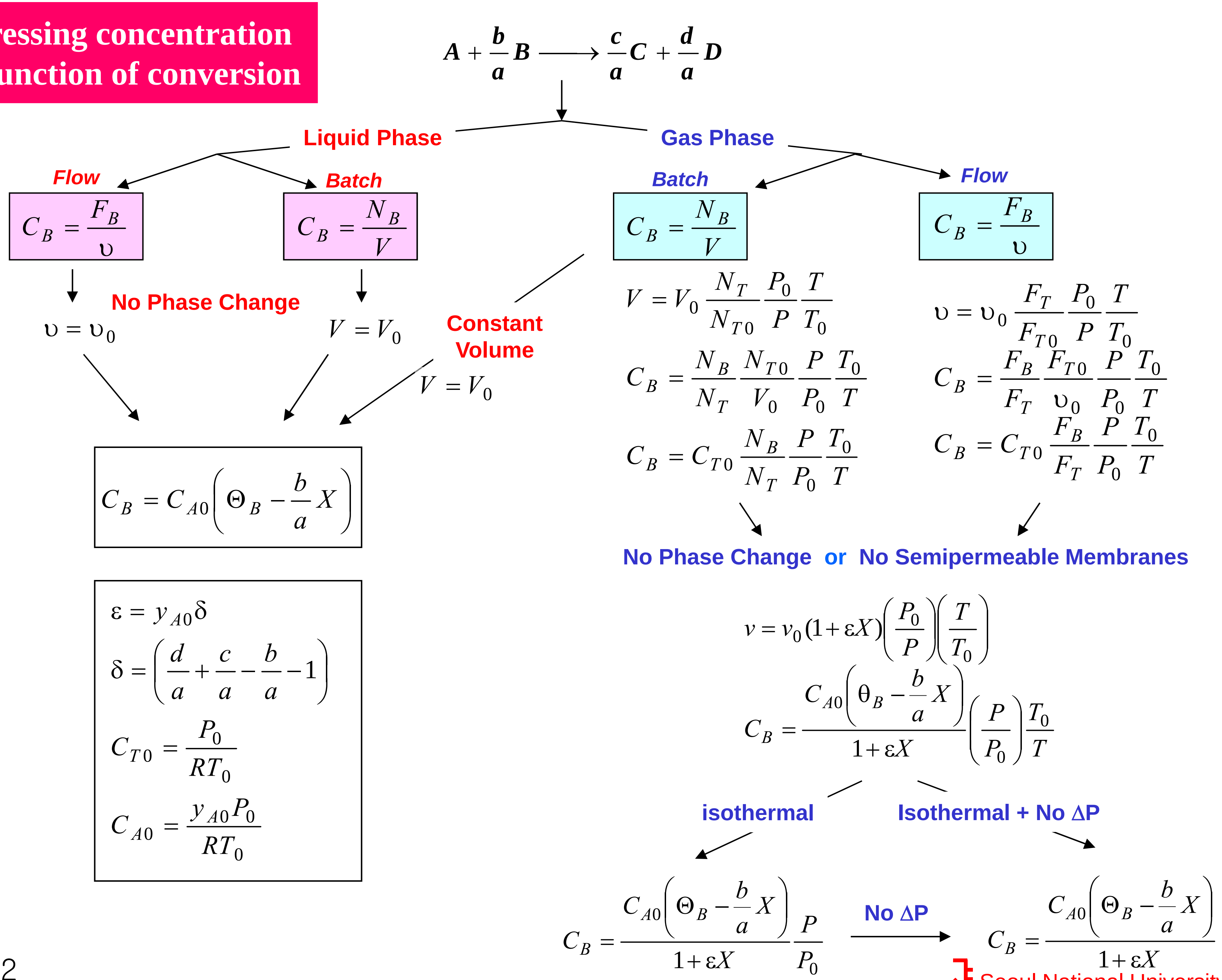
Concentration as a function of conversion

variable-volume flow system

One of the major objective of this chapter is to learn how to express any given rate law $-r_A$ as a function of conversion. The schematic diagram in Figure 3-6 helps to summarize our discussion on this point.

