15.1 Standard enthalpy changes of reaction (HL)
Standard enthalpy change of formation \((\Delta H_f^\Theta)\)

- The enthalpy change when 1 mol of a compound is formed from its elements in their standard states at 298 K and 1 atm pressure.

- The standard state (the reference state) is generally the most stable form of the element.

- Ex. The enthalpy change of formation of silver bromide, AgBr.

  \[
  \text{Ag(s) + } \frac{1}{2} \text{Br}_2(l) \rightarrow 1 \text{AgBr(s)} \quad \Delta H_f^\Theta = -99.5 \text{ kJ mol}^{-1}
  \]
• $\Delta H_f^\theta$ for elements (in their standard states) are zero, because no reaction is involved in their formation.

$$\text{O}_2 \ (g) \rightarrow \text{O}_2 \ (g) \quad \Delta H_f^\theta = \ 0 \ \text{kJ mol}^{-1}$$
• $\Delta H_f^\Theta$ are usually difficult to measure in practice, but for water it can be directly determined.

$$\text{H}_2 \text{ (g)} + \frac{1}{2} \text{O}_2 \text{ (g)} \rightarrow 1 \text{H}_2\text{O (l)} \quad \Delta H_f^\Theta = -286 \text{ kJ mol}^{-1}$$
Standard enthalpy change of combustion ($\Delta H^\Theta_c$)

- The enthalpy change when 1 mol of a substance is completely combusted in oxygen under standard conditions.

$$\text{1 CH}_4 (g) + 2 \text{ O}_2 (g) \rightarrow \text{ CO}_2 (g) + 2 \text{ H}_2\text{O (l)} \quad \Delta H^\Theta_c = -890 \text{ kJ mol}^{-1}$$
Determining the enthalpy changes of a reaction using $\Delta H_f^\circ$

The enthalpy change of any reaction can be calculated by using Hess law and the enthalpy changes of formation.

$$\sum \Delta H_{\text{reaction}}^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$$
Determining the enthalpy changes of a reaction using $\Delta H^\Theta_c$

- The standard enthalpy change of a reaction can be calculated by using Hess law and the standard enthalpy changes of combustion. (But only if the substances on both sides of the equation can be burned in oxygen).

$$\sum \Delta H^\Theta_{\text{reaction}} = \sum \Delta H^\Theta_c(\text{reactants}) - \sum \Delta H^\Theta_c(\text{products})$$
Using Hess’s law to calculate the enthalpy change of a reaction

Ex. Calculate the enthalpy change for the conversion of graphite to diamond under standard thermodynamic conditions.

\[
\begin{align*}
\text{C (graphite)} + \text{O}_2 (g) & \rightarrow \text{CO}_2 (g) \quad \Delta H^\theta = -393 \text{ kJ mol}^{-1} \\
\text{C (diamond)} + \text{O}_2 (g) & \rightarrow \text{CO}_2 (g) \quad \Delta H^\theta = -395 \text{ kJ mol}^{-1}
\end{align*}
\]
a) Energy-cycle method

\[ \Delta H_1 = (\Delta H_2 - \Delta H_3) \]

\[ \Delta H_2 = -393 \text{ kJ mol}^{-1} \]

\[ \Delta H_3 = -395 \text{ kJ mol}^{-1} \]

\[ \Delta H_1 = (-393)-(-395) = +2 \text{ kJ mol}^{-1} \]
b) Algebraic method

The two equations are added together. Reversing the direction of the reaction reverses the sign of ΔH!

\[
\begin{align*}
\text{C (graphite)} + \text{O}_2 (g) & \rightarrow \text{CO}_2 (g) \quad -393 \text{ kJ mol}^{-1} \\
\text{CO}_2 & \rightarrow \text{C (diamond)} + \text{O}_2 (g) \quad +395 \text{ kJ mol}^{-1} \\
\hline
\text{C (graphite)} & \rightarrow \text{C (diamond)} \quad +2 \text{ kJ mol}^{-1}
\end{align*}
\]
Enthalpy of atomization ($\Delta H_{\text{atom}}^\Theta$)

- The heat change when one mole of gaseous atoms of the element is formed from the element in its standard state under standard conditions.

