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.

\[
aA + bB \rightarrow cC + dD \quad (2-1)
\]

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."

\[
A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D \quad (2-2)
\]

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

\[
-r_A = -\frac{r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d} \quad (3-1)
\]
Let’s 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

$$-r_A(T, C) = k_A(T) \times f(C_A, C_B, ...)$$

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

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.

$$-r_A = k_A C_A^a C_B^0$$

3-3

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

The order of a reaction refers to the powers to which the concentrations are raised in the kinetic rate law.
농도 대 활동도 (concentration vs. activity)

반응속도는 활동도 \( a_i \) \( (a_i = \gamma_i C_i) \)의 항으로 나타남

\[
-r_A = k'_A a_A^\alpha a_B^\beta
\]

많은 반응계의 경우에 활동도계수 \( \gamma_i \)는 반응이 진행되는 동안 현저하게 변화하지 않으므로 반응속도 \( k_A \)에 흡수.

\[
-r_A = k'_A a_A^\alpha a_B^\beta = k'_A (\gamma_A C_A)^\alpha (\gamma_B C_B)^\beta = (k'_A \gamma_A^\alpha \gamma_B^\beta) C_A^\alpha C_B^\beta = k_A C_A^\alpha C_B^\beta
\]

\[
-r_A = k_A C_A^\alpha C_B^\beta
\]

Unit of Specific Reaction Rate

The unit of the specific reaction rate, \( k_A \), vary with the order of the reaction.

\[ k = \frac{(\text{Concentration})^n}{\text{Time}} \]

\[
A \rightarrow \text{products} \quad k = \frac{\text{mol}}{(\text{dm}^3) \cdot \text{s}} \quad (3-4)
\]

0차  Zero - order : \(- r_A = k_A \) \( \{k\} = \frac{\text{mol}}{(\text{dm}^3) \cdot \text{s}} \)

1차  First - order : \(- r_A = k_A C_A \) \( \{k\} = \frac{1}{s} \) \( (3-5) \)

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

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

허가없이 본 수업자료의 무단 배포 및 사용을 불허합니다.
Elementary and Non-elementary Reaction

**Kinetic rate raw**

“**Elementary reaction**”

기초반응

\[ \text{O}^\bullet + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O}^\bullet + \text{OH}^\bullet \]

\[ -r_{\text{O}^\bullet} = k_{\text{O}^\bullet} \cdot C_{\text{CH}_3\text{OH}} \]

1\text{st} \text{ order w.r.t. atomic oxygen}

1\text{st} \text{ order w.r.t. methanol}

overall is 2\text{nd} \text{ order reaction}

“**Non-elementary reaction**”

비기초반응

\[ \text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2 \]

\[ -r_{\text{CO}} = k_{\text{CO}} \cdot C_{\text{Cl}_2}^{3/2} \]

1\text{st} \text{ order w.r.t. carbon monoxide}

3/2 \text{ order w.r.t. chorine}

overall is 5/2 \text{ order reaction}

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

---

Reversible Reactions

_All rate raws for reversible reactions must reduce to the thermodynamic relationship relating the reacting species concentrations at equilibrium._ At equilibrium, the rate of reaction is identically zero for all species (i.e., \(-r_A = 0\)). For the general reaction

\[
aA + bB \rightleftharpoons cC + dD
\]

The concentrations at equilibrium are related by the thermodynamic relationship

\[
K_c = \frac{C_c^c \cdot C_d^d}{C_a^a \cdot C_b^b} \quad \left[ \frac{(mol/ dm^3)^{d+c-b-a}}{} \right]
\]

---
### Reversible Reactions

\[
2C_6H_6 \xrightarrow{k_f} C_{12}H_{10} + H_2 \\
2B \xrightarrow{k_r} D + H_2
\]

<table>
<thead>
<tr>
<th>The rate of disappearance of benzene</th>
<th>The rate of formation of benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>[2C_6H_6 \xrightarrow{k_f} C_{12}H_{10} + H_2]</td>
<td>[C_{12}H_{10} + H_2 \xrightarrow{k_r} 2C_6H_6]</td>
</tr>
<tr>
<td>[r_{B,,\text{forward}} = -k_B C_B^2]</td>
<td>[r_{B,,\text{reverse}} = k_B C_D C_{H_2}]</td>
</tr>
</tbody>
</table>

