Comments Transient Energy Balances
General form of the “stuff” balance equation

\[
\begin{align*}
\text{Rate of Accumulation} &= \text{Rate In} - \text{Rate Out} + \text{Rate of Generation} - \text{Rate of Consumption}
\end{align*}
\]
Word form of the energy balance equation

\[
\left\{ \text{Rate of Accumulation} \right\} = \left\{ \text{Convection Energy In} \right\} - \left\{ \text{Convection Energy Out} \right\} \pm \left\{ \text{Heat Across Boundary} \right\} \pm \left\{ \text{Work Across Boundary} \right\}
\]
Transient energy balance equation

\[ \frac{dE}{dt} = \sum_{i:\text{inlet}} \dot{E}_i - \sum_{j:\text{outlet}} \dot{E}_j + \sum_k Q_k - \sum_m W_{s,m} \]

\[ \frac{d(U + K + P)}{dt} = \sum_{i:\text{inlet}} \rho_i F_i \dot{H}_i - \sum_{j:\text{outlet}} \rho_j F_j \dot{H}_j + \sum_k Q_k - \sum_m W_{s,m} \]

\[ \frac{d(\rho \dot{H} V)}{dt} \approx \frac{d(\rho \dot{U} V)}{dt} = \sum_{i:\text{inlet}} \rho_i F_i \dot{H}_i - \sum_{j:\text{outlet}} \rho_j F_j \dot{H} + \sum_k Q_k - \sum_m W_{s,m} \]

![Diagram showing energy flow and terms in the transient energy balance equation](image)
Where does heat of reaction come from? Use of heat capacity for enthalpy

The enthalpy form of the energy balance is the same whether or not there is a chemical reaction, heat of mixing, heat of absorption, etc.

These effects are artifacts of describing the enthalpy of a mixture using the heat capacity.

\[
\left( \frac{\partial H}{\partial T} \right)_p \equiv \tilde{C}_p \quad \Rightarrow \quad \tilde{H} - \tilde{H}_{\text{ref}} = \int_{T_{\text{ref}}}^{T} \tilde{C}_p \, dT \approx \tilde{C}_p \left( T - T_{\text{ref}} \right)
\]

\[
\hat{H} - \hat{H}_{\text{ref}} = \int_{T_{\text{ref}}}^{T} \hat{C}_p \, dT \approx \hat{C}_p \left( T - T_{\text{ref}} \right)
\]
Where does heat of reaction come from?
Use of heat capacity for enthalpy

No reaction:

\[
\rho V \frac{d\hat{H}}{dt} = \rho F \hat{H}_0 - \rho F \hat{H}_1 + Q
\]

\[
\rho V\hat{C}_p \frac{dT}{dt} = \rho F\left[\hat{C}_p (T_0 - T_{ref}) + H_{ref}\right] - \rho F\left[\hat{C}_p (T_1 - T_{ref}) + H_{ref}\right] + Q
\]

\[
\rho V\hat{C}_p \frac{dT}{dt} = \rho F\hat{C}_p (T_0 - T_1) + Q
\]

With chemical reaction, the reference enthalpies are different:

\[
\rho V\hat{C}_p \frac{dT}{dt} = \rho F\left[\hat{C}_p (T_0 - T_{ref}) + \hat{H}_{ref,0}\right] - \rho F\left[\hat{C}_p (T_1 - T_{ref}) + \hat{H}_{ref,1}\right] + Q
\]

\[
\rho V\hat{C}_p \frac{dT}{dt} = \rho F\hat{C}_p (T_0 - T_1) + \rho F\left[\hat{H}_{ref,0} - \hat{H}_{ref,1}\right] + Q
\]
Where does heat of reaction come from? Use of heat capacity for enthalpy

What if the reactants have different heat capacities then the products?

\[
\rho V \frac{d(\hat{C}_p T_1)}{dt} = \rho F \left[ \hat{C}_p (T_0 - T_{ref}) + \hat{H}_{ref,0} \right] - \rho F \left[ \hat{C}_p (T_1 - T_{ref}) + \hat{H}_{ref,1} \right] + Q
\]

\[
\rho V \frac{d(\hat{C}_p T_1)}{dt} = \rho F \left[ \hat{C}_p (T_0 - T_{ref}) - \hat{C}_p (T_1 - T_{ref}) \right] + \rho F \left[ \hat{H}_{ref,0} - \hat{H}_{ref,1} \right] + Q
\]
Where does heat of reaction come from?

