2A Enthalpy

Lattice enthalpy

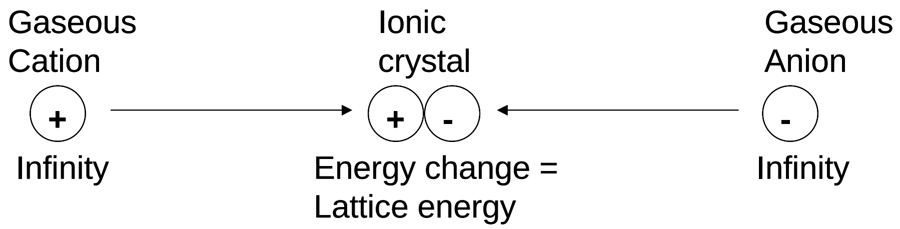
- In AS we looked at ionic bonding and learned that:

Ionic bonds are strong
Due to strong electrostatic forces of attraction

- This means that the melting and boiling points of ionic compounds are very high.
- This is due to the **lattice enthalpy, ΔH^{θ}_{LE}:**

Definition – Lattice enthalpy

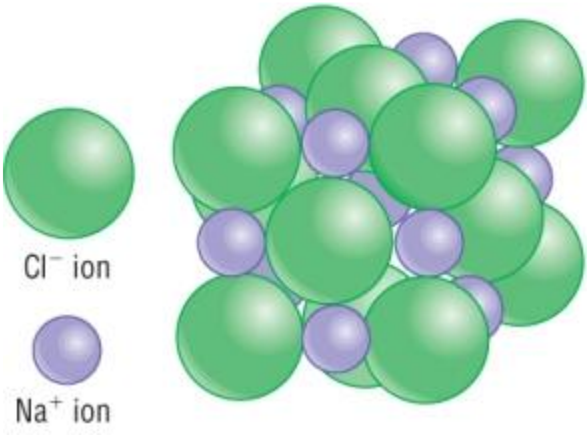
The lattice enthalpy is the enthalpy change when 1 mole of an ionic compound is formed from its gaseous ions under standard conditions (298K, 100kPa).



- For sodium chloride:

$$Na^{+}_{(g)} \quad + \quad Cl^{-}_{(g)} \rightarrow NaCl_{(s)} \quad \Delta H^{\theta}_{LE} = -781\ KjMol^{-1}$$

Features of lattice enthalpy:



- Lattice enthalpy is an **exothermic process** as large amounts of energy is released upon the formation of the lattice from gaseous ions.
- Lattice enthalpy indicates the strength of ionic bonds in a compound lattice structure.
- Lattice enthalpy is impossible to measure directly as it is impossible to have gaseous ions.
- Covalent compounds cannot have lattice enthalpies due to the nature of the bonding.
- As it is not possible to calculate directly, a special type of **Hess's cycle** is used.
- This is called a **Born - Haber cycle**.
- These cycles require many more types of enthalpy changes:

Key enthalpy changes:

1) Standard enthalpy change of formation, ΔH^{θ}_{f} :

1 mole of compound is formed from its constituent elements in their standard state.

Example - usually exothermic

$$K_{(s)} + 1/2Cl_{2(g)} \rightarrow KCl_{(s)}\ \Delta H^{\theta}_{f} = -\ 437\ KJ\ Mol^{-1}$$

2) The standard enthalpy change of atomisation,ΔH^{θ}_{at} :

1 mole of gaseous atoms are formed from the element in its standard state.

Example - Always endothermic as bonds have to be broken:

$$Mg_{(s)} \rightarrow Mg_{(g)}\ \Delta H^{\theta}_{at} = +148\ KJ\ Mol^{-1}$$

3) First ionisation energy, ΔH^{θ}_{I1} :

1 mole of gaseous 1+ ions is formed from gaseous atoms

Example - Always endothermic as an electron has to overcome the attraction from the nucleus:

$$Li_{(g)} \rightarrow Li^{+}_{(g)} + e^{-}\ \Delta H^{\theta}_{I1} = +\ 520\ KJ\ Mol^{-1}$$

4) Second ionisation energy, ΔH^{θ}_{I2} :

1 mole of gaseous 2+ ions is formed from 1 mole gaseous 1+ ions

Example - Always endothermic as an electron has to overcome the attraction from the nucleus:

$$Ca^{1+}_{(g)} \rightarrow Ca^{2+}_{(g)} + e^{-}\ \Delta H^{\theta}_{I2} = +\ 1145\ KJ\ Mol^{-1}$$

5) First Electron affinity, ΔH^{θ}_{EA1} :

1 mole of gaseous 1- ions formed from gaseous atoms

Example - Is exothermic as an electron is attracted to the outer shell by the nucleus:

$$Cl_{(g)} + e^{-} \rightarrow Cl^{-}_{(g)}\ \Delta H^{\theta}_{EA1} = -\ 349\ KJ\ Mol^{-1}$$

6) Second Electron affinity, ΔH^{θ}_{EA2} :

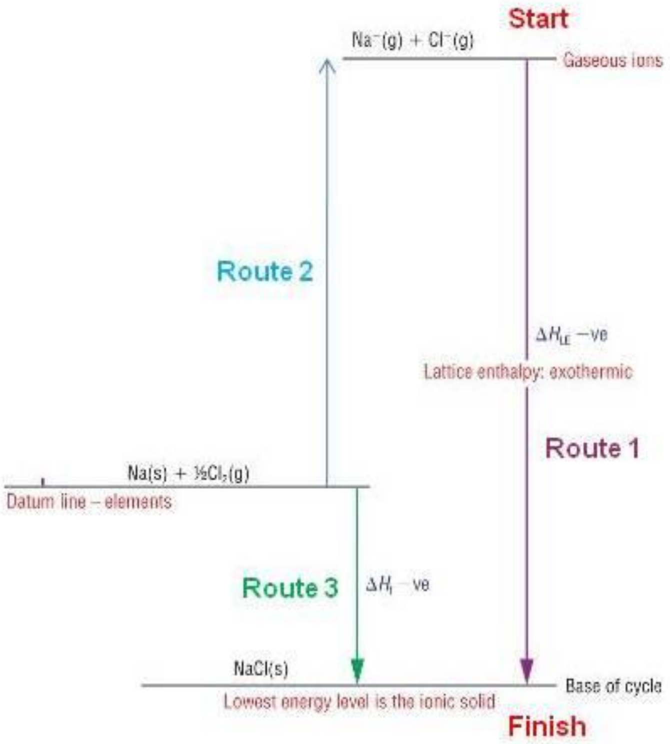
1 mole of gaseous 2- ions formed from 1 mole gaseous 1- ions

