Chemical Reaction Engineering

Dr. Yahia Alhamed
Kinetics and Reaction Rate

What is reaction rate?
It is the rate at which a species loses its chemical identity per unit volume.

The rate of a reaction can be expressed as:-
- The rate of disappearance of a reactant or
- The rate of appearance of a product.
Reaction Rate

Consider species A:

\[ \text{A} \rightarrow \text{B} \]

\[-r_A = \text{the rate of formation of species A per unit volume}\]
\[r_B = \text{the rate of formation of species B per unit volume}\]

EXAMPLE: If B is being formed at 0.2 moles per decimeter cubed per second, i.e., \( r_B = 0.2 \text{ mole/dm}^3/\text{s} \)

Then A is disappearing at the same rate:
\[-r_A = 0.2 \text{ mole/dm}^3/\text{s} \]

The rate of formation (generation of A) is \( r_A = -0.2 \text{ mole/dm}^3/\text{s} \)
Reaction Rate

Consider species $j$:

• $r_j$ is the rate of formation of species $j$ per unit volume [e.g. mol/dm$^3$*s]

• $r_j$ is a function of concentration, temperature, pressure, and the type of catalyst (if any)

• $r_j$ is independent of the type of reaction system (batch, plug flow, etc.)

• $r_j$ is an algebraic equation, not a differential equation
Rate Law Basics

- A rate law describes the behavior of a reaction. The rate of a reaction is a function of temperature (through the rate constant) and concentration.
Reaction Rate for solid catalytic reactions

• For a catalytic reaction, we refer to \(-r_A\)', which is the rate of disappearance of species A on a per mass of catalyst basis.

• \(-r_A' = r_A/\text{bulk density of the catalyst (}\rho_b)\)
Rate Law Basics

- A rate law describes the behavior of a reaction. The rate of a reaction is a function of temperature (through the rate constant) and concentration.

- **Power Law Model**

  - $k$ is the specific reaction rate (constant)

  - $k$ is given by the Arrhenius Equation:

    $$ k = A e^{-E_{A}RT} $$

    Where:
    - $E = \text{activation energy (cal/mol)}$
    - $R = \text{gas constant (cal/mol*K)}$
    - $T = \text{temperature (K)}$
    - $A = \text{frequency factor (units of A, and k, depend on overall reaction order)}$
General Mole Balance on System Volume $V$

\[
\text{In} - \text{Out} + \text{Generation} = \text{Accumulation}
\]

\[
F_{A_0} - F_A + \int r_A dV = \frac{dN_A}{dt}
\]
Batch Reactor Mole Balance

\[
F_{A0} - F_A + \int r_A \, dV = \frac{dN_A}{dt}
\]

\[
F_{A0} = F_A = 0
\]

Well mixed

\[
\int r_A \, dV = r_A V
\]

\[
\frac{dN_A}{dt} = r_A V
\]
Constantly Stirred Tank Reactor Mole Balance

CSTR or MFR

\[
F_{A0} - F_A + \int r_A dV = \frac{dN_A}{dt}
\]

CSTR

Steady State

\[
\frac{dN_A}{dt} = 0
\]

Well mixed

\[
\int r_A dV = r_A V
\]

\[
F_{A0} - F_A + r_A V = 0
\]

V = \frac{F_{A0} - F_A}{-r_A}
Plug Flow Reactor (PFR) Mole Balance

The integral form is:

\[
V = \int_{F_{A0}}^{F_A} \frac{dF_A}{r_A}
\]

This is the volume necessary to reduce the entering molar flow rate (mol/s) from \( F_{A0} \) to the exit molar flow rate of \( F_A \).
Packed Bed Reactor Mole Balance

The integral form to find the catalyst weight is:

\[ W = \int_{F_{A0}}^{F_A} \frac{dF_A}{r'_A} \]

\[ \frac{dN_A}{dt} = 0 \]

\[ F_{A0} - F_A + \int r'_A dW = 0 \]

