AQA A Level Chemistry

Your notes

Thermodynamics

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Defining Thermodynamic Terms

- **Thermodynamics** is the branch of physical chemistry concerned with heat energy, temperature, and energy changes in chemical and physical processes
- Energy cycles, such as **Born–Haber cycles**, are diagrams used to represent enthalpy changes for ionic compounds using **Hess's Law**
- To understand these cycles, you must know the definitions of several key enthalpy changes
- The **enthalpy change** (**Δ*H***) is the heat energy transferred during a reaction at constant pressure
- Key enthalpy definitions include:
  - Enthalpy of formation
  - Ionisation energy
  - Enthalpy of atomisation
  - Bond enthalpy
  - Electron affinity

Enthalpy of formation

- The standard **enthalpy of formation** (**$\Delta_f H^{\ominus}$**) is the enthalpy change when **one mole** of a **compound** is formed from its elements in their **standard states** under **standard conditions**
- In this specification, standard conditions are 298 K and a pressure of 100 kPa
- The value of $\Delta_f H^{\ominus}$ can be **positive** (**endothermic**) or **negative** (**exothermic**), depending on the balance between **bond breaking** and **bond formation** during the reaction
- An equation must show the formation of exactly one mole of the compound from its elements in their standard states
- For example, the standard enthalpy of formation of sodium chloride is:

$$Na(s) + \tfrac{1}{2}Cl_2(g) \rightarrow NaCl(s) \qquad \Delta_f H^{\ominus} = -411\ kJ\ mol^{-1}$$

- The enthalpy of formation applies only to compounds
  - By definition, the standard enthalpy of formation of an element in its standard state is zero

Ionisation energy

- The **ionisation energy** of an element is the amount of energy required to remove an electron from a gaseous atom of an element to form a gaseous ion under standard

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conditions

- **Ionisation enthalpy** is always endothermic, as energy is needed to overcome the attraction between an electron and the nucleus
- The **first ionisation energy** is the energy required to remove **one mole of electrons** from one mole of gaseous atoms of an element to form one mole of gaseous 1+ ions
  - E.g., the first ionisation energy of gaseous sodium:

$$Na\,(g) \rightarrow Na^{+}\,(g) + e^{-} \qquad \Delta H^{\ominus} = +500\ kJ\ mol^{-1}$$

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Enthalpy of atomisation

- The standard **enthalpy of atomisation** is the enthalpy change when **one mole** of **gaseous atoms** is formed from an **element** in its standard state under standard conditions
- Atomisation is always endothermic because energy is required to break the bonds holding the atoms together in the element
  - Therefore, $\Delta H^{\ominus}$ always has a positive value
- An equation for atomisation must show the formation of one mole of gaseous atoms
- For example, sodium is a solid in its standard state. Its standard enthalpy of atomisation is:

$$Na\,(s) \rightarrow Na\,(g) \qquad \Delta H^{\ominus} = +108\ kJ\ mol^{-1}$$

- This represents the energy required to form one mole of gaseous sodium atoms from solid sodium

Worked Example

Writing equations for the standard enthalpy of atomisation

Write down the equations for the standard enthalpy of atomisation ($\Delta H^{\ominus}$) for:

(i) Potassium

(ii) Mercury

Answer

Answer 1: Potassium in its elemental form is a **solid**, therefore the standard enthalpy of atomisation is the energy required to form 1 mole of K(g) from K(s)

$$K(s) \rightarrow K(g)$$

Answer 2: Mercury in its elemental form is a **liquid**, so the standard enthalpy change of atomisation of mercury is the energy required to form 1 mole of Hg(g) from Hg(l)

$$Hg(l) \rightarrow Hg(g)$$

Bond enthalpy

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- **Bond enthalpy** (also called **bond dissociation enthalpy**) is the energy required to break one mole of a specific covalent bond in the gaseous state
- It is usually represented as ***E*(bond)**, for example:
  - *E*(H–H) is the bond enthalpy of one mole of H–H bonds
- Bond enthalpy values are always quoted as **positive** because breaking bonds is an **endothermic process**
- When considering bond formation, the same value is used but with a negative sign, since bond **formation** is **exothermic**
- For example, chlorine exists as Cl_2 (g).
  - The bond enthalpy of chlorine is:

$$Cl_2\,(g) \rightarrow 2Cl\,(g) \quad E(Cl\text{–}Cl) = +242\ kJ\ mol^{-1}$$

- This looks similar to the atomisation enthalpy of chlorine, but there is an important difference
- Bond enthalpy refers to breaking one mole of bonds
  - Atomisation enthalpy refers to the formation of one mole of gaseous atoms
  - Therefore, the atomisation enthalpy of chlorine is half the bond enthalpy:

$$\tfrac{1}{2}Cl_2\,(g) \rightarrow Cl\,(g) \quad \Delta H^{\ominus} = +121\ kJ\ mol^{-1}$$

