Thermochemistry

Chapter 2 of Atkins: *The First Law: Concepts*

Sections 2.7- 2.9 of Atkins

Assignment:
Exercises 2.29(a), 2.30(a), 2.39(a), 2.40(a), 2.43(a), 2.46(a)
Problems 2.13, 2.19
Thermochemistry

Chapter 2 of Atkins: *The First Law: Concepts*

Sections 2.7-2.9 of Atkins

*Standard Enthalpy Changes*

Enthalpies of Physical Change
Enthalpies of Chemical Change
Hess’ Law

*Standard Enthalpies of Formation Changes*

Reaction Enthalpy & Enthalpy of Formation
Group Contributions

Temperature Dependence of Reaction Enthalpies
Thermochemistry

Thermochemistry is the branch of thermodynamics which studies heats of reaction: heat produced by or required for a chemical reaction. In thermochemistry, chemical reactions are divided into two categories:

**exothermic reaction**

$q_{rxn} < 0$; heat is produced by the reacting system (i.e., the temperature of the system is higher right after the reaction than initially; heat must be transferred from the system to the surroundings in order to return the system to its initial temperature)

**endothermic reaction**

$q_{rxn} > 0$; heat is absorbed by the reacting system (i.e., the temperature of the system is lower right after the reaction than initially; heat must be transferred from the surroundings to the system in order to return the system to its initial temperature)

These reactions can also be described in terms of change in **enthalpy**, $\Delta H$
Standard Enthalpy Changes

Numerical values describing $\Delta U$ or $\Delta H$ of a system when some chemical or physical change occurs depend upon the nature of the reaction, as well as the physical states of reactants and products.

It is useful to define a **standard enthalpy change**, $\Delta H^\Theta$, which is the change in enthalpy for a process (chemical or physical) where initial and final substances are in **standard states**.

**Standard states**: pure form of a substance at specified temperature at pressure of 1 bar, e.g. standard state of liquid water at 298 K is pure liquid water at 298 K and 1 bar.

**Examples**: The standard enthalpy of vaporization, $\Delta_{vap} H^\Theta$, is change in enthalpy per mole when pure liquid vaporizes to pure gas at pressure of 1 bar. The standard enthalpy of fusion, $\Delta_{fus} H^\Theta$, is enthalpy change accompanying change from solid to liquid.

$$
\begin{align*}
H_2O(l) & \rightarrow H_2O(g) \quad \Delta_{vap} H^\Theta (373 K) = +40.86 \text{ kJ mol}^{-1} \\
H_2O(s) & \rightarrow H_2O(l) \quad \Delta_{fus} H^\Theta (273 K) = +6.01 \text{ kJ mol}^{-1}
\end{align*}
$$

$\Delta H^\Theta$ can be reported at any temperature, convention is at 298.15 K.
Enthalpy of Physical Change

**standard enthalpy of transition**, $\Delta_{\text{trs}}H^\Theta$:

Standard enthalpy change accompanying a phase change

(a) Enthalpy is a *state function*, independent of path between initial and final states:

same value of $\Delta H^\Theta$ occurs regardless of how change occurs!

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction</th>
<th>$\Delta H^\Theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>melting</td>
<td>$\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l)$</td>
<td>$\Delta_{\text{fus}} H^\Theta$</td>
</tr>
<tr>
<td>Boiling</td>
<td>$\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$</td>
<td>$\Delta_{\text{vap}} H^\Theta$</td>
</tr>
<tr>
<td>sublimation</td>
<td>$\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(g)$</td>
<td>$\Delta_{\text{sub}} H^\Theta = \Delta_{\text{fus}} H^\Theta + \Delta_{\text{vap}} H^\Theta$</td>
</tr>
</tbody>
</table>

(b) Enthalpy is a *state function*, so $\Delta H^\Theta$ differs only in sign for forward and reverse processes

Example: At 298 K,

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction</th>
<th>$\Delta H^\Theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>condensing</td>
<td>$\text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{O}(l)$</td>
<td>$-\Delta_{\text{vap}} H^\Theta = -44 \text{ kJ mol}^{-1}$</td>
</tr>
<tr>
<td>boiling</td>
<td>$\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$</td>
<td>$\Delta_{\text{vap}} H^\Theta = +44 \text{ kJ mol}^{-1}$</td>
</tr>
</tbody>
</table>
Graphical Depiction of Enthalpies of Transition

(A) Same \( \Delta H^\circ \), regardless of pathway

(B) Forward & reverse processes, \( \Delta H^\circ \) differs only in sign
Enthalpies of Fusion and Vapourization

See Table 2.3 Atkins 7th Ed. at back of book for a listing of enthalpies of fusion and vaporization, with freezing and boiling temperatures.