**Steady State**

Differentiate with respect to \( W \) and rearrange

\[ \frac{dF_A}{dW} = r'_A \]

The integral form to find the catalyst weight is:

\[ W = \int_{F_{A0}}^{F_A} \frac{dF_A}{r'_A} \]
Space time and space velocity

\[ F_{A0} = C_{A0} \cdot v_o \]

\[ \theta = \text{is called space time (s)} = \frac{V}{v_o} \]

Space velocity = \( \frac{1}{\theta} \), where:

- \( F_{A0} \) = Molar feed rate of key reactant A (mol/s)
- \( C_{A0} \) = Concentration of key reactant A in the feed (mol/m³)
- \( v_o \) = Volumetric flow rate of feed to the reactor (m³/s)
- \( V \) = Volume of the reactor

For constant volume systems \( v = v_o \) where \( v \) is volumetric flow rate leaving the reactor
# Reactor Mole Balance Summary

<table>
<thead>
<tr>
<th>Reactor</th>
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<tbody>
<tr>
<td>Batch</td>
<td>( \frac{dN_A}{dt} = r_A V )</td>
<td>( t = \int_{N_{A_0}}^{N} \frac{dN_A}{r_A V} )</td>
<td><img src="image" alt="Graph showing the relationship between time (t) and mole number (N_A)" /></td>
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<td>$t = \int_{N_{A_0}}^{N_A} \frac{dN_A}{r_A \cdot V}$</td>
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<td>CSTR</td>
<td>$V = \frac{F_{A_0} - F_A}{-r_A}$</td>
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| Batch   | \[
\frac{dN_A}{dt} = r_A \sqrt{V} 
\] | \[
t = \int_{N_A_0}^{N_A} \frac{dN_A}{r_A \sqrt{V}} 
\] | ![Graph of N_A vs t] |
| CSTR    | \[
\sqrt{V} = \frac{F_{A_0} - F_A}{-r_A} 
\] |  |  |
| PFR     | \[
\frac{dF_A}{dV} = r_A 
\] | \[
V = \int_{F_A_0}^{F_A} \frac{dF_A}{r_A} 
\] | ![Graph of F_A vs V] |
# Reactor Mole Balance Summary

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<td>$\frac{dN_A}{dt} = r_A \nu$</td>
<td>$t = \int_{N_{A0}}^{N_A} \frac{dN_A}{r_A \nu}$</td>
<td>![Graph of $N_A$ vs. $t$]</td>
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<tr>
<td>CSTR</td>
<td>$\nu = \frac{F_{A0} - F_A}{-r_A}$</td>
<td>![Graph of $\nu$ vs. $V$]</td>
<td></td>
</tr>
<tr>
<td>PFR</td>
<td>$\frac{dF_A}{dV} = -r_A$</td>
<td>$V = \int_{F_{A0}}^{F_A} \frac{dF_A}{r_A}$</td>
<td>![Graph of $F_A$ vs. $V$]</td>
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<tr>
<td>PBR</td>
<td>$\frac{dF_A}{dW} = r_A$</td>
<td>$W = \int_{F_{A0}}^{F_A} \frac{dF_A}{r_A}$</td>
<td>![Graph of $F_A$ vs. $W$]</td>
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Reactor Mole Balance
Summary

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<td>$t = \int_{N_{A0}}^{N_A} \frac{dN_A}{r_A V}$</td>
<td>$N_A$</td>
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<tr>
<td></td>
<td></td>
<td></td>
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<tr>
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<tr>
<td>PFR</td>
<td>$\frac{dF_A}{dV} = r_A$</td>
<td>$V = \int_{F_{A0}}^{F_A} \frac{dF_A}{r_A}$</td>
<td>$F_A$</td>
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<td></td>
<td>$V$</td>
</tr>
<tr>
<td>PBR</td>
<td>$\frac{dF_A}{dw} = r_A$</td>
<td>$W = \int_{F_{A0}}^{F_A} \frac{dF_A}{r_A}$</td>
<td>$F_A$</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>$w$</td>
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Conversion

Consider the general reaction: \( aA + bB \rightarrow cC + dD \)

We will choose A as bases of calculation (i.e. Key reactant)

The limiting reactant is usually taken as the key reactant

Then: \( A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D \)

\( X_A = \text{moles reacted/moles fed} \)

**Flow**

\[ X = \frac{(F_{A_0} - F_A)}{F_{A_0}} \]

**Batch**

\[ X = \frac{(N_{A_0} - N_A)}{N_{A_0}} \]

For irreversible reactions, the maximum value of \( X \) is that for complete conversion, i.e. \( X=1.0 \).

