

3.5/3.6 – Enthalpy and entropy

Definitions

Enthalpy change of atomisation, $\Delta_{\text{at}}H^\theta$

This is the enthalpy change when one mole of gaseous atoms forms from an element in its standard state.



You may see **bond dissociation enthalpy** – the enthalpy needed to break one mole of the bond to give separated atoms, with everything being in the gaseous state.



For a diatomic element, bond dissociation enthalpy is $2 \times$ atomisation enthalpy

Ionisation energy

The first ionisation energy is the enthalpy change when one mole of gaseous positive ions forms from one mole of gaseous atoms.



The second ionisation energy involves gaseous ions with a +2 charge forming from gaseous ions with a +1 charge.

Electron affinity

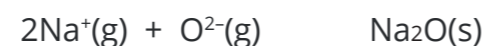
The first electron affinity is the enthalpy change when one mole of gaseous negative ions forms from one mole of gaseous atoms.



The second electron affinity involves gaseous ions with a -2 charge forming from gaseous ions with a -1 charge.

Enthalpy change of lattice formation, $\Delta_{\text{latt}}H^\theta$

This is the enthalpy change when one mole of an ionic compound forms from its constituent gaseous ions.

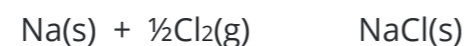


You may see the enthalpy change of lattice breaking, which is the reverse of this process.



Enthalpy change of formation, $\Delta_f H^\theta$

This is the enthalpy change when one mole of a compound forms from its constituent elements in their standard state.



Enthalpy change of hydration, $\Delta_{\text{hyd}}H^\theta$

This is the enthalpy change when one mole of gaseous ions dissolves in enough water to give an infinitely dilute solution.



Enthalpy change of solution, $\Delta_{\text{sol}}H^\theta$

This is the enthalpy change when one mole of an ionic substance dissolves completely in water to form a solution.



If you need to define standard enthalpies, add 'under standard conditions' to the definition.

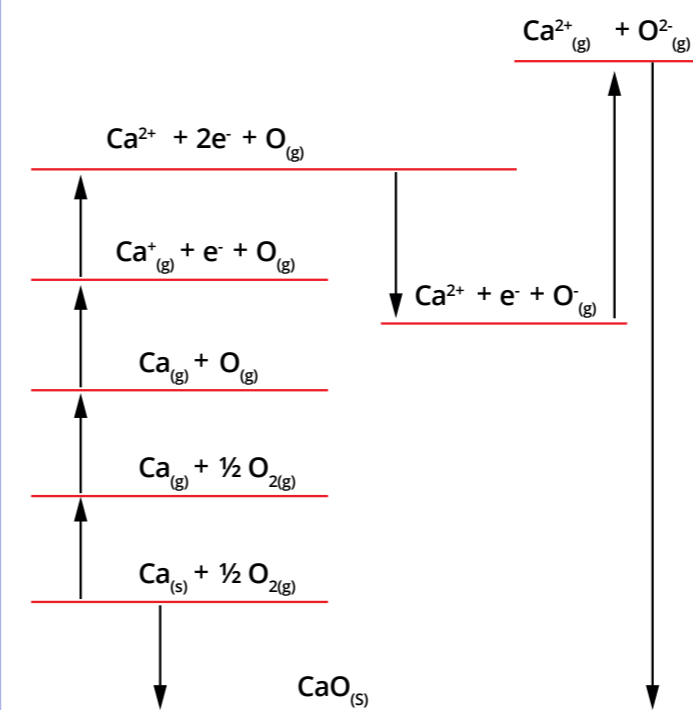
Born-Haber cycle

The formation of ionic compounds from their elements depends on the enthalpy changes involved in a number of steps. These steps are combined in an energy cycle – the Born-Haber cycle.

The elements are turned into gaseous atoms – this is the enthalpy of atomisation (endothermic).

The gaseous atoms are turned to cations – ionisation energy (endothermic) – and anions – electron affinity (1st electron affinity exothermic, 2nd electron affinity endothermic).

The gaseous ions are combined to form a solid – lattice enthalpy (exothermic).

