2. How far? Entropy

Entropy change ($\Delta S$)

A SPONTANEOUS PROCESS (e.g. diffusion) will proceed on its own without any external influence.

A problem with $\Delta H$

A reaction that is exothermic will result in products that are more thermodynamically stable than the reactants. This is a driving force behind many reactions and causes them to be spontaneous (occur without any external influence).

Some spontaneous reactions, however, are endothermic. How can this be explained?

We need to consider something called entropy

Entropy, $S^\circ$

Substances with more ways of arranging their atoms and energy (more disordered) have a higher entropy.

System and Surroundings

When considering entropy it is useful to split the system (the chemicals) from the surroundings.

A system will consist of reactants and then products. It does not change temperature or pressure, and mass cannot be transferred to the surroundings. Energy can be transferred to the surroundings.

Entropy of the System, $S^\circ_{\text{system}}$

<table>
<thead>
<tr>
<th>Elements</th>
<th>Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simpler compounds</td>
<td>Complex compounds</td>
</tr>
<tr>
<td>Pure substances</td>
<td>Mixtures</td>
</tr>
</tbody>
</table>

Solids have lower entropies than liquids which are lower than gases. When a solid increases in Temperature its entropy increases as the particles vibrate more.

There is a bigger jump in entropy with boiling than that with melting. Gases have large entropies as they are much more disordered.

Entropy is a description of the number of ways atoms can share quanta of energy. If number of ways of arranging the energy ($W$) is high, then system is disordered and entropy ($S$) is high.
Calculating $\Delta S_{\text{system}}$ quantitatively

Data books lists standard entropies ($S^0$) per mole for a variety of substances. It is not possible for a substance to have a standard entropy of less than zero. Elements in their standard states do not have zero entropy. Only perfect crystals at absolute zero ($T = 0$ K) will have zero entropy:

$$\Delta S_{\text{system}}^0 = \sum S^0_{\text{products}} - \sum S^0_{\text{reactants}}$$

The unit of entropy is $\text{J K}^{-1} \text{mol}^{-1}$

Example

Calculate $\Delta S^0$ for the following reaction at 25°C:

$$2\text{Fe}_2\text{O}_3 (s) + 3\text{C} (s) \rightarrow 4\text{Fe} (s) + 3\text{CO}_2 (g)$$

$$\Delta S_{\text{system}}^0 = \sum S^0_{\text{products}} - \sum S^0_{\text{reactants}}$$

$$= (3 \times 213.6 + 4 \times 27.3) - (2 \times 87.4 + 3 \times 5.7)$$

$$= + 558.1 \text{ J K}^{-1} \text{mol}^{-1} = + 558 \text{ J K}^{-1} \text{mol}^{-1} (3 \text{ S.F.})$$

Note: the entropy change is very positive as a large amount of gas is being created increasing disorder.

Entropy of the Surroundings $\Delta S_{\text{surrounding}}$

The surroundings are the container, air, solvent.

In an exothermic reaction energy is given out into the surroundings. The number of ways of arranging the energy therefore increases and so $\Delta S_{\text{surrounding}}$ increases and is positive.

$$\Delta S_{\text{surrounding}} = - \frac{\Delta H \text{ reaction}}{T}$$

converted into Jmol$^{-1}$ by x1000

in K

Convert $^\circ$C into K by +273

Total Entropy change $\Delta S_{\text{total}}$

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

For any reaction to be spontaneous then $\Delta S_{\text{total}}$ must be positive. If a reaction is not spontaneous i.e. it doesn’t go, then $\Delta S_{\text{total}}$ will be negative.
Example: Data for the following reaction, which represents the reduction of aluminium oxide by carbon, are shown in the table.

\[
\text{Al}_2\text{O}_3(s) + 3\text{C}(s) \rightarrow 2\text{Al}(s) + 3\text{CO}(g)
\]

Calculate the values of \(\Delta S_{\text{system}}\), \(\Delta H\), \(\Delta S_{\text{surroundings}}\) and \(\Delta S_{\text{Total}}\) for the above reaction at 298 K.