The concentration of B expressed as a function of conversion in both flow and batch systems, for various conditions of temperature, pressure, and volume.

Expressing concentration as a function of conversion



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

Liquid Phase

Flow

$$C_B = \frac{F_B}{\upsilon}$$

$$\upsilon = \upsilon_0$$

Batch

$$C_B = \frac{N_B}{V}$$

$$V = V_0$$

No Phase Change

Constant Volume

$$V = V_0$$

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

$$\varepsilon = y_{A0}\delta$$

$$\delta = \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1\right)$$

$$C_{T0} = \frac{P_0}{RT_0}$$

$$C_{A0} = \frac{y_{A0}P_0}{RT_0}$$

Gas Phase

Batch

$$C_B = \frac{N_B}{V}$$

$$V = V_0 \frac{N_T}{N_{T0}} \frac{P_0}{P} \frac{T}{T_0}$$

$$C_B = \frac{N_B}{N_T} \frac{N_{T0}}{V_0} \frac{P}{P_0} \frac{T_0}{T}$$

$$C_B = C_{T0} \frac{N_B}{N_T} \frac{P}{P_0} \frac{T_0}{T}$$

Flow

$$C_B = \frac{F_B}{\upsilon}$$

$$\upsilon = \upsilon_0 \frac{F_T}{F_{T0}} \frac{P_0}{P} \frac{T}{T_0}$$

$$C_B = \frac{F_B}{F_T} \frac{F_{T0}}{\upsilon_0} \frac{P}{P_0} \frac{T_0}{T}$$

$$C_B = C_{T0} \frac{F_B}{F_T} \frac{P}{P_0} \frac{T_0}{T}$$

No Phase Change or No Semipermeable Membranes

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

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

isothermal

Isothermal + No ΔP

$$C_B = \frac{C_{A0}\left(\Theta_B - \frac{b}{a}X\right)}{1+\varepsilon X}\frac{P}{P_0} \xrightarrow{\text{No } \Delta P} C_B = \frac{C_{A0}\left(\Theta_B - \frac{b}{a}X\right)}{1+\varepsilon X}$$

pp112

Volume as a function of conversion

variable-volume flow system

From Table 3-3, the total molar flow rate can be written in terms of X

$$F_T = F_{T0} + F_{A0}\delta X \tag{3-43}$$

$$\upsilon = \upsilon_0 \frac{F_{T0} + F_{A0}\delta X}{F_{T0}} \left(\frac{P_0}{P}\right) \frac{T}{T_0}$$

$$= \upsilon_0 \left(1 + \frac{F_{A0}}{F_{T0}}\delta X\right)\left(\frac{P_0}{P}\right)\frac{T}{T_0} = \upsilon_0 \left(1 + y_{A0}\delta X\right)\left(\frac{P_0}{P}\right)\frac{T}{T_0} \tag{3-44}$$

$$\boxed{\upsilon = \upsilon_0 (1 + \varepsilon X)\left(\frac{P_0}{P}\right)\frac{T}{T_0}} \tag{3-45}$$

Volume as a function of conversion

variable-volume flow system

The concentration of species *j* is

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

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

$$= F_{A0}\left(\Theta_j + \nu_j X\right)$$

$$\upsilon = \upsilon_0 (1 + \varepsilon X)\left(\frac{P_0}{P}\right)\frac{T}{T_0}$$

$$\boxed{C_j = \frac{F_{A0}\left(\Theta_j + \nu_j X\right)}{\upsilon_0\left((1+\varepsilon X)\frac{P_0}{P}\frac{T}{T_0}\right)}} \qquad (3\text{-}46)$$

Concentration as a function of conversion

Multiple gas-phase reaction and membrane reactor

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

Substituting for F_j and F_T in terms of conversion in Eq. (3-45) yields

$$C_j = C_{T0}\frac{F_{A0}\left(\Theta_j + v_j X\right)}{F_{T0} + F_{A0}\delta X}\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right)$$

