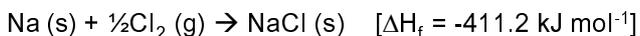


# 1: THERMODYNAMICS

## Definitions of enthalpy changes

### Enthalpy change of formation

The enthalpy change when 1 mole of a compound is formed from its elements in their standard states under standard conditions



### Enthalpy of atomisation

The enthalpy of atomisation of an element is the enthalpy change when 1 mole of gaseous atoms is formed from the element in its standard state



The enthalpy change for a solid metal turning to gaseous atoms can also be called the **Enthalpy of sublimation** and will numerically be the same as the enthalpy of atomisation

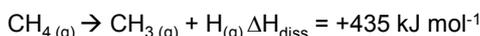


### Bond dissociation enthalpy

The bond dissociation enthalpy is the standard molar enthalpy change when one mole of a covalent bond is broken into two gaseous atoms (or free radicals)



Or

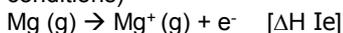


For diatomic molecules the  $\Delta H_{\text{diss}}$  of the molecule is the same as  $2x \Delta H_{\text{at}}$  of the element



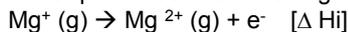
### First Ionisation energy

The first ionisation energy is the energy required to remove 1 mole of electrons from 1 mole of gaseous atoms to form 1 mole of gaseous ions with a +1 charge (under standard conditions)



### Second Ionisation energy

The second ionisation energy is the energy required to remove 1 mole of electrons from one mole of gaseous 1+ ions to produce one mole of gaseous 2+ ions.



### First Electron affinity

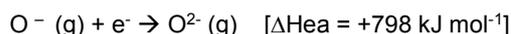
The first electron affinity is the enthalpy change that occurs when 1 mole of gaseous atoms gain 1 mole of electrons to form 1 mole of gaseous ions with a -1 charge (under standard conditions)



*The first electron affinity is exothermic for atoms that normally form negative ions because the ion is more stable than the atom*

### second electron affinity

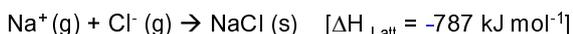
The second electron affinity is the enthalpy change when one mole of gaseous 1- ions gains one electron per ion to produce gaseous 2- ions.



The second electron affinity for oxygen is **endothermic** because it takes energy to overcome the **repulsive force** between the **negative ion and the electron**

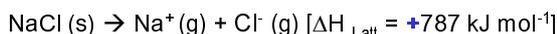
### Enthalpy of lattice formation

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 (under standard conditions).



### Enthalpy of lattice dissociation

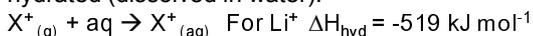
The Enthalpy of lattice dissociation is the standard enthalpy change when 1 mole of an ionic crystal lattice is separated into its constituent ions in gaseous form (under standard conditions).



Note the conflicting definitions and the sign that always accompanies the definitions

### Enthalpy of Hydration $\Delta H_{\text{hyd}}$

Enthalpy change when one mole of gaseous ions become hydrated (dissolved in water).