Table 2.3*  Standard enthalpies of fusion and vaporization at the transition temperature, $\Delta_{\text{trs}}H^\circ/(\text{kJ mol}^{-1})$

<table>
<thead>
<tr>
<th></th>
<th>$T_f$/K</th>
<th>Fusion</th>
<th>$T_b$/K</th>
<th>Vaporization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>83.81</td>
<td>1.188</td>
<td>87.29</td>
<td>6.506</td>
</tr>
<tr>
<td>C$_6$H$_6$</td>
<td>278.61</td>
<td>10.59</td>
<td>353.2</td>
<td>30.8</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>273.15</td>
<td>6.008</td>
<td>373.15</td>
<td>40.656 44.016 at 298 K</td>
</tr>
<tr>
<td>He</td>
<td>3.5</td>
<td>0.021</td>
<td>4.22</td>
<td>0.084</td>
</tr>
</tbody>
</table>

* More values are given in the Data section.
Enthalpies of Transition

There are many different types of transitions, each of which has an associated change in enthalpy.

**Table 2.4 Enthalpies of transition**

<table>
<thead>
<tr>
<th>Transition</th>
<th>Process</th>
<th>Symbol*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transition</td>
<td>Phase $\alpha \rightarrow$ phase $\beta$</td>
<td>$\Delta_{\text{trs}} H$</td>
</tr>
<tr>
<td>Fusion</td>
<td>$s \rightarrow l$</td>
<td>$\Delta_{\text{fus}} H$</td>
</tr>
<tr>
<td>Vaporization</td>
<td>$l \rightarrow g$</td>
<td>$\Delta_{\text{vap}} H$</td>
</tr>
<tr>
<td>Sublimation</td>
<td>$s \rightarrow g$</td>
<td>$\Delta_{\text{sub}} H$</td>
</tr>
<tr>
<td>Mixing of fluids</td>
<td>Pure $\rightarrow$ mixture</td>
<td>$\Delta_{\text{mix}} H$</td>
</tr>
<tr>
<td>Solution</td>
<td>Solute $\rightarrow$ solution</td>
<td>$\Delta_{\text{sol}} H$</td>
</tr>
<tr>
<td>Hydration</td>
<td>$X^\circ(g) \rightarrow X^\circ(aq)$</td>
<td>$\Delta_{\text{hyd}} H$</td>
</tr>
<tr>
<td>Atomization</td>
<td>Species(s, l, g) $\rightarrow$ atoms(g)</td>
<td>$\Delta_{\text{at}} H$</td>
</tr>
<tr>
<td>Ionization</td>
<td>$X(g) \rightarrow X^+(g) + e^-(g)$</td>
<td>$\Delta_{\text{ion}} H$</td>
</tr>
<tr>
<td>Electron gain</td>
<td>$X(g) + e^-(g) \rightarrow X(g)$</td>
<td>$\Delta_{\text{eg}} H$</td>
</tr>
<tr>
<td>Reaction</td>
<td>Reactants $\rightarrow$ products</td>
<td>$\Delta_r H$</td>
</tr>
<tr>
<td>Combustion</td>
<td>Compound(s, l, g) + $O_2(g) \rightarrow CO_2(g), H_2O(l, g)$</td>
<td>$\Delta_c H$</td>
</tr>
<tr>
<td>Formation</td>
<td>Elements $\rightarrow$ compound</td>
<td>$\Delta_f H$</td>
</tr>
<tr>
<td>Activation</td>
<td>Reactants $\rightarrow$ activated complex</td>
<td>$\Delta^I H$</td>
</tr>
</tbody>
</table>

* IUPAC recommendations. In common usage, the transition subscript is often attached to $\Delta H$, as in $\Delta H_{\text{trs}}$. 
Enthalpies of Chemical Change