Dividing numerator and denominator by F_{T0}, we have

$$C_j = C_{T0}\left(\frac{F_{A0}}{F_{T0}}\right)\frac{\Theta_j + v_j X}{1+(F_{A0}/F_{T0})\delta X}\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right)$$

Concentration as a function of conversion

Multiple gas-phase reaction and membrane reactor

Recalling $y_{a0}=F_{A0}/F_{T0}$ and $C_{A0}=y_{A0}C_{T0}$, then

$$\boxed{C_j = \frac{C_{A0}\left(\Theta_j + v_j X\right)}{1+\varepsilon X}\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right)} \qquad (3\text{-}46)$$

where v_i is the stoichiometric coefficient, which is negative for reactants and positive for products.

For example, for the reaction

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

$v_A = -1,\ \ v_B = -b/a,\ \ v_C = c/a,\ \ v_D = d/a,$ and $\Theta_j = F_{j0}/F_{A0}$.

Concentration as a function of conversion

variable-volume gas flow system

Table 3-4

$$C_A = \frac{F_A}{\upsilon} = \frac{F_{A0}(1-X)}{\upsilon} = \frac{F_{A0}(1-X)}{\upsilon_0(1+\varepsilon X)}\left(\frac{T_0}{T}\right)\frac{P}{P_0} = C_{A0}\frac{(1-X)}{(1+\varepsilon X)}\left(\frac{T_0}{T}\right)\frac{P}{P_0}$$

$$C_B = \frac{F_B}{\upsilon} = \frac{F_{A0}\left[\Theta_B-(b/a)X\right]}{\upsilon} = \frac{F_{A0}\left[\Theta_B-(b/a)X\right]}{\upsilon_0(1+\varepsilon X)}\left(\frac{T_0}{T}\right)\frac{P}{P_0} = C_{A0}\left(\frac{\Theta_B-(b/a)X}{1+\varepsilon X}\right)\frac{T_0}{T}\left(\frac{P}{P_0}\right)$$

$$C_C = \frac{F_C}{\upsilon} = \frac{F_{A0}\left[\Theta_C+(c/a)X\right]}{\upsilon} = \frac{F_{A0}\left[\Theta_C+(c/a)X\right]}{\upsilon_0(1+\varepsilon X)}\left(\frac{T_0}{T}\right)\frac{P}{P_0} = C_{A0}\left(\frac{\Theta_C+(c/a)X}{1+\varepsilon X}\right)\frac{T_0}{T}\left(\frac{P}{P_0}\right)$$

$$C_D = \frac{F_D}{\upsilon} = \frac{F_{A0}\left[\Theta_D+(d/a)X\right]}{\upsilon} = \frac{F_{A0}\left[\Theta_D+(d/a)X\right]}{\upsilon_0(1+\varepsilon X)}\left(\frac{T_0}{T}\right)\frac{P}{P_0} = C_{A0}\left(\frac{\Theta_D+(d/a)X}{1+\varepsilon X}\right)\frac{T_0}{T}\left(\frac{P}{P_0}\right)$$

$$C_I = \frac{F_I}{\upsilon} = \frac{F_{A0}\Theta_I}{\upsilon} = \frac{F_{A0}\Theta_I}{\upsilon_0(1+\varepsilon X)}\left(\frac{T_0}{T}\right)\frac{P}{P_0} = \frac{C_{A0}\Theta_I}{1+\varepsilon X}\left(\frac{T_0}{T}\right)\frac{P}{P_0}$$

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Example 3-4: Manipulation of the Equation $C_j = f_j(X)$

Show under what conditions and manipulation the expression for C_B for a gas flow system reduces to the following equation in Table 3-5.

