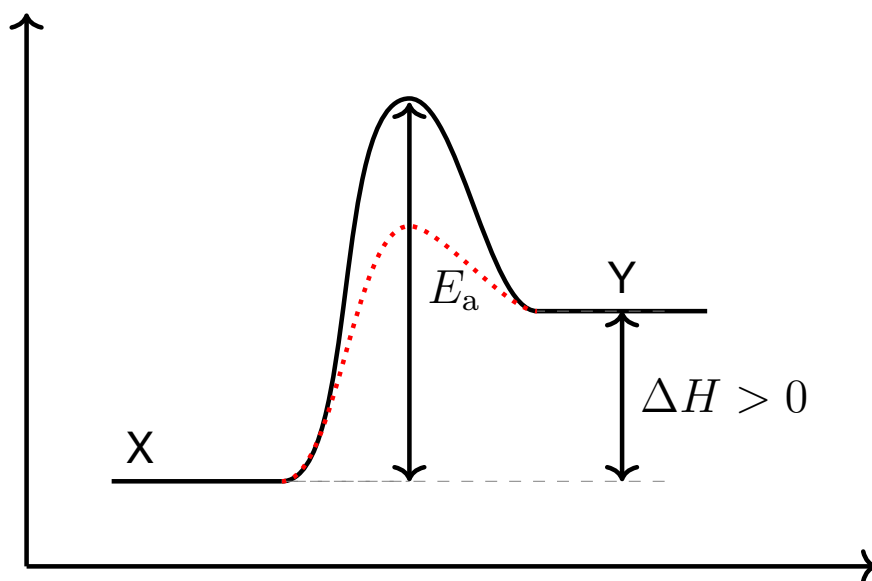# Physical Chemistry

$$\Delta G = \Delta H - T \times \Delta S$$

Chapters 5 to 7

Contents

Enthalpies

1 Enthalpy Change

Enthalpy refers to the total energy content of a given substance. When reacting two or more compounds together, the bonds within must first be broken, before new bonds are formed. This process involves the transfer of energy, which is measured as the *enthalpy change*.

Enthalpy change, or ΔH, measures the difference in energy content between the reactants and the products of a reaction.

For an exothermic reaction, the energy content of the products is less than that of the reactants. Since the most stable state is that with the least amount of energy, exothermic reactions are said to be *more energetically favoured* — $\Delta H < 0$. Heat is released into the surroundings, and generally, temperature increases.
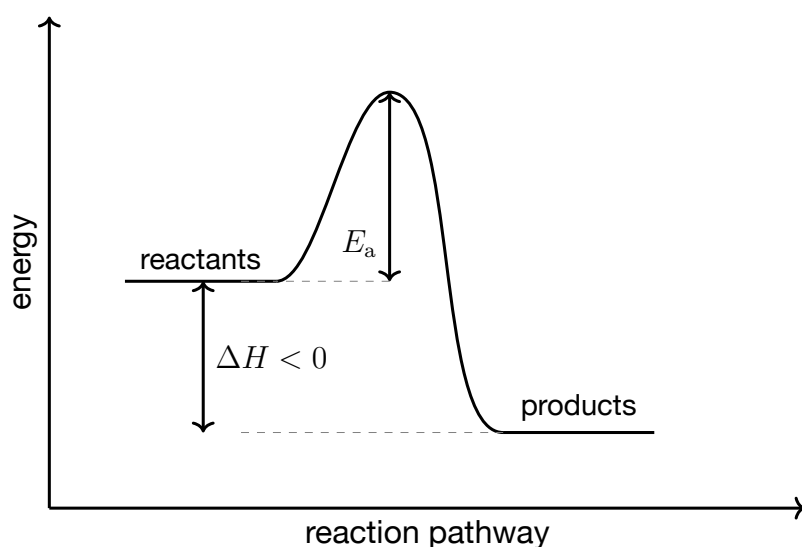
Conversely, for an endothermic reaction, the reverse is true — the energy content of the final products is greater than that of the reactants. Thus, these reactions are somewhat *less energetically favoured*, and less likely to happen. $\Delta H > 0$, and heat is absorbed from the surroundings to feed the reaction.
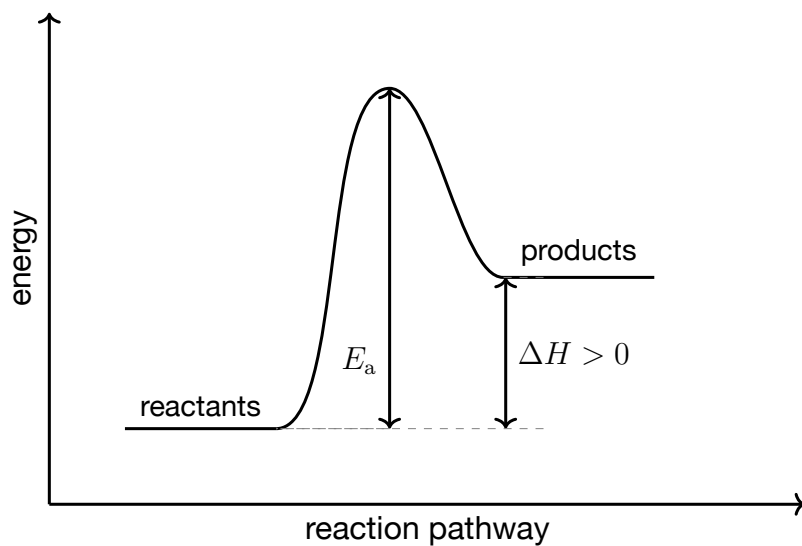
1.1   Activation Energy

