

## 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).

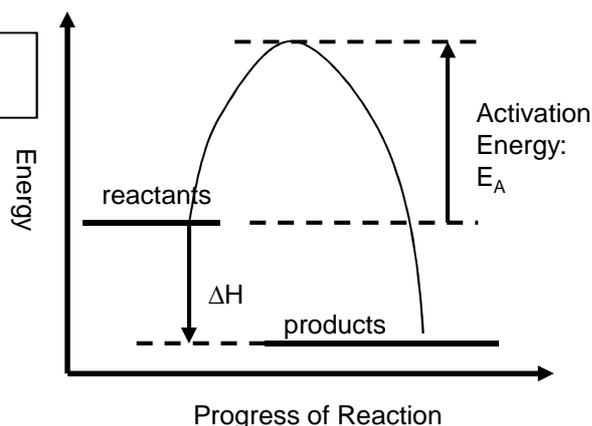
Some spontaneous reactions, however, are endothermic.

#### 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.

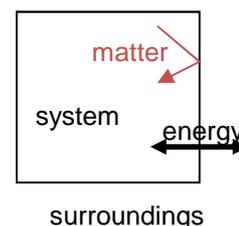


Entropy is a description of the number of ways atoms can share quanta of energy. If number of ways of arranging the energy ( $W$ ) is *high*, then system is *disordered* and entropy ( $S$ ) is *high*.

### 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.



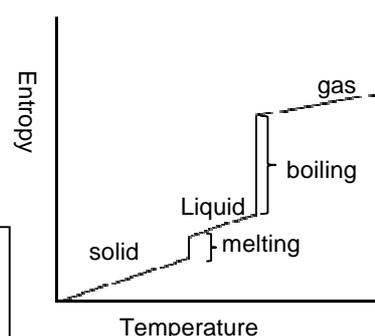
#### Entropy of the System, $S^\circ_{system}$

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. 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**



At 0K substances have zero entropy. There is no disorder as particles are stationary

## Predicting Change in entropy ' $\Delta S_{\text{system}}$ ' Qualitatively

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

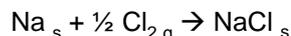
Balanced chemical equations can often be used to predict if  $\Delta S^{\circ}_{\text{system}}$  is positive or negative.

**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.



$$\Delta S^{\circ}_{\text{system}} = +\text{ve}$$

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



$$\Delta S^{\circ}_{\text{system}} = -\text{ve}$$

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

## Calculating $\Delta S^{\circ}_{\text{system}}$ 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.

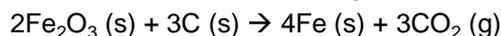
Elements in their standard states do *not* have zero entropy. **Only perfect crystals at absolute zero ( $T = 0 \text{ K}$ ) will have zero entropy:**

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

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

### Example

Calculate  $\Delta S^{\circ}$  for the following reaction at  $25^{\circ}\text{C}$ :



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

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

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

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

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

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

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

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

## Entropy of the Surroundings $\Delta S^{\ominus}_{\text{surrounding}}$

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.

In an endothermic reaction energy is transferred from the surroundings. The number of ways of arranging the energy in the surroundings therefore decreases and so  $\Delta S_{\text{surrounding}}$  decreases and is negative.

$$\Delta S^{\ominus}_{\text{surrounding}} = \frac{-\Delta H_{\text{reaction}}}{T}$$

converted into  $\text{J mol}^{-1}$  by  $\times 1000$

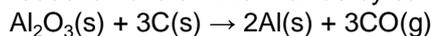
in K  
Convert  $^{\circ}\text{C}$  into K  
by  $+273$

## Total Entropy change $\Delta S^{\ominus}_{\text{total}}$

$$\Delta S^{\ominus}_{\text{total}} = \Delta S^{\ominus}_{\text{system}} + \Delta S^{\ominus}_{\text{surrounding}}$$

For any reaction to be **spontaneous** then  $\Delta S^{\ominus}_{\text{total}}$  **must be positive**. If a reaction is not spontaneous i.e. it doesn't go, then  $\Delta S^{\ominus}_{\text{total}}$  will be negative.

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



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  $\Delta S_{\text{system}}$**

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

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

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

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

**3. Calculate  $\Delta S_{\text{surroundings}}$**

$$\begin{aligned} \Delta S_{\text{surrounding}} &= - \frac{\Delta H_{\text{reaction}}}{T} \\ &= -1336000/298 \\ &= -4483 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

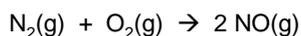
**4. Calculate  $\Delta S_{\text{Total}}$**

$$\begin{aligned} \Delta S_{\text{total}} &= \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} \\ &= 581 - 4483 \\ &= -3902 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$\Delta S_{\text{Total}}$  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



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

The reaction will be feasible when  $\Delta S_{\text{Total}} \geq 0$

Make  $\Delta S_{\text{Total}} = 0$  in the following equation

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

$$0 = -\Delta H/T + \Delta S_{\text{system}}$$

$$\text{So } T = \Delta H / \Delta S_{\text{system}}$$

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

The T must be >7200K which is a high Temp!