1. Calculate \(\Delta S_{\text{system}}\)

\[
\Delta S_{\text{system}} = \Sigma S_{\text{products}} - \Sigma S_{\text{reactants}}
\]

\[
= (2 \times 28 + 3 \times 198) - (51 + 3 \times 6) = 581 \text{ J K}^{-1} \text{mol}^{-1} \quad (3 \text{ S.F.})
\]

2. Calculate \(\Delta H\)

\[
\Delta H = \Sigma \Delta H_{\text{products}} - \Sigma \Delta H_{\text{reactants}}
\]

\[
= (3 \times -111) - (-1669) = 1336 \text{ kJ mol}^{-1}
\]

\(\Delta S_{\text{Total}}\) is negative. The reaction is not feasible.

Calculating the temperature a reaction will become feasible

Calculate the temperature range that this reaction will be feasible.

\[
\text{CH}_4(g) \rightarrow \text{CH}_4(l) \quad \Delta H = 0.94 \text{ kJ mol}^{-1} \quad \Delta S = 10.3 \text{ J mol}^{-1} \text{K}^{-1}
\]

Make \(\Delta S_{\text{Total}} = 0\) in the following equation:

\[
\Delta S_{\text{Total}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}
\]

\[
0 = \frac{-\Delta H}{T} + \Delta S_{\text{system}}
\]

\[
T = 917 \text{ K}
\]

Effect of Temperature on feasibility

\[
\Delta S_{\text{Total}} = -\Delta H/T + \Delta S_{\text{system}}
\]

Changing temperature will change the value of \(-\Delta H/T\) in the above equation.

If the reaction involves an increase in entropy of the system (\(\Delta S_{\text{system}}\) is +ve) then increasing temperature will make the -\(\Delta H/T\) have a smaller magnitude and it will more likely that \(\Delta S_{\text{Total}}\) will be positive and more likely that the reaction occurs e.g. \(\text{NaCl (aq)} + \text{Na}^+(aq) + \text{Cl}^-(aq)\)

If the reaction involves a decrease in entropy (\(\Delta S_{\text{system}}\) is -ve) then increasing temperature will make it more less likely that \(\Delta S_{\text{Total}}\) will be positive because the -\(\Delta H/T\) will have a smaller magnitude and will be less likely to compensate for the negative \(\Delta S_{\text{system}}\) It will be less likely for the reaction to occur. E.g. \(\text{HCl(g)} + \text{NH}_3(g) \rightarrow \text{NH}_4\text{Cl(s)}\)

If the reaction has a \(\Delta H\) close to zero then temperature will not have a large effect on the feasibility of the reaction as -\(\Delta H/T\) will be small and \(\Delta S_{\text{Total}}\) won’t change much.
**Enthalpy of lattice formation**

The Enthalpy of lattice formation is the standard enthalpy change when 1 mole of an ionic crystal lattice is formed from its constituent ions in gaseous form.

\[
\text{Na}^+ (g) + \text{Cl}^- (g) \rightarrow \text{NaCl} (s) \quad [\Delta H_{\text{Latt}} = -787 \text{ kJ mol}^{-1}]
\]

**Enthalpy of solution**

The enthalpy of solution is the standard enthalpy change when one mole of an ionic solid dissolves in an large enough amount of water to ensure that the dissolved ions are well separated and do not interact with one another.

\[
\text{NaCl} (s) + \text{aq} \rightarrow \text{Na}^+ (aq) + \text{Cl}^- (aq)
\]

**Enthalpy of Hydration \(\Delta H_{\text{hyd}}\)**

- Enthalpy change when one mole of gaseous ions become hydrated such that further dilution causes no further heat change

\[
\begin{align*}
\text{For Li}^+ \quad \Delta H_{\text{hyd}} &= -519 \text{ kJ mol}^{-1} \\
\text{or} \quad \text{For F}^- \quad \Delta H_{\text{hyd}} &= -506 \text{ kJ mol}^{-1}
\end{align*}
\]

This always gives out energy (exothermic, -ve) because bonds are made between the ions and the water molecules.

**Trends in Lattice Enthalpies**

The strength of an enthalpy of lattice formation depends on the following factors:

1. **The sizes of the ions:**
   - The larger the ions, the less negative the enthalpies of lattice formation (i.e. a weaker lattice). As the ions are larger the charges become further apart and so have a weaker attractive force between them.