Regardless of the enthalpy change of the reaction, some energy must always be input, and thus the activation energy, E_a , is always positive. This is because bonds must always be broken, which requires energy input, before new bonds can be formed.

However, the E_a for endothermic reactions is generally much higher than that for exothermic reactions, since its reactants are generally more stable.

1.2   Thermochemical Equations

A thermochemical equation is simply a normal, balanced chemical equation that has an enthalpy change of reaction associated with it. State symbols must also be included, since a change in state necessitates a change in the enthalpy of the substance.

$$H_2SO_{4\,(aq)} \; + \; 2\,NaOH_{(aq)} \quad \longrightarrow \quad Na_2SO_{4\,(aq)} \; + \; 2\,H_2O_{(l)}$$
$$\Delta H = -114.2 \, \text{kJ} \, \text{mol}^{-1}$$
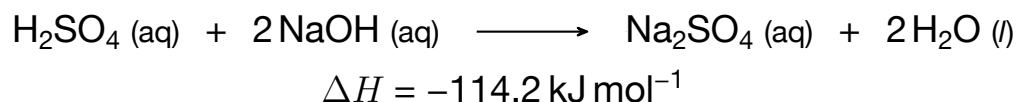
Note that the enthalpy change is per mole *of reaction*, not per mole of any one substance. Thus, if the above reaction were to be rewritten using 1 mole of NaOH instead:

$$\tfrac{1}{2}\,H_2SO_{4\,(aq)} \; + \; NaOH_{(aq)} \quad \longrightarrow \quad \tfrac{1}{2}\,Na_2SO_{4\,(aq)} \; + \; H_2O_{(l)}$$
$$\Delta H = -57.1 \, \text{kJ} \, \text{mol}^{-1}$$
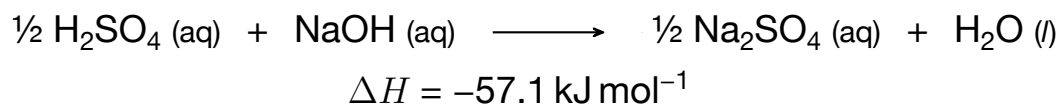
The enthalpy change of the reaction is now half the previous value.

1.3 Bond Dissociation Energy

Bond dissociation energy is the energy required to break *1 mole* worth of *covalent bonds* between two atoms in the *gaseous state*. Note that this value is always positive, since energy is required to break bonds. The larger the value, the stronger the bond.

Bonds are complex beasts; breaking seemingly identical bonds successively will require differing amounts of energy. For instance, the bond dissociation energy for the first $C-H$ bond in CH_4 is $425\,kJ\,mol^{-1}$, while that of the second $C-H$ bond (in what is now CH_3) is $470\,kJ\,mol^{-1}$.

Naturally, the bond dissociation energies can vary by significant amounts between different molecules — the BDE for a $C-H$ bond in CH_4 is smaller than that of the $C-H$ bond in $CH_2=CH_2$.

1.4 Bond Energy

Due to these problems, the *bond energy* is more frequently used. It is simply the *average* of the bond dissociation energies of the particular bond, sampled from a large variety of molecules.

Thus, it is defined as the *average energy* required to break *1 mole* worth of *covalent bonds* between two atoms in the *gaseous state*.

Furthermore, if the bond in question is between two atoms in a diatomic molecule in the gaseous state, then the bond energy and the enthalpy change of atomisation (ΔH_{atom}, below) are related: The bond energy is twice the enthalpy change of atomisation.