or



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

### Enthalpy of solution

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

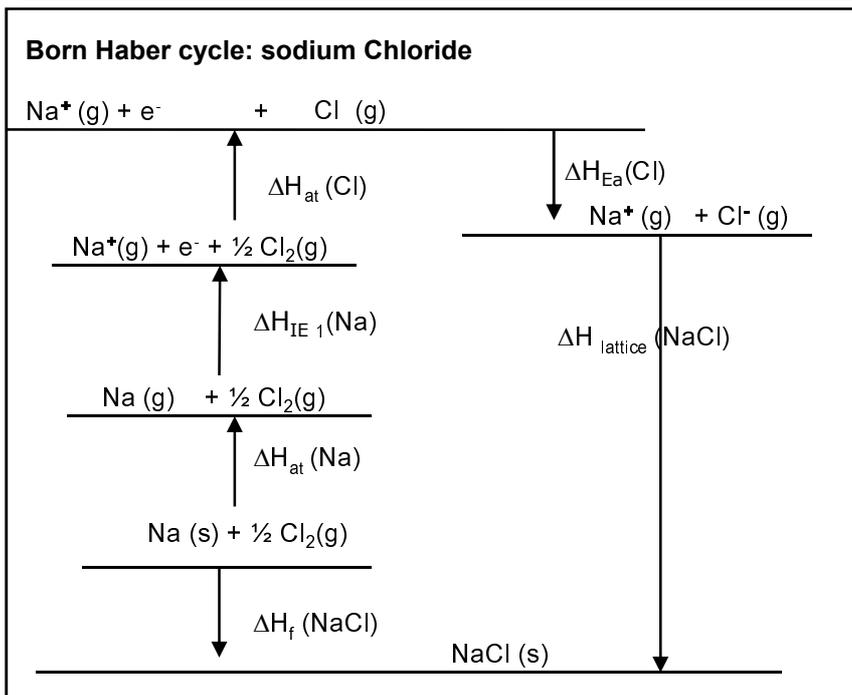


## BORN HABER CYCLES

The lattice enthalpy cannot be determined directly. We calculate it indirectly by making use of changes for which data are available and link them together in an enthalpy cycle the Born Haber cycle

Pay attention to state symbols and direction of arrows.

Usually all pieces of data are given except the one that needs to be calculated

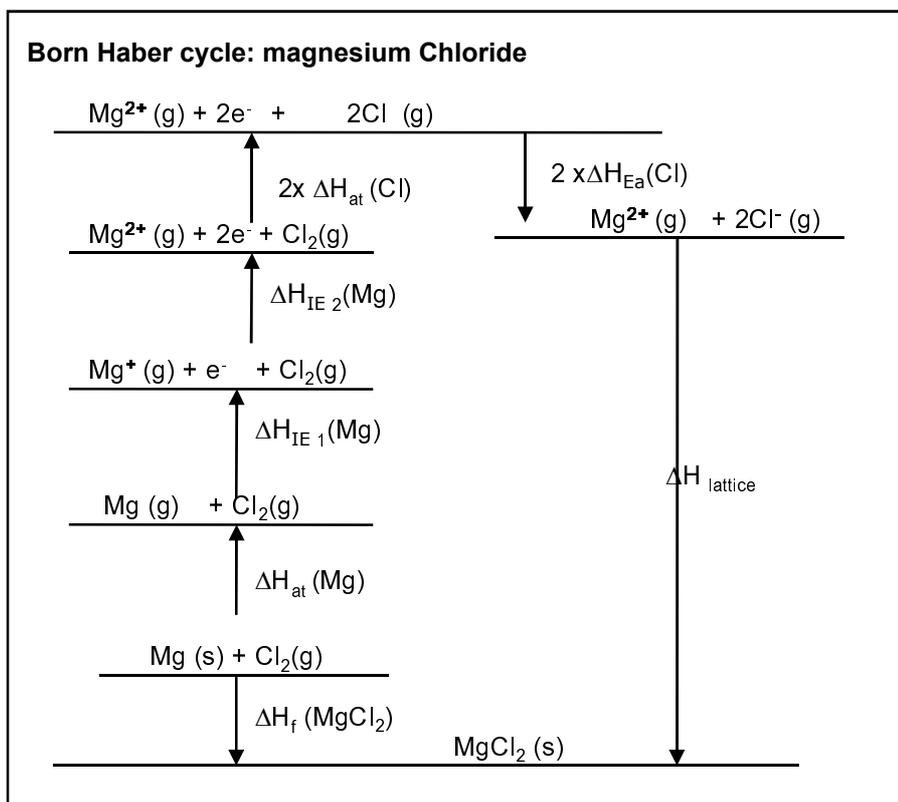


By applying Hess's law the heat of formation equals to the sum of everything else

$$\Delta H_f = \Delta H_{at} \text{Na} + \Delta H_{IE} \text{Na} + \Delta H_{at} \text{Cl} + \Delta H_{Ea} \text{Cl} + \Delta H_{latt}$$

Rearrange to give  $\Delta H_{latt} = \Delta H_{formation} - (\Delta H_{atm} \text{Na} + \Delta H_{IE} \text{Na} + \Delta H_{atm} \text{Cl} + \Delta H_{Ea} \text{Cl})$

$$\Delta H_{lattice} = -411 - (+107 + 496 + 122 + -349) = -787 \text{ kJmol}^{-1}$$