Fe (s) $\rightarrow$ 1 Fe (g) $\Delta H_{\text{atom}}^\Theta$ = +418 kJ mol$^{-1}$

$\frac{1}{2}$ Br$_2$ (g) $\rightarrow$ 1 Br (g) $\Delta H_{\text{atom}}^\Theta$ = + 96.5 kJ mol$^{-1}$

$\frac{1}{2}$ Cl$_2$ (g) $\rightarrow$ Cl (g)
Enthalpies of physical change

- When a gas condenses to liquid, intermolecular bonds form (e.g. dipole-dipole bonds). Therefore, energy is released.
- When a liquid vaporizes, energy is absorbed.
- e.g. the enthalpy change of vaporization of water is the enthalpy change when 1 mol of H\textsubscript{2}O vaporizes from liquid to gas.

\[ \Delta H_{vap}^\Theta = +44 \text{ kJmol}^{-1} \]
The first ionization energy, $\Delta H_i^0$

- The energy required to remove one mole of electrons from one mole of isolated gaseous atoms to form one mole of gaseous unipositive ions under standard conditions:

$$\text{Na} (g) \rightarrow \text{Na}^+ (g) + 1 \text{ e}^- (g)$$
The first electron affinity, $\Delta H_{ee}^\Theta$

- The enthalpy change when one mole of gaseous atoms attracts one mole of electrons:

$$\text{Cl} \ (g) + e^- \ (g) \rightarrow \text{Cl}^- \ (g)$$
\[
\text{Na (g)} \rightarrow \text{Na}^+ (g) + \text{e}^- (g) \quad \Delta H_i^\Theta = + 496 \text{ kJmol}^{-1}
\]

\[
\text{Cl (g)} + \text{e}^- (g) \rightarrow \text{Cl}^- (g) \quad \Delta H_e^\Theta = -349 \text{ kJmol}^{-1}
\]
The Lattice enthalpy $\Delta H_{\text{lat}}^\Theta$

- Ionic compounds form because the oppositely charged ions are strongly attracted to each other and form an ionic lattice. This process is extremely exothermic.

$$\text{Na}^+ (g) + \text{Cl}^- (g) \rightarrow \text{NaCl} (s) \quad \Delta H_{\text{latt}}^\Theta = -790 \text{ kJmol}^{-1}$$
• $\Delta H_{\text{latt}}^\Theta$ of an ionic compound is the heat absorbed when one mole of a solid ionic compound is decomposed to form gaseous ions (infinite distance from each other) under standard conditions = the reversed process to the formation of the lattice.

$$\text{NaCl (s) } \rightarrow \text{ Na}^+ (g) + \text{ Cl}^- (g) \quad \Delta H_{\text{latt}}^\Theta = ?$$

• The lattice enthalpy of an ionic compound can not be determined experimentally, but it can be calculated using a Born-Haber cycle.
15.2 Born-Haber cycle

• An energy cycle for the formation of ionic compounds. It contains a number of separate steps of measurable enthalpy values, such as the enthalpy of ionization and enthalpy of atomization.

It can be used for calculating experimental lattice enthalpy (="the missing value") from other enthalpy changes.
Experimental lattice enthalpies: the Born-Haber cycle for NaCl

Na (s) + ½ Cl₂ (g) → NaCl (s)
Theoretical lattice enthalpies

The value of lattice enthalpy is effected by

1) the charge of the ions
2) the size of the ions
3) the structure of the crystal lattice

Lattice enthalpy is a measure of the strength of the electrostatic attraction between all the ions in the crystal structure.

E.g. \( \Delta H_{\text{latt}}^\circ (\text{MgO}) = -3889 \text{ kJ/mol} \)
\( \Delta H_{\text{latt}}^\circ (\text{NaCl}) = -771 \text{ kJ/mol} \)
Born-Haber cycles are used in the
1) calculation of an unknown value in cycle,
2) determination of degree of ionic character of a
   salt (two values of lattice enthalpy are
   compared: that from a Born-Haber cycle and a
   theoretical value which takes into account ionic
   size, charge and packing.)

<table>
<thead>
<tr>
<th></th>
<th>NaCl</th>
<th>AgCl</th>
<th>AgI</th>
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</thead>
<tbody>
<tr>
<td>Difference in electronegativity</td>
<td>2.1</td>
<td>1.1</td>
<td>0.6</td>
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<tr>
<td>Theor. value for $H_{\text{latt}}$</td>
<td>766</td>
<td>770</td>
<td>736</td>
</tr>
<tr>
<td>Exp. value for $H_{\text{latt}}$</td>
<td>771</td>
<td>905</td>
<td>876</td>
</tr>
</tbody>
</table>

If there is a big difference between the two values, then the compound has a considerable degree of covalent character.
15.3 Entropy
• Energy and matter has a natural tendency to disperse and the universe becomes more disordered.