For reversible reactions, the maximum value of \( X \) is the equilibrium conversion, i.e. \( X=X_e \).
Batch Reactor Conversion

\[
\frac{dN_A}{dt} = r_A V
\]

\[
N_A = N_{A0} - N_{A0}X
\]

\[
dN_A = -N_{A0}dX
\]

\[
N_{A0} \frac{dX}{dt} = -r_A V
\]

\[
t = N_{A0} \left[ \int_0^X \frac{dX}{-r_A V} \right]
\]
CSTR Conversion

CSTR

\[ F_A = F_{A0} - F_{A0}X \]

\[ V = \frac{F_{A0} - F_A}{-r_A} = \frac{F_{A0} - (F_{A0} - F_X)}{-r_A} \]

Algebraic Form:

\[ V = \frac{F_{A0}X}{-r_A} \]

There is no differential or integral form for a CSTR.
PFR Conversion

\[ \frac{dF_A}{dV} = r_A \]

\[ F_A = F_{A0} (1 - X) \]

Differential Form:
\[ dF_A = -F_{A0}dX \]

Rearranging

Integral Form:
\[ V = F_{A0} \int_0^X \frac{dX}{-r_A} = \int_0^X \frac{F_{A0}dX}{-r_A} \]
Design Equations

The following design equations are for single reactions only. Design equations for multiple reactions will be discussed later.

**Reactor Mole Balances in Terms of Conversion**

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<td>$V = \frac{F_{A0} \cdot X}{-r_A}$</td>
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<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>
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Reactor Sizing (CSTR)

- Given \(-r_A\) as a function of conversion, \(-r_A=f(X)\), one can size any type of reactor.
- We do this by constructing a Levenspiel plot.
- Here we plot either \(\frac{F_{A0}}{-r_A}\) or \(\frac{1}{-r_A}\) as a function of X.
- Volume of a CSTR is:
  \[ V = \frac{F_{A0}(X-0)}{-r_A}_{\text{EXIT}} \]
Reactor Sizing (PFR)

For PFR the volume of the reactor needed is given by the area under the curve

\[ V_{PFR} = \int_{0}^{X} \frac{F_{A0}}{-r_{A}} \, dX \]

=area
## Summary

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<td><strong>Batch</strong></td>
<td>$N_{A0} \frac{dX}{dt} = -r_A V$</td>
<td>$t = N_{A0} \int_0^x \frac{dX}{-r_A V}$ and</td>
<td>$\int_0^t V(t) , dt = N_{A0} \int_0^x \frac{dX}{-r_A}$</td>
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<td><strong>CSTR</strong></td>
<td>[ V = \frac{F_{A0}(X_{out} - X_{in})}{(-r_A)_{out}} ]</td>
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<td><strong>PFR</strong></td>
<td>$F_{A0} \frac{dX}{dV} = -r_A$</td>
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<td>$F_{A0} \frac{dX}{dW} = -r'_A$</td>
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Rate Law Basics

• A rate law describes the behavior of a reaction. The rate of a reaction is a function of temperature (through the rate constant) and concentration.