Standard reaction enthalpy, $\Delta_r H^\Theta$:
Change in enthalpy when reactants in standard states change to products in standard states:

pure unmixed reactants in their standard states $\quad \rightarrow \quad$ pure separated products their standard states

Example:

$$C_3H_6(g) + \frac{9}{2} O_2(g) \rightarrow 3 \text{ CO}_2(g) + 3 \text{ H}_2\text{O}(l)$$

$\Delta H^\Theta = -2058 \text{ kJ}$

$\Delta_r H^\Theta = -2058 \text{ kJ mol}^{-1}$

The change in enthalpy for the above thermochemical equation is for 1 mole of pure CH$_4$(g) reacting with 4.5 moles of pure O$_2$(g) at 1 bar to produce 3 mole of pure CO$_2$(g) and 3 moles of pure H$_2$O(l) at 1 bar.

Changes in enthalpies of mixing and separation are insignificant compared to the standard reaction enthalpy, and may be neglected in this case.
Standard Molar Enthalpies

Consider the reaction:

\[ 2A + B \rightarrow 3C + D \]

Standard enthalpy is calculated from:

\[ \Delta_r H^\circ = \{3H_m^\circ(C) + H_m^\circ(D)\} - \{2H_m^\circ(A) + H_m^\circ(B)\} \]

Or, more generally:

\[ \Delta_r H^\circ = \sum_{\text{products}} v_j H_m^\circ(J) - \sum_{\text{reactants}} v_j H_m^\circ(J) \]

where \( H_m^\circ(J) \) is standard molar enthalpy of species \( J \) and \( v_j \) the "stoichiometric numbers" - wait, we will REDEFINE these.
Consider the reaction:

\[ 2A + B \rightarrow 3C + D \]

We can rewrite this:

\[ 0 \rightarrow 3C + D - 2A - B \]

Now if J denotes substances and \( \nu_J \) the stoichiometric numbers:

\[ \nu_A = -2 \quad \nu_B = -1 \quad \nu_C = 3 \quad \nu_D = 1 \]

Thus, standard reaction enthalpy is:

\[ \Delta_r H^\oplus = \sum_J \nu_J H_m^\oplus (J) \]
Hess’ Law

The standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which the overall reaction may be divided – individual steps may not be “real” reactions, but must balance

Standard reaction enthalpy for hydrogenation of propene: -124 kJ mol\(^{-1}\)

\[
\text{CH}_2=\text{CHCH}_3(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3(\text{g})
\]

Standard reaction enthalpy for combustion of propane: -2220 kJ mol\(^{-1}\)

\[
\text{CH}_3\text{CH}_2\text{CH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})
\]

Calculate the standard enthalpy of combustion of propene:

\[
\text{C}_3\text{H}_6(\text{g}) + (9/2) \text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})
\]
**Hess’ Law**

$$\Delta_r H^\Theta/(kJ \ mol^{-1})$$

<table>
<thead>
<tr>
<th>Chemical Reaction</th>
<th>$\Delta_r H^\Theta/(kJ \ mol^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CH_2=CHCH_3(g) + H_2(g) \rightarrow CH_3CH_2CH_3(g)$</td>
<td>-124</td>
</tr>
<tr>
<td>$CH_3CH_2CH_3(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$</td>
<td>-2220</td>
</tr>
<tr>
<td>$H_2O(l) \rightarrow H_2(g) + 1/2 O_2(g)$</td>
<td>+286</td>
</tr>
<tr>
<td>$CH_2=CHCH_3(g) + (9/2) O_2(g) \rightarrow 3CO_2(g) + 3H_2O(l)$</td>
<td>-2058</td>
</tr>
</tbody>
</table>
Hess’ Law - Further Example

The standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which the overall reaction may be divided – individual steps may not be “real” reactions, but must balance

Standard reaction enthalpy for combustion of glucose: \(-2809.1 \text{ kJ mol}^{-1}\)

\[
\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})
\]

Standard reaction enthalpy for combustion of maltose: \(-5645.5 \text{ kJ mol}^{-1}\)

\[
\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s}) + 12\text{O}_2(\text{g}) \rightarrow 12\text{CO}_2(\text{g}) + 11\text{H}_2\text{O}(\text{l})
\]

Calculate the standard enthalpy of conversion:

\[
\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) \rightarrow 1/2 \text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s}) + 1/2 \text{H}_2\text{O}(\text{l})
\]
### Hess’ Law - Further Example