• Spontaneous processes occur without the need to do work.
• Entropy is simply a measure of disorder or dispersal of energy in a system:

- arrangement of particles (atoms, ions or molecules)
- the kinetic energy of the particles in a system.

Low entropy

High entropy
The second law of thermodynamics

- The total entropy of the universe tends to increase.
The third law of thermodynamics

- At absolute zero all matter would be in perfectly ordered crystalline solid state and the particles would not vibrate.

- The particles would have the maximum order (no disorder) and the entropy would be zero.
Predicting entropy changes

a) Increasing temperature increases the entropy (+).
b) The entropy increases from solid to liquid to gas (+).
c) If the number of particles increases, disorder and hence entropy increases (+).

\[
\text{N}_2\text{O}_4 (g) \rightarrow 2 \text{NO}_2 (g)
\]
d) Entropy increases (+) when particles are mixed during melting or dissolving.
Entropy change, \( \Delta S \)

- Entropy values are absolute values that can be measured experimentally (under standard thermodynamic conditions) and calculated theoretically.

\[
\Delta S^\circ = \Sigma S^\circ(\text{products}) - \Sigma S^\circ(\text{reactants})
\]

- \( \Delta S > 0 \) increased entropy, more disorder
- \( \Delta S < 0 \) decreased entropy, more order
Ex. Calculate the entropy change that occurs during the complete combustion of ethane:

\[ C_2H_6 (g) + 3.5 O_2 (g) \rightarrow 2 CO_2 (g) + 3 H_2O (l) \]

\[ S^\ominus = 230 \text{ JK}^{-1}\text{mol}^{-1} \]
\[ 205\text{ JK}^{-1}\text{mol}^{-1} \]
\[ 214\text{ JK}^{-1}\text{mol}^{-1} \]
\[ 69.9\text{ JK}^{-1}\text{mol}^{-1} \]

\[ \Delta S^\ominus = \Sigma S^\ominus (\text{products}) - \Sigma S^\ominus (\text{reactants}) \]
15.4 Spontaneity

- Calculate ΔS° for the reaction of ammonia with hydrochloric acid.

\[
\text{NH}_3(g) + \text{HCl} (g) \rightarrow \text{NH}_4\text{Cl} (s)
\]

- The reaction is spontaneous even though the entropy decreases.
• When considering the total entropy change of a reaction, the entropy change into the surrounding universe has to be taken into account.

• The heat given out in exothermic reactions increases the disorder of the surroundings

\[ \Delta S_{\text{surrounding}} \propto -\Delta H_{\text{sys}} \]
The change in disorder of the surrounding by addition of heat depends on the present state of disorder (= the temperature).

The colder the surrounding (lower temperature), the more dramatic the change in disorder caused by addition of extra heat.

\[ \Delta S_{\text{surrounding}} \propto \frac{1}{T} \]

Combining both expressions: \( \Delta S_{\text{surrounding}} = -\frac{\Delta H_{\text{sys}}}{T} \)
• For a spontaneous change the entropy increases:

\[ \Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surrounding}} > 0 \]

\[ \Delta S_{\text{total}} = \Delta S_{\text{sys}} - \Delta H_{\text{sys}} / T > 0 \]

• Order may increase in local areas but only at the expense of greater disorder elsewhere in the universe

e.g. photosynthesis
The Gibbs free energy

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$\Delta G < 0$  spontaneous reaction

$\Delta G = 0$  chemical equilibrium

$\Delta G > 0$  non-spontaneous reaction
The Gibbs free energy is a useful quantity that predicts whether a process (e.g. a chemical reaction) carried out at constant temperature and pressure can or cannot occur.

When the value of Gibbs free energy is negative it is equal to the maximum amount of energy given out in a reaction that is available for useful work.
## Possible combinations for free energy changes

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

<table>
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<th>$\Delta H^\circ$</th>
<th>$\Delta S^\circ$</th>
<th>$T$</th>
<th>$T\Delta S^\circ$</th>
<th>$\Delta H^\circ - T\Delta S^\circ$</th>
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<tr>
<td>+</td>
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<td>0 - (-)</td>
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</tbody>
</table>
a) Calculating $\Delta G^\Theta_{\text{reaction}}$ from $\Delta G^\Theta_f$ at 298K

$$\Delta G^\Theta_{\text{reaction}} = \sum G^\Theta_f(\text{products}) - \sum G^\Theta_f(\text{reactants})$$
b) Calculating $\Delta G^\Theta_{\text{reaction}}$ at all temperatures

$$\Delta G^\Theta = \Delta H^\Theta - T \Delta S^\Theta$$

Homework: 43, 44, 45-47