**$\Delta S_{\text{Total}}$  during phase changes**

As physical phase changes like melting and boiling are equilibria, the  $\Delta S_{\text{Total}}$  for such changes is zero.

What temperature would methane melt at?



Make  $\Delta S_{\text{Total}} = 0$  in the following equation

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

$$0 = -\Delta H/T + \Delta S_{\text{system}}$$

$$\text{So } T = \Delta H / \Delta S_{\text{system}}$$

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

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

**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.**  $\text{NaCl} + \text{aq} \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$

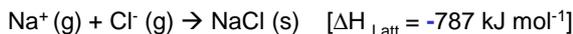
If the reaction involves an decrease in entropy ( $\Delta S_{\text{system}}$  **is -ve**) then increasing Temperature will make it more **less likely** that  $\Delta S_{\text{total}}$  **will be positive** because the  $-\Delta H/T$  will have a smaller magnitude and will be less likely to compensate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

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**

## Solubility of ionic substances

### 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**.



### 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



### 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



or



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 a 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).

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  $\text{MgCl}_2$ ) have lattice enthalpies of around -2000 to -3500

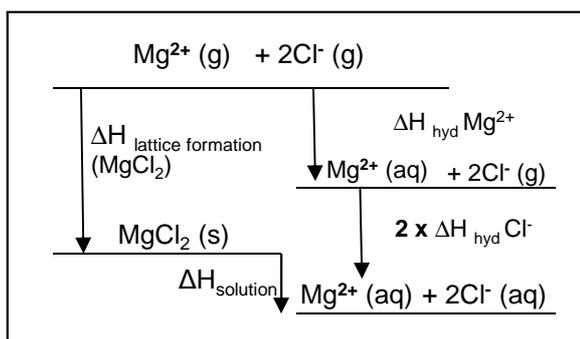
group 2 oxides eg MgO have lattice enthalpies of around -3000 to -4500  $\text{kJ mol}^{-1}$

## 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  $\text{MgCl}_2(\text{s}) + \text{aq} \rightarrow \text{Mg}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq})$



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**.

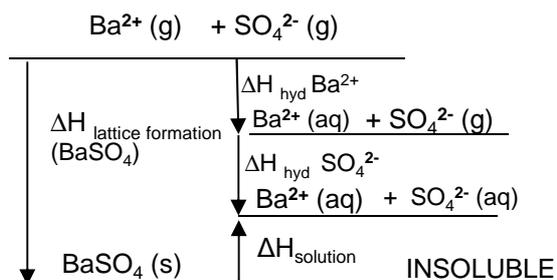
The size of the lattice enthalpy depends on the size and charge on the ion. The smaller the ion and the higher its charge the stronger the lattice

$$\Delta H_{\text{solution}} = -\Delta H_{\text{L formation}} + \sum \Delta H_{\text{hyd}}$$

Example . 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

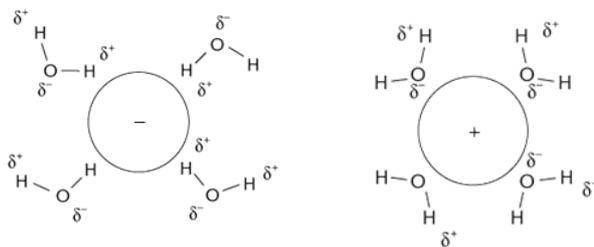
$$\begin{aligned}\Delta H_{\text{sol}} &= -\Delta H_{\text{Latt formation}} + \Sigma\Delta H_{\text{hyd}} \\ &= -(-771) + (-406-364) \\ &= +1 \text{ kJmol}^{-1}\end{aligned}$$

**$\Delta H$  solution endothermic.**



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**.

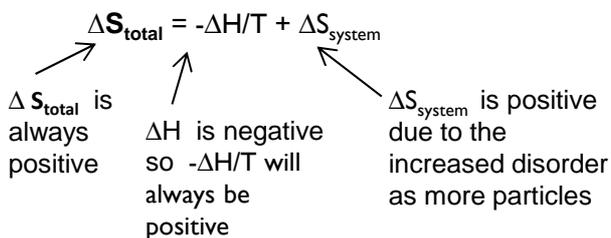
If a substance is insoluble it is often because the lattice enthalpy is much larger than the hydration enthalpy and it is not energetically favourable to break up the lattice, making  $\Delta H_{\text{solution}}$  **endothermic**.

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

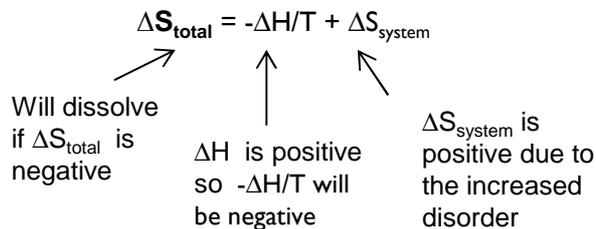
When a solid dissolves into ions the **entropy increases** as there is **more disorder** as solid changes to solution and **number of particles increases**.

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



For salts where  $\Delta H_{\text{solution}}$  is endothermic the salt may dissolve depending on whether the  $\Delta S$  value is more positive than  $-\Delta H/T$  is negative



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