- If an element is a liquid in its standard state, its atomisation enthalpy would also include the enthalpy of vaporisation before bond breaking occurs

Enthalpy of Lattice Formation and Dissociation

- Lattice enthalpy can be defined either as **lattice formation enthalpy** or **lattice dissociation enthalpy**
- Because **strong electrostatic attractions** form between oppositely charged ions in the solid lattice, a large amount of energy is released
  - Therefore, the enthalpy of lattice formation is exothermic and has a **large negative value**
  - The large negative value indicates that the ionic lattice is much **more stable** than the separated gaseous ions
  - In the gas phase, the ions are far apart, and there are no strong electrostatic attractions between them
- The **more exothermic** the lattice enthalpy, the **stronger** the **ionic bonding** in the lattice
- Lattice enthalpy cannot be measured directly in a single experiment
  - Instead, it is determined indirectly using a **Born–Haber cycle** and other experimentally measured enthalpy changes
- For example, for sodium chloride:

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$$Na^+(g) + Cl^-(g) \rightarrow NaCl(s) \quad \Delta H^{\ominus} = -776 \text{ kJ mol}^{-1}$$

- This equation represents the enthalpy change when one mole of solid sodium chloride is formed from its gaseous ions

Your notes

Worked Example

Writing equations for lattice energy

Write down the equations that represent the enthalpy of lattice formation for:

(i) magnesium oxide

(ii) lithium chloride

Answer

Answer 1: $Mg^{2+}(g) + O^{2-}(g) \rightarrow MgO(s)$

Answer 2: $Li^+(g) + Cl^-(g) \rightarrow LiCl(s)$

Electron Affinity

- The **electron affinity** of an element is the enthalpy change when **one mole** of **electrons** is added to one mole of **gaseous atoms** to form one mole of **gaseous negative ions** under standard conditions
- For example, the first electron affinity of chlorine is:

$$Cl(g) + e^- \rightarrow Cl^-(g) \qquad \Delta H^{\ominus} = -364 \text{ kJ mol}^{-1}$$

- The **first electron affinity** is usually **exothermic** because energy is released when an electron is attracted to the positively charged nucleus of a gaseous atom
- However, the **second electron affinity** is always **endothermic**
  - For example, for oxygen:

$$O^-(g) + e^- \rightarrow O^{2-}(g) \qquad \Delta H^{\ominus} = +844 \text{ kJ mol}^{-1}$$

- This is because energy must be supplied to overcome the **electrostatic repulsion** between the negatively charged ion and the incoming electron

Examiner Tips and Tricks

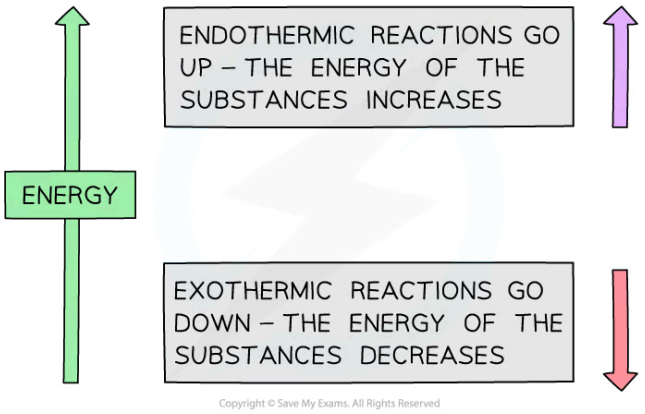
Make sure the correct **state symbols** are stated when writing these equations – you must use these correctly throughout this entire topic.

