Calculation of Enthalpy Changes

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As shown previously, the change in enthalpy can be calculated using the heat capacity $C_P$.

\[ \Delta H = \int C_P dT \]

To give the heat capacity some physical meaning, $C_P$ represents the amount of energy required to increase the temperature of a given amount of substance by 1 degree.

Common units for $C_P$:

- kJ/kmol $\cdot$ K
- Btu/lbmol $\cdot$ °F
## Heat Capacities of Ideal Gases

<table>
<thead>
<tr>
<th>Type of Molecule</th>
<th>High Temperature</th>
<th>Low Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoatomic</td>
<td>$\frac{5R}{2}$</td>
<td>$\frac{5R}{2}$</td>
</tr>
<tr>
<td>Polyatomic, linear</td>
<td>$(3n - \frac{3}{2})R$</td>
<td>$\frac{7R}{2}$</td>
</tr>
<tr>
<td>Polyatomic, nonlinear</td>
<td>$(3n - 2)R$</td>
<td>$4R$</td>
</tr>
</tbody>
</table>

$n =$ number of atoms per molecule ; $R =$ ideal gas constant ; $C_V = C_P - R$
For gas mixtures, the $C_P$ of the mixture is the mole weighted average of the heat capacities of the components:

$$(C_P)_{avg} = \sum_{i=1}^{N} x_i C_{Pi}$$

If $C_P$ is not constant for the given temperature range, it may be expressed as a function of temperature in a power series such as:

$$C_P = \alpha + \beta T + \gamma T^2$$

where $\alpha$, $\beta$, and $\gamma$ are constants specific to a particular substance (Appendix E.1, Basic Principles and Calculations in Chemical Engineering, 6th edition, by David M. Himmelblau)
Example 14–1. Calculation of \( \Delta H \) for a Gas Mixture

An economic feasibility study indicates that solid municipal waste can be burned to a gas of the following composition (on a dry basis):

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)</td>
<td>9.2%</td>
</tr>
<tr>
<td>CO</td>
<td>1.5%</td>
</tr>
<tr>
<td>O(_2)</td>
<td>7.3%</td>
</tr>
<tr>
<td>N(_2)</td>
<td>82.0%</td>
</tr>
</tbody>
</table>

What is the enthalpy difference for this gas per lbmol between the bottom and the top of the stack if the temperature at the bottom of the stack is 550\(^0\)F and the temperature at the top is 200\(^0\)F.
The heat capacity equations for the gases are:
[T in $^0$F; $C_p$ in Btu/(lbmol)($^0$F)]

$\text{N}_2$: $C_p = 6.895 + 0.7624 \times 10^{-3}T - 0.7009 \times 10^{-7}T^2$

$\text{O}_2$: $C_p = 7.104 + 0.7851 \times 10^{-3}T - 0.5528 \times 10^{-7}T^2$

$\text{CO}$: $C_p = 6.865 + 0.8024 \times 10^{-3}T - 0.7367 \times 10^{-7}T^2$

$\text{CO}_2$: $C_p = 8.448 + 5.757 \times 10^{-3}T - 21.59 \times 10^{-7}T^2$
$+ 3.059 \times 10^{-10}T^3$
Example 14–1. Calculation of $\Delta H$ for a Gas Mixture

Basis: 1.00 lbmol of gas mixture

The enthalpy difference ($\Delta H$) is calculated as:

$$\Delta H = \int C_P dT$$

The $C_P$ of the gas mixture is determined from the equation:

$$\left( C_P \right)_{\text{avg}} = \sum_{i=1}^{N} x_i C_{P_i}$$

$$\left( C_P \right)_{\text{avg}} = x_{N2} C_{P_{N2}} + x_{O2} C_{P_{O2}} + x_{CO2} C_{P_{CO2}} + x_{CO} C_{P_{CO}}$$
Example 14–1. Calculation of $\Delta H$ for a Gas Mixture

$$x_{N_2}C_{P_{N_2}} = (0.82)(6.895 + ....)$$

$$x_{O_2}C_{P_{O_2}} = (0.073)(7.104 + ....)$$

$$x_{CO_2}C_{P_{CO_2}} = (0.092)(8.448 + ....)$$

$$x_{CO}C_{P_{CO}} = (0.015)(6.865 + ....)$$

Obtaining $\Sigma x_i C_{P_i}$:

$$\left( C_p \right)_{avg} = 7.053 + 1.2242 \times 10^{-3}T - 2.6124 \times 10^{-7}T^2$$

$$+ 0.2814 \times 10^{-10}T^3$$
Solving for $\Delta H$:

$$
\Delta H = \int_{550}^{200} \left( 7.053 + 1.2242 \times 10^{-3} T - 2.6124 \times 10^{-7} T^2 
- 0.2814 \times 10^{-10} T^3 \right) \, dT
$$

$$
\Delta H = 7.053 (200 - 550) + \frac{1.2242 \times 10^{-3}}{2} (200^2 - 550^2)
- \frac{2.6124 \times 10^{-7}}{3} (200^3 - 550^3) + \frac{0.2814 \times 10^{-10}}{4} (200^4 - 550^4)
$$

$$
\Delta H = -2616 \text{ Btu} / \text{lbmol}
$$
Enthalpies at various temperatures can also be obtained from tables.

