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

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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

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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, \( \Delta H \)

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Thermochemistry

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**, \( \Delta H^\circ \), 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, \( \Delta H^\circ \) (vap), is change in enthalpy per mole when pure liquid vaporizes to pure gas at pressure of 1 bar. The standard enthalpy of vaporization, \( \Delta H^\circ \) (vap), is enthalpy change accompanying change from solid to liquid:
  \[ \text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(g) \quad \Delta H^\circ \text{(vap)}(273 K) = +40.86 \text{ kJ mol}^{-1} \]
  \[ \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g) \quad \Delta H^\circ \text{(vap)}(273 K) = +6.01 \text{ kJ mol}^{-1} \]

\( \Delta H^\circ \) can be reported at any temperature, convention is at 298.15 K

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Enthalpy of Physical Change

standard enthalpy of transition, \( \Delta_{\text{trs}}H^0 \):

Standard enthalpy change accompanying a phase change

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

same value of \( \Delta H \) occurs regardless of how change occurs!

- melting: \( H_2O(s) \rightarrow H_2O(l) \) \( \Delta_{\text{fus}}H^0 \)
- sublimation: \( H_2O(s) \rightarrow H_2O(g) \) \( \Delta_{\text{sub}}H^0 \)

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

Example: At 298 K,

- condensing: \( H_2O(g) \rightarrow H_2O(l) \) \( -\Delta_{\text{vap}}H^0 = 44 \text{ kJ mol}^{-1} \)
- boiling: \( H_2O(l) \rightarrow H_2O(g) \) \( \Delta_{\text{vap}}H^0 = 44 \text{ kJ mol}^{-1} \)

Graphical Depiction of Enthalpies of Transition

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

(B) Forward & reverse processes, \( \Delta H \) 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>
<thead>
<tr>
<th>Substance</th>
<th>( T_f ) (K)</th>
<th>( \Delta_{\text{fus}}H^0 ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>183.81</td>
<td>1.188</td>
</tr>
<tr>
<td>C(_2)H(_2)</td>
<td>278.64</td>
<td>19.59</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>273.15</td>
<td>6.008</td>
</tr>
</tbody>
</table>

Enthalpies of Transition

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

**Standard reaction enthalpy** $\Delta \text{H}^\circ$:

Change in enthalpy when reactants in standard states change to products in standard states:

- Pure unmixed reactants in their standard states
- Pure separated products in their standard states

Example:

\[
\text{C}_3\text{H}_6(g) + \frac{9}{2} \text{O}_2(g) \rightarrow 3 \text{CO}_2(g) + 3 \text{H}_2\text{O}(l)
\]

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

$\Delta \text{rH}^\circ = -2058 \text{ kJ mol}^{-1}$

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.

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**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:

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

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

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

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

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

Calculate the standard enthalpy of combustion of propene:

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

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta H^\circ ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_2=\text{CHCH}_3(g) + \text{H}_2(g) \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3(g) )</td>
<td>-124</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CH}_2\text{CH}_3(g) + 5\text{O}_2(g) \rightarrow 3\text{CO}_2(g) + 4\text{H}_2\text{O}(l) )</td>
<td>-2220</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}(l) \rightarrow \text{H}_2(g) + \frac{1}{2}\text{O}_2(g) )</td>
<td>+286</td>
</tr>
<tr>
<td>( \text{CH}_2=\text{CHCH}_3(g) + \frac{9}{2}\text{O}_2(g) \rightarrow 3\text{CO}_2(g) + 3\text{H}_2\text{O}(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 kJ mol\(^{-1}\)
\( \text{C}_6\text{H}_{12}\text{O}_6(s) + 6\text{O}_2(g) \rightarrow 6\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \)

Standard reaction enthalpy for combustion of maltose: -5645.5 kJ mol\(^{-1}\)
\( \text{C}_{12}\text{H}_{22}\text{O}_{11}(s) + 12\text{O}_2(g) \rightarrow 12\text{CO}_2(g) + 11\text{H}_2\text{O}(l) \)

Calculate the standard enthalpy of conversion:
\( \text{C}_6\text{H}_{12}\text{O}_6(s) \rightarrow \frac{1}{2}\text{C}_{12}\text{H}_{22}\text{O}_{11}(s) + \frac{1}{2}\text{H}_2\text{O}(l) \)