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Constructing Born-Haber Cycles

- A **Born-Haber cycle** is a specific application of Hess's Law used for ionic compounds. It allows the calculation of lattice enthalpy, which cannot be measured directly by experiment
- The basic principle of constructing the cycle is to draw a diagram in which energy increases upwards

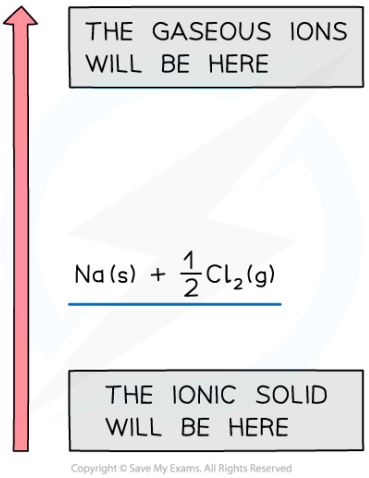


The energy flows in a Born-Haber cycle

- The cycle shows all the enthalpy changes required to convert elements into gaseous ions and then form the ionic lattice from those ions
- The alternative route to the ionic lattice starts from the enthalpy of formation of the compound from its elements in their standard states

Drawing the cycle for sodium chloride

- A good starting point is to draw the elements, with their state symbols, about one-third of the way up the diagram
- These appear on the left-hand side of the equation for the process being represented
- This position is marked by a horizontal line, which represents the starting energy level



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The first step in drawing a Born-Haber cycle

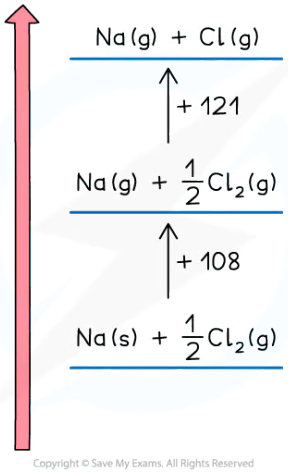
- Next, the gaseous ions must be formed
- This occurs in two steps: first, gaseous atoms are produced, and then these atoms are converted into ions
- The formation of gaseous atoms involves bond breaking, so these steps are represented by arrows drawn upwards on the diagram
- It does not matter whether sodium or chlorine is considered first
- The enthalpy of atomisation of sodium is:

$$Na\,(s) \rightarrow Na\,(g) \qquad \Delta H_{at}^{\ominus} = +108\ kJ\ mol^{-1}$$

- The enthalpy of atomisation of chlorine is

$$\tfrac{1}{2}Cl_2\,(g) \rightarrow Cl\,(g) \qquad \Delta H_{at}^{\ominus} = +121\ kJ\ mol^{-1}$$

- The products of each step are shown on horizontal lines, with the enthalpy change written next to the vertical arrow connecting the energy levels



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The second step in a Born-Haber cycle – creating the gaseous atoms

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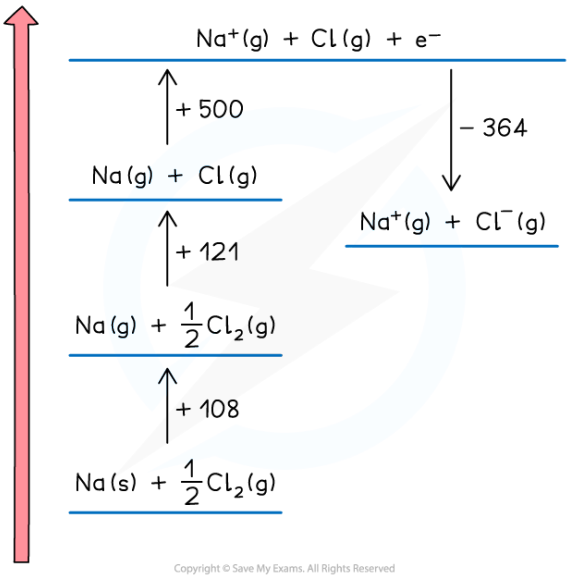
- Next, the gaseous ions are formed
- The sodium atom loses an electron, so this energy change corresponds to the first ionisation energy of sodium:

$$Na\,(g) \rightarrow Na^{+}\,(g) + e^{-} \qquad \Delta H_{ie}^{\ominus} = +500\ kJ\ mol^{-1}$$

- This process is endothermic, so the arrow is drawn upwards on the diagram
- The chlorine atom gains an electron, which is the electron affinity of chlorine:

$$Cl\,(g) + e^{-} \rightarrow Cl^{-}\,(g) \qquad \Delta H_{ea}^{\ominus} = -364\ kJ\ mol^{-1}$$

- This change is exothermic, so the arrow is drawn downwards
- The electron affinity step is often displaced to the right on the diagram to improve clarity and avoid overlapping arrows



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Third step in a Born–Haber cycle step– creating the gaseous ions