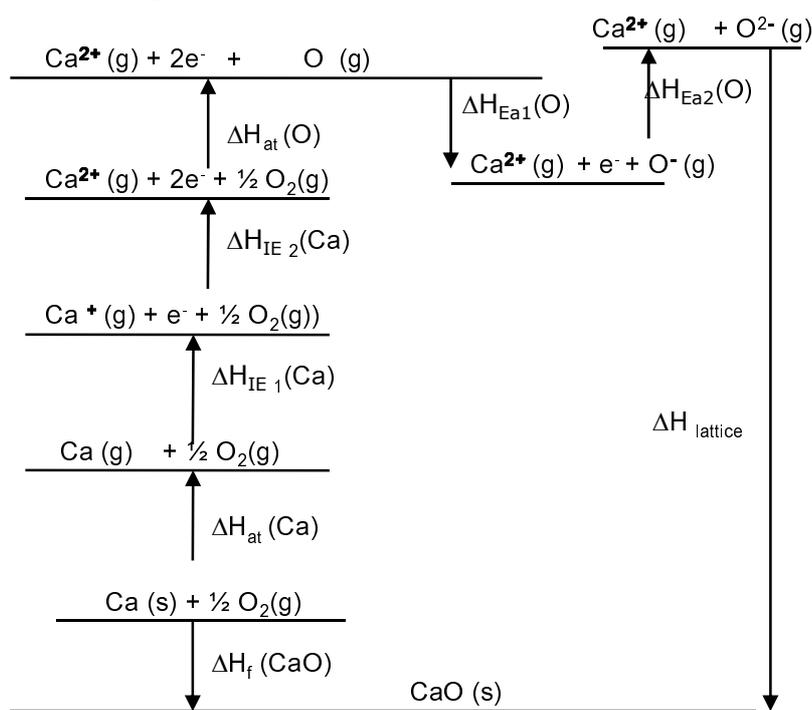


The data for the  $\Delta H_{at}(\text{Cl})$  could also be given as the bond energy for  $\text{E}(\text{Cl}-\text{Cl})$  bond.

Remember :

$$\text{E}(\text{Cl}-\text{Cl}) = 2 \times \Delta H_{at}(\text{Cl})$$

## Born Haber cycle: calcium oxide



Notice the second electron affinity for oxygen is **endothermic** because it takes energy to overcome the **repulsive force** between the **negative ion and the electron**

## Trends in Lattice Enthalpies

The strength of a lattice enthalpy depends on the following factors

### 1. The sizes of the ions:

The larger the ions, the less negative the lattice enthalpy (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).

The lattice enthalpies become less negative down any group.  
e.g. LiCl, NaCl, KCl, RbCl

e.g. group 1 halides (eg NaF, KI) have lattice enthalpies of around -700 to -1000

group 2 halides (eg MgCl<sub>2</sub>) have lattice enthalpies of around -2000 to -3500

group 2 oxides eg MgO have lattice enthalpies of around -3000 to -4500 kJmol<sup>-1</sup>

## Differences between theoretical and Born Haber lattice enthalpies

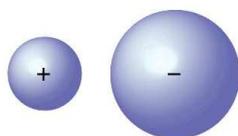
Theoretical lattice enthalpies assume the ions are 100% ionic and spherical. The Born Haber lattice enthalpy is the real experimental value.

When a compound shows covalent character, the theoretical and the Born Haber lattice enthalpies differ. The more the covalent character the bigger the difference between the values.

There is a tendency towards covalent character in ionic substances when

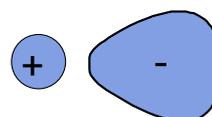
- the positive ion is small
- the positive ion has multiple charges
- the negative ion is large
- the negative ion has multiple negative charges.

When the negative ion becomes distorted and more covalent we say it becomes polarised. The metal cation that causes the polarisation is called more polarising if it polarises the negative ion.



100% ionic

The theoretical and the Born Haber lattice enthalpies will be the same



Ionic with covalent character

The theoretical and the Born Haber lattice enthalpies will differ

## Why does Calcium chloride have the formula $\text{CaCl}_2$ and not $\text{CaCl}$ or $\text{CaCl}_3$ ?

It is useful to draw out the born haber cycles for each potential case.

We need to calculate an enthalpy of formation for each case.