Example - Is endothermic as the electron being put in is repelled by the 1- ion:

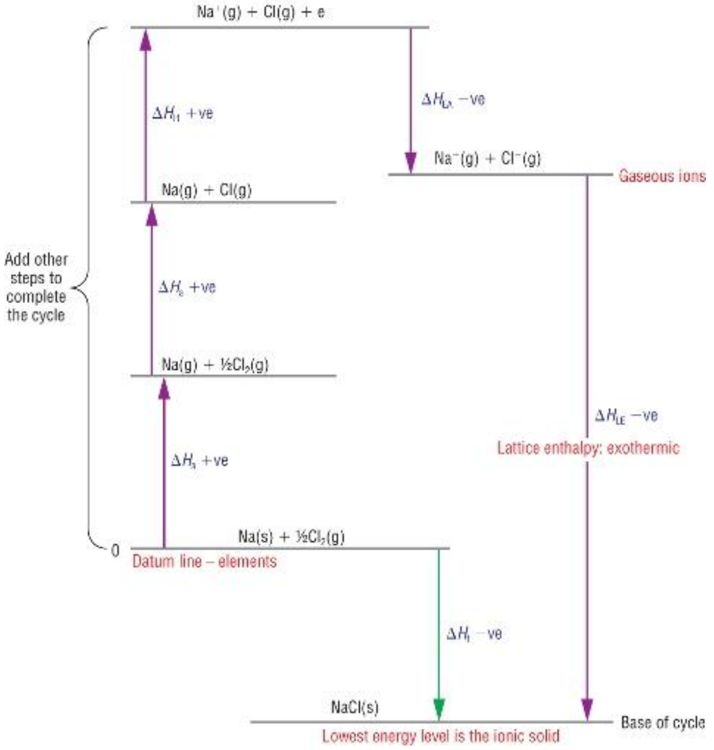
$$O^{-}_{(g)} + e^{-} \rightarrow O^{2-}_{(g)}\ \Delta H^{\theta}_{EA2} = -\ 798\ KJ\ Mol^{-1}$$

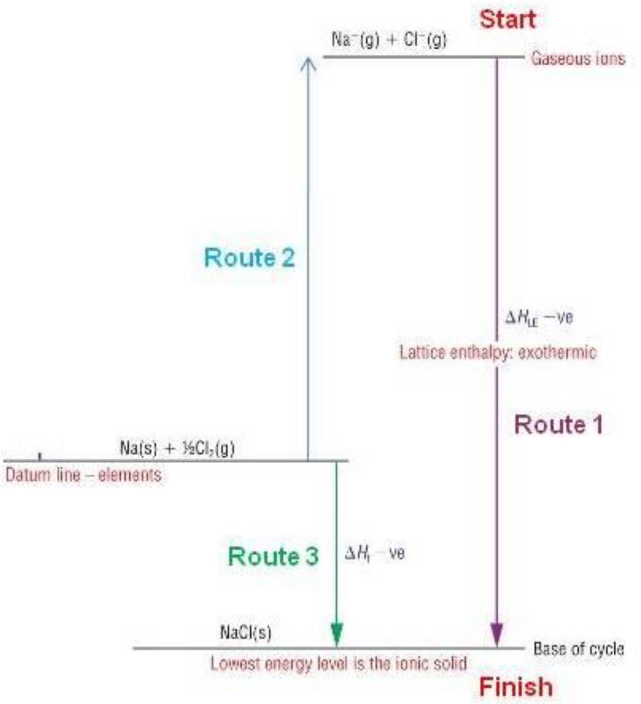
Constructing Born - Haber cycles

- **Born - Haber cycles** are basically a form of **Hess's cycle** particularly for calculating lattice enthalpies.
- Start with the elements at **'zero energy'** - called the **datum line**.
- **Endothermic processes go up**
- **Exothermic processes go down**
- A simple view of the **Born - Haber** cycle is shown below:



- **Route 2** is actually a multi - step process changing elements to gases then to ions





- **Route 2** has to be calculated in stages using a combination of enthalpy changes.
- Taking one element at a time use enthalpy changes to convert each element into gaseous atoms.
- From there, use successive ionisation energies or electron affinities to convert the gaseous atoms into gaseous ions.
- Apply Hess's cycle to calculate the **Lattice energy**.

Calculation:

Route 1 = - Route 2 + Route 3
Route 1 = Route 3 - Route 2

Lattice enthalpy, $\Delta H^{\theta}_{LE} = \Delta H^{\theta}_{f}$ - Route 2 (the rest)

Or better - rearranged:

$\Delta H^{\theta}_{LE} = \Delta H^{\theta}_{f}$ - (SUM OF ΔH^{θ} THE REST)

Other rules:

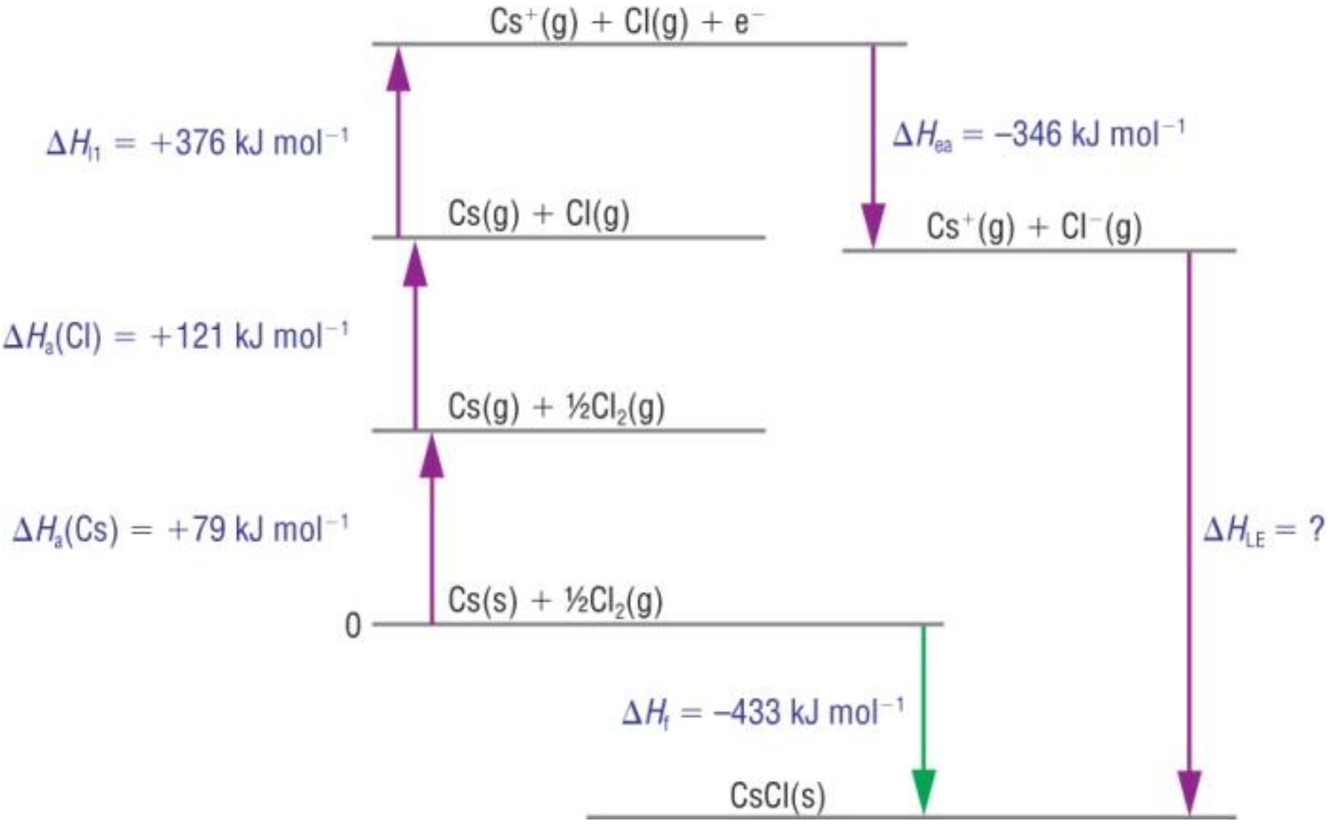
2 ions of the same formula, $MgCl_2$ – You need to count the enthalpies from the atom in its standard state to the ion in its gaseous state **TWICE**.

More than 1 charge on the ion – you need to 2 ionisation energies or electron affinities: eg Mg → Mg^{+} → Mg^{2+} or O → O^{-} → O^{2-}

Born - Haber cycle calculation

- Worked examples:

1) Caesium chloride:



Calculation:

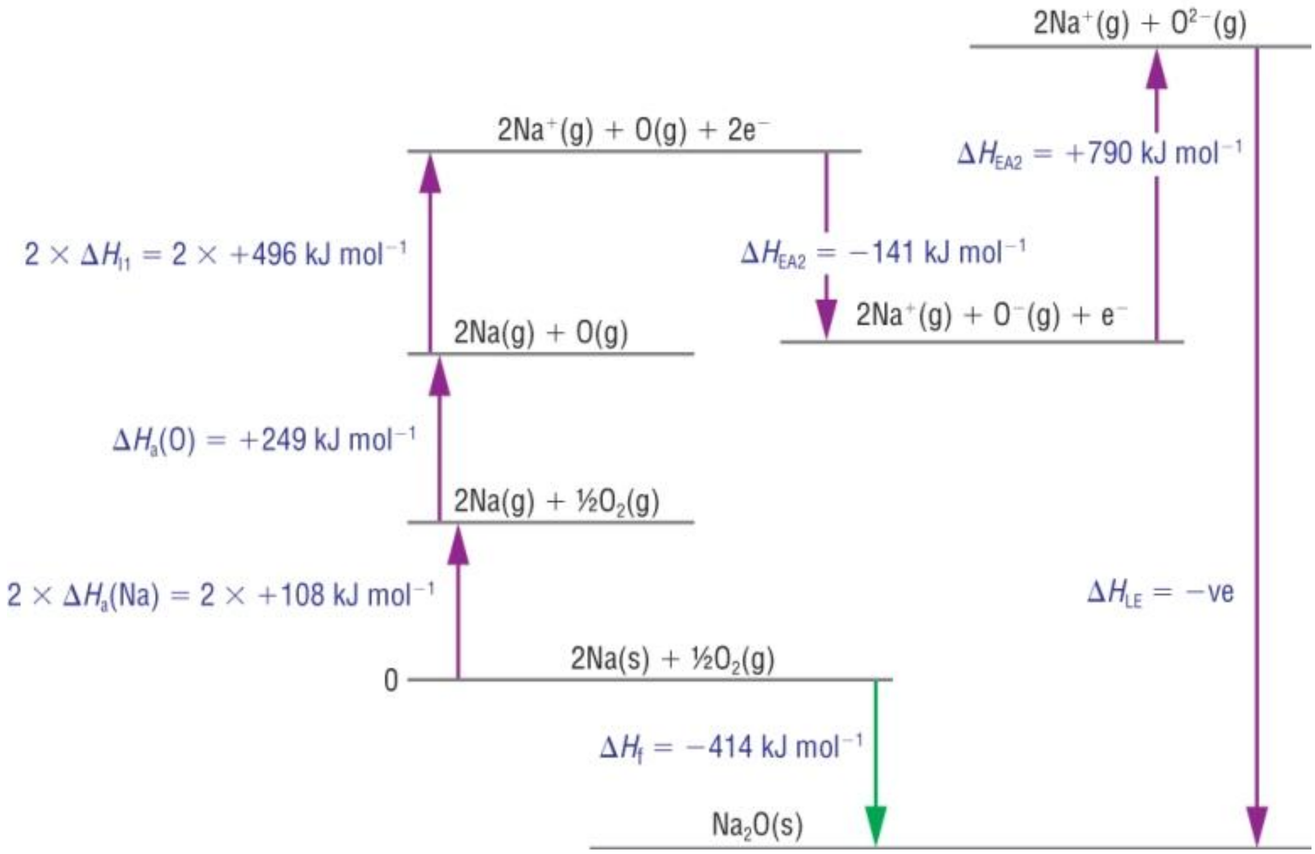
ΔH^θ_{LE} = ΔH^θ_f - (SUM OF ΔH^θ THE REST)

ΔH^θ_{LE} = - 433 - (+79 + 121 + 376 + - 346)

ΔH^θ_{LE} = - 433 - (+79 + 121 + 376 - 346)

ΔH^θ_{LE} = - 663 Kj mol^{-1}

2) Sodium oxide:



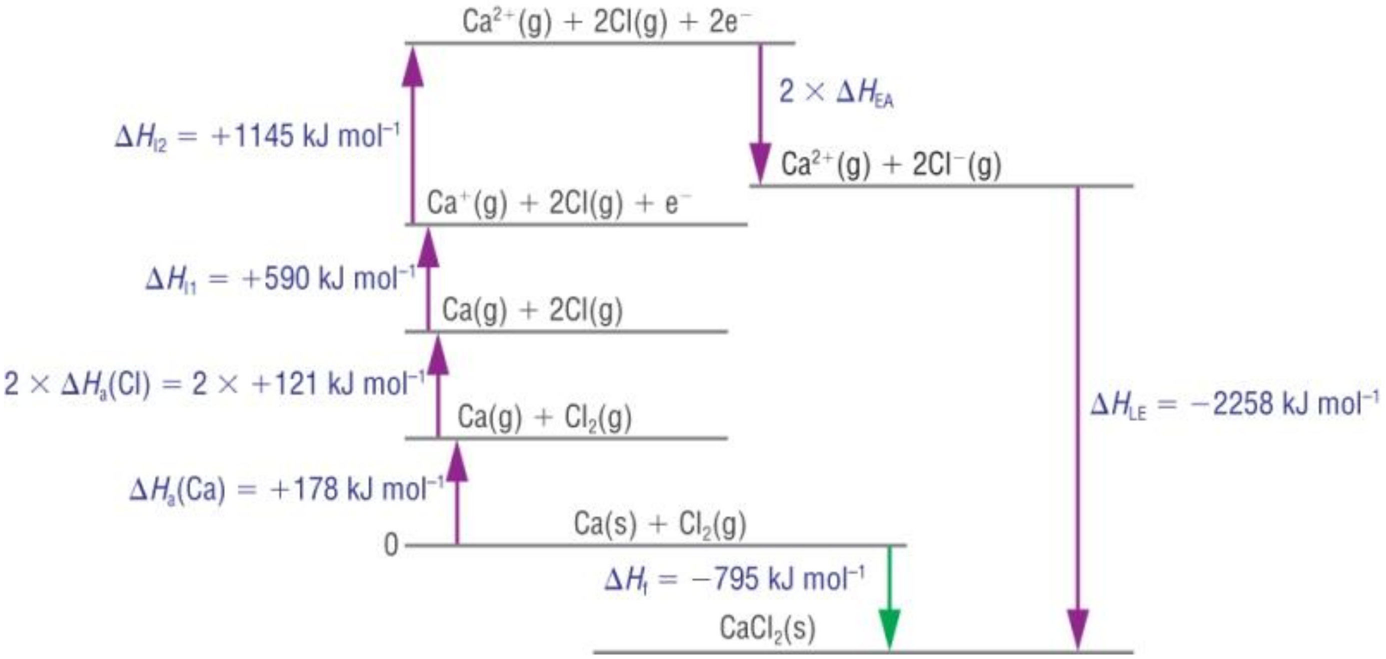
Calculation:

ΔH^{θ}_{LE} = ΔH^{θ}_{f} - (SUM OF ΔH^{θ} THE REST)
ΔH^{θ}_{LE} = - 414 - (+216 + 249 + 992 + - 141 + 790)
ΔH^{θ}_{LE} = - 414 - (+216 + 249 + 992 - 141 + 790)
ΔH^{θ}_{LE} = - 2520 Kj mol^{-1}

Further examples of Born - Haber cycles

3) Calcium chloride:

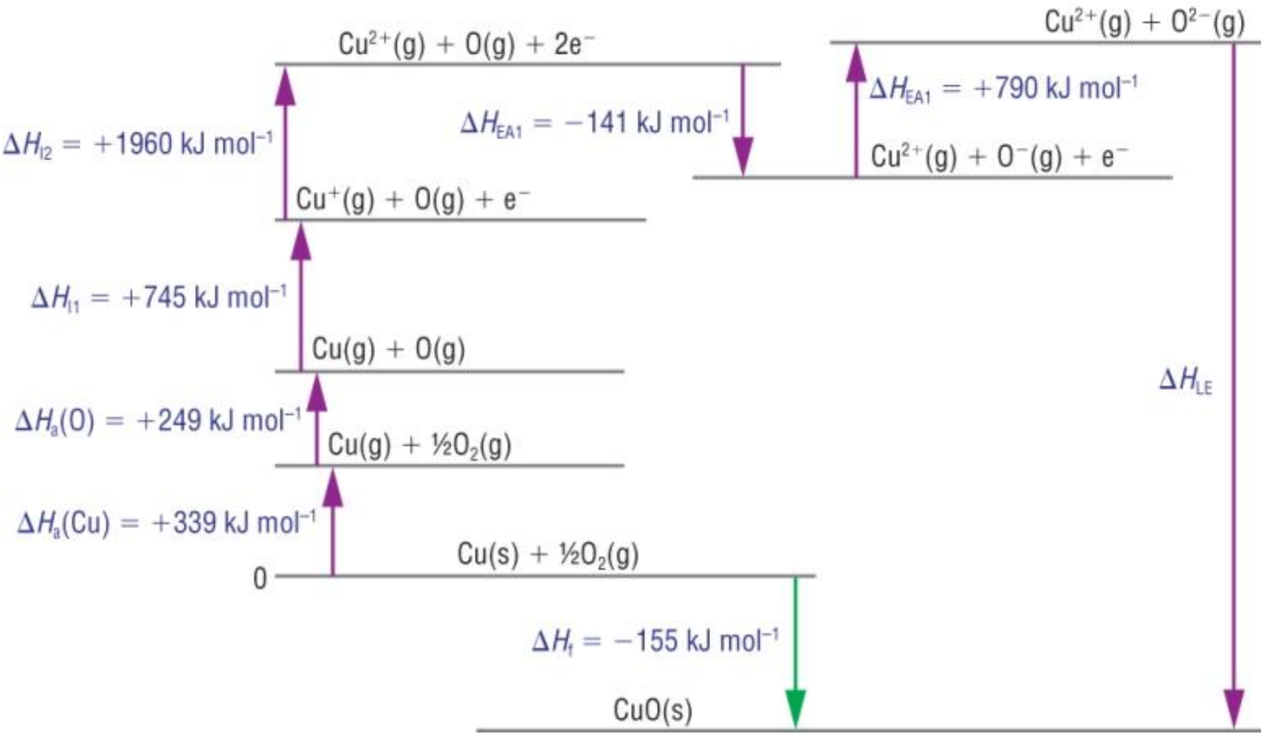
- These cycles can be used to calculate other unknowns:



Calculation:

ΔH^{θ}_{LE} = ΔH^{θ}_{f} - (SUM OF ΔH^{θ} THE REST)
-2258 = - 795 - (+178 + 242 + 590 + 1145 + (2 x ΔH^{θ}_{EA}))
-2258 = - 795 - (+ 2155 + (2 x ΔH^{θ}_{EA}))
-2258 = - 795 - 2155 - (2 x ΔH^{θ}_{EA})
-2258 = - 2950 - (2 x ΔH^{θ}_{EA})
2 x ΔH^{θ}_{EA} = - 2950 + 2258
2 x ΔH^{θ}_{EA} = - 692
ΔH^{θ}_{EA} = - 346 Kj mol^{-1}

4) Copper (II) oxide:



Calculation:

ΔH^{θ}_{LE} = ΔH^{θ}_{f} - (SUM OF ΔH^{θ} THE REST)

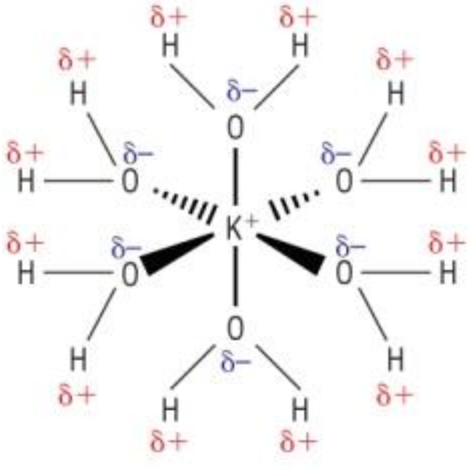
ΔH^{θ}_{LE} = - 155 - (+339 + 249 + 745 + 1960 + -141 + 790)

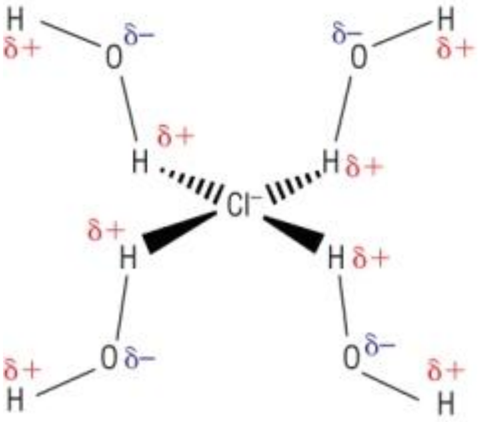
ΔH^{θ}_{LE} = - 155 - (+339 + 249 + 745 + 1960 - 141 + 790)

ΔH^{θ}_{LE} = - 4097 Kj mol^{-1}

Enthalpy change of solution

- When ionic compounds dissolve in water the ions separate.





- If the electrostatic forces of attraction are so strong, how is this possible?
- The clue comes with the temperature changes that occur when they dissolve.
- Calcium chloride gives us an exothermic reaction.
- Ammonium nitrate gives us an endothermic reaction.
- The energy produced when water surrounds the ions must be about the same as the electrostatic forces of attraction between the ions.
- If there is energy left over it is given out as heat energy.
- If there is not enough energy it is taken in from the surroundings
- These can all be calculated in another type of Hess's cycle but some other enthalpy changes are required first:

1) Enthalpy change of solution, ΔH^{θ}_{s}

1 Mole of compound → Aqueous ions

1 mole of a compound is dissolved in water under standard conditions

Example - This process can be endothermic or exothermic:

$$KCl_{(s)} + aq \rightarrow K^{+}_{(aq)} + Cl^{-}_{(aq)}$$

2) Enthalpy change of hydration, ΔH^{θ}_{hyd}

Gaseous ions → 1 Mole aqueous ions

1 mole of aqueous ions are formed from their gaseous ions under standard conditions

Example - This process is an exothermic process:

$$K^{+}_{(g)} + aq \rightarrow K^{+}_{(aq)}$$

$$Cl^{-}_{(g)} + aq \rightarrow Cl^{-}_{(aq)}$$

What happens when a solid dissolves:

- In terms of a Hess's cycle:

1) Ionic lattice breaks down into gaseous ions, E_{in}:

- This is the opposite of the lattice enthalpy:

$K^+_{(g)} + Cl^-_{(g)} \rightarrow KCl_{(s)} \quad \Delta H^{\theta}_{LE} = -771\ KjMol^{-1}$

- Opposite of this:

$KCl_{(s)} \rightarrow K^+_{(g)} + Cl^-_{(g)} \quad \Delta H^{\theta}_{LE} = +771\ KjMol^{-1}$

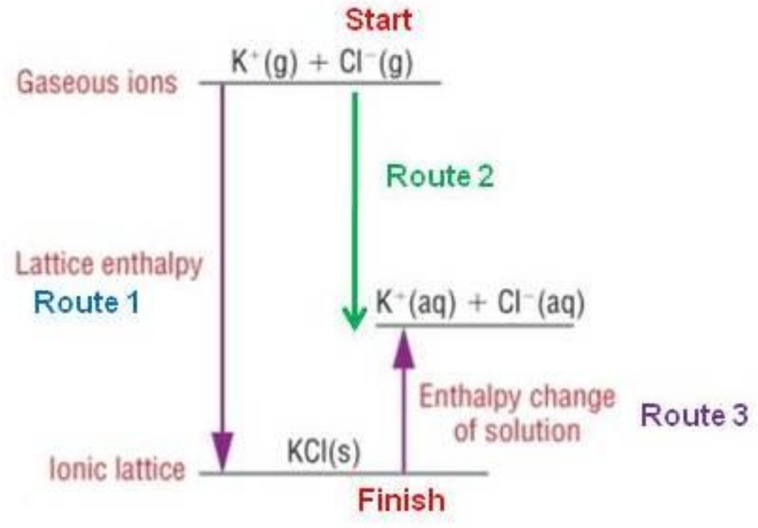
2) Hydration of gaseous ions, E_{out}:

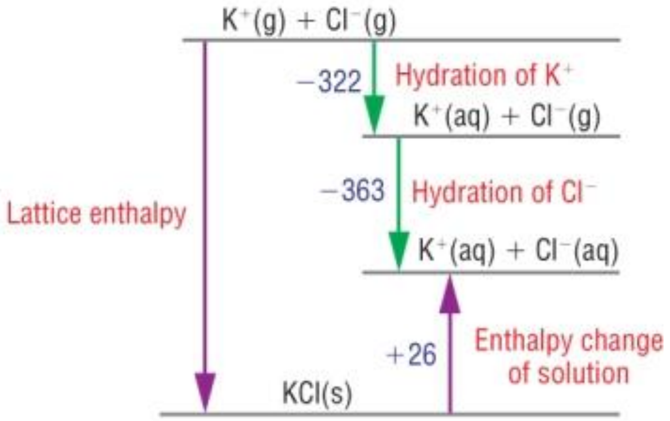
$K^+_{(g)} + aq \rightarrow K^+_{(aq)}$

$Cl^-_{(g)} + aq \rightarrow Cl^-_{(aq)}$

- The resulting enthalpy change is known as the **enthalpy change of solution**

Calculating a lattice enthalpy from enthalpy changes of solution and hydration:





Route 1 = Route 2 + - Route 3

Route 1 = Route 2 - Route 3

$\Delta H^{\theta}_{LE} = \text{Route 2} - \Delta H^{\theta}_{s}$

- **Route 2 is made up of 2 steps:**

$\Delta H^{\theta}_{LE} = (\text{SUM OF } \Delta H^{\theta}_{hyd} \text{ ions}) - \Delta H^{\theta}_{s}$

$\Delta H^{\theta}_{LE} = (-322 + -363) - +26$

$\Delta H^{\theta}_{LE} = (-322 - 363) - 26$

$\Delta H^{\theta}_{LE} = -685 - 26$

$\Delta H^{\theta}_{LE} = -711\ Kj\ mol^{-1}$

Understanding hydration and lattice enthalpies

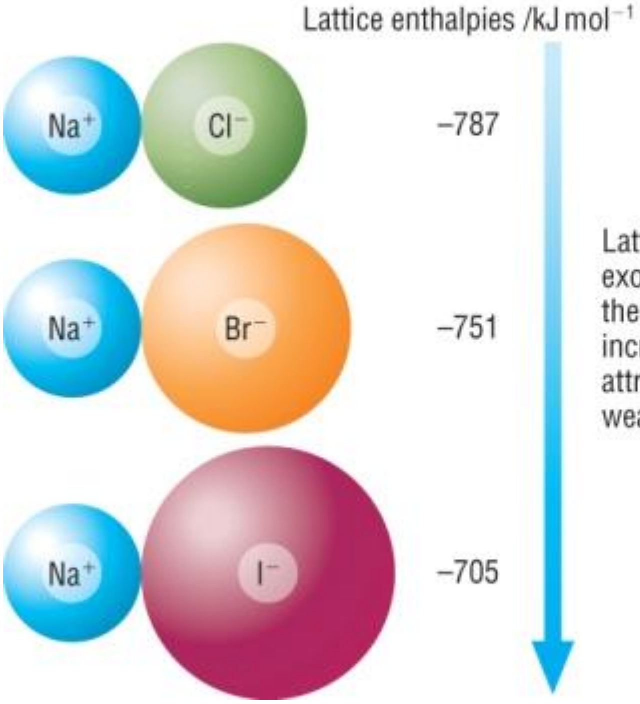
Lattice enthalpies

- Lattice enthalpy is due to strong electrostatic forces of attraction between oppositely charged ions.
- This means that 2 things can effect the value of the lattice enthalpy:

1. **Ionic size**
2. **Ionic charge**

Ionic size

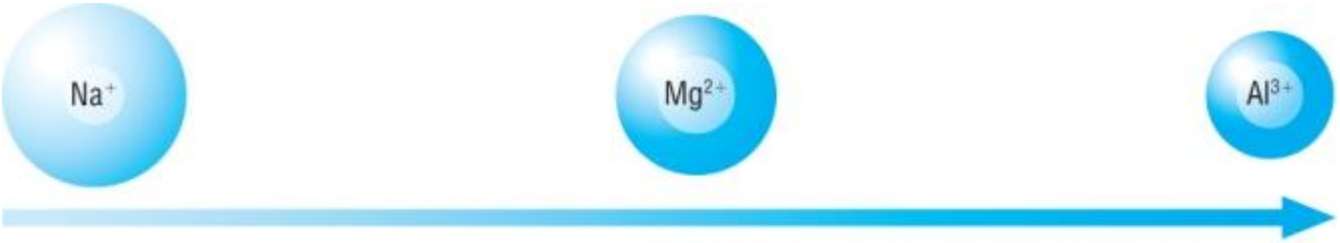
- Small ions can pack together closer.
- This gives a stronger electrostatic force of attraction.
- As ions become larger down a group, the attraction decreases.
- This means that the lattice enthalpy will be less exothermic:



Lattice enthalpy becomes less exothermic and *less negative* as the size of the negative ions increases. This indicates weaker attraction between ions and hence weaker ionic bonding

Ionic charge

- The larger the charge on the ion, the stronger electrostatic force of attraction between the ions.
- As the ionic charge increases, the electrostatic forces of attraction also increases.
- This means that the lattice enthalpy will be more exothermic:



Charge increases and produces a greater attraction between these positive ions and negative ions. The ionic radius decreases resulting in the ions in the lattice being closer together producing more attraction. Lattice enthalpies become more exothermic – *more negative*

Enthalpy change of hydration:

- Enthalpy change of hydration is due to attractive forces between ions and water.
- This means that 2 things can effect the value of the lattice enthalpy:

1. **Ionic size**
2. **Ionic charge**

Ionic size

- Small ions attract water molecules closer.
- This gives a stronger force of attraction.
- As ions become **larger** down a Group, the **attraction decreases**.
- This means that the hydration enthalpy will be l**ess exothermic**:

Down the group, size increases, ΔH^{θ}_{hyd} gets less exothermic	**Ion**	**ΔH^{θ}_{hyd}**
	Cl^-	**-363**
	Br^-	**-336**
	I^-	**-295**

Ionic charge

- A **greater charge** on ions attract water molecules stronger.
- This gives a **stronger force of attraction**.
- The ions also become smaller across a Period, the attraction increases further.
- This means that the hydration enthalpy will be **more exothermic**:

Across a Period, charge increases and size decreases, ΔH^{θ}_{hyd} gets more exothermic	**Ion**	**ΔH^{θ}_{hyd}**
	Na^+	**-406**
	Mg^{2+}	**-1921**
	Al^{3+}	**-4665**

Entropy

What is entropy:

- Entropy is a measure of **disorder** in a system.
- There is always some degree of disorder as particles always have some sort of motion, so values are always **positive**.
- As motion is related to enthalpy (energy) then the 2 are related.
- As entropy is due to disorder and so enthalpy (energy) it can be described as the dispersal of energy.

