Objectives

- Review rates of reactions.
- Understand rate law and order of reaction.
- Determination of zero-, first-, and second-order reactions.
- Apply temperature corrections to chemical and biochemical reactions.
- Discuss three types of flow regimes.
- Review ideal batch, complete-mix, and plug flow reactors.

Rates of Reaction: stoichiometric coefficients are unity

\[ 
A + B \rightarrow C 
\]

\[ r = \frac{d}{dt} \left( \frac{C}{dt} \right) = -\frac{d}{dt} \left( \frac{A}{dt} \right) = -\frac{d}{dt} \left( \frac{B}{dt} \right) \]

\( r \) = rate of reaction, moles/(L·time), and 
[ ] = concentration, moles/L or M.

Rate of Reaction: stoichiometric coefficients are not unity

\[ 
2A \rightarrow 3C 
\]

\[ r = \frac{1}{3} \frac{d}{dt} \left( \frac{C}{dt} \right) = -\frac{1}{2} \frac{d}{dt} \left( \frac{A}{dt} \right) \]
Rate Equation & Reaction Order

\[ aA + bB \rightarrow cC \]

\[ r = -k \ A^\alpha \ B^\beta = k \ C^\gamma \]

Overall order of the reaction based on the reactants A and B is \( \alpha + \beta \). Reaction is said to be \( \alpha \)-order with respect to A and \( \beta \)-order with respect to B. Reaction order based on product formation is \( \gamma \) or \( \gamma \)-order with respect to C.

EXAMPLE 5.5 Determination of reaction order

For the rate law equation given below, determine the order of the reaction with respect to each chemical species and give the overall order of the reaction.

\[ r = \frac{dA}{dt} = k \ A^1 \ B^2 \]

Solution

The reaction is considered to be first-order with respect to A and second-order with respect to B. The overall order of the reaction is third.

Relationship among rate of reaction \( (r) \), reactant concentration \( (conc) \), and reaction order \( (n) \).

\[ r = Conc^n \]

\[ \ln r = n \ln Conc \]

Plotting \( \ln(r) \) versus \( \ln(C) \)
Zero-Order Reactions

\[ A \rightarrow P \]

\[ r = - \frac{dC}{dt} = k C^0 = k \]

\( \frac{dC}{dt} \) = rate of change in the concentration of A with time or rate of disappearance of A (mass)/(volume/time) and \( k \) = reaction rate constant, (mass)/(volume/time).

Differential and Integrated Forms of Zero-Order Reaction

\[ \int_{C_0}^{C_i} dC = -k \int_0^t dt \]

\[ C_t - C_0 = -k t \]

Plot of Zero-Order Removal Reaction

Y-intercept = \( C_0 \)
Slope = - \( k \)

Plot of Zero-Order Production Reaction

Y-intercept = \( C_0 \)
Slope = \( k \)
First-Order Reactions

\[ A \rightarrow P \]

\[ r = - \frac{dC}{dt} = k \ C^1 \]

Differential and Integrated Forms of First-Order Removal Reaction

\[
\int_{C_0}^{C_t} \frac{1}{C} dC = - k \int_0^t dt
\]

\[ \ln(C_t) - \ln(C_0) = - k \ t \]

Arithmetic Plot of First-Order Removal Reaction

Y-intercept = \(C_0\)

Semi-log Plot of First-Order Removal Reaction

Y-intercept = \(\ln(C_0)\)

Slope = \(k\)
**Arithmetic Plot of First-Order Production Reaction**

- $C_t$ vs. Time ($t$)

**Semi-log Plot of First-Order Production Reaction**

- $\ln(C_t)$ vs. Time ($t$)
  - Y-intercept = $\ln(C_0)$
  - Slope = $k$

**Exponential Equation Form**

- $\ln(C_t) - \ln(C_o) = -kt$
- $C_t = C_o e^{-kt}$

**Half-life Equation**

- $C_t = C_o e^{-kt}$
- $0.5 C_o = C_o e^{-kt}$
- $t_{1/2} = \frac{-\ln(0.5)}{k} = \frac{0.693}{k}$
Second-Order Reactions