The one with the **most exothermic enthalpy of formation** will be the one that forms as it will be the most thermodynamically stable

Theoretical lattice enthalpies have been calculated for each case

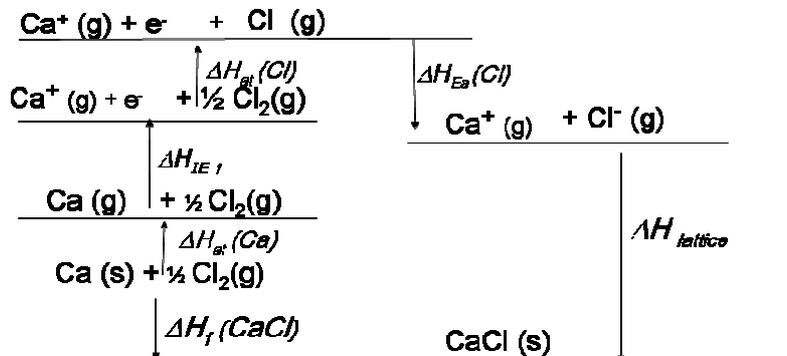
Theoretical lattice enthalpies  
 $\Delta H_{\text{latt}} \text{CaCl} = -719 \text{ kJ mol}^{-1}$   
 $\Delta H_{\text{latt}} \text{CaCl}_2 = -2218 \text{ kJ mol}^{-1}$   
 $\Delta H_{\text{latt}} \text{CaCl}_3 = -4650 \text{ kJ mol}^{-1}$

These get larger as the positive charge on the calcium ion becomes bigger.

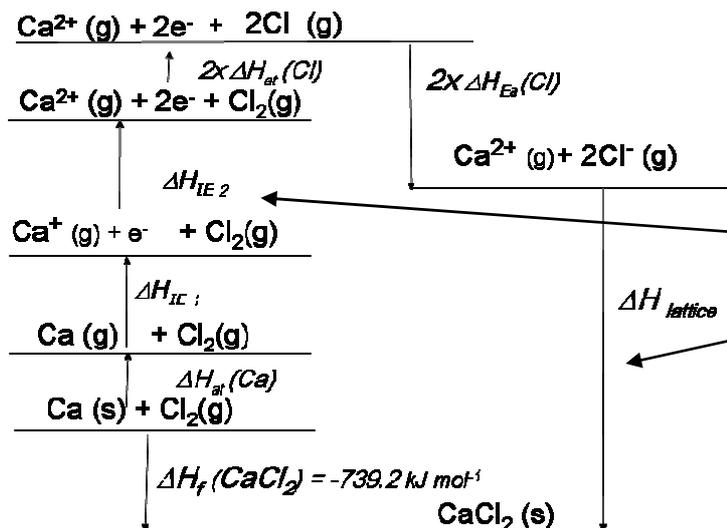
The enthalpy of formation is largely a balance of the ionisation energy and lattice enthalpy.

$\Delta H_f(\text{CaCl})$  is  $-163.1 \text{ kJ mol}^{-1}$ .  
This is exothermic.

### Born Haber Cycle for $\text{CaCl}$



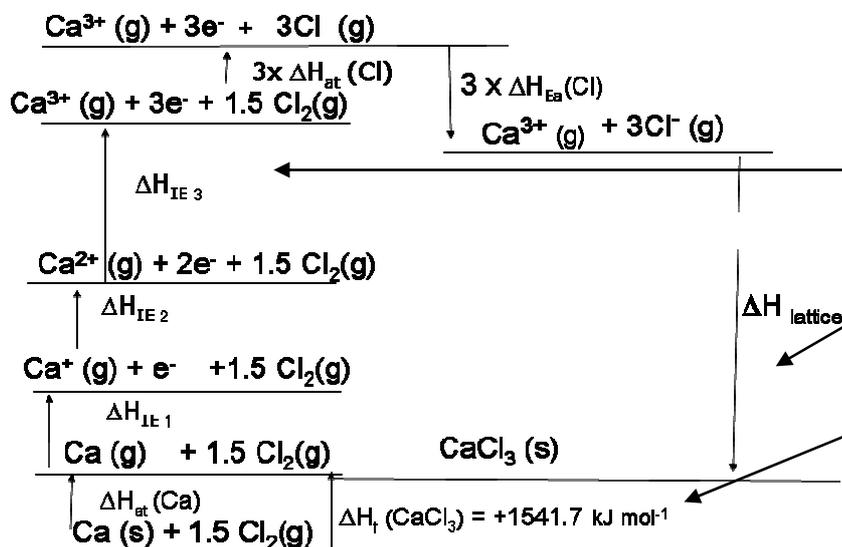
### Born Haber Cycle for $\text{CaCl}_2$