Entropy:

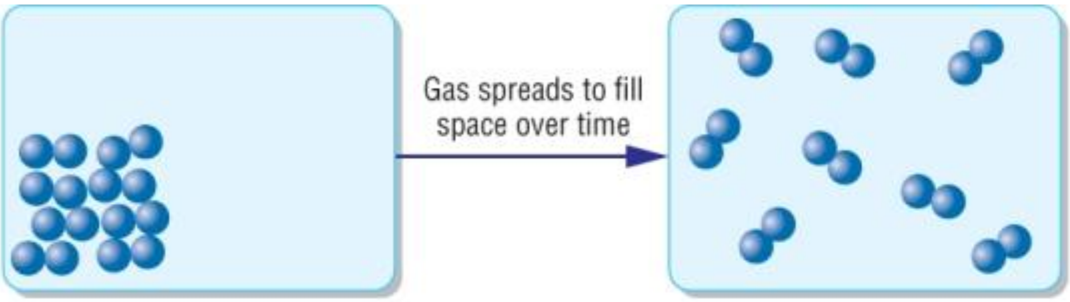
- There are many naturally occurring events that lead to disorder:

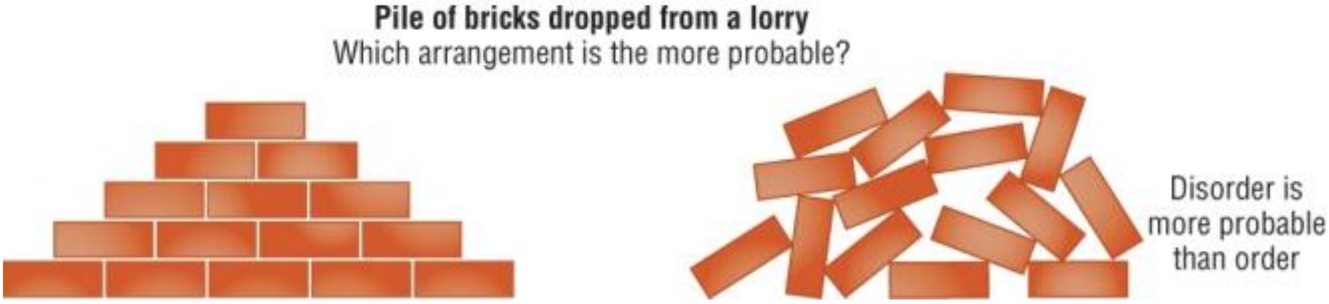
Melting ice cream
Smell of cooking spreading

- These are occasions when natural processes lead to disorder.
- There is a tendency in nature for processes to lead to disorder:

Your bedroom

Expanding Universe





What can entropy tell us?

- All these processes start off ordered and become disordered
- The entropy starts of with a low value (ordered) and leads to a higher value (disordered)
- This means that reactants and products will have an **entropy content.**
- As Chemists we are interested in the change in entropy of a chemical system.
- This gives us an idea as to whether a reaction will occur or not

Order	**State**	**Explanation**	**Entropy**
Ordered (O)	**Solids**	Vibrating in fixed position	**Low**
Disordered (DO)	**Liquids/ Aqueous**	Free moving but closely packed	**Medium**
Very Disordered (VDO)	**Gases**	As far apart as possible, moving lots	**High**

Using Entropy:

Reaction	$NH_4NO_{3(s)}$	+	aq	→	$NH_4^+{}_{(aq)}$	+	$NO_3^-{}_{(aq)}$
Order	**Ordered**		**Disordered**	→	**Disordered**		**Disordered**
Overall	**Ordered**			→	**Disordered**		

LIKELY TO HAPPEN

Reaction	$MgCO_{3(s)}$	→	$MgO_{(s)}$	+	$CO_{2(g)}$
Order	**Ordered**	→	**Ordered**		**Very disordered**
Overall	**Ordered**	→	**Disordered**		

LIKELY TO HAPPEN

Calculating entropy:

- Standard entropy content of a substance can be looked up in a data book.
- They have the units **J Mol K^{-1}**
- The difference in entropy content between the products and reactants will give a value.

$$\Delta S^{\theta}{}_{system} = \Sigma S^{\theta}{}_{products} - \Sigma S^{\theta}{}_{reactants}$$

- If the value is **positive** it means that the system is moving to more **disorder - LIKELY TO HAPPEN**
- If the value is **negative** it means that the system is moving towards more **order - UNLIKELY TO HAPPEN**

Worked example:

- For the reaction:

Reaction	$N_{2(g)}$	+	$3H_{2(g)}$	→	$2NH_{3(g)}$
Entropy content	**+ 192**		**+ 131**		**+ 193**

$$\Delta S^{\theta}{}_{system} = \Sigma S^{\theta}{}_{products} - \Sigma S^{\theta}{}_{reactants}$$

$$\Delta S^{\theta}{}_{system} = (2 \times +193) - [\,(+192) + (3 \times +131)\,]$$

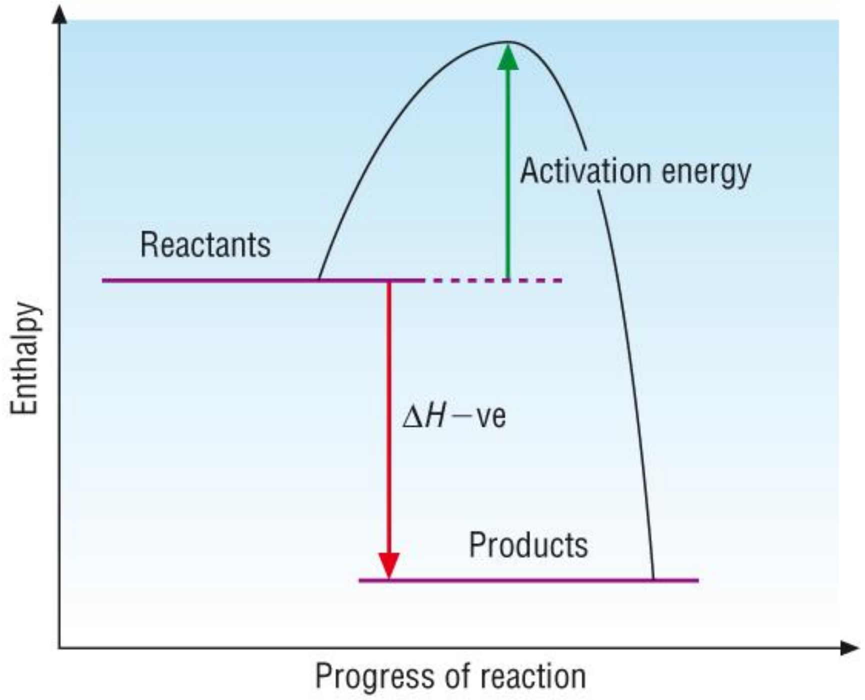
$$\Delta S^{\theta}{}_{system} = -199 \text{ J K}^{-1} \text{ mol}^{-1}$$