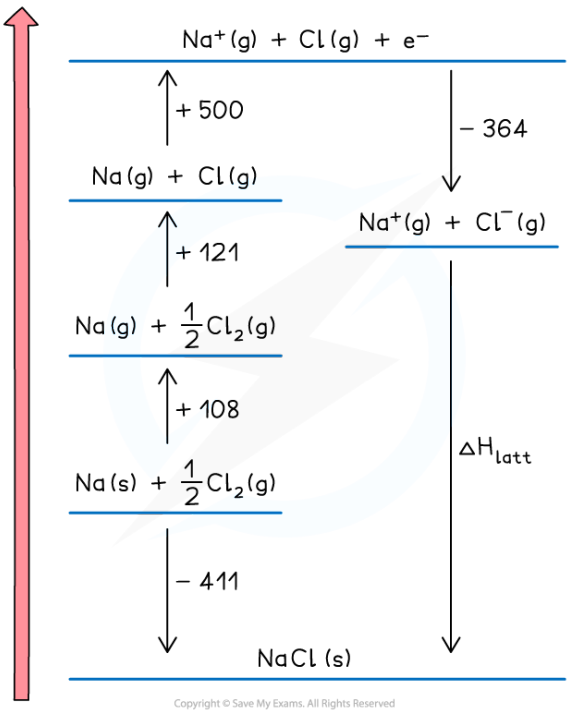
- The two remaining parts of the cycle can now be completed.
- The enthalpy of formation of sodium chloride is added at the bottom of the diagram:

$$Na(s) + \tfrac{1}{2}Cl_2\,(g) \rightarrow NaCl\,(s) \qquad \Delta H_{f}^{\ominus} = -411\ kJ\ mol^{-1}$$

- This is an exothermic change for sodium chloride, so the arrow is drawn downwards
- Enthalpy of formation can be either exothermic or endothermic. If it is endothermic, the arrow must be drawn upwards and is often displaced to the right of the diagram for clarity
- The final step is the lattice enthalpy, which can be shown as the enthalpy change for lattice formation or dissociation
  - For sodium chloride, the formation equation is:

$$Na^{+}(g) + Cl^{-}(g) \rightarrow NaCl\,(s)\ \Delta H_{latt}^{\ominus}$$

Your notes



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Fourth step in a Born-Haber cycle - completing the cycle

- The cycle is now complete
- It is most commonly used to calculate the lattice enthalpy of an ionic solid, but it can also be used to determine other enthalpy changes if the lattice enthalpy is known

Examiner Tips and Tricks

Lattice enthalpy can be defined as either the enthalpy of lattice dissociation or the enthalpy of lattice formation.

Lattice dissociation is a bond-breaking process, so the equation always shows the ionic solid changing into the gaseous ions in an endothermic reaction:

$$NaCl(s) \rightarrow Na^+(g) + Cl^-(g) \quad \Delta H_{latt}^{\ominus} = +ve$$

Lattice formation is bond forming, so gaesous ions change into the ionic solid in an exothermic reaction

$$Na^+(g) + Cl^-(g) \rightarrow NaCl(s) \quad \Delta H_{latt}^{\ominus} = -ve$$

Examiners use both processes in past paper questions.