The increased ionisation enthalpy to form  $\text{Ca}^{2+}$  is more than compensated for by the stronger lattice enthalpy

The enthalpy of formation is therefore more exothermic. This is the most stable form

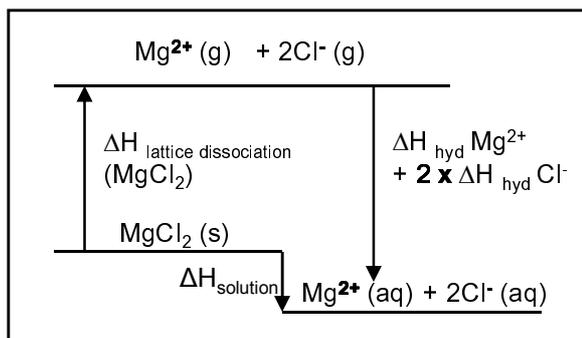
### Born Haber Cycle for $\text{CaCl}_3$



The big increase in ionisation enthalpy to remove the 3<sup>rd</sup> electron is not compensated for by the stronger lattice enthalpy

The enthalpy of formation is therefore endothermic. This is the least stable form

## Using Hess's law to determine enthalpy changes of solution



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**.

Hydration enthalpies are **exothermic** as energy is given out as water molecules bond to the metal ions.

The higher the **charge density** the greater the hydration enthalpy (e.g. smaller ions or ions with larger charges)

**In general**

$$\Delta H_{\text{sol}} = \Delta H_{\text{L dissociation}} + \Sigma \Delta H_{\text{hyd}}$$

**OR**

$$\Delta H_{\text{sol}} = -\Delta H_{\text{L formation}} + \Sigma \Delta H_{\text{hyd}}$$

Sometimes in questions  $\Delta H_{\text{L formation}}$  is given instead of  $\Delta H_{\text{L dissociation}}$  in order to catch you out. Remember the difference between the two.

**What does  $\Delta H_{\text{solution}}$  tell us?**

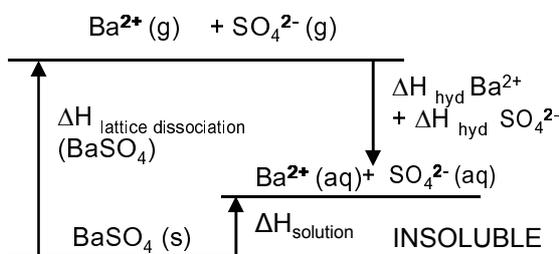
Generally  $\Delta H_{\text{solution}}$  is not very exo or endothermic so the hydration enthalpy is about the same as lattice enthalpy.

In general the substance is thought to **be soluble** if the  **$\Delta H_{\text{solution}}$  is exothermic**

If a substance is insoluble it is often because the lattice enthalpy is 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

**$\Delta H_{\text{solution}}$  endothermic.**



Example 1. Calculate the enthalpy of solution of NaCl given that the lattice enthalpy of formation of NaCl is  $-771 \text{ kJmol}^{-1}$  and the enthalpies of hydration of sodium and chloride ions are  $-406$  and  $-364 \text{ kJmol}^{-1}$  respectively

$$\begin{aligned} \Delta H_{\text{sol}} &= -\Delta H_{\text{L formation}} + \Sigma \Delta H_{\text{hyd}} \\ &= -(-771) + (-406 - 364) \\ &= +1 \text{ kJmol}^{-1} \end{aligned}$$

## Mean Bond energies

The Mean bond energy is the enthalpy needed **to break** the bond into **gaseous atoms, averaged over different** molecules

We use values of **mean** bond energies because in reality every single bond in a compound has a slightly different value. E.g. In  $\text{CH}_4$  there are 4 C-H bonds. Breaking each one will require a different amount of energy. However, we use an average value for the C-H bond for all hydrocarbons.