Enthalpy of formation as reference enthalpy

Total enthalpy is component average of individual enthalpies (if no mixing effect)

\[ H = \sum_{i=1}^{N} m_i \tilde{H}_i = \sum_{i=1}^{N} n_i \tilde{H}_i \quad \Rightarrow \quad C_p = \sum_{i=1}^{N} m_i \tilde{C}_{pi} = \sum_{i=1}^{N} n_i \tilde{C}_{pi} \]

For constant heat capacities for each chemical species

\[
\frac{dH_1}{dt} = \dot{H}_0 - \dot{H}_1 + Q \\
\frac{dH_1}{dt} = \sum_{i=1}^{N} \dot{n}_{i,0} \tilde{H}_{i,0} - \sum_{i=1}^{N} \dot{n}_{i,1} \tilde{H}_{i,1} + Q \\
\frac{dH_1}{dt} = \sum_{i=1}^{N} \dot{n}_{i,0} \tilde{C}_{p,i} (T_0 - T_{ref}) - \sum_{i=1}^{N} \dot{n}_{i,1} \tilde{C}_{p,i} (T_1 - T_{ref}) + \sum_{i=1}^{N} (\dot{n}_{i,0} - \dot{n}_{i,1}) (\Delta \tilde{H}_f)_i + Q
\]
Where does heat of reaction come from?
Heat of formation or combustion as reference

Reference state enthalpies can be the enthalpy of formation or the heat of combustion

- Take care whether the heat of combustion is reported as a negative or positive value (positive value consistent with report as heating value)

Can separate the terms for the reacting & non-reacting species

- Written with heat of combustion as negative value

\[
\frac{dH_1}{dt} = \sum_{i=1}^{N_{\text{Reacting}}} \dot{n}_{i,0} \tilde{C}_{p,i} \left( T_0 - T_{\text{ref}} \right) - \sum_{i=1}^{N_{\text{Reacting}}} \dot{n}_{i,1} \tilde{C}_{p,i} \left( T_1 - T_{\text{ref}} \right) + \sum_{i=1}^{N_{\text{Reacting}}} \left( \dot{n}_{i,0} - \dot{n}_{i,1} \right) \left( \Delta \tilde{H}_c \right)_i \\
+ \sum_{i=1}^{N_{\text{Nonreacting}}} \dot{n}_{i,0} \tilde{C}_{p,i} \left( T_0 - T_1 \right) + Q
\]
Latent heat effects

There are other latent heat effects that look like “generation” terms – changes in enthalpy not due to temperature changes.

Heats associated with phase change, e.g., vaporization (solidification, dissolution, absorption, etc. are similar)

\[ \int_{T_0}^{T_{vap}} dH = \int_{T_0}^{T_{vap}} \tilde{C}_{p,L} dT + (\Delta H)_{vap} + \int_{T_{vap}}^{T_1} \tilde{C}_{p,V} dT \]

\[ = \tilde{C}_{p,L} (T_{vap} - T_0) + (\Delta H)_{vap} + \tilde{C}_{p,L} (T_1 - T_{vap}) \]

Heat of mixing

\[ \tilde{H} = \sum_{i=1}^{N} x_i \tilde{H}_i + (\Delta H)_{mix} \approx \sum_{i=1}^{N} x_i \tilde{H}_i + x_R (\Delta \tilde{H})_{mix,R} \]
How to calculate the effect of heat of reaction

Heat of reaction effects are determined by the indirect path:

- Determine enthalpy change to take reactants to reference temperature
- Determine the change in enthalpy @ reference temperature
- Determine enthalpy change to take products from the reference temperature

![Diagram showing the calculation of heat of reaction](Image)

Figure 5.2

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Pauline Doran, Elsevier Science & Technology
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Calculating heat of reaction from heats of combustion (values in Table C.8)

Use the heat of combustion as the reference

Example: Glucose → Ethanol

\[ \text{C}_6\text{H}_{12}\text{O}_6 \text{ (s)} \rightarrow 2 \text{C}_2\text{H}_5\text{OH} \text{ (l)} + 2 \text{CO}_2 \text{ (g)} \]

<table>
<thead>
<tr>
<th>Compound (state)</th>
<th>( \Delta H^0_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(<em>6)H(</em>{12})O(_6) (s)</td>
<td>-2805.0 kJ/mol</td>
</tr>
<tr>
<td>C(_2)H(_5)OH (l)</td>
<td>-1366.8 kJ/mol</td>
</tr>
<tr>
<td>CO(_2) (g)</td>
<td>0 kJ/mol</td>
</tr>
</tbody>
</table>

\[
\Delta \tilde{H}^0_{rxn} = \sum_{\text{reactants}} n_i \Delta \tilde{H}^0_c - \sum_{\text{products}} n_i \Delta \tilde{H}^0_c \\
= [1 \cdot (-2805.0)] - [2 \cdot (-1366.8) + 2 \cdot (0)] \\
= -71.4 \frac{\text{kJ}}{\text{mol glucose}}
\]
Heat of reaction with cell growth

Estimated from available electrons

\[-\Delta \tilde{H}_c = -q \gamma x_c\]

\[q \approx 111 \text{ to } 115 \frac{\text{kJ}}{\text{g.mol}}\]