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

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Example 3-4: Manipulation of the Equation $C_j=h_j(X)$

$$C_B = \frac{F_B}{\upsilon}$$

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

$$\upsilon = \upsilon_0(1+\varepsilon X)\left(\frac{P_0}{P}\right)\frac{T}{T_0} \qquad \text{(3-45)}$$

$$C_B = \frac{F_{A0}\left(\Theta_B - (b/a)X\right)}{\upsilon_0\left((1+\varepsilon X)\frac{P_0}{P}\frac{T}{T_0}\right)} \qquad \text{(E3-4.4)}$$

$$\boxed{C_B = C_{A0}\left[\frac{\Theta_B - (b/a)X}{1+\varepsilon X}\right]\frac{P}{P_0}\left(\frac{T_0}{T}\right)}$$

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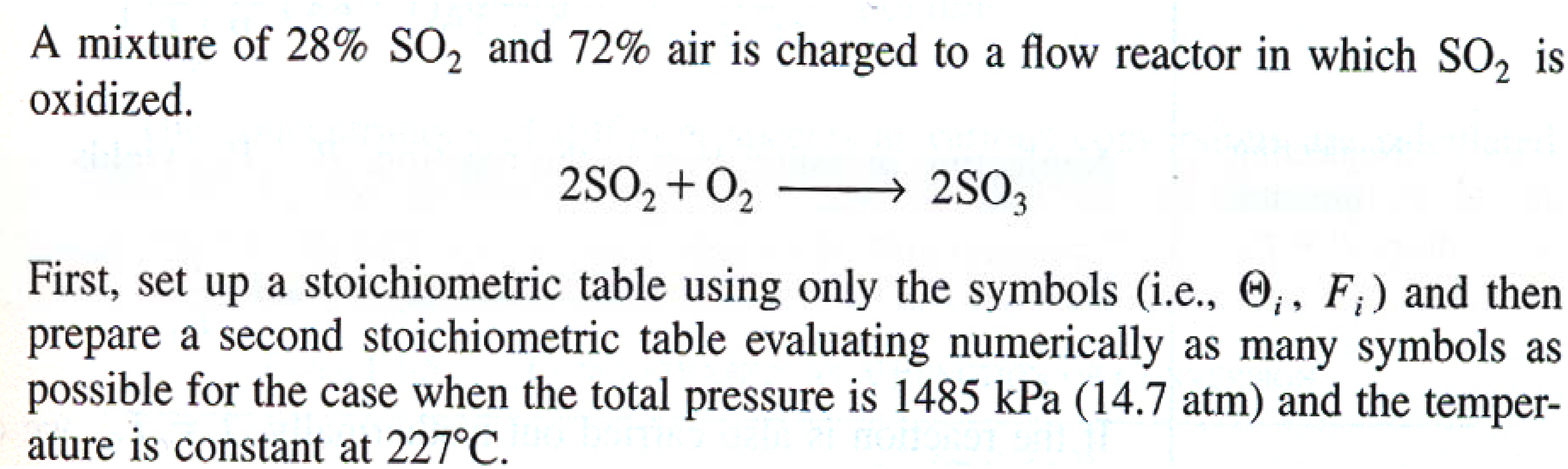
Example 3-5: Determination of $C_j = h_j(X)$ for a Gas-Phase Reaction



A mixture of 28% SO_2 and 72% air is charged to a flow reactor in which SO_2 is oxidized.

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

First, set up a stoichiometric table using only the symbols (i.e., Θ_i, F_i) and then prepare a second stoichiometric table evaluating numerically as many symbols as possible for the case when the total pressure is 1485 kPa (14.7 atm) and the temperature is constant at 227°C.

Isothermal

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

Example 3-5: Determination of $C_j=h_j(X)$ for a Gas-Phase Reaction

Taking SO_2 as the basis of calculation, we divide the reaction through by the stoichiometric coefficient of our chosen basis of calculation:

$$\underset{\textbf{A}}{SO_2} + \tfrac{1}{2}\underset{\textbf{B}}{O_2} \longrightarrow \underset{\textbf{C}}{SO_3}$$

$$-r_A = kC_A C_B$$

The initial stoichiometric table is given as Table E3-5.1. Initially, 72% of the total number of moles is air containing (21% O_2 and 79% N_2) along with 28% SO_2.

$$y_{A0} = 0.28$$

$$F_{A0} = (0.28)(F_{T0})$$

$$F_{B0} = (0.72)(0.21)(F_{T0})$$

$$\Theta_B = \frac{F_{B0}}{F_{A0}} = \frac{(0.72)(0.21)}{0.28} = 0.54$$

$$\Theta_I = \frac{F_{I0}}{F_{A0}} = \frac{(0.72)(0.79)}{0.28} = 2.03$$

From the definition of conversion, we substitute not only for the molar flow rate of SO_2 (A) in terms of conversion but also for the volumetric flow rate as a function of conversion.