The net rate of formation of benzene

\[r_B \equiv r_{B,\,\text{net}} = r_{B,\,\text{forward}} + r_{B,\,\text{reverse}}\]

\[r_B = -k_B C_B^2 + k_B C_D C_{H_2}\]

### Reversible Reactions

The rate law for the rate of disappearance of benzene

\[-r_B = k_B C_B^2 - k_{-B} C_D C_{H_2} = k_B \left(C_B^2 - \frac{k_B}{k_{-B}} C_D C_{H_2}\right)\]

\[-r_B = k_B \left(C_B^2 - \frac{C_D C_{H_2}}{K_C}\right)\]

\[k_B k_{-B} = K_C = \text{concentration equilibrium constant}\]
Arrhenius equation

\[ k_A(T) = A e^{-\frac{E}{RT}} \]

Specific reaction rate (constant)

Activation energy, J/mol or cal/mol

Frequency factor or pre-exponential factor

Mathematical number \( e = 2.71828 \ldots \)

Gas constant

8.314 J/mol \( \cdot \) K
1.987 cal/mol \( \cdot \) K
8.314 kPa \( \cdot \) dm\(^3\)/mol \( \cdot \) K

Absolute Temperature, K

Arrhenius equation

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

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

\( T \rightarrow 0, k_A \rightarrow 0 \)
\( T \rightarrow \infty, k_A \rightarrow A \)
**Present Status of Our Approach to Reactor Sizing and Design**

**Design Equations**

<table>
<thead>
<tr>
<th></th>
<th><strong>Differential form</strong></th>
<th><strong>Algebraic form</strong></th>
<th><strong>Integral form</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Batch</strong></td>
<td>( N_{A0} \frac{dX}{dt} = -r_AV )</td>
<td>( t = N_{A0} \int_0^X \frac{dX}{-r_AV} )</td>
<td></td>
</tr>
<tr>
<td><strong>CSTR</strong></td>
<td>( V = \frac{F_{A0}X}{-r_A} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>PFR</strong></td>
<td>( F_{A0} \frac{dX}{dW} = -r_A )</td>
<td>( V = F_{A0} \int_0^X \frac{dX}{-r_A} )</td>
<td></td>
</tr>
<tr>
<td><strong>PBR</strong></td>
<td>( F_{A0} \frac{dX}{dW} = -r_A' )</td>
<td>( W = F_{A0} \int_0^X \frac{dX}{-r_A'} )</td>
<td></td>
</tr>
</tbody>
</table>

**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.

\[ aA + bB \longrightarrow cC + dD \]  \hspace{1cm} (2-1)

\[ \frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d} \]  \hspace{1cm} (3-1)

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

\[ \frac{b}{a} B \longrightarrow \frac{c}{a} C + \frac{d}{a} D \]  \hspace{1cm} (2-2)

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

**허가없이 본 수업자료의 무단 배포 및 사용을 불허합니다.**
Stoichiometric Table for a Batch System

<table>
<thead>
<tr>
<th>Species</th>
<th>Initially (mol)</th>
<th>Change (mol)</th>
<th>Remaining (mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>$N_{A0}$</td>
<td>$-(N_{A0}X)$</td>
<td>$N_A = N_{A0} - N_{A0}X$</td>
</tr>
<tr>
<td>$B$</td>
<td>$N_{B0}$</td>
<td>$- \frac{b}{a} (N_{A0}X)$</td>
<td>$N_B = N_{B0} - \frac{b}{a} N_{A0}X$</td>
</tr>
<tr>
<td>$C$</td>
<td>$N_{C0}$</td>
<td>$+ \frac{c}{a} (N_{A0}X)$</td>
<td>$N_C = N_{C0} + \frac{c}{a} N_{A0}X$</td>
</tr>
<tr>
<td>$D$</td>
<td>$N_{D0}$</td>
<td>$+ \frac{d}{a} (N_{A0}X)$</td>
<td>$N_D = N_{D0} + \frac{d}{a} N_{A0}X$</td>
</tr>
<tr>
<td>$I$ (inert)</td>
<td>$N_{I0}$</td>
<td></td>
<td>$N_I = N_{I0}$</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>$N_{T0}$</td>
<td></td>
<td>$N_T = N_{T0} + \left( \frac{d}{a} + \frac{c}{a} - \frac{b}{a} + 1 \right) N_{A0}X$</td>
</tr>
</tbody>
</table>