<table>
<thead>
<tr>
<th>Chemical Reaction</th>
<th>( \Delta_r H^\Theta/\text{(kJ mol}^{-1}\text{)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) )</td>
<td>-2809.1</td>
</tr>
<tr>
<td>( \frac{1}{2} {12CO_2(g) + 11H_2O(l) \rightarrow C_{12}H_{22}O_{11}(s) + 12O_2(g) } )</td>
<td>( \frac{1}{2} ) (5645.5)</td>
</tr>
<tr>
<td>( C_6H_{12}O_6(s) \rightarrow \frac{1}{2} C_{12}H_{22}O_{11}(s) + \frac{1}{2} H_2O(l) )</td>
<td>13.7</td>
</tr>
</tbody>
</table>
Standard Enthalpies of Formation

**standard enthalpy of formation, \( \Delta_f H^\Theta \):**
Change in enthalpy for formation of compound from its constituent elements in their *reference states*

**reference state:** the most stable state of an element at the specified temperature and 1 bar pressure

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Delta_f H^\Theta ) (kJ mol(^{-1}))</th>
<th>( \Delta_c H^\Theta ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene, C(_5)H(_6)(l)</td>
<td>+49.0</td>
<td>−3268</td>
</tr>
<tr>
<td>Ethane, C(_2)H(_6)(g)</td>
<td>−84.7</td>
<td>−1560</td>
</tr>
<tr>
<td>Glucose, C(_6)H(_12)O(_6)(s)</td>
<td>−1274</td>
<td>−2808</td>
</tr>
<tr>
<td>Methane, CH(_4)(g)</td>
<td>−74.8</td>
<td>−890</td>
</tr>
<tr>
<td>Methanol, CH(_3)OH(l)</td>
<td>−238.7</td>
<td>−726</td>
</tr>
</tbody>
</table>

* More values are given in the Data section.
Standard Enthalpies of Formation

**standard enthalpy of formation, \( \Delta_f H^\Theta \):**
Change in enthalpy for formation of compound from its constituent elements in their reference states

**reference state:** the most stable state of an element at the specified temperature and 1 bar pressure

Table 2.6* Standard enthalpies of formation of inorganic compounds, \( \Delta_f H^\Theta / (\text{kJ mol}^{-1}) \), at 298 K

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Delta_f H^\Theta ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O(l)</td>
<td>-285.83</td>
</tr>
<tr>
<td>H(_2)O(_2)(l)</td>
<td>-187.78</td>
</tr>
<tr>
<td>NH(_3)(g)</td>
<td>-46.11</td>
</tr>
<tr>
<td>N(_2)H(_4)(l)</td>
<td>+50.63</td>
</tr>
<tr>
<td>NO(_2)(g)</td>
<td>+33.18</td>
</tr>
<tr>
<td>N(_2)O(_4)(g)</td>
<td>+9.16</td>
</tr>
<tr>
<td>NaCl(s)</td>
<td>-411.15</td>
</tr>
<tr>
<td>KCl(s)</td>
<td>-436.75</td>
</tr>
</tbody>
</table>

* More values are given in the Data section.
Standard Enthalpies of Formation

Reference states: Examples

Nitrogen \( N_2(g) \)
Mercury \( Hg(l) \)
Carbon \( C(s), \) graphite
Tin white metallic tin
Phosphorus white phosphorus (most reproducible)

Examples of Formation Reactions:

\[
6C(s, \text{graphite}) + 3H_2 \rightarrow C_6H_6 \text{ (l)} \quad \Delta_f^\Theta H = +49.0 \text{ kJ mol}^{-1}
\]

\[
N_2(g) \rightarrow N_2(g) \quad \Delta_f^\Theta H = 0
\text{null, reference state}
\]
Reaction Enthalpy in Terms of Formation

Conceptual Reaction: Decompose the reactants into their elements, form these elements into products.