$$\frac{1}{2}\ H-H\ _{(g)} \longrightarrow H\ _{(g)}$$

$$\Delta H_{atom} = \frac{1}{2}\ BE(H-H)$$
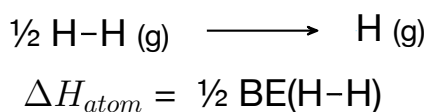
Indeed, since reactions at a fundamental level simply involve breaking and forming bonds, the enthalpy change of a given reaction can be calculated (somewhat inaccurately, due to bond energy being an average) taking the difference between the energies of the bonds formed, and that of the bonds broken.
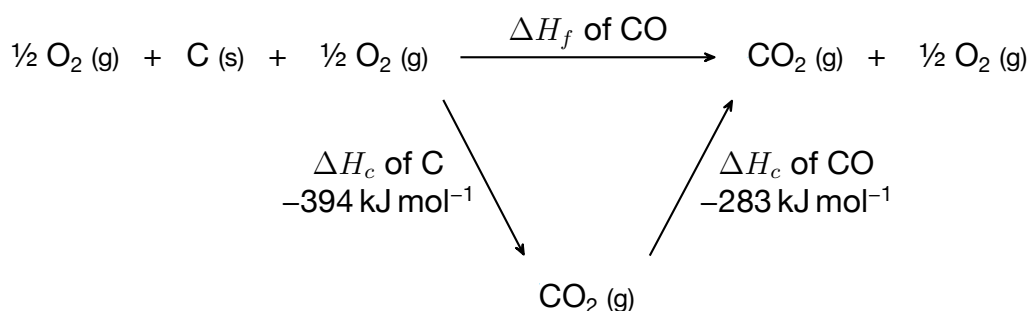
$$\Delta H_r = \Sigma\ BE(broken) - \Sigma\ BE(formed)$$

Accounting for any required changes in state can be done by adding the enthalpy change of either fusion or vaporisation on either side.

1.5 The Law of Hess

Hess's Law of *Constant Heat Summation* states that the enthalpy change of any given reaction is determined only by the enthalpy change between the initial state and final state, regardless of the steps taken in between.

Therefore, whether the reactants reacted directly or through some convoluted pathway to get to the final state, the enthalpy change will be the same. To make use of this, typically an energy cycle diagram is drawn, inserting whatever intermediate reaction is required (with known enthalpies) to get to the final product.

$$\frac{1}{2} O_2\ _{(g)}\ +\ C\ _{(s)}\ +\ \frac{1}{2} O_2\ _{(g)} \xrightarrow{\ \Delta H_f \text{ of CO}\ } CO_2\ _{(g)}\ +\ \frac{1}{2} O_2\ _{(g)}$$

ΔH_c of C
$-394\ \text{kJ mol}^{-1}$

ΔH_c of CO
$-283\ \text{kJ mol}^{-1}$

$$CO_2\ _{(g)}$$

Half a mole of O_2 was added on both sides of the primary reaction to balance it.

Note that the direction of the arrow can be manipulated *at will*, simply by reversing the sign of the associated enthalpy change. Indeed, extra reactants can be introduced too, as long as they are accounted for in all reactions.

1.6 Standard Enthalpy Change

For enthalpy change to have any meaning, it must be defined in terms of a set of standard conditions. In this case, the standard enthalpy change, $\Delta H^{\ominus}$, is defined as the enthalpy change at *298 K*, and a pressure of *1 atm*.

An element or substance in its standard state has the least amount of energy, and is physically stable. Elements in their standard states (C $_{(s)}$, Br$_2$ $_{(l)}$, N$_2$ $_{(g)}$, etc.) are assigned an enthalpy value of *0*.

The unit of enthalpy change is usually kJ mol^{-1} (kilojoules per mole). This means that it is always determined per mole of some substance; the greater the number of moles of substance reacting, the greater the total enthalpy change will be, in kJ.

1.7 Determination of Enthalpy Change

Since heat is released or absorbed when a reaction takes place, the enthalpy change, which is the change in energy of the compounds involved, can be determined through the measurement of temperature. Using the formula to determine heat change, q, enthalpy change is then heat change per mole.

$$q = mc\Delta T$$
$$\Delta H = \pm \frac{q}{n}$$

q   Heat change of the reaction.
m   Mass of the solution — in a polystyrene cup experiment, this excludes solids.
c   Specific heat capacity of the solution (usually assumed to be $4.18\,\mathrm{J\,g^{-1}\,K^{-1}}$)
ΔT   Change in temperature of the solution (before and after reaction)
ΔH   Enthalpy change of reaction.

While heat change is a scalar value and is always positive, enthalpy change has a sign, which is decided by whether the reaction is exothermic or endothermic. This can be inferred from the direction of the change in temperature.

1.8 Types of Enthalpy Change

1.8.1 Enthalpy Change of Fusion and Vaporisation

The enthalpy change of fusion is the change in enthalpy when *1 mole* of a substance in the *solid state* is heated, at a constant temperature (the melting point), until it becomes a liquid. Similarly, the enthalpy change of vaporisation is the change in enthalpy when *1 mole* of a substance in the *liquid state* is heated at a constant temperature (the boiling point), until it becomes a gas.

These are known as *latent* heats, because the temperature of the substance remains constant at either the melting or boiling points — no heat is actually released. However, since enthalpy measures the actual, total energy content of the compound, enthalpy still increases since the internal energy increases.