A → P

\[ r = - \frac{dC}{dt} = k \cdot C^2 \]

Differential and Integrated Forms of Second-Order Removal Reaction

\[ \int_{C_0}^{C_t} \frac{1}{C^2} dC = k \int_0^t dt \]

\[ \frac{1}{C_t} = \frac{1}{C_0} + k \cdot t \]

Plot of Second-Order Removal Reaction

\[ \frac{1}{C_t} \]

Slope = \( k \)

Y-intercept = \( \frac{1}{C_0} \)

Plot of Second-Order Production Reaction

\[ \frac{1}{C_t} \]

Slope = \( k \)
Temperature Corrections

\[
\frac{k_2}{k_1} = \theta (T_2 - T_1)
\]

\(\theta\) = temperature correction coefficient
\(k_2\) = reaction rate constant at temperature \(T_2\), and
\(k_1\) = reaction rate constant at temperature \(T_1\).

Flow Regimes

- **Ideal Plug**: all elements pass through the reactor at the same time; pipe flow; no longitudinal mixing along length of the reactor.
- **Ideal Complete-Mix**: all fluid particles instantaneously mixed upon entering the reactor.
- **Dispersed Flow**: somewhere between ideal plug flow and ideal complete-mix.

Ideal Detention Time

\[
\tau = \frac{V}{Q}
\]

\(\tau\) = ideal hydraulic detention time, hr or d,
\(V\) = volume of the tank, lake, or reactor, ft\(^3\), m\(^3\), L, gal, and
\(Q\) = volumetric flow rate, ft\(^3\) d\(^{-1}\), m\(^3\) d\(^{-1}\), L d\(^{-1}\), gal d\(^{-1}\).

Material Balances

\[
[\text{accumulation}] = [\text{inputs}] - [\text{outputs}] + [\text{reaction}]
\]
Mass Balance: Batch Reactor

\[
\left( \frac{dC}{dt} \right)_{\text{accum}} = QC_o - QC_t + \left( \frac{dC}{dt} \right)\nu
\]

\[
\left( \frac{dC}{dt} \right)_{\text{accum}} = 0 - 0 + -k \nu
\]

\[
\left( \frac{dC}{dt} \right)_{\text{accum}} = -k
\]

EXAMPLE 5.9 Complete-mix batch reactor design

A CMBR is to be designed to pre-treat a food-processing wastewater that contains 500 mg/L of biochemical oxygen demand (BODs). A treatability study performed on the food-processing wastewater determined the kinetics for BODs removal to be zero-order with a rate constant of 40 mg/(L-h).

Determine:

a) Reaction or treatment time necessary to reduce the BODs of the wastewater to 100 mg/L.

b) The volume of the reactor to treat 6000 m³ of wastewater daily.

Solution Part A

\[ t = \frac{500 - 100 \text{ mg/L}}{40 \text{ mg/(L-h)}} = 10 \text{ h} \]

Solution Part B

Assume that two batches of wastewater will be processed each day with 3000 m³ of wastewater per batch. This will allow the reactor to be filled in 1 hour and drained in 1 hour resulting in a total time of 12 hours for each batch of processed wastewater.
EXAMPLE 5.6 Determination of rate equation


As noted earlier, the rate law must be determined experimentally. Consider the following overall chemical reaction:

\[ 2 \text{NO}_2 + \text{O}_2 \rightarrow 2 \text{NO}_2 \ g \]

The proposed rate law for this reaction is as follows:

\[ r = k \ \text{NO}_2 \ O_2 \]

Three experimental runs were performed to confirm the proposed rate law presented above. The table below shows the data collected during each run.

