Chemical Reaction Engineering (CRE) is the field that studies the rates and mechanisms of chemical reactions and the design of the reactors in which they take place.
Today’s lecture

- **Membrane Reactors:** Used for Thermodynamically Limited Reactions

- Balances in Terms of Molar Flow Rates
  - Block 1: Mole Balances
    Balance Equation on Every Species
  - Block 2: Rate Laws
    Relative Rates
    Transport Laws
  - Block 3: Stoichiometry
  - Block 4: Combine
# Reactor Mole Balance Summary

The GMBE applied to the four major reactor types (and the general reaction $A \rightarrow B$)

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Differential</th>
<th>Algebraic</th>
<th>Integral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch</td>
<td>$\frac{dN_A}{dt} = r_A V$</td>
<td>$N_A(t) = \int_{t_0}^{t} \frac{dN_A}{r_A V}$</td>
<td></td>
</tr>
<tr>
<td>CSTR</td>
<td>$V = \frac{F_{A0} - F_A}{-r_A}$</td>
<td>$V = \int_{F_{A0}}^{F_A} \frac{dF_A}{dr_A}$</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></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></td>
</tr>
</tbody>
</table>
Mole Balance

1. Write mole balance on each species.\(^\dagger\)

\[
\frac{dF_A}{dV} = r_A, \quad \frac{dF_B}{dV} = r_B, \quad \frac{dF_C}{dV} = r_C
\]

Rate Law

2. Write rate law in terms of concentration.

\[
e_{g} = -r_A = k_A \left( C_A C_B^2 - \frac{C_C}{K_C} \right)
\]

Relative Rates

3. Relate the rates of reaction of each species to one another.

\[
\frac{-r_A}{1} = \frac{-r_B}{2} = \frac{r_C}{1}
\]

\(\text{e.g.}, r_B = 2r_A, \quad r_C = -r_A\)

Stoichiometry

4. (a) Write the concentrations in terms of molar flow rates for isothermal \textit{gas-phase} reactions.

\[
e_{g} = C_A = C_{T_0} \frac{F_A}{F_T} \frac{P}{P_0}, \quad C_B = C_{T_0} \frac{F_B}{F_T} \frac{P}{P_0}
\]

\(\text{with } F_T = F_A + F_B + F_C\)

(b) For \textit{liquid-phase} reactions, use concentration, e.g., \(C_A, C_B\)

Pressure Drop

5. Write the \textit{gas-phase} pressure drop term in terms of molar flow rates.

\[
\frac{dy}{dW} = -\frac{\alpha}{2y} \frac{F_T}{F_{T_0}} , \quad \text{with } y = \frac{P}{P_0}
\]

Combine

6. Use an ODE solver or a nonlinear equation solver (e.g., Polymath) to combine Steps 1 through 5 to solve for, for example, the profiles of molar flow rates, concentration, and pressure.

\(\dagger\) For PBR, use \(\frac{dF_A}{dW} = r_A, \quad \frac{dF_B}{dW} = r_B, \quad \frac{dF_C}{dW} = r_C.\)
Membrane Reactors

Membrane reactors can be used to achieve conversions greater than the original equilibrium value. These higher conversions are the result of Le Chatelier’s principle; you can remove the reaction products and drive the reaction to the right.

To accomplish this, a membrane that is permeable to that reaction product, but impermeable to all other species, is placed around the reacting mixture.
Membrane reactors

Dehydrogenation Reaction:

\[ \text{C}_3\text{H}_8 \leftrightarrow \text{H}_2 + \text{C}_3\text{H}_6 \quad \text{A} \leftrightarrow \text{B} + \text{C} \]

Thermodynamically Limited:

exothermic

\[ X_C \]

endothermic

\[ X_C \]
Membrane reactors

\[ W = \rho_b V \]

\[ \rho_b = (1-\phi)\rho_C \]

A, C stay behind since they are too big
Membrane reactors

Mole Balance:

Species A: \( \text{In} - \text{out} + \text{generation} = 0 \)

\[
F_{A0}\big|_V - F_{A0}\big|_{V+\Delta V} - r_A \Delta V = 0
\]

A: \[
\frac{dF_A}{dV} = r_A
\]
Species B: In – out – out membrane + generation = 0

\[ F_B\big|_V - F_B\big|_{V+\Delta V} - R_B \Delta V + r_B \Delta V = 0 \]

