“Chemical Engineers are not gentle people, they like high temperatures and high pressures.” - Steve LeBlanc

How does the algorithm change?

1. Mole Balance (design equation)
2. Rate Law (Arrhenius)
3. Stoichiometry
4. Combine
5. Energy Balance
Energy Balance

• First law of Thermodynamics

• Closed System – no mass crosses the system boundaries

• Open System – mass crosses (continuous flow reactors)

\[
\frac{d \hat{E}_{\text{system}}}{dt} = \dot{Q} - \dot{W} + \sum_{i=1}^{n} E_i F_i \bigg|_{\text{in}} - \sum_{i=1}^{n} E_i F_i \bigg|_{\text{out}}
\]
Lets evaluate each of the terms in our energy balance

Work Term

What kind of work do we have?

- Flow work
- Other work

\[
\dot{W} = - \sum_{i=1}^{n} F_i P \tilde{V}_i \bigg|_{\text{in}} + \sum_{i=1}^{n} F_i P \tilde{V}_i \bigg|_{\text{out}} + \dot{W}_s
\]

\[
\frac{d\hat{E}}{dt} = \dot{Q} - \dot{W} + \sum_{i=1}^{n} E_i F_i \bigg|_{\text{in}} - \sum_{i=1}^{n} E_i F_i \bigg|_{\text{out}}
\]

\[
\frac{d\hat{E}_{\text{system}}}{dt} = \dot{Q} - \dot{W}_s + \sum_{i=1}^{n} (E_i + P\tilde{V}_i) F_i \bigg|_{\text{in}} - \sum_{i=1}^{n} (E_i + P\tilde{V}_i) F_i \bigg|_{\text{out}}
\]
How do we describe energy, $E$?

$$E_i = U_i + \frac{u_i^2}{2} + g z_i + \text{other}$$

$$E_i = U_i$$

$$H_i = U_i + P \tilde{V}_i$$

$$\frac{d \hat{E}_{\text{system}}}{dt} = \dot{Q} - \dot{W}_s + \sum_{i=1}^{n} \left( E_i + P \tilde{V}_i \right) F_i \bigg|_{\text{in}} - \sum_{i=1}^{n} \left( E_i + P \tilde{V}_i \right) F_i \bigg|_{\text{out}}$$

$$\frac{d \hat{E}_{\text{system}}}{dt} = \dot{Q} - \dot{W}_s + \sum_{i=1}^{n} \left( H_i \right) F_i \bigg|_{\text{in}} - \sum_{i=1}^{n} \left( H_i \right) F_i \bigg|_{\text{out}}$$

$$\frac{d \hat{E}_{\text{system}}}{dt} = \dot{Q} - \dot{W}_s + \sum_{i=1}^{n} H_{i0} F_{i0} - \sum_{i=1}^{n} H_i F_i$$
We are going to go thru the derivation!
This way you apply the assumptions, and arrive at the correct energy expression!

$\frac{d\hat{E}_{\text{system}}}{dt} = \dot{Q} - \dot{W}_s + \sum_{i=1}^{n} H_{i0} F_{i0} - \sum_{i=1}^{n} H_i F_i$

What two terms do we need to look at?

$H_i$ (Molar enthalpies – fcn (T))
$F_i$ (Molar flow rates)
Consider flow systems that are operated at steady state

\[
\dot{Q} - \dot{W}_s + \sum_{i=1}^{n} H_{i0} F_{i0} - \sum_{i=1}^{n} H_i F_i = 0
\]

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

\[
\sum H_{i0} F_{i0} = H_{A0} F_{A0} + H_{B0} F_{B0} + H_{C0} F_{C0} + H_{D0} F_{D0} + H_{I0} F_{I0}
\]

\[
\sum H_i F_i = H_A F_A + H_B F_B + H_C F_C + H_D F_D + H_I F_I
\]

Write the molar flow rates in terms of conversion

\[
F_i = F_{A0} (\Theta_i + \nu_i X)
\]
\[
\sum_{i=1}^{n} H_{i0} F_{i0} - \sum_{i=1}^{n} H_i F_i = \\
F_{A0} \left[ (H_{A0} - H_A) + (H_{B0} - H_B) \Theta_B + (H_{C0} - H_C) \Theta_C + (H_{D0} - H_D) \Theta_D + (H_{I0} - H_I) \Theta_I \right] \\
- \left( \frac{d}{a} H_D + \frac{c}{a} H_C - \frac{b}{a} H_B - H_A \right) F_{A0} X
\]

Heat of reaction at temperature T, we call it $\Delta H_{Rx}$

\[
\sum_{i=1}^{n} H_{i0} F_{i0} - \sum_{i=1}^{n} H_i F_i = F_{A0} \sum_{i=1}^{n} \Theta_i (H_{i0} - H_i) - \Delta H_{Rx} (T) F_{A0} X
\]

\[
\dot{Q} - \dot{W}_s + F_{A0} \sum_{i=1}^{n} \Theta_i (H_{i0} - H_i) - \Delta H_{Rx} (T) F_{A0} X_i = 0
\]
Enthalpies - How do we find?