<table>
<thead>
<tr>
<th>Run Number</th>
<th>Rate of Reaction, M/s</th>
<th>Initial [NO] Concentration, M</th>
<th>Initial [O(_2)] Concentration, M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.2 \times 10^{-6}</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>2</td>
<td>2.4 \times 10^{-6}</td>
<td>0.10</td>
<td>0.20</td>
</tr>
<tr>
<td>3</td>
<td>1.08 \times 10^{-7}</td>
<td>0.30</td>
<td>0.10</td>
</tr>
</tbody>
</table>

SOLUTION

To develop the rate law, pick the first two runs and determine how the rate of reaction is affected by doubling the concentration of oxygen since the concentration of nitrous oxide (NO) is held constant. The rate of reaction has doubled by doubling the concentration of \([\text{O}_2]\). Showing this mathematically as follows:

\[
\frac{1.08 \times 10^{-7}}{1.2 \times 10^{-8}} = 9
\]

Therefore, the value of \(x\) must be equal to 1 and the order of the reaction with respect to oxygen is 1. Now select Runs 1 and 3 in which the concentration of oxygen is held constant at 0.10 M and the rate of reaction increases by a factor of 9.

The rate of reaction increases nine-fold while the concentration of nitrous oxide is tripled. This is expressed mathematically as follows:

\[
\frac{1.08 \times 10^{-7}}{0.30 \ M} \times \frac{0.10 \ M}{1.08 \times 10^{-7}} = 9
\]

Therefore, the value of \(x\) must be 2; this means that the order of reaction with respect to [NO] is 2. The proposed rate law is correct.

Determine the value of the reaction rate constant, \(k\), using data from one of the runs. Let’s use the data from Run #3.

\[
r = k \ \text{NO}_2 \ O_2
\]

\[
k = \frac{r}{\text{NO}_2 \ O_2} = \frac{1.08 \times 10^{-7} \ M/s}{0.30 \ M^2 \ 0.10 \ M}
\]

\[
k = 1.2 \times 10^{-5} \ M^2 s^{-1}
\]

Complete-Mix Flow Reactor
First-Order Removal CMFR

\[ r = - \frac{dC}{dt} = k \ C^1 \]

\[ \text{[accumulation]} = \text{[inputs]} - \text{[outputs]} + \text{[reaction]} \]

\[ \left( \frac{dC}{dt} \right)_{\text{accum}} = QC_0 - QC_t + r \ V \]

**EXAMPLE 5.10 Complete-mix flow reactor design**

A complete-mix flow reactor is to be designed to treat an influent stream containing 200 mg/L of chemical oxygen demand (COD) at a flow rate of 200 gallons per minute (gpm). COD represents the total quantity of oxygen required to oxidize organic matter to carbon dioxide and water. COD removal follows a first-order removal reaction with a rate constant \( k \) of 0.45 h\(^{-1}\).

**Determine:**

a) The detention time in hours if the effluent is to contain 15 mg/L of COD.

b) The volume of the reactor in ft\(^3\) if the effluent is to contain 15 mg/L of COD.

**Solution Part A**

\[ \tau = \frac{C_0 - C_t}{k C_t} = \frac{200 \text{ mg/L}}{0.45 \text{ h}^{-1} \times 15 \text{ mg/L}} = 24.7 \text{ h} \]

**Solution Part B**

\[ V = \tau Q = 27.4 \text{ h} \times \left( \frac{200 \text{ gal}}{\text{min}} \times \frac{\text{min}}{60 \text{ min}} \times \frac{1 \text{ ft}^3}{7.48 \text{ gal}} \right) = 44,000 \text{ ft}^3 \]

**EXAMPLE 5.11 Complete-mix flow reactor design**

A complete-mix flow reactor is to be designed to treat domestic wastewater with an influent five-day biochemical oxygen demand (BOD\(_5\)) concentration of 150 mg/L and a flow rate of 545 m\(^3\)/d. A 90% removal in BOD\(_5\) is to be achieved. The concentration of microorganisms (\( X \)) in the reactor is maintained at 2500 mg/L. Assuming that substrate utilization can be modeled by the following equation:

\[ \frac{dS}{dt} = \frac{k X S}{K_s + S} \]

**Determine:**

a) The equation for detention time by performing a mass balance on substrate.

b) The detention time in hours.
\[
\left( \frac{dS}{dt} \right)_{\text{accum}} = Q S_0 - Q S_t - r V
\]

\[
\left( \frac{dS}{dt} \right)_{\text{accum}} = Q S_0 - S_t - \left( \frac{k X S_t}{K_S + S_t} \right) V
\]