B: \[ \frac{dF_B}{dV} = (r_B - R_B) \]

\[ R_B = \frac{\text{moles of B through sides}}{\text{volume of reactor}} \]
Membrane reactors

\[ W_B = k'_C (C_B - C_{BS}) \quad \left[ \frac{\text{mol}}{m^2 \cdot \text{s}} \right] \]

\[ a = \frac{\text{membrane surface area}}{\text{reactor volume}} = \frac{\pi DL}{\frac{\pi D^2}{4} L} = \frac{4}{D} \quad \left[ \frac{m^2}{m^3} \right] \]

\[ R_B = W_B a = k'_C a [C_B - C_{BS}] \]

\[ k'_C = k_C a \]

\[ R_B = k_C \left[ C_B - C_{BS} \right] \quad \left[ \frac{\text{mol}}{m^3 \cdot \text{s}} \right] \]

Neglected most of the time
Membrane reactors

**Mole Balance:**

1. \[ \frac{dF_A}{dV} = r_A \]
2. \[ \frac{dF_B}{dV} = r_B - R_B \]
3. \[ \frac{dF_C}{dV} = r_C \]

**Rate Laws:**

4. \[ r_A = -k \left[ C_A - \frac{C_B C_C}{K_C} \right] \]
Membrane reactors

Relative Rates: \[ \frac{-r_A}{1} = \frac{r_B}{1} = \frac{r_C}{1} \]

Net Rates:

\[ r_A = -r_B, \quad r_A = -r_C \] (5)

Transport Law:

\[ R_B = k_c C_B \] (6)

Stoichiometry:

\[ C_A = C_{T0} \frac{F_A}{F_T} \] (7)

\[ C_B = C_{T0} \frac{F_B}{F_T} \] (8)

\[ C_C = C_{T0} \frac{F_C}{F_T} \] (9)

\[ F_T = F_A + F_B + F_C \] (10)

Parameters: \( C_{TO} = 0.2, \quad F_{A0} = 5, \quad k = 4, \quad K_C = 0.0004, \quad k_C = 8 \)
Membrane Reactors

Example: The following reaction is to be carried out isothermally in a membrane reactor with no pressure drop. The membrane is permeable to product C, but impermeable to all other species.

\[
C_6H_{12} \Leftrightarrow C_6H_6 + 3H_2 \\
A \Leftrightarrow B + 3C
\]

For membrane reactors, we cannot use conversion. We have to work in terms of the molar flow rates \( F_A, F_B, F_C \).
Membrane Reactors

Mole Balances:

\[
\frac{dF_A}{dW} = r_A'
\]

\[
\frac{dF_B}{dW} = r_B'
\]

\[
\frac{dF_C}{dW} = r_C' - k_C C_C
\]
Membrane Reactors

Rates:

Rate Law:

\[- r'_A = k_A \left[ C_A - \frac{C_B C_C^3}{K_C} \right] \]

Relative Rates:

\[ \frac{r'_A}{-1} = \frac{r'_B}{1} = \frac{r'_C}{3} \]

Net Rate:

\[ r'_B = -r'_A \]

\[ r'_C = -3r'_A \]
Membrane Reactors

**Stoichiometry:**
Isothermal, no pressure drop

\[
C_{T0} = \frac{P_0}{RT_0}
\]

\[
C_A = C_{T0} \frac{F_A}{F_T}
\]

\[
C_B = C_{T0} \frac{F_B}{F_T}
\]

\[
C_C = C_{T0} \frac{F_C}{F_T}
\]

\[
F_T = F_A + F_B + F_C
\]
Membrane Reactors

Combine: – Use Polymath

Parameters:

\[ C_{T0} = 0.2 \frac{\text{mol}}{\text{dm}^3} \]
\[ F_{A0} = 10 \frac{\text{mol}}{\text{s}} \]
\[ k_A = 10 \frac{\text{dm}^3}{\text{kg cat s}} \]
\[ k_C = 0.5 \frac{\text{dm}^3}{\text{kg cat s}} \]
\[ K_C = 200 \frac{\text{mol}^2}{\text{dm}^6} \]
Membrane Reactors
End of Lecture 9