Free energy

Spontaneous process

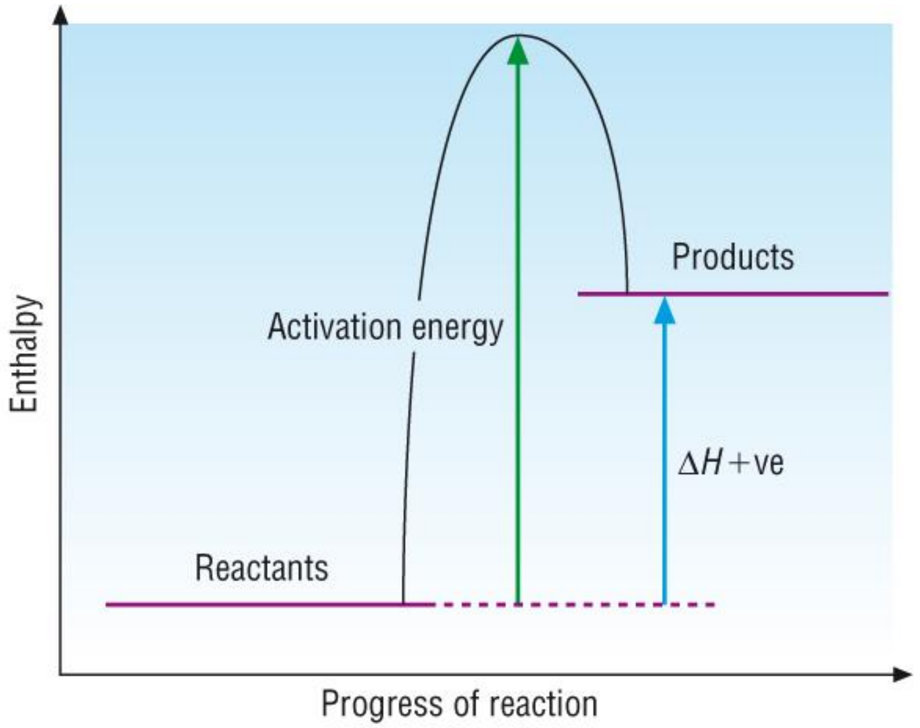
- Spontaneous reactions occur on their own and move to products with a lower energy and more stability.

Exothermic reactions:



- Are usually spontaneous at room temperature.
- The enthalpy content decreases during the reaction and the excess energy being released to the surroundings.
- There is an increase in stability.

Endothermic reactions:



- Some endothermic reactions are also spontaneous at room temperature.
- The enthalpy content increases during the reaction with energy being taken in from the surroundings.
- Overall this must also increase in stability.

- The fact that endothermic reactions are spontaneous too means that there must be more than just enthalpy involved in increasing stability.
- A reaction is spontaneous if a chemical system becomes more stable **and** its overall energy increases
- In fact stability is derived from the contributions from **enthalpy** and **entropy**.

Enthalpy	**Deals with the contribution of energy of the surroundings**
Entropy	**Deals with the contribution of energy of the system**

Energy from entropy

- The entropy contribution to the overall energy depends on temperature, **T** in kelvins.

Energy derived from entropy = $T\Delta S$

- As temperature increases, the energy derived from entropy becomes more significant.

Free energy and feasibility:

- 3 factors contribute to whether a reaction will be spontaneous:

1 Temperature in k	**T**
2 Entropy change of the system	**ΔS**
3 Enthalpy change with the surroundings	**ΔH**

- The relationship between these 3 factors is expressed by Gibbs **Free energy, ΔG:**

$$\Delta G = \underset{\text{Surroundings}}{\Delta H} - \underset{\text{System}}{T\Delta S}$$

- For there to be a **decrease in (free) energy**, leading to **more stability**:

$\Delta G < 0$ Negative

ΔH	ΔS	ΔG	Feasibility / spontaneous
(-)ve	**(+)ve**	**(-)ve**	**Feasible**
(+)ve	**(-)ve**	**(+)ve**	**Never feasible**
(-)ve	**(-)ve**	**(-)ve at low temps**	**Feasible at low temps**
(+)ve	**(+)ve**	**(-)ve at high temps**	**Feasible at high temps**

- Most exothermic reactions are feasible / spontaneous as enthalpy contributes more to **ΔG**.

How do endothermic reactions take place:

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

- For an endothermic reaction to take place, **ΔS must be positive**
- The temperature must be high enough to make, **$T\Delta S > \Delta H$**

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

$$\Delta H < T\Delta S$$

$$(+)\text{ve} < T\Delta S$$

- This will make **ΔG negative and therefore spontaneous**.

Example:

At what temperature will $ZnCO_3$ decompose?

Reaction $ZnCO_{3(s)} \rightarrow ZnO_{(s)} + CO_{2(g)}$ $\Delta H = +71$ KJ mol^{-1}
Entropy, ΔS +82 +44 +214

1) Calculate $\Delta S^{\theta}_{system}$:

$\Delta S^{\theta}_{system} = \Sigma S^{\theta}_{products} - \Sigma S^{\theta}_{reactants}$

$\Delta S^{\theta}_{system} = (+44 + +214) - +82$

$\Delta S^{\theta}_{system} = 176$ J K^{-1} mol^{-1}

$\Delta S^{\theta}_{system} = 0.176$ KJ K^{-1} mol^{-1} COMMON ERROR - MUST COVERT TO KJ

2) Assume $\Delta G = 0$ to calculate T:

$\Delta G = \Delta H - T\Delta S$
$0 = +71 - T \times 0.176$

$T \times 0.176 = +71$

$$T = \frac{+71}{0.176}$$

T = 403 k (-273 for ^{o}C)
T = 130 ^{o}C