$N_T = N_{T0} + 6N_{A0}X$

허가없이 본 수업자료의 무단 배포 및 사용을 불허합니다.

Constant Volume Batch Reactor (=constant density system)

\[ V = V_0 \]

\[ C_A = \frac{N_{A0}(1-X)}{V_0} = C_{A0}(1-X) \]  \hspace{1cm} (4-6)

\[ C_B = N_{A0} \frac{[(N_{B0}/N_{A0}) - (b/a)X]}{V_0} = N_{A0} \frac{[\Theta_B - (b/a)X]}{V_0} = C_{A0} \left( \Theta_B - \frac{b}{a}X \right) \]  \hspace{1cm} (4-7)

\[ C_C = N_{A0} \frac{[(N_{C0}/N_{A0}) + (c/a)X]}{V_0} = C_{A0} \left( \Theta_C + \frac{c}{a}X \right) \]  \hspace{1cm} (4-8)

\[ C_D = N_{A0} \frac{[(N_{D0}/N_{A0}) + (d/a)X]}{V_0} = C_{A0} \left( \Theta_D + \frac{d}{a}X \right) \]  \hspace{1cm} (4-9)

\[ \Theta_i = \frac{N_{I0}}{N_{A0}} = \frac{C_{I0}}{C_{A0}} = \frac{y_{I0}}{y_{A0}} \]

허가없이 본 수업자료의 무단 배포 및 사용을 불허합니다.
Flow Systems

Entering
\[ A + \frac{b}{a} B \rightarrow \frac{c}{a} C + \frac{d}{a} D \]

Leaving
\[ F_A \quad F_B \quad F_C \quad F_D \quad F_I \]

Molar flow rate
\[ C_A = \frac{F_A}{V} = \frac{\text{moles/time}}{\text{liters/time}} = \frac{\text{moles}}{\text{liter}} \]

Volumetric flow rate
\[ \Theta_i = \frac{F_i0}{V} = \frac{C_{i0}V_0}{C_{A0}V_0} = \frac{C_{i0}}{C_{A0}} \frac{y_{i0}}{y_{A0}} \]

Equations for Concentrations in Flow Systems

Batch System
\[ A + \frac{b}{a} B \rightarrow \frac{c}{a} C + \frac{d}{a} D \]

Flow System

\[ C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X)}{V} \]
\[ C_B = \frac{N_B}{V} = \frac{N_{B0}-(b/a)N_{A0}X}{V} \]
\[ C_C = \frac{N_C}{V} = \frac{N_{C0}+(c/a)N_{A0}X}{V} \]
\[ C_D = \frac{N_D}{V} = \frac{N_{D0}+(d/a)N_{A0}X}{V} \]

\[ C_A = \frac{F_A}{V} = \frac{F_{A0}(1-X)}{V} \]
\[ C_B = \frac{F_B}{V} = \frac{F_{B0}-(b/a)F_{A0}X}{V} \]
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\[ C_D = \frac{F_D}{V} = \frac{F_{D0}+(d/a)F_{A0}X}{V} \]
### Stoichiometric Table for a Flow System

<table>
<thead>
<tr>
<th>Species</th>
<th>Feed rate to reactor (mol/time)</th>
<th>Change in reactor (mol/time)</th>
<th>Effluent rate from reactor (mol/time)</th>
</tr>
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<td>$-(F_{A0}X)$</td>
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<td>B</td>
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<td>$-\frac{b}{a}(F_{A0}X)$</td>
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$$F_T = F_{T0} + F_{A0}\delta X$$

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