TABLE E3-5.1. STOICHIOMETRIC TABLE FOR $SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3$

Species	*Symbol*	*Initially*	*Change*	*Remaining*
SO_2	A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$
O_2	B	$F_{B0} = \Theta_B F_{A0}$	$-\frac{F_{A0}X}{2}$	$F_B = F_{A0}\left(\Theta_B - \frac{1}{2}X\right)$
SO_3	C	$F_{C0}=0$	$+F_{A0}X$	$F_C = F_{A0}X$
N_2	I	$F_{I0} = \Theta_I F_{A0}$	—	$F_I = F_{I0} = \Theta_I F_{A0}$
		F_{T0}		$F_T = F_{T0} - \frac{F_{A0}X}{2}$

$$\delta = 1 - \frac{1}{2} - 1 = -\frac{1}{2}$$

$$F_T = F_{T0} + F_{A0}\delta X = F_{T0} - \frac{F_{A0}X}{2}$$

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

Recalling Equation (3-45), we have

$$v = v_0(1+\varepsilon X)\frac{P_0}{P}\left(\frac{T}{T_0}\right) \tag{3-45}$$

Neglecting pressure drop in the reaction, $P = P_0$, yields

$$v = v_0(1+\varepsilon X)\frac{T}{T_0}$$

If the reaction is also carried out isothermally, $T = T_0$, we obtain

$$v = v_0(1+\varepsilon X)$$

$$C_A = \frac{F_{A0}(1-X)}{v_0(1+\varepsilon X)} = C_{A0}\left(\frac{1-X}{1+\varepsilon X}\right)$$

The concentration of A initially is equal to the mole fraction of A initially multiplied by the total concentration. The total concentration can be calculated from an equation of state such as the ideal gas law. Recall that $y_{A0} = 0.28$, $T_0 = 500$ K, and $P_0 = 1485$ kPa.

= 227+273

$$C_{A0} = y_{A0} C_{T0} = y_{A0}\left(\frac{P_0}{RT_0}\right)$$

$$= 0.28\left[\frac{1485\ \text{kPa}}{8.314\ \text{kPa}\cdot\text{dm}^3/(\text{mol}\cdot\text{K}) \times 500\ \text{K}}\right]$$

$$= 0.1\ \text{mol/dm}^3$$

The total concentration is

$$C_T = \frac{F_T}{v} = \frac{F_{T0} + y_{A0}\delta X F_{T0}}{v_0(1+\varepsilon X)} = \frac{F_{T0}(1+\varepsilon X)}{v_0(1+\varepsilon X)} = \frac{F_{T0}}{v_0} = C_{T0} = \frac{P_0}{RT_0}$$

$$= \frac{1485 \text{ kPa}}{[8.314 \text{ kPa}\cdot\text{dm}^3/(\text{mol}\cdot\text{K})](500 \text{ K})} = 0.357 \frac{\text{mol}}{\text{dm}^3}$$

We now evaluate ε .

$$\varepsilon = y_{A0}\,\delta = (0.28)\,(1 - 1 - \tfrac{1}{2}) = -0.14$$

$$C_A = C_{A0}\left(\frac{1-X}{1+\varepsilon X}\right) = 0.1\left(\frac{1-X}{1-0.14X}\right) \text{mol/dm}^3$$

$$C_B = C_{A0}\left(\frac{\Theta_B - \frac{1}{2}X}{1+\varepsilon X}\right) = \frac{0.1\,(0.54-0.5X)}{1-0.14X} \text{ mol/dm}^3$$

$$C_C = \frac{C_{A0}X}{1+\varepsilon X} = \frac{0.1X}{1-0.14X} \text{ mol/dm}^3$$

$$C_I = \frac{C_{A0}\Theta_I}{1+\varepsilon X} = \frac{(0.1)\,(2.03)}{1-0.14X} \text{ mol/dm}^3$$

The concentrations of different species at various conversions are calculated in Table E3-5.2 and plotted in Figure E3-5.1. *Note* that the concentration of N_2 is changing even though it is an inert species in this reaction!!