As one might expect, the enthalpy changes of fusion and vaporisation are almost always positive, since they involve moving a compound to a higher energy, and thus less stable, state. There are, however, a certain number of exceptions to this. The negative of these enthalpy changes would represent the amount of energy that needs to be removed, per mole, to change the substance from liquid to solid, and gas to liquid respectively.

1.8.2 Enthalpy Change of Formation

The standard enthalpy change of formation a compound is the heat evolved when *1 mole* of it is formed from its constituent elements, all in their standard states, under standard conditions. This disregards the actual method of forming the compound, and instead only accounts for simply mashing elements together. For example:

$$2\,C_{(s)} \;+\; 3\,H_{2\,(aq)} \;+\; \tfrac{1}{2}\,O_{2\,(g)} \longrightarrow C_2H_5OH_{(l)}$$
$$\Delta H = -298\,\text{kJ mol}^{-1}$$
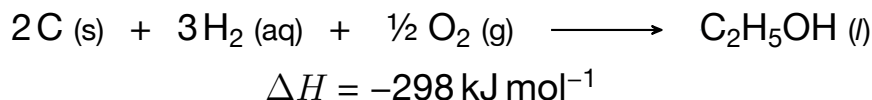
If the enthalpy change of formation of a substance, ΔH_f is > 0, then the compound is less stable than its constituent elements, meaning it is more likely to decompose — the reverse is true if $\Delta H_f < 0$. Note that ΔH_f of elements in their standard states is 0, by definition.

1.8.3 Enthalpy Change of Combustion

The enthalpy change of combustion of a compound is the heat evolved when *1 mole* of it is completely burned in excess oxygen, under standard conditions. This enthalpy change is always negative — heat is always released when things are combusted.

$$CH_{4\,(g)} \;+\; 2\,O_{2\,(g)} \longrightarrow CO_{2\,(g)} \;+\; 2\,H_2O_{(l)}$$
$$\Delta H_c = -866\,\text{kJ mol}^{-1}$$
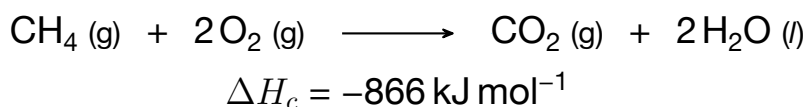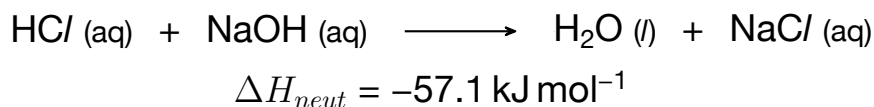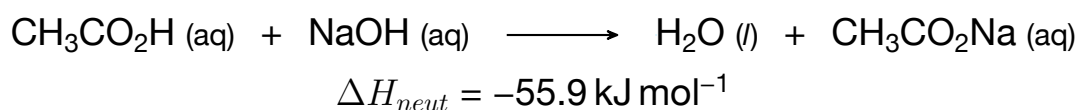
1.8.4 Enthalpy Change of Neutralisation

The enthalpy change of neutralisation is the heat evolved when *1 mole* of H_2O is formed when an acid and a base are reacted. Normally, it is the reaction between H^+ ions and OH^- ions in aqueous solution.

$$H^+_{(aq)} \;+\; OH^-_{(aq)} \longrightarrow H_2O_{(l)}$$
$$\Delta H_{neut} = -57.1\,\text{kJ mol}^{-1}$$
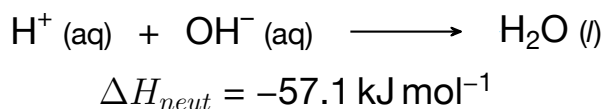
This reaction between H^+ ions and OH^- ions underlies the majority of reactions between acids and bases.

$$HCl \text{ (aq)} + NaOH \text{ (aq)} \longrightarrow H_2O \text{ (l)} + NaCl \text{ (aq)}$$
$$\Delta H_{neut} = -57.1 \text{ kJ mol}^{-1}$$

In general, the enthalpy change of neutralisation of all strong acid-base reactions will be the same, at $-57.1 \text{ kJ mol}^{-1}$. However, for weak acids, the H^+ and OH^- ions only dissociate partially — energy is thus needed to break these partially dissociated bonds, which decreases the enthalpy change of neutralisation of weak acids and bases.

$$CH_3CO_2H \text{ (aq)} + NaOH \text{ (aq)} \longrightarrow H_2O \text{ (l)} + CH_3CO_2Na \text{ (aq)}$$
$$\Delta H_{neut} = -55.9 \text{ kJ mol}^{-1}$$

1.8.5 Enthalpy Change of Atomisation

The enthalpy change of atomisation for an element is the energy required to create *1 mole* of gaseous atoms from the element in question in the standard state.

$$\tfrac{1}{2} Cl_2 \text{ (g)} \longrightarrow Cl \text{ (g)}$$
$$\Delta H_{atom} = 122 \text{ kJ mol}^{-1}$$
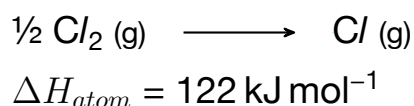
For elements that are already gaseous at their standard state, such as F_2 (g), the enthalpy change of atomisation would simply be the bond energy, in this case of the $F-F$ bond. For elements that are monatomic in the gaseous state, such as noble gases, the ΔH_{atom} is 0.