*From Basic Principles and Calculations in Chemical Engineering by David M. Himmelblau (6th edition):*

**Table D.2**  Enthalpies of Paraffinic Hydrocarbons ($C_1 - C_6$)

**Table D.3**  Enthalpies of Other Hydrocarbons (ethylene, propylene, butene, acetylene, benzene)

**Table D.4**  Enthalpies of Nitrogen and Some of its Oxides

**Table D.5**  Enthalpies of Sulfur Compounds

**Table D.6**  Enthalpies of Combustion Gases
The enthalpy from a standard reference state is given by

\[
H = H_f^\circ + \int_{T_R}^{T} C_P \, dT
\]

where \( H_f^\circ \) is the standard heat of formation and \( T_R \) is the reference temperature.

For a mixture,

\[
H_{\text{mixture}} = \sum_{i=1}^{N} \left( H_f^\circ + \int_{T_R}^{T} C_P \, dT \right)
\]
The standard heat of formation ($\Delta H_f^\circ$) is the special enthalpy for the formation of 1 mole of a compound from its constituents elements, for example

$$C(s) + 0.5O_2(g) \rightarrow CO(g)$$

The reactants and products must be at 25°C and 1 atm.

The reaction may not represent a real reaction. By definition, the heat of formation for the elements is zero in the standard state.

From *Basic Principles and Calculations in Chemical Engineering* by David M. Himmelblau (6th edition):

**Table F.1** Heats of Formation and Combustion
Consider an open system with no chemical reaction:

\[
\Delta H = H_{\text{out}} - H_{\text{in}} = (H_{A2} + H_{B2}) - (H_{A1} + H_{B1})
\]
14.3 Enthalpy Calculations from Standard Heat of Formation

Calculating the enthalpies from standard heat of formation

$$\Delta H = \left[ \left( H_{fA}^\circ + \int_{T_R}^{T_2} C_{PA} \, dT \right) + \left( H_{fB}^\circ + \int_{T_R}^{T_2} C_{PB} \, dT \right) \right]$$

$$- \left[ \left( H_{fA}^\circ + \int_{T_R}^{T_1} C_{PA} \, dT \right) + \left( H_{fB}^\circ + \int_{T_R}^{T_1} C_{PB} \, dT \right) \right]$$

Simplifying,

$$\Delta H = \int_{T_1}^{T_2} C_{PA} \, dT + \int_{T_1}^{T_2} C_{PB} \, dT$$
Consider an open system with chemical reaction:

\[ A + B \rightarrow C + D \]

Input, \( T_1 \)

A: \( H_A \)
B: \( H_B \)

Open System

Output, \( T_2 \)

C: \( H_C \)
D: \( H_D \)

The enthalpy difference between inlet and outlet will be

\[ \Delta H = H_{out} - H_{in} = (H_C + H_D) - (H_A + H_B) \]
Calculating the enthalpies from standard heat of formation

\[
\Delta H = \left[ \left( H_f^{\circ} + \int_{T_R}^{T_2} C_{PC} dT \right) + \left( H_f^{\circ} + \int_{T_R}^{T_2} C_{PD} dT \right) \right] \\
- \left[ \left( H_f^{\circ} + \int_{T_R}^{T_1} C_{PA} dT \right) + \left( H_f^{\circ} + \int_{T_R}^{T_1} C_{PB} dT \right) \right]
\]

Rearranging the terms,

\[
\Delta H = \left[ \left( H_f^{\circ} + H_f^{\circ} \right) - \left( H_f^{\circ} + H_f^{\circ} \right) \right] + \int_{T_R}^{T_2} C_{PC} dT \\
+ \int_{T_R}^{T_2} C_{PD} dT - \int_{T_R}^{T_1} C_{PA} dT - \int_{T_R}^{T_1} C_{PB} dT
\]
The group of terms involving the standard heats of formation is called the standard heat of reaction, $\Delta H^o_R$.

In general,

$$\Delta H^o_R = \sum_{products} \left( nH^o_f \right) - \sum_{reactants} \left( nH^o_f \right)$$

The $n$ in the equation is the stoichiometric coefficient of species $i$ in the chemical reaction.

The standard heat of reaction is the difference between the heats of formation of the products and that of the reactants.
Example 14-2. Calculation of Standard Heat of Reaction

Calculate $\Delta H^\circ_R$ for the following reaction:

$$4 \text{NH}_3(g) + 5 \text{O}_2(g) \implies 4 \text{NO}(g) + 6 \text{H}_2\text{O}(g)$$

The standard heats of formation of the products and reactants are:

- $\text{NH}_3$: $-46.191$ kJ/mol
- $\text{NO}$: $+90.374$ kJ/mol
- $\text{O}_2$: $0$
- $\text{H}_2\text{O}$: $-241.826$ kJ/mol

And the standard heat of reaction:

$$\Delta H^\circ_R = [4(90.374) + 6(-241.826)] - [4(-46.191) + 5(0)]$$

$$\Delta H^\circ_R = -904.696 \text{ kJ}/4 \text{ mol NH}_3$$