Value of $\Delta_r H^\Theta$ for reaction is sum of forming and "unforming" enthalpies:

$$\Delta_r H^\Theta = \sum_{j} \nu_j \Delta_f H^\Theta (J)$$

Remember:

$\nu_j$ negative for reactants
Reaction Enthalpy in Terms of Formation

\[ \Delta_r H^\ominus = \sum_j v_j \Delta_f H^\ominus (J) \]

Example:

\[ 2 \text{HN}_3(\text{l}) + 2 \text{NO}(\text{g}) \rightarrow \text{H}_2\text{O}_2(\text{l}) + 4 \text{N}_2(\text{g}) \]

\[ \Delta_r H^\ominus = \Delta_f H^\ominus (\text{H}_2\text{O}_2(\text{l})) + 4 \Delta_f H^\ominus (\text{N}_2(\text{g})) \]

\[ - 2 \Delta_f H^\ominus (\text{HN}_3(\text{l})) - 2 \Delta_f H^\ominus (\text{NO}(\text{g})) \]

\[ = [1(-187.78) + 4 (0) - 2 (264.0) - 2 (90.25)] \text{kJ mol}^{-1} \]

\[ = -896.3 \text{kJ mol}^{-1} \]
Group Contributions

Sometimes it is difficult to exactly (thermodynamically) break enthalpies of formation down into contributions from individual atoms and bonds

**mean bond enthalpies,**  $H(A-B)$ enthalpy change associated with breaking of a specific bond, $A-B$

This is an *unreliable method,* since $H(A-B)$ are average values for series of unrelated compounds (different geometries, isomers, etc.)

**thermochemical groups**
atom or physical group of atoms bound to at least two other atoms

enthalpy of formation is associated with sum of contributions associated with all of the thermochemical groups into which the molecule can be divided – sometimes called **Benson thermochemical groups**
**Benson Group Contributions**

### Table 2.7* Benson thermochemical groups

<table>
<thead>
<tr>
<th>Group</th>
<th>$\Delta_f H^\circ$ (kJ mol$^{-1}$)</th>
<th>$C_p,m^\circ$ (J K$^{-1}$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(H)$_3$(C)</td>
<td>-42.17</td>
<td>25.9</td>
</tr>
<tr>
<td>C(H)$_2$(C)$_2$</td>
<td>-20.7</td>
<td>22.8</td>
</tr>
<tr>
<td>C(H)(C)$_3$</td>
<td>-6.91</td>
<td>18.7</td>
</tr>
<tr>
<td>C(C)$_4$</td>
<td>+8.16</td>
<td>18.2</td>
</tr>
</tbody>
</table>

*More values are given in the *Data section.*
Benson Group Contributions

Example:

Estimate standard enthalpy of formation for hexane (gas and liquid) at 298 K.

Decomposition:

Two C(H)₃(C)
Four C(H)₂(C)₂

\[ \Delta_r H^\ominus (C_6H_{14}, g) = [2(-42.17) + 4 (-20.7)] \text{ kJ mol}^{-1} \]

\[ = -167.1 \text{ kJ mol}^{-1} \]

\[ \Delta_{vap} H^\ominus (C_6H_{14}) = 33.1 \text{ kJ mol}^{-1} \]

\[ \Delta_r H^\ominus (C_6H_{14}, l) = [-167.1 - 33.1] \text{ kJ mol}^{-1} \]

\[ = -200.2 \text{ kJ mol}^{-1} \]

Experimental value is -198.7 kJ mol⁻¹
Temperature Dependence of Reaction Enthalpies

Standard enthalpies have been measured at many temperatures for many substances - however, in absence of such information, the standard enthalpies of reactions may be estimated from heat capacities.

\[
\left( \frac{\partial H}{\partial T} \right)_p = C_p
\]

\[
H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p \, dT
\]

Here, we have heated from \( T_1 \) to \( T_2 \) and assumed no phase transitions over this temperature range. We also assume that the \( C_p \) is independent of \( T \) over this range.
Temperature Dependence of Reaction Enthalpies

\[ H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p \, dT \]

Because the above equation is assumed to apply to all substances in the reaction, it follows that:

\[ \Delta_r H^\oplus (T_2) = \Delta_r H^\oplus (T_1) + \int_{T_1}^{T_2} \Delta_r C_p^\oplus \, dT \]

This equation is known as **Kirchoff’s Law**.

The quantity \( \Delta_r C_p^\oplus \) is the difference in heat capacities between reactants and products under standard conditions, weighted by stoichiometric coefficients:

\[ \Delta_r C_p^\oplus = \sum_J v_J C_p^{\oplus,m} (J) \]