The enthalpy change of atomisation of a non-elemental compound, on the other hand, is the energy required to create gaseous atoms of its constituent elements, from the compound in its standard state. For example:

$$CH_4 \text{ (g)} \longrightarrow C \text{ (g)} + 4H \text{ (g)}$$
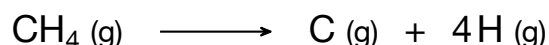
Of course, for compounds not initially in the gaseous state, they must first be converted, and the appropriate enthalpy change (of fusion or vaporisation) taken into account.

1.8.6 Enthalpy Change of Hydration

The enthalpy change of hydration is the energy released when *1 mole* of gaseous ions is dissolved in an *infinite volume* of water, under standard conditions. ΔH_{hyd} is always negative, as it involves the formation of ion-dipole interactions between the ions in question and the water molecules.

$$\Delta H_{hyd} \propto \frac{q}{r}$$

The enthalpy change of hydration is proportional to the charge density of the ions; the higher the charge density, the stronger the ion-dipole interactions and thus the larger the enthalpy change.

1.8.7 Enthalpy Change of Solution

The enthalpy change of solution is the enthalpy change when *1 mole* of a substance is dissolved in an *infinite volume* of solvent, under standard conditions. The solute and solvent can be anything, even though the solute is usually an ionic compound, and the solvent water.

If ΔH_{sol} is highly positive, then the solute is likely to be insoluble in the solvent, since the reaction would be endothermic. On the other hand, if ΔH_{sol} is negative, then the solute is likely to be soluble in the solvent.

1.8.8 Ionisation Energy

Ionisation energy is the energy required to remove *1 mole* of electrons from *1 mole* of gaseous atoms, forming *1 mole* of *gaseous cations*. The first ionisation energy involves the removal of electrons from neutral atoms, forming singly-charged gaseous cations; the second ionisation energy involves removing electrons from singly-charged gaseous cations, forming doubly-charged gaseous cations, and so on.

As should be obvious, ionisation energy increases with the number of electrons already removed. It is always positive, since energy is required to remove electrons from an atom.

1.8.9 Electron Affinity

Electron affinity is essentially the reverse of ionisation energy, measuring the enthalpy change when *1 mole* of electrons is added to *1 mole* of gaseous atoms, forming *1 mole* of *gaseous anions*. As with ionisation energy, the energy required to do this increases

with the number of electrons previously added.

The first electron affinity is usually negative, due to the slight electrostatic attraction between the neutral atom (rather, its nucleus) and the incoming electron. Subsequent electron affinities are usually positive, since energy is required to move a negative electron towards a negatively charged atom.

1.9 Lattice Energy

Lattice energy is the heat released when *1 mole* of an solid ionic compound is formed from its constituent ions in the gaseous state. It is *always negative*, since it involves the formation of ionic bonds between atoms.

The magnitude of lattice energy is a measure of the strength of the ionic bond — the more exothermic it is, the stronger the ionic bond. Ionic bond strength depends on two factors; the magnitude of the charge on both ions, and the ionic radius of the atoms.

$$LE \propto \frac{q_+ \times q_-}{r_+ + r_-}$$

q_+ and q_- represent the charge of the respective ion, and r_+ and r_- represent the ionic radius. Thus, the maximum lattice energy is achieved with the highest charge magnitude and the smallest ionic radius.

## 1.9.1 Theoretical vs. Experimental Lattice Energies

There exists no truly ionic compound — all ionic bonds will have some degree of covalent character, due to the behaviour of electrons. Naturally, some ionic bonds exhibit greater covalent character than others. This is related to the charge density of the cation and the ionic radius of the anion.

If the cation has a high charge density and the ionic radius of the anion is relatively large, then the large electron cloud will be attracted towards the cation (due to higher polarisability, shielding effect, etc.). This creates a situation where the charge is more spread out over the participating ions, resulting in a smaller ionic character and thus greater covalent character. Conversely, if the anion as a small electron cloud, it will be less polarisable, and tend to exhibit greater ionic character.

The calculation of lattice energy assumes a model where the bond is completely ionic, ie. zero covalent character. As this is clearly *not* the case, there are often discrepancies between theoretical and experimental values (from Born-Haber cycles) of lattice energy. If the discrepancy is small, then the ionic bond in question has a large ionic character. Else, it has a larger covalent character.