• **Power Law Model**

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

\(\alpha\) order in \(A\)
\(\beta\) order in \(B\)

Overall Reaction Order = \(\alpha + \beta\)

\(k\) is the specific reaction rate (constant)
Examples of Rate Laws

• First Order Reactions
  
  (1) Homogeneous irreversible elementary gas phase reaction

\[ C_2H_6 \rightarrow C_2H_4 + H_2 \]

\[ -r_A = kC_{C_2H_6} \quad \text{with} \quad k = 0.072s^{-1}e^{\frac{82kcal/mol}{1000\left(1 - \frac{1}{T}\right)}} \]
Examples of Rate Laws

• First Order Reactions

(1) Homogeneous irreversible elementary gas phase reaction

\[ C_2H_6 \rightarrow C_2H_4 + H_2 \]

\[ -r_A = kC_{C_2H_6} \]

with \( k = 0.072 \text{s}^{-1} e^{\frac{82 \text{kcal}}{\text{mol} \cdot \left( \frac{1}{1000} \frac{1}{T} \right)}} \)

(2) Homogeneous reversible elementary reaction

\[ n - C_4H_{10} \leftrightarrow i - C_4H_{10} \]

\[ -r_n = k\left[C_{nC_4} - C_{iC_4} / K_c\right] \]

with \( k = 31.1 \exp \left[7900 \left(\frac{T - 360}{360T}\right)\right] \) and \( K_c = 3.03 \exp \left[-830.3 \left(\frac{T - 333}{333T}\right)\right] \)
Examples of Rate Laws

• First Order Reactions

(1) Homogeneous irreversible elementary gas phase reaction

\[ \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 \]

\[-r_A = kC_{\text{C}_2\text{H}_6} \quad \text{with} \quad k = 0.072 \text{s}^{-1} e^{\frac{82 \text{ kcal}}{\text{mol} \left( \frac{1}{1000} - \frac{1}{T} \right)}}\]

(2) Homogeneous reversible elementary reaction

\[ n - \text{C}_4\text{H}_{10} \leftrightarrow i - \text{C}_4\text{H}_{10} \]

\[-r_n = k \left[ C_{\text{nC}_4} - C_{\text{iC}_4} / K_c \right] \]

\[ \text{with} \quad k = 31.1 \exp \left[ 7900 \left( \frac{T - 360}{360T} \right) \right] \quad \text{and} \quad K_c = 3.03 \exp \left[ -830.3 \left( \frac{T - 333}{333T} \right) \right] \]

• Second Order Reactions

(1) Homogeneous irreversible non-elementary reaction

\[ \text{ONCB} + 2\text{NH}_3 \rightarrow \text{ONCB} + \text{NH}_4\text{Cl} \]

\[-r_A = kC_{\text{ONCB}} C_{\text{NH}_3} \quad \text{with} \quad k = 0.0017 \frac{\text{m}^3}{\text{kmol.min}} \quad \text{and} \quad E = 11273 \frac{\text{cal}}{\text{mol}} \quad \text{At} \ 188^\circ \text{C} \]

This is first order in ONCB, first order in ammonia and overall second order.
Examples of Rate Laws

• Second Order Reactions

(2) Homogeneous irreversible elementary reaction

\[ \text{CNBr} + \text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3\text{Br} + \text{NCNH}_2 \quad \text{with} \quad k = \frac{2.2 \text{dm}^3}{\text{s.mol}} \]

\[ -r_A = kC_{\text{CNBr}} C_{\text{CH}_3\text{NH}_2} \]
Examples of Rate Laws

• Second Order Reactions

(2) Homogeneous irreversible elementary reaction

\[ \text{CNBr} + \text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3\text{Br} + \text{NCNH}_2 \quad \text{with} \quad k = \frac{2.2 \text{dm}^3}{\text{s.mol}} \]

\[ -r_A = kC_{\text{CNBr}} C_{\text{CH}_3\text{NH}_2} \]

This reaction is first order in CNBr, first order in \( \text{CH}_3\text{NH}_2 \) and overall second order.

(3) Heterogeneous catalytic reaction: The following reaction takes place over a solid catalyst:

\[ \text{Cumene} (C) \rightarrow \text{Benzene} (B) + \text{Proplene} (P) \]

\[ -r_C = \frac{k[P_C - P_B P_P/K_P]}{1 + K_B P_B + K_C P_C} \]