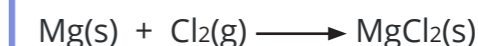


The second electron affinity for oxygen is positive because you are forcing an electron into an already negative ion. You have to put in energy to perform this change.

$$\begin{aligned} \Delta_f H(\text{CaO}) &= \Delta_{\text{at}}H(\text{Ca}) + \Delta_{\text{at}}H(\text{O}) + \text{IE}(\text{Ca}) \\ &\quad + \text{EA}(\text{O}) + \Delta_{\text{latt}}H(\text{CaO}) \\ &= 178 + 248 + 1735 + 702 - 3498 \\ &= -635 \text{ kJ mol}^{-1} \end{aligned}$$

The more **negative** the enthalpy change of formation of a compound, the more **stable** it is.

For a compound such as MgCl_2 , since the equation for the enthalpy change of formation is



and for the atomisation of chlorine is



when you calculate $\Delta_f H$ you must double $\Delta_{\text{at}}H(\text{Cl})$ and $\text{EA}(\text{Cl})$, i.e.

$$\begin{aligned} \Delta_f H(\text{MgCl}_2) &= \Delta_{\text{at}}H(\text{Mg}) + 2\Delta_{\text{at}}H(\text{Cl}) + \text{IE}(\text{Mg}) \\ &\quad + 2\text{EA}(\text{Cl}) + \Delta_{\text{latt}}H(\text{MgCl}_2) \end{aligned}$$

3.5/3.6 – Enthalpy and entropy

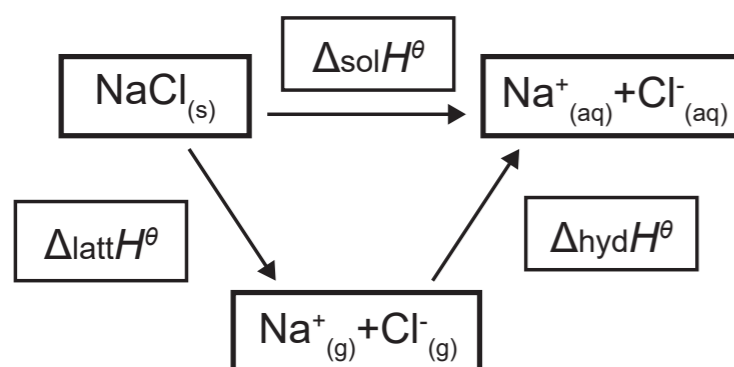
Solubility

Generally, if the enthalpy change of solution, $\Delta_{sol}H^\theta$, is negative, an ionic compound will be soluble. The more negative, the more soluble a compound is likely to be.

Enthalpy change of solution depends on two factors:

- enthalpy change of lattice breaking (endothermic)
- enthalpy change of hydration (exothermic)

If the enthalpy change of hydration is greater than the enthalpy change of lattice breaking, the compound will dissolve.



$$\Delta_{sol}H^\theta = \Delta_{latt}H^\theta + \Delta_{hyd}H^\theta$$

Entropy

Entropy is represented by the symbol S and has the unit $\text{J K}^{-1} \text{mol}^{-1}$.

It is the disorder in a system, or a measure of the freedom possessed by particles within a system.

Particles that can move freely in any direction have a much higher entropy than particles that are constrained.

$$S(\text{gas}) > S(\text{liquid}) > S(\text{solid})$$

Gibbs free energy

Chemical reactions tend to occur when the enthalpy change is negative, i.e. they are exothermic, but some endothermic reactions also occur. To explain this, enthalpy and entropy need to be considered together. The balance between enthalpy, entropy and temperature is the Gibbs free energy change, ΔG . If $\Delta G < 0$, a reaction will occur spontaneously.

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

ΔG and ΔH are normally measured in kJ mol^{-1} but ΔS is measured in $\text{J K}^{-1} \text{mol}^{-1}$. T is measured in kelvin (K).

For a reaction with a positive ΔG , changing the temperature might cause a reaction to occur.

The temperature when a reaction becomes feasible is when the value of ΔG changes from positive to negative. At this point $\Delta G = 0$. Since $\Delta G = \Delta H - T\Delta S = 0$

$$\Delta H = T\Delta S \text{ or } T = \Delta H / \Delta S$$

ΔH	ΔS	ΔG	Feasibility
+ve	-ve	always +ve	never feasible
-ve	+ve	always -ve	feasible
+ve	+ve	only -ve if $T\Delta S > \Delta H$	feasible at high temps
-ve	-ve	only -ve if $\Delta H > T\Delta S$	feasible at low temps