TABLE E3-5.2. CONCENTRATION AS A FUNCTION OF CONVERSION

Species		C_i (mol/dm^3)				
		$X = 0.0$	$X = 0.25$	$X = 0.5$	$X = 0.75$	$X = 1.0$
SO_2	$C_A =$	0.100	0.078	0.054	0.028	0.000
O_2	$C_B =$	0.054	0.043	0.031	0.018	0.005
SO_3	$C_C =$	0.000	0.026	0.054	0.084	0.116
N_2	$C_I =$	0.203	0.210	0.218	0.227	0.236
	$C_T =$	0.357	0.357	0.357	0.357	0.357

We are now in a position to express $-r_A$ as a function of X. For example, *if* the rate law for this reaction *were* first order in SO_2 (i.e., A) and in O_2 (i.e., B), with $k = 200\ \text{dm}^3/\text{mol}\cdot\text{s}$, then the rate law becomes

$$-r_A = kC_AC_B = kC_{A0}^2\frac{(1-X)(\Theta_B - 0.5X)}{(1+\varepsilon X)^2} = \frac{2(1-X)(0.54-0.5X)}{(1-0.14X)^2} \quad \text{(E3-5.1)}$$

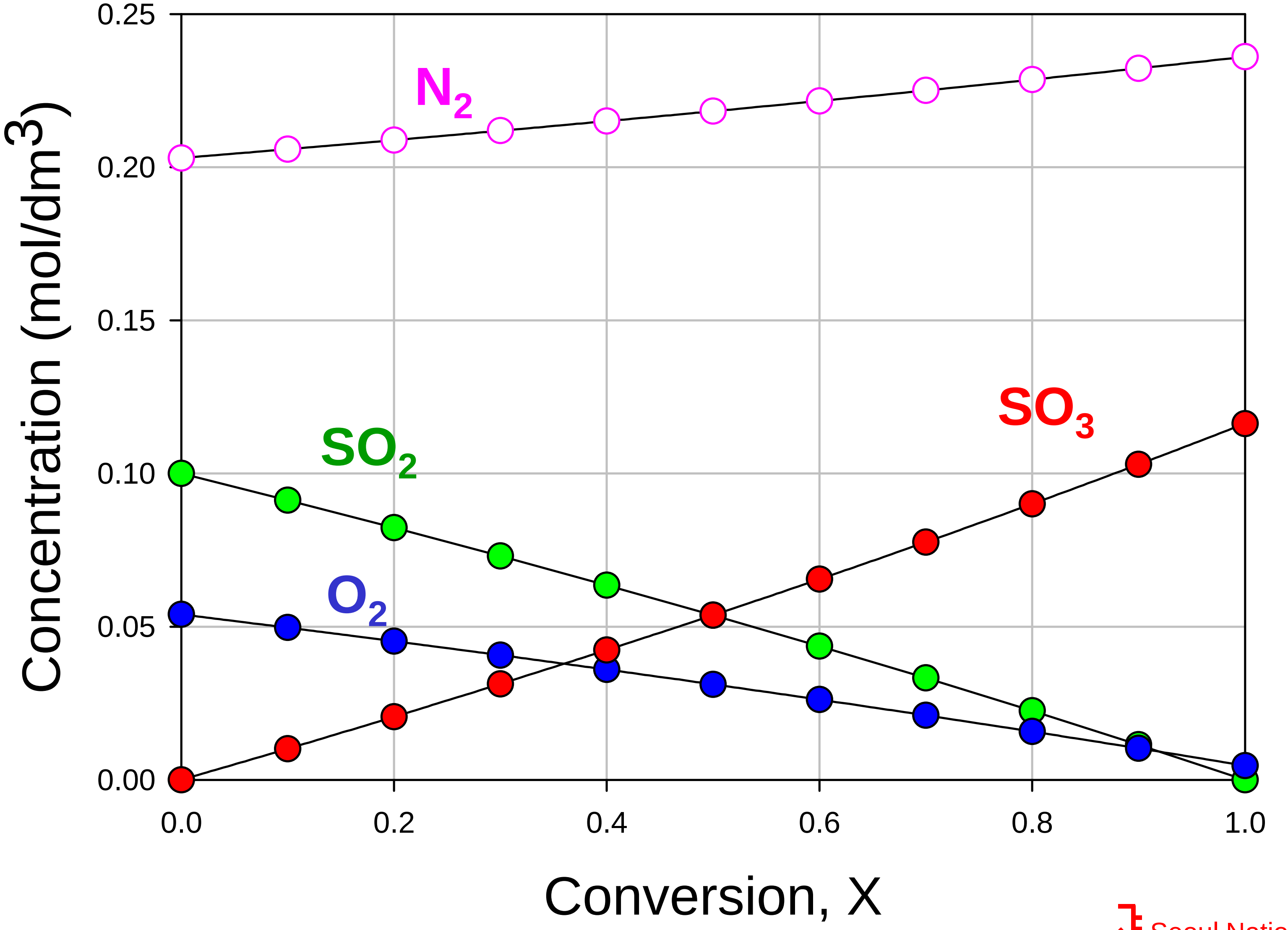
Concentrations as a function of conversion