1.9.2 Born-Haber Cycles

Since it is impractical to determine lattice energy directly by reacting gaseous ions together, the *Law of Hess* can be applied to calculate lattice energy indirectly, using a Born-Haber cycle, which really is just a glorified energy-level diagram.
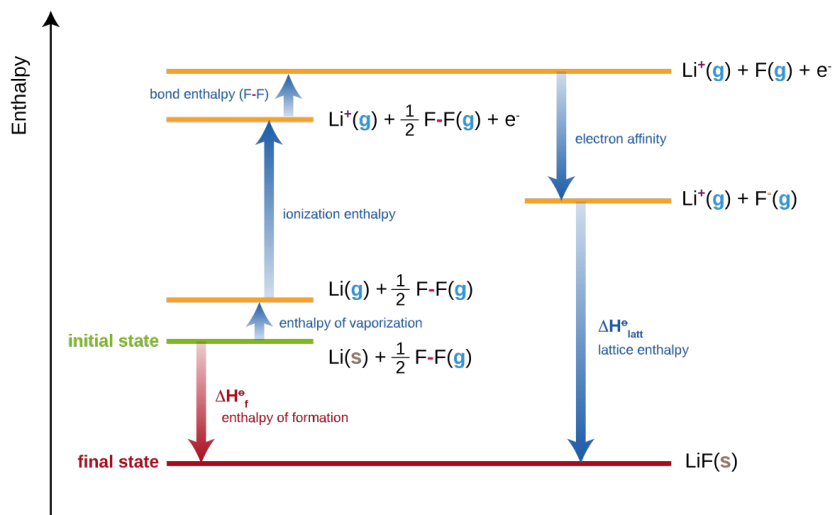

In the example above, the lattice energy of LiF, ΔH_{latt} is being calculated indirectly using various enthalpy changes. The initial state is given an enthalpy of 0. To put into words:
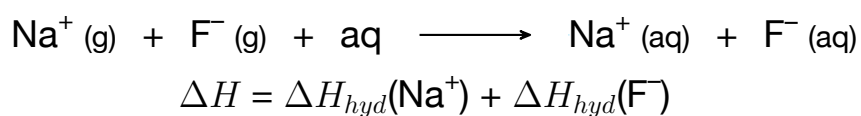
1. Atoms are at their initial, standard state; Li (s) and ½ F$_2$ (g).
   $\Delta H = 0$.

2. Li (s) is heated into the gaseous state, forming Li (g).
   $\Delta H = \Delta H_{fus} + \Delta H_{vap}$.

3. One mole of electrons is removed from Li (g), forming Li$^+$ (g) and e$^-$.
   $\Delta H = \Delta H_{fus} + \Delta H_{vap}$ + First IE (Li).

4. The F−F bond is broken, forming F (g).
   $\Delta H = \Delta H_{fuS} + \Delta H_{vap}$ + First IE (Li) + BE(F−F).

5. One mole of electrons is added to F (g), forming F$^-$ (g).
   $\Delta H = \Delta H_{fuS} + \Delta H_{vap}$ + First IE (Li) + BE(F−F) + First EA (F).

6. LiF (s) is formed from its constituent gaseous ions, Li$^+$ (g) and F$^-$ (g).
   $\Delta H = \Delta H_{fuS} + \Delta H_{vap}$ + First IE (Li) + BE(F−F) + First EA (F) + ΔH_{latt}.

7. To determine ΔH_{latt}, ΔH_f is used — the enthalpy change of formation of LiF (s) from constituent elements in their standard state.

8. Thus, applying the *Law of Hess* — $\Delta H_f = \Delta H_{fus} + \Delta H_{vap}$ + First IE (Li) + BE(F−F) + First EA (F) + ΔH_{latt}. Rearrange to solve for ΔH_{latt}.

1.9.3 Lattice Energy, ΔH_{sol} and ΔH_{hyd}

These three energies are related; dissolving a solid, ionic compound in water can be split into two sequential processes. First, the formation of gaseous ions form the solid ionic compound:

$$NaF_{(s)} \longrightarrow Na^+_{(g)} + F^-_{(g)}$$
$$\Delta H = -LE$$
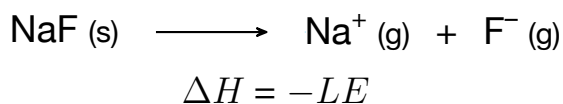
Second, the gaseous are hydrated.

$$Na^+_{(g)} + F^-_{(g)} + aq \longrightarrow Na^+_{(aq)} + F^-_{(aq)}$$
$$\Delta H = \Delta H_{hyd}(Na^+) + \Delta H_{hyd}(F^-)$$