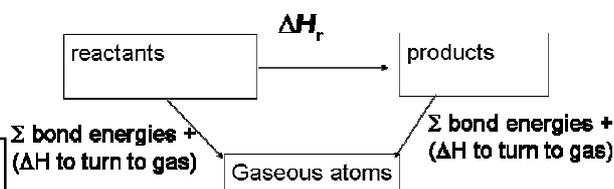
These values are positive because energy is required to break a bond.

The definition only applies when the **substances start and end in the gaseous state**.

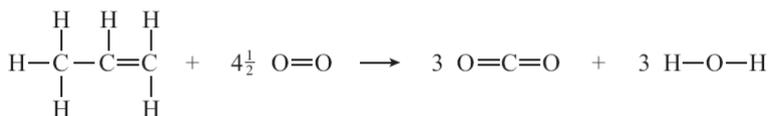
**In general** (if all substances are gases)

$$\Delta H_{\text{r}} = \Sigma \text{bond energies broken} - \Sigma \text{bond energies made}$$

$\Delta H$  values calculated using this method will be less accurate than using formation or combustion data because the mean bond energies are not exact



Example 2. Using the following mean bond enthalpy data to calculate the heat of combustion of propene



$\Delta H = \Sigma \text{ bond energies broken} - \Sigma \text{ bond energies made}$

$$= [\text{E}(\text{C}=\text{C}) + \text{E}(\text{C}-\text{C}) + 6 \times \text{E}(\text{C}-\text{H}) + 4.5 \times \text{E}(\text{O}=\text{O})] - [6 \times \text{E}(\text{C}=\text{O}) + 6 \times \text{E}(\text{O}-\text{H})]$$

$$= [612 + 348 + (6 \times 412) + (4.5 \times 496)] - [(6 \times 743) + (6 \times 463)]$$

$$= -1752 \text{ kJ mol}^{-1}$$

Bond	Mean enthalpy (kJ mol <sup>-1</sup> )
C=C	612
C-C	348
O=O	496
O=C	743
O-H	463
C-H	412

Example 3. Using the following mean bond enthalpy data to calculate the heat of formation of NH<sub>3</sub>

$\frac{1}{2} \text{N}_2 + 1.5 \text{H}_2 \rightarrow \text{NH}_3$  (note the balancing is to agree with the definition of heat of formation (i.e. one mole of product))

$$\text{E}(\text{N}\equiv\text{N}) = 944 \text{ kJ mol}^{-1} \quad \text{E}(\text{H}-\text{H}) = 436 \text{ kJ mol}^{-1} \quad \text{E}(\text{N}-\text{H}) = 388 \text{ kJ mol}^{-1}$$

$\Delta H = \Sigma \text{ bond energies broken} - \Sigma \text{ bond energies made}$

$$= [0.5 \times \text{E}(\text{N}\equiv\text{N}) + 1.5 \times \text{E}(\text{H}-\text{H})] - [3 \times \text{E}(\text{N}-\text{H})]$$

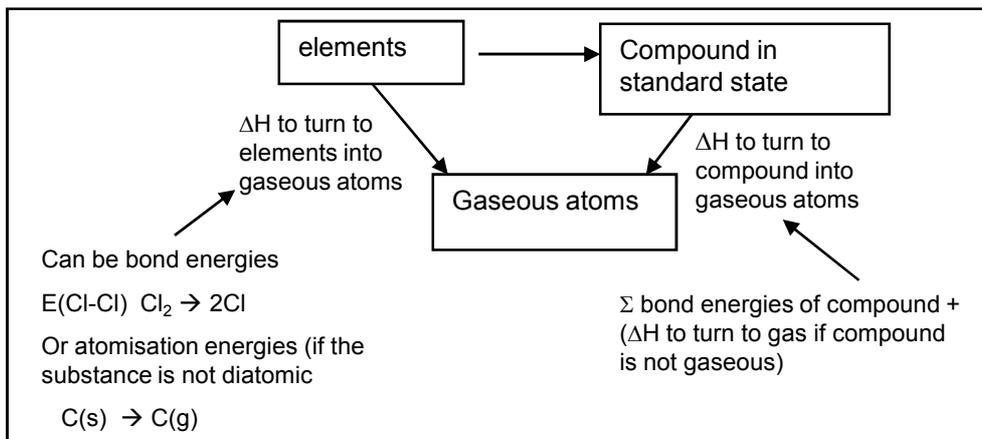
$$= [(0.5 \times 944) + (1.5 \times 436)] - [3 \times 388]$$

$$= -38 \text{ kJ mol}^{-1}$$

### More complicated examples that may occur at A2

Working out  $\Delta H_f$  of a compound using bond energies and other data

This is a more complicated example of the type in example 3



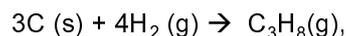
The  $\Delta H$ 's can be combinations of different data

Example 4

Calculate  $\Delta H_f$  for propane,  $\text{C}_3\text{H}_8(\text{g})$ , given the following data.