X	C_A	C_B	C_C	C_I	C_T
0	0.1000	0.0540	0.0000	0.2030	0.3570
0.1	0.0913	0.0497	0.0101	0.2059	0.3570
0.2	0.0823	0.0453	0.0206	0.2088	0.3570
0.3	0.0731	0.0407	0.0313	0.2119	0.3570
0.4	0.0636	0.0360	0.0424	0.2150	0.3570
0.5	0.0538	0.0312	0.0538	0.2183	0.3570
0.6	0.0437	0.0262	0.0655	0.2216	0.3570
0.7	0.0333	0.0211	0.0776	0.2251	0.3570
0.8	0.0225	0.0158	0.0901	0.2286	0.3570
0.9	0.0114	0.0103	0.1030	0.2323	0.3570
1	0.0000	0.0047	0.1163	0.2360	0.3570

↑

Limiting reactant

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$$



Reaction rates as a function of conversion

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$$

$$-r_A = kC_A C_B$$

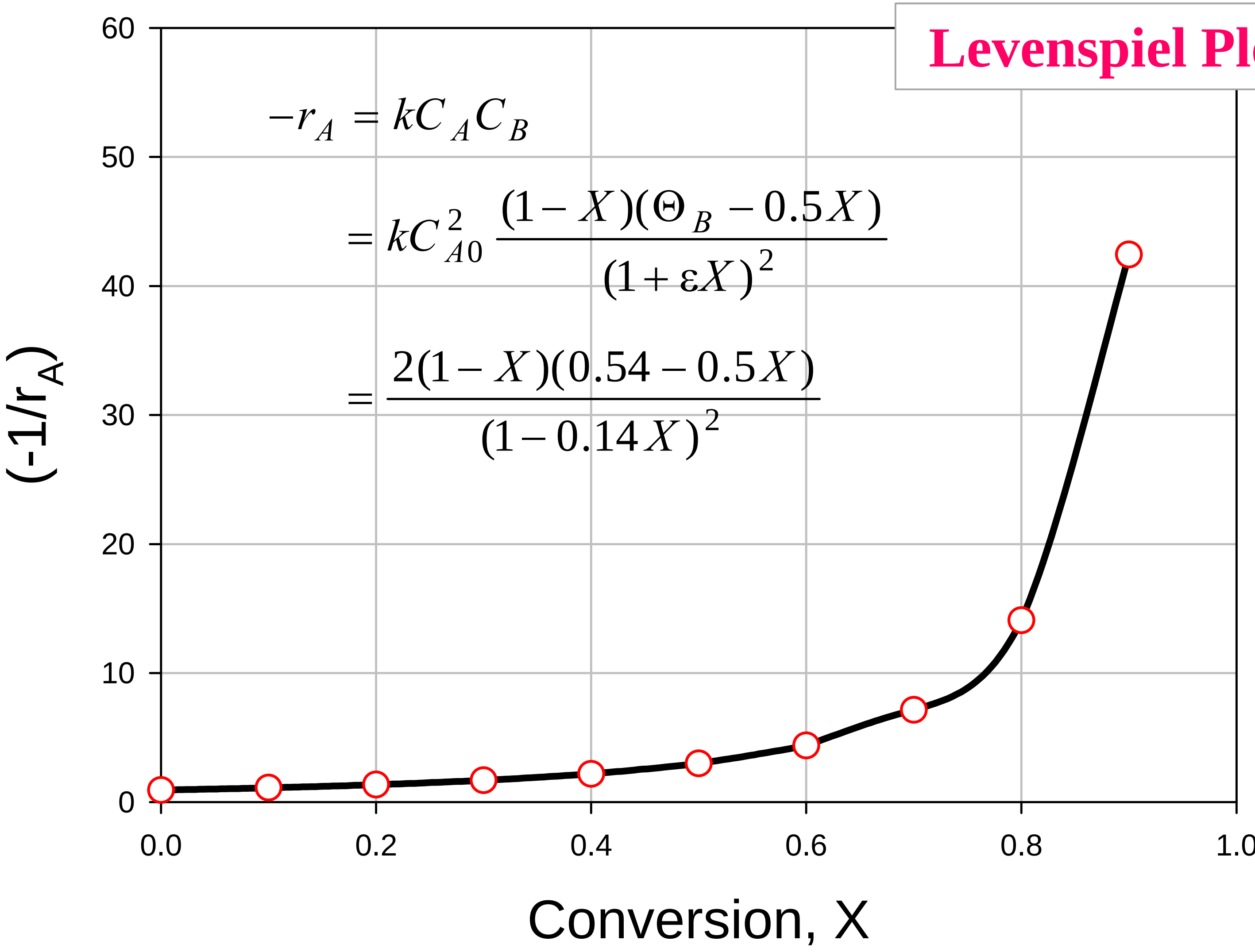
$$= kC_{A0}^2 \frac{(1-X)(\Theta_B - 0.5X)}{(1+\varepsilon X)^2}$$

$$= \frac{2(1-X)(0.54-0.5X)}{(1-0.14X)^2}$$