$H_i$ – expressed in term of an enthalpy of formation at some reference temperature, $T_R$ plus the change in enthalpy, $\Delta H_{Qi}$ that results when the temperature is raised from $T_R$ to some temperature $T$.

$$H_i = H_i^o(T_R) + \Delta H_{Qi}$$

Look this value up  
Use heat capacity

$$H_i = H_i^o(T_R) + \int_{T_R}^{T} C_{pi}dT$$

Enthalpy of species $i$ at temperature $T$ - NO PHASE CHANGE
What about if you have phase change?

\[ H_i = H_i^\circ (T_R) + \Delta H_{Qi} \]

\[ H_i = H_i^\circ (T_R) + \int_{T_R}^{T_m} C_{Pi} \, dT + \Delta H_{mi} (T_m) + \int_{T_m}^{T_b} C_{Pi} \, dT + \Delta H_{vi} (T_b) + \int_{T_b}^{T} C_{Pi} \, dT \]

Constant or changing heat capacity?

\[ C_{Pi} = \alpha_i + \beta_i T + \gamma_i T^2 \]

Properties of liquids and gases

\[ H_{i0} - H_i = (H_i^\circ (T_R) + C_{Pi}[T_{i0} - T_R]) - (H_i^\circ (T_R) + C_{Pi}[T - T_R]) \]

\[ H_{i0} - H_i = C_{Pi}[T_{i0} - T] \]

\[ \dot{Q} - \dot{W}_s + F_{A0} \sum_{i=1}^{n} \Theta_i C_{Pi} [T_{i0} - T] - \Delta H_{Rx} (T) F_{A0} X_i = 0 \]
We have to do the same thing for $\Delta H_{Rx}$

$$H_i = H_i^\circ (T_R) + C_{Pi}[T - T_R]$$

$$\Delta H_{Rx}(T) = \Delta H_{Rx}^\circ (T_R) + \Delta C_P[T - T_R]$$

$$\dot{Q} - \dot{W}_s + F_{A0} \sum_{i=1}^{n} \Theta C_{Pi}[T_{i0} - T] - [\Delta H_{Rx}^\circ (T_R) + \Delta C_P(T - T_R)]F_{A0}X_i = 0$$

Finally, a form of the energy balance where we can look everything up that we need OR calculate it!
Let's look at an example:

![Chemical structure diagram](image)

Calculate the heat of reaction at 298 K, 473 K, 673 K, 873 K, 1073 K

<table>
<thead>
<tr>
<th>Heat Capacities:</th>
<th>Heat of Formation (25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylbenzene = 299 J/mol K</td>
<td>29,920 J/mol</td>
</tr>
<tr>
<td>Styrene = 273 J/mol K</td>
<td>147,360 J/mol</td>
</tr>
<tr>
<td>Hydrogen = 30 J/mol K</td>
<td>0 J/mol</td>
</tr>
</tbody>
</table>
Equilibrium constants – How do we find?

True equilibrium constant

\[-RT \ln K = \Delta G\]

Van’t Hoff’s equation

\[
\frac{d \ln K_P}{dT} = \frac{\Delta H_{Rx}(T)}{RT^2}
\]

\[
\ln \frac{K_P(T)}{K_P(T_1)} = \frac{\Delta H_{Rx}^\circ(T_R) - T_R \Delta \hat{C}_P}{R} \left( \frac{1}{T_1} - \frac{1}{T} \right) + \frac{\Delta \hat{C}_P}{R} \ln \frac{T}{T_1}
\]

Neglect $\Delta C_p$

\[
K_P(T) = K_P(T_1) \exp \left[ \frac{\Delta H_{Rx}^\circ(T_R)}{R} \left( \frac{1}{T_1} - \frac{1}{T} \right) \right]
\]
Let's look at an example:

![Chemical Reaction Diagram]

Calculate the equilibrium coefficient, $K$

<table>
<thead>
<tr>
<th>Heat Capacities:</th>
<th>Gibbs Free Energy (25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylbenzene = 299 J/mol K</td>
<td>130,890 J/mol</td>
</tr>
<tr>
<td>Styrene = 273 J/mol K</td>
<td>213,900 J/mol</td>
</tr>
<tr>
<td>Hydrogen = 30 J/mol K</td>
<td>0 J/mol</td>
</tr>
</tbody>
</table>

What is the equilibrium coefficient $K$, at $T = 873$ K?