Heat of reaction with oxygen as electron acceptor (aerobic, combustion))

\[\Delta \tilde{H}_{rxn} = -460 \frac{\text{kJ}}{\text{g.mol } O_2}\]
Heat of combustion for bacteria & yeast

Can be estimated as:

\[
\left( \Delta \tilde{H}_c \right)_{bacteria} \approx -23.2 \frac{kJ}{g}
\]

\[
\left( \Delta \tilde{H}_c \right)_{yeast} \approx -21.2 \frac{kJ}{g}
\]

For general biomass

\[(CH_{1.8}O_{0.5}N_{0.2})\]:

\[
\left( \Delta \tilde{H}_c \right)_{biomass} \approx -21.3 \frac{kJ}{g}
\]
Calculating heat of reaction from heats of combustion (values in Table C.8)

Use the heat of combustion as the reference

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\[
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<tr>
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<td>-1366.8 kJ/mol</td>
</tr>
<tr>
<td>\text{CO}_2 \text{ (g)}</td>
<td>0 kJ/mol</td>
</tr>
</tbody>
</table>

\[
\Delta \tilde{H}_{rxn}^0 = \sum_{\text{reactants}} n_i \Delta \tilde{H}_c^0 - \sum_{\text{products}} n_i \Delta \tilde{H}_c^0
\]

\[
= \left[ 1 \cdot (-2805.0) \right] - \left[ 2 \cdot (-1366.8) + 2 \cdot 0 \right]
\]

\[
= -71.4 \frac{\text{kJ}}{\text{mol glucose}}
\]
Example energy balance – Continuous Ethanol Fermentation

*Saccharomyces cerevisiae* is grown anaerobically in continuous culture at 30°C. Glucose is used as the carbon source; ammonia is the nitrogen source. A mixture of glycerol and ethanol is produced.

<table>
<thead>
<tr>
<th>Compound</th>
<th>In [kg/h]</th>
<th>Out [kg/h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>36.0</td>
<td></td>
</tr>
<tr>
<td>NH$_3$</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>Cells</td>
<td></td>
<td>2.81</td>
</tr>
<tr>
<td>Glycerol</td>
<td></td>
<td>7.94</td>
</tr>
<tr>
<td>Ethanol</td>
<td></td>
<td>11.9</td>
</tr>
<tr>
<td>CO$_2$</td>
<td></td>
<td>13.6</td>
</tr>
<tr>
<td>Produced H$_2$O</td>
<td></td>
<td>0.15</td>
</tr>
</tbody>
</table>

What is the cooling requirement to keep @ 30°C?
Example energy balance – Continuous Ethanol Fermentation

We’ll calculate the heat of reaction at the standard temperature (25°C) & assume this is close enough

- For more accuracy we would need to cool reactants to 25°C, calculate heat of reaction @ 25°C, & then heat up products to 30°C

Heat of reaction:

\[ \Delta H_{rxn} = -570000 - (-556025) \]
\[ = -13,977 \text{ kJ/h} \]

Since negative this heat to be removed

<table>
<thead>
<tr>
<th>Compound</th>
<th>In [kg/h]</th>
<th>Out [kg/h]</th>
<th>Mol Wt</th>
<th>( \Delta H_c ) [kJ/mol]</th>
<th>( \Delta H_c ) [kJ/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>36</td>
<td></td>
<td>180</td>
<td>-2805.0</td>
<td>-15,583</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.4</td>
<td></td>
<td>17</td>
<td>-382.6</td>
<td>-22,506</td>
</tr>
<tr>
<td>Cells</td>
<td>2.81</td>
<td></td>
<td></td>
<td></td>
<td>-21,200</td>
</tr>
<tr>
<td>Glycerol</td>
<td>7.94</td>
<td>92</td>
<td></td>
<td>-1655.4</td>
<td>-17,993</td>
</tr>
<tr>
<td>Ethanol</td>
<td>11.9</td>
<td>46</td>
<td></td>
<td>-1366.8</td>
<td>-29,713</td>
</tr>
<tr>
<td>CO₂</td>
<td>13.6</td>
<td></td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Produced H₂O</td>
<td>0.15</td>
<td></td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>TOTAL</td>
<td>36.4</td>
<td>36.4</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

\[ \Sigma m \Delta H_c = -570,002 - -556,025 \]
Other topics from supplemental text

Use of steam tables

- How much steam might be needed to heat a reactor or stream
- How much heat is carried away by evaporated water
Closing comments

Remember that the heat of reaction is energy released not energy generated

- Unless we are working with nuclear reactions we do not create nor destroy energy

Using heat of combustion (i.e., change in enthalpy upon combustion) is a valid reference state, just like enthalpy of formation

- Take care whether the values are reported as negative (consistent with $\Delta H_{\text{rxn}}$) or positive (reported as heating value)
- For biological reactions make sure you choose the higher heating value (i.e., where any product water is in the liquid state)

Many times you can ignore the actual reactor temperature & just use the heat of reaction at standard conditions