Therefore, the total enthalpy change for this process is simply the sum of the enthalpy change of hydration of each ion, less the lattice energy of the final ionic compound. This can be summed up with the following energy level diagram:
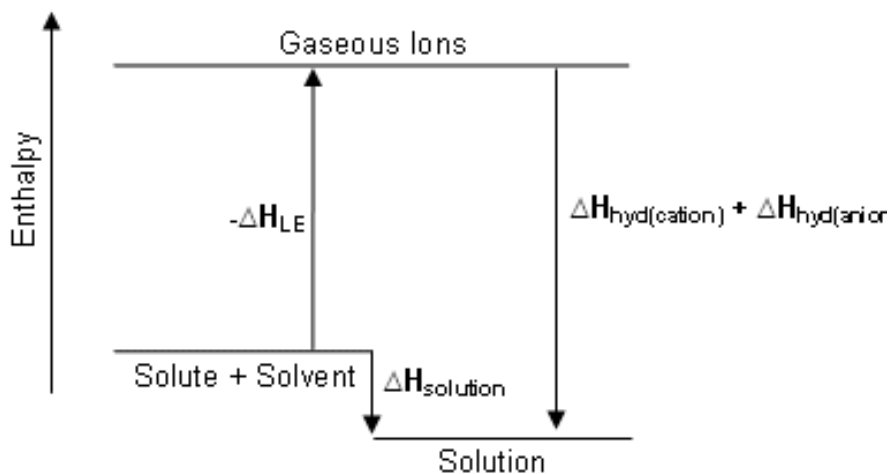
II Gibbs Free Energy and Entropy

1 Entropy and Spontaneity

The Second Law of Thermodynamics states that for a process to be spontaneous, the total entropy of the system must increase. Entropy, represented by *S*, is a measure of the number of ways energy can be distributed in a given system. This is often manifested through the motion of particles.

In a solid, movement is restricted and the kinetic energy of particles can only have so many permutations. Entropy is the smallest in the solid state.

In a gas, movement is almost unrestricted, and the possible range of kinetic energies for particles within the system is huge. Thus, entropy is the greatest. The difference in entropy between a gas and a liquid is much greater than that between a solid and a liquid.

1.1 Change in Entropy (ΔS)

The entropy change of a given reaction or action is determined mainly by the effect on the number of ways to distribute energy in the system. The ways in which entropy is changed include changing the *temperature*, *number of moles of gas*, or the *state* of one or more compounds present in the system.

Throughout this terrible, tedious chapter, it is important to note that S $\neq \Delta S$. The units of ΔS are typically $J\,mol^{-1}$ (joules per mole).

1.1.1 Change in Temperature

Increasing the temperature of a system of molecules increases their average kinetic energy, and hence the range of possible energies within the system.

As such, the amount of ways to distribute energy in the system increases, resulting in greater entropy. ($\Delta S > 0$)
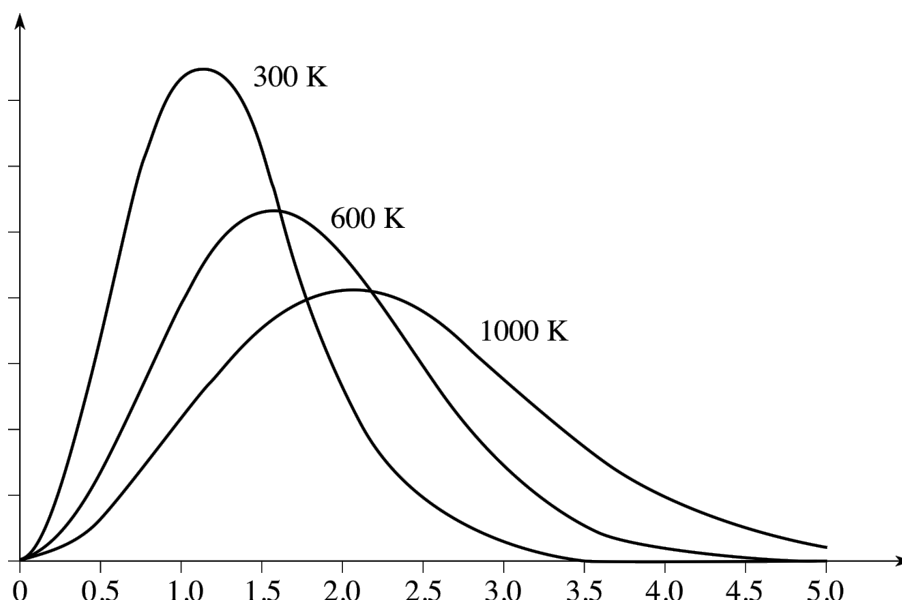
The Maxwell-Boltzmann curve above shows that as temperature increases, the possible range of kinetic energies of the system also increases, thus increasing entropy.