Standard Enthalpies of Formation

Change in enthalpy for formation of compound from its constituent elements in their reference state

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 H^\circ ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene, ( \text{C}_6\text{H}_6 )</td>
<td>-326.0</td>
</tr>
<tr>
<td>Methylene, ( \text{CH}_2 )</td>
<td>-386.9</td>
</tr>
<tr>
<td>Chlorine, ( \text{Cl}_2 )</td>
<td>-174.8</td>
</tr>
<tr>
<td>Methane, ( \text{CH}_4 )</td>
<td>-74.8</td>
</tr>
<tr>
<td>Methanol, ( \text{CH}_3\text{OH} )</td>
<td>-237.7</td>
</tr>
</tbody>
</table>

*Values are given in the discussion.
Standard Enthalpies of Formation

**standard enthalpy of formation, \( \Delta_f^\circ \):**
Change in enthalpy for formation of compound from its constituent elements in their reference state.

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

<table>
<thead>
<tr>
<th>Inorganic Compound</th>
<th>( \Delta_f^\circ ) (kJ mol(^{-1})) at 298 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{O}(l) )</td>
<td>-285.83</td>
</tr>
<tr>
<td>( \text{N}_2\text{O}_4(g) )</td>
<td>+46.11</td>
</tr>
<tr>
<td>( \text{NO}(g) )</td>
<td>+33.18</td>
</tr>
<tr>
<td>( \text{NaCl}(s) )</td>
<td>-411.15</td>
</tr>
</tbody>
</table>

* More values are given in the Data sections.

**Examples of Formation Reactions:**

- \( 6\text{C}(s, \text{graphite}) + 3\text{H}_2 \rightarrow \text{C}_6\text{H}_6(l) \) \( \Delta_f^\circ = +49.0 \text{ kJ mol}^{-1} \)
- \( \text{N}_2(g) \rightarrow \text{N}_2(g) \) \( \Delta_f^\circ = 0 \) null, reference state

Reaction Enthalpy in Terms of Formation

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

Value of \( \Delta_r^\circ \) for reaction is sum of forming and "unforming" enthalpies

\[
\Delta_r^\circ = \sum_j n_j \Delta_f^\circ(J)
\]

Remember:

- \( n_j \) negative for reactants

Example:

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

\[
\Delta_r^\circ = \Delta_f^\circ(\text{H}_2\text{O}_2(l)) + 4 \Delta_f^\circ(\text{N}_2(g)) - 2 \Delta_f^\circ(\text{H}_2\text{O}(l)) - 2 \Delta_f^\circ(\text{NO}(g))
\]

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

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

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

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

This is an unreliable method, since $\Delta H(A-B)$ 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*

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**Benson Group Contributions**

**Example:**

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

Decomposition: Two $\text{CH}_3\text{C}_3$  
Four $\text{CH}_2\text{C}_2$

$\Delta_r H^\circ(\text{C}_6\text{H}_{14},g) = [2(-42.17) + 4(-20.7)] \text{kJ mol}^{-1}$

$= -167.1 \text{kJ mol}^{-1}$

$\Delta_{vap} H^\circ(\text{C}_6\text{H}_{14}) = 33.1 \text{kJ mol}^{-1}$

$\Delta_r H^\circ(\text{C}_6\text{H}_{14},l) = [-167.1 - 33.1] \text{kJ mol}^{-1}$

$= -200.2 \text{kJ mol}^{-1}$

Experimental value is -198.7 kJ mol$^{-1}$

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**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.

$\left( \frac{\partial }{\partial T} \right)_p \Delta_r H = C_p$

$H(T_f) - H(T_i) = \int_{T_i}^{T_f} C_p dT$

Here, we have heated from $T_i$ to $T_f$ 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

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

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

\[ \Delta_rH^\circ(T_2) = \Delta_rH^\circ(T_1) + \int_{T_1}^{T_2} \Delta_rC_p^\circ \, dT \]

This equation is known as Kirchoff's Law.

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

\[ \Delta_rC_p^\circ = \sum_j v_j C_p^\circ_{p,j} (T) \]