X	C_A	C_B	C_C	C_I	C_T	$(-r_A)$	$1/(-r_A)$
0	0.1000	0.0540	0.0000	0.2030	0.3570	1.0800	0.9259
0.1	0.0913	0.0497	0.0101	0.2059	0.3570	0.9072	1.1023
0.2	0.0823	0.0453	0.0206	0.2088	0.3570	0.7451	1.342
0.3	0.0731	0.0407	0.0313	0.2119	0.3570	0.5949	1.6809
0.4	0.0636	0.0360	0.0424	0.2150	0.3570	0.4578	2.1842
0.5	0.0538	0.0312	0.0538	0.2183	0.3570	0.3353	2.9824
0.6	0.0437	0.0262	0.0655	0.2216	0.3570	0.2288	4.3701
0.7	0.0333	0.0211	0.0776	0.2251	0.3570	0.1401	7.1369
0.8	0.0225	0.0158	0.0901	0.2286	0.3570	0.0710	14.081
0.9	0.0114	0.0103	0.1030	0.2323	0.3570	0.0236	42.438
1	0.0000	0.0047	0.1163	0.2360	0.3570	0.0000	

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$$

Levenspiel Plot



$$-r_A = kC_A C_B$$

$$= kC_{A0}^2 \frac{(1-X)(\Theta_B - 0.5X)}{(1+\varepsilon X)^2}$$

$$= \frac{2(1-X)(0.54-0.5X)}{(1-0.14X)^2}$$