2. **The charges on the ion:**
   - The bigger the charge of the ion, the greater the attraction between the ions so the stronger the lattice enthalpy (more negative values).

**Enthalpies of solution**

Using Hess’s law to determine enthalpy changes of solution

When an ionic lattice dissolves in water it involves breaking up the bonds in the lattice and forming new bonds between the metal ions and water molecules.

For \(\text{MgCl}_2\) the ionic equation for the dissolving is \(\text{MgCl}_2 (s) + \text{aq} \rightarrow \text{Mg}^{2+} (aq) + 2\text{Cl}^- (aq)\)

\[
\begin{align*}
\Delta H_{\text{Lattice formation}} (\text{MgCl}_2) &\quad \Delta H_{\text{hyd}} \text{Mg}^{2+} \\
\text{MgCl}_2 (s) &\quad \text{Mg}^{2+} (aq) + 2\text{Cl}^- (g) \\
\Delta H_{\text{solution}} &\quad 2 \times \Delta H_{\text{hyd}} \text{Cl}^- \\
&\quad \text{Mg}^{2+} (aq) + 2\text{Cl}^- (aq)
\end{align*}
\]

\[\Delta H_{\text{solution}} = - \Delta H_{\text{Lattice formation}} + \Sigma \Delta H_{\text{hyd}}\]

When an ionic substance dissolves the lattice must be broken up. The enthalpy of lattice dissociation is equal to the energy needed to break up the lattice (to gaseous ions). This step is **endothermic**.

The size of the lattice enthalpy depends on the size and charge on the ion. The smaller the ion and the higher its charge the stronger the lattice.
Example. Calculate the enthalpy of solution of NaCl given that the lattice enthalpy of formation of NaCl is -771 kJmol\(^{-1}\) and the enthalpies of hydration of sodium and chloride ions are -406 and -364 kJmol\(^{-1}\) respectively.

\[
\Delta H_{\text{sol}} = -\Delta H_{\text{lattice formation}} + \Sigma \Delta H_{\text{hyd}} = -(-771) + (-406-364) = +1 \text{ kJmol}^{-1}
\]

Hydration enthalpies are **exothermic** as energy is given out as water molecules bond to the metal ions. The **negative** ions are attracted to the \(\delta^+\) hydrogens on the **polar water** molecules and the positive ions are attracted to the \(\delta^-\) oxygen on the polar water molecules.

The higher the **charge density** the greater the hydration enthalpy (e.g. **smaller ions** or **ions with larger charges**) as the ions attract the water molecules more strongly.

e.g. Fluoride ions have more negative hydration enthalpies than chloride ions

Magnesium ions have a more negative hydration enthalpy than barium ions

### What does \(\Delta H_{\text{solution}}\) tell us?

Generally \(\Delta H_{\text{solution}}\) is not very exo or endothermic so the hydration enthalpy is about the same as lattice enthalpy. In general the substance is more likely to be **soluble** if the \(\Delta H_{\text{solution}}\) is exothermic. If a substance is insoluble it is often because the lattice enthalpy is much larger than the hydration enthalpy and it is not energetically favourable to break up the lattice, making \(\Delta H_{\text{solution}}\) endothermic.

We must consider **entropy**, however, to give us the full picture about solubility.

When a solid dissolves into ions the **entropy increases** as there is **more disorder** as solid changes to solution and the **number of particles increases**.

This positive \(\Delta S_{\text{system}}\) can make \(\Delta S_{\text{total}}\) positive even if \(\Delta H_{\text{solution}}\) is endothermic, especially at higher temperatures.

For salts where \(\Delta H_{\text{solution}}\) is exothermic the salt will always dissolve at all Temperatures

\[
\Delta S_{\text{total}} = -\Delta H/T + \Delta S_{\text{system}}
\]

\(\Delta S_{\text{total}}\) is always positive

\(\Delta H\) is negative so \(-\Delta H/T\) will always be positive

\(\Delta S_{\text{system}}\) is positive due to the increased disorder as more particles

Increasing the Temperature will make it more likely that \(\Delta S_{\text{total}}\) will become positive, making the reaction feasible and the salt dissolve