1.1.2 Change in Number of Gas Particles

From the diagram above, it should be obvious that, since gaseous molecules have a much greater entropy, an increase in the number of gas particles will also result in an increase in the entropy of the system ($\Delta S > 0$).

Simply put, if the reaction results in a greater number of gaseous products than reactants, then there will be a net increase in entropy. For example:

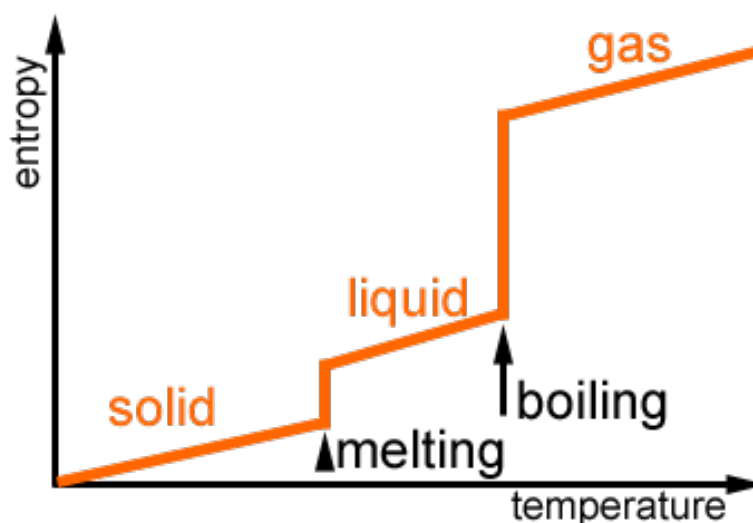$$2\,NaN_3 \text{ (s)} \longrightarrow 2\,Na \text{ (s)} + 3\,N_2 \text{ (g)}$$

Here, the number of moles of gas *increased* from 0 to 3, hence $\Delta S > 0$. The reverse is also true, naturally — if the number of moles of gas decreases, then the entropy change will be negative.

1.1.3 Change in Phase

When a particular substance melts, boils, condenses or freezes, the entropy of the system changes accordingly. The diagram below aptly illustrates this.

As a substance melts, its molecules are no longer constrained by the structure of the solid state; average kinetic energy increases, and $\Delta S > 0$. As the substance boils, the molecules are completely free to move; naturally, the change in entropy is much greater than for melting. $\Delta S > 0$, obviously.

1.1.4 Change in Volume

If the available volume of a gas increases (at a constant temperature, which implies a decrease in pressure), then the entropy of the system will also increase. The possible distributions of each molecule of gas increases, and hence entropy increases ($\Delta S > 0$). Naturally, the opposite is also true; if the pressure of a system increases at a constant temperature, then the entropy will decrease ($\Delta S < 0$).

Note that when two containers containing two different gases are mixed, the entropy of the system also increases — the total volume that each gas occupies is increased as well.

1.1.5 Dissolution of Ionic Solids

When solid ionic compounds are dissolved in water (or another polar solvent), the total entropy of the system will also change. However, it depends on the interposition of two separate factors; when the ionic compound is dissolved, the constituent ions are able to move around, thus increasing the entropy.

However, the water molecules that are interacting with the dissolved ions are now restricted in movement, and hence entropy decreases as well. Thus, the net change in entropy of the system depends on which of the above factors is more significant. For singly-charged ions, the net change in entropy is usually an increase ($\Delta S > 0$).

1.2 Gibbs Free Energy

Since the enthalpy change (ΔH) and the change in entropy (ΔS) are both crucial in determining whether a given reaction will be spontaneous (occurring without external energy input), they are used together to calculate the change in Gibbs free energy, ΔG. If you paid attention to the cover page, then this equation should be familiar to you:

$$\Delta G = \Delta H - T \times \Delta S$$

In short, the change in Gibbs energy of a given reaction is determined by the temperature, and the changes in both enthalpy and entropy, of the reaction. The units of ΔG are typically kJ mol^{-1} (kilojoules per mole), and that for temperature is K (kelvins).

Exergonic reactions, where ΔG < 0, are said to be energetically feasible, and take place spontaneously. Conversely, endergonic reactions where $\Delta G > 0$ are energetically infeasible, and do not take place spontaneously. ΔG can be 0, for example during melting or boiling.

1.2.1 Effect of Gibbs Free Energy

Given the sign (positive or negative, duh) of both ΔH and ΔS, it is possible to determine if ΔG will increase or decrease with temperature. Thus, it is possible to predict if the reaction will be more or less spontaneous (and thus energetically feasible) with a change in temperature.

A *disgusting* and *abhorrent* table below summarises the four possible scenarios:

ΔH	ΔS	ΔG	Feasibility
< 0	< 0	always < 0	All temperatures
< 0	> 0	always > 0	Never
> 0	< 0	depends	Low temperatures
> 0	> 0	depends	High temperatures

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