0 = Q \left( S_0 - S_t \right) - \left( \frac{k X S_t}{K_S + S_t} \right) V

\[
\frac{S_0 - S_t}{\tau} = \left( \frac{k X S_t}{K_S + S_t} \right)
\]

\[
S_t = 150 \frac{\text{mg}}{\text{L}} \cdot 1 - 0.9 \cdot 45.0 \frac{\text{mg}}{\text{L}}
\]

\[
\tau = S_0 - S_t = \frac{(50 - 15 \text{mg/L}) \cdot (0 + 15 \text{mg/L})}{5 \text{d}^{-1} \times 2500 \text{mg/L} \times 15 \text{mg/L}} = 0.0468 \text{d}
\]

\[
\tau = 0.0468 \text{d} \times \left( \frac{24 \text{h}}{\text{d}} \right) = 11 \text{h}
\]

**CMFR in Series**

**CM Reactors in Series**

\[
C_t = \frac{C_0}{1 + k \tau}
\]

\[
C_1 = \frac{C_0}{1 + k \tau}
\]

\[
C_2 = \frac{C_1}{1 + k \tau}
\]

\[
C_3 = \frac{C_2}{1 + k \tau}
\]

\[
C_n = C_0 \left( \frac{1}{1 + k \tau} \right)^n
\]
Example: CMFRs in Series

10 CMFRs in series; \( k = 0.35 \text{ h}^{-1} \) and detention time = 0.667 hours per reactor.
Calculate the effluent COD concentration if the influent COD concentration is 150 mg/L.

\[
C_n = C_0 \left( \frac{1}{1 + k \tau} \right)^n
\]

\[
C_{10} = 150 \text{ mg/L} \left( \frac{1}{1 + 0.35 \text{ h}^{-1} \times 0.667 \text{ h}} \right)^{10}
\]

\[
C_{10} = \frac{18 \text{ mg/L}}{L}
\]

One-Dimensional Plug Flow

\[
\left( \frac{\partial C}{\partial t} \right) \Delta V = QC|_X - QC|_{X + \Delta X} + r \Delta V
\]

\[\Delta V = \text{ elemental volume, L}^3; \]
\[A = \text{ cross-sectional area of the reactor, width times the depth, L}^2; \text{ and} \]
\[\Delta X = \text{ width or thickness of the elemental area, L.} \]

\[
\left( \frac{\partial C}{\partial t} \right) \Delta V = QC - \left( C + \frac{\Delta C}{\Delta X} \Delta X \right) + r \Delta V
\]

One-Dim. Plug Flow

\[
\left( \frac{\partial C}{\partial t} \right) A \Delta X = QC - QC - \left( Q \frac{\Delta C}{\Delta X} \Delta X \right) + r A \Delta X
\]

Dividing both sides of the above equation by \( A \Delta X \)

\[
\left( \frac{\partial C}{\partial t} \right) = - \left( Q \frac{\Delta C}{A \Delta X} \right) + r
\]

General form for the One-Dimensional Plug Flow Equation

\[
\left( Q \frac{\Delta C}{A \Delta X} \right) = r
\]
Second-Order Removal Plug Flow

\[
r = \frac{dC}{dt} = -kC^2
\]

\[
\left( \frac{Q}{A} \frac{dC}{dX} \right) = -kC^2
\]

\[- \frac{A}{Q} \int_0^L dX = \frac{1}{k} \int_0^{C_e} \frac{1}{C^2} dC
\]

**Detention Time for 2\textsuperscript{nd} Order Removal Plug Flow Reactor**

\[
- \frac{AL}{Q} = -\frac{\nu}{Q} = -\tau = \frac{1}{k} \left[ \left( \frac{1}{C_i} \right) - \left( \frac{1}{C_o} \right) \right]
\]

\[
\tau = \frac{1}{k} \left[ \left( \frac{1}{C_i} \right) - \left( \frac{1}{C_o} \right) \right]
\]

**EXAMPLE 5.7 Plug flow reactor design**

A continuous PFR is to be designed to treat an influent stream containing 250 mg/L of acetic acid at a flow rate of 300 liters per minute (lpm). A second-order removal reaction is occurring where the rate constant \( k \) is 0.0075 L/(mg·h).