Bond	C-C	C-H	H-H
kJ mol <sup>-1</sup>	348	412	436



$$\Delta H_f = \Delta H \text{ to turn to elements into gaseous atoms} - \Delta H \text{ to turn to compound into gaseous atoms}$$

$$\Delta H_f = (3 \times \Delta H_{\text{at}}[\text{C}] + 4 \times \text{E}[\text{H}-\text{H}]) - (2 \times \text{E}[\text{C}-\text{C}] + 8 \times \text{E}[\text{C}-\text{H}])$$

$$= (3 \times 715 + 4 \times 436) - (2 \times 348 + 8 \times 412)$$

$$= -103 \text{ kJ mol}^{-1}$$

## Free-energy change ( $\Delta G$ ) and entropy change ( $\Delta S$ )

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

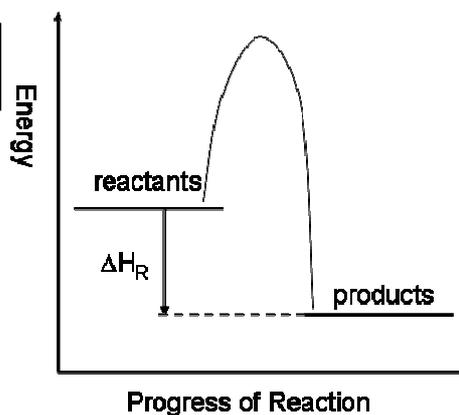
### A problem with $\Delta H$

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, $S^\circ$

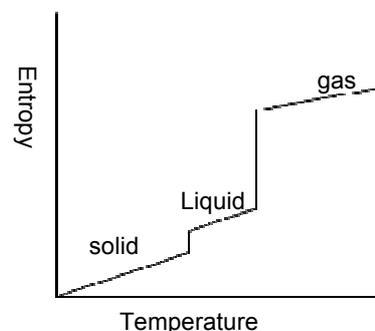
Substances with more ways of arranging their atoms and energy (*more disordered*) have a higher entropy.

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*.

Elements	...tend to have lower entropies than...	Compounds
Simpler compounds		Complex compounds
Pure substances		Mixtures

Solids have lower entropies than liquids which are lower than gases. There is a bigger jump in entropy with boiling than that with melting.

**Gases have large entropies**



### Predicting Change in entropy ' $\Delta S$ ' Qualitatively

An **increase** in disorder and **entropy** will lead to a positive entropy change  $\Delta S^\circ = +ve$

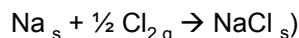
Balanced chemical equations can often be used to predict if  $\Delta S^\circ$  is positive or negative.

**In general**, a significant increase in the entropy will occur if:  
 - there is a **change of state** from **solid or liquid to gas**  
 - there is a significant **increase in number of molecules** between products and reactants.



$$\Delta S^\circ = +ve$$

- change from solid reactant to gaseous products
  - increase in number of molecules
- both will increase disorder



$$\Delta S^\circ = -ve$$

- change from gaseous and solid reactant to solid
  - decrease in number of molecules
- both will decrease disorder

### Calculating $\Delta S^\circ$ quantitatively

Data books lists standard entropies ( $S^\circ$ ) **per mole** for a variety of substances. It is not possible for a substance to have a standard entropy of less than zero.

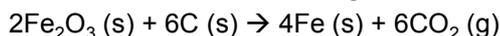
The unit of entropy is  $\text{J K}^{-1} \text{mol}^{-1}$

Elements in their standard states do *not* have zero entropy. **Only perfect crystals at absolute zero ( $T = 0 \text{ K}$ ) will have zero entropy:**

$$\Delta S^\circ = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

### Example

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



$$\begin{aligned} \Delta S^\circ &= S^\circ_{\text{products}} - S^\circ_{\text{reactants}} \\ &= (6 \times 213.6 + 4 \times 27.3) - (2 \times 87.4 + 6 \times 5.7) \\ &= +1181.8 \text{ J K}^{-1} \text{ mol}^{-1} = \mathbf{+1180 \text{ J K}^{-1} \text{ mol}^{-1}} \text{ (3 S.F.)} \end{aligned}$$

$$S[\text{Fe}_2\text{O}_3] = 87.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S[\text{C}] = 5.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S[\text{Fe}] = 27.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S[\text{CO}_2] = 213.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

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

### Gibbs Free Energy Change, $\Delta G$

The balance between entropy and enthalpy determines the feasibility of a reaction.

This is given by the relationship :

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

For any spontaneous change,  $\Delta G$  will be **negative**.

Gibbs free energy is a term that combines the effect of enthalpy and entropy into one number

A reaction that has increasing entropy (+ve  $\Delta S$ ) and is exothermic (-ve  $\Delta H$ ) will make  $\Delta G$  be **negative** and will always be feasible

Convert from °C to K (+ 273)

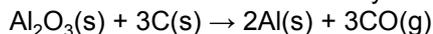
Unit of S =  $\text{J K}^{-1} \text{ mol}^{-1}$

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

Units:  $\text{KJ mol}^{-1}$       Units:  $\text{KJ mol}^{-1}$       Units:  $\text{KJ mol}^{-1}$

Need to convert to  $\text{KJ K}^{-1} \text{ mol}^{-1}$  ( $\div 1000$ )

**Example** : Data for the following reaction, which represents the reduction of aluminium oxide by carbon, are shown in the table.



Calculate the values of  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  for the above reaction at 298 K

#### 1. Calculate $\Delta S$

$$\begin{aligned} \Delta S^\circ &= S^\circ_{\text{products}} - S^\circ_{\text{reactants}} \\ &= (2 \times 28 + 3 \times 198) - (51 + 3 \times 6) \\ &= +581 \text{ J K}^{-1} \text{ mol}^{-1} \text{ (3 S.F.)} \end{aligned}$$

#### 2. Calculate $\Delta H^\circ$

$$\begin{aligned} \Delta H^\circ &= \Delta H^\circ_f [\text{products}] - \Delta H^\circ_f [\text{reactants}] \\ &= (3 \times -111) - (-1669) \\ &= +1336 \text{ kJ mol}^{-1} \end{aligned}$$

Substance	$\Delta H_f / \text{kJ mol}^{-1}$	$\Delta S / \text{JK}^{-1} \text{ mol}^{-1}$
$\text{Al}_2\text{O}_3(\text{s})$	-1669	51
C(s)	0	6
Al(s)	0	28
CO(g)	-111	198

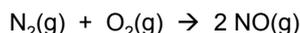
#### 3. Calculate $\Delta G$

$$\begin{aligned} \Delta G &= \Delta H - T\Delta S \\ &= +1336 - 298 \times 0.581 \\ &= +1163 \text{ kJ mol}^{-1} \end{aligned}$$

$\Delta G$  is positive. The reaction is not feasible

### Calculating the temperature a reaction will become feasible

Calculate the temperature range that this reaction will be feasible



$$\Delta H = 180 \text{ kJ mol}^{-1} \quad \Delta S = 25 \text{ J K}^{-1} \text{ mol}^{-1}$$

The reaction will be feasible when  $\Delta G \leq 0$

Make  $\Delta G = 0$  in the following equation  $\Delta G = \Delta H - T\Delta S$

$$0 = \Delta H - T\Delta S$$

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

$$\begin{aligned} T &= 180 / (25/1000) \\ &= 7200 \text{ K} \end{aligned}$$

The T must be  $>7200 \text{ K}$

### $\Delta G$ during phase changes

As physical phase changes like melting and boiling are equilibria, the  $\Delta G$  for such changes is zero.

What temperature would methane melt at?



Make  $\Delta G = 0$  in the following equation  $\Delta G = \Delta H - T\Delta S$

$$0 = \Delta H - T\Delta S$$

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

$$T = 0.94 / (10.3 \div 1000)$$

$$T = 91 \text{ K}$$