Determine:

a) The detention time in hours to achieve 90% removal of acetic acid.

b) The volume of the reactor in m\(^3\) to achieve 90% removal of acetic acid.

**Solution Part A**

percent removal \( \% = \frac{C_{out} - C_{in}}{C_{in}} \times 100 \)

90\% = \frac{250 \text{ mg/L} - C_{out}}{250 \text{ mg/L}} \times 100

\[ C_{out} = 25 \text{ mg/L} \]

**Solution Part B**

\[
\tau = \frac{1}{k} \left[ \left( \frac{1}{C_i} \right) - \left( \frac{1}{C_o} \right) \right] = \frac{1}{0.0075 \text{ L/mg·h}} \left[ \frac{1}{25 \text{ mg/L}} - \frac{1}{250 \text{ mg/L}} \right]
\]

\[
\tau = \frac{4.8 \text{ h}}{}
\]

\[
\psi = \tau \times Q = 4.8 \text{ h} \left( \frac{300 \text{ L}}{60 \text{ min}} \right) \left( \frac{1 \text{ m}^3}{1000 \text{ L}} \right) = 86.4 \text{ m}^3
\]
EXAMPLE: Derivation of $\tau$ equation for PFR with a first-order removal reaction

Derive an equation for calculating the detention time in a continuous flow, plug flow reactor which has a first-order removal reaction occurring within.

\[
\left( \frac{Q}{A} \frac{dC}{dX} \right) = -r = -kC
\]
\[
\frac{Q}{A} \frac{dC}{dX} = -kC
\]

Derivation of $\tau$ equation for PFR with a first-order removal reaction continued.

\[
\int_{C_0}^{C_f} \frac{1}{C} dC = \frac{-kA}{Q} \int_0^\tau dX
\]
\[
\ln \frac{C_f}{C_0} = \frac{-k A L}{Q}
\]
\[
\ln C_f - \ln C_0 = \frac{kV}{Q}
\]

Example: Comparison of 10 CMFRs in Series versus one PF

10 CMFRs in series; $k = 0.35$ h$^{-1}$ and detention time= 0.667 hr per reactor resulted in effluent COD concentration of 18 mg/L.

\[
\ln \left( \frac{C_f}{C_0} \right) = -k \tau
\]
\[
C_f = C_0 e^{-k\tau} = \frac{150 \text{ mg}}{L} e^{-0.35 \text{ h}^{-1} \times 0.667 \text{ h}} < 15 \text{ mg/L}
\]
\[
C_f = 15 \text{ mg/L}
\]
Example Continued: Show % Removal or % Conversion

\[
\text{% Conversion} = \frac{C_{\text{in}} - C_{\text{out}} \times 100}{C_{\text{in}}}
\]

\[
\text{% Conversion} = \frac{150 - 18 \text{ mg/L} \times 100}{150 \text{ mg/L}} = 88\% \text{ CMFRs in Series}
\]

\[
\text{% Conversion} = \frac{150 - 15 \text{ mg/L} \times 100}{150 \text{ mg/L}} = 90\% \text{ PFR}
\]

\[
\text{% Conversion} = \frac{88\%}{90\%} = 98\% \text{ CMFRs}
\]

CMFRs yield 98% performance of PFR.

Pulse Addition of Dye to Complete-Mix Reactor

\[
\left( \frac{dC}{dt} \right) = - \frac{Q}{\nu} C_0 - Q C + r \nu
\]

\[
\left( \frac{dC}{dt} \right) = 0 - Q C + 0
\]

\[
\frac{dC}{dt} = -\frac{Q C}{\nu}
\]

\[
\int_{C_0}^{C} \frac{1}{C} dC = -\frac{Q}{\nu} \int_0^t dt
\]

\[
\ln C - \ln C_0 = -\frac{t}{\tau}
\]

\[
C = C_0 e^{-t/\tau}
\]
Complete-mix reactor response to step addition of dye

Batch reactor response to pulse addition of dye

Residence time curve for pulse addition of dye to a PFR