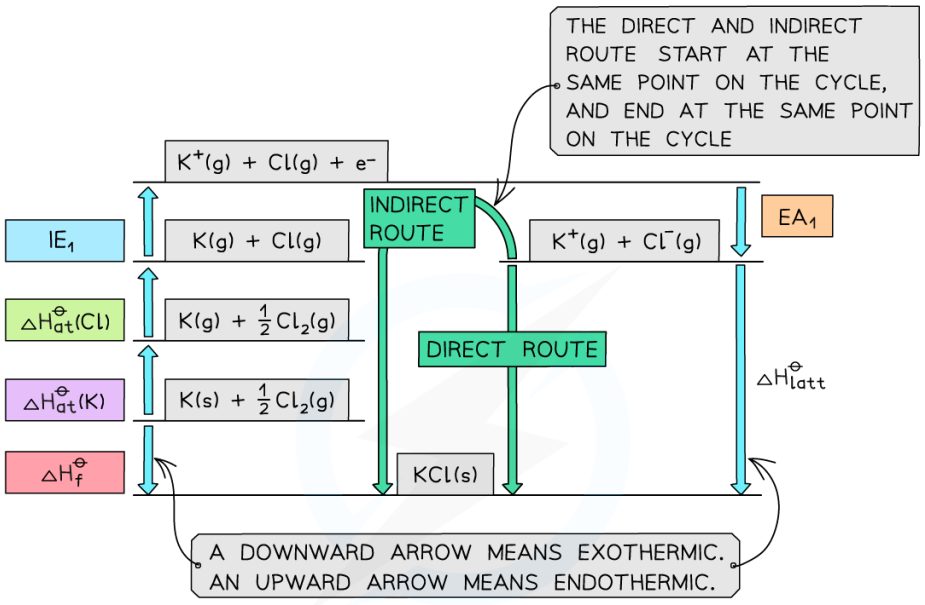
Worked Example

Your notes

Construct a Born-Haber Cycle which can be used to calculate the lattice energy of potassium chloride.

Step	Equation	Enthalpy Change
Convert $K_{(s)}$ atoms into $K_{(g)}$ atoms	$K_{(s)} \rightarrow K_{(g)}$	ΔH^{θ}_{at}
Convert $K_{(g)}$ atoms into $K^{+}_{(g)}$ ions	$K_{(g)} \rightarrow K^{+}_{(g)} + e^{-}$	IE_{1st}
Convert $Cl_{2(g)}$ molecules into $Cl_{(g)}$ atoms	$\frac{1}{2}Cl_{2(g)} \rightarrow Cl_{(g)}$	ΔH^{θ}_{at}
Convert $Cl_{(g)}$ atoms into $Cl^{-}_{(g)}$ ions	$Cl_{(g)} + e^{-} \rightarrow Cl^{-}_{(g)}$	EA_{1st}
Add up all values to get ΔH^{θ}_{1}		ΔH^{θ}_{1}
Apply Hess's Law to find ΔH^{θ}_{latt}		ΔH^{θ}_{latt}

Answer



$$\Delta H_f^{\ominus} = \left(\Delta H_{at}^{\ominus}(K)\right) + \left(\Delta H_{at}^{\ominus}(Cl)\right) + \left(IE_1\right) + \left(EA_1\right) + \left(\Delta H_{latt}^{\ominus}\right)$$

$$\therefore \Delta H_{latt}^{\ominus} = \left(\Delta H_f^{\ominus}\right) - \left(EA_1\right) - \left(IE_1\right) - \left(\Delta H_{at}^{\ominus}(Cl)\right) - \left(\Delta H_{at}^{\ominus}(K)\right)$$

$$\Delta H_1^{\ominus}$$

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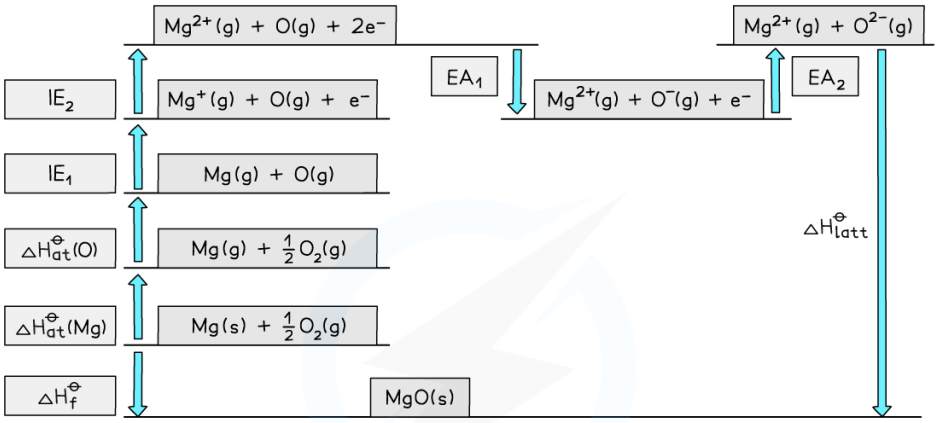
Worked Example

Your notes

Construct a Born-Haber Cycle which can be used to calculate the lattice energy of magnesium oxide.

Convert $Mg_{(s)}$ atoms into $Mg_{(g)}$ atoms	$Mg_{(s)} \rightarrow Mg_{(g)}$	ΔH^{θ}_{at}
Convert $Mg_{(g)}$ atoms into $Mg^{+}_{(g)}$ ions	$Mg_{(g)} \rightarrow Mg^{+}_{(g)} + e^{-}$	IE_{1st}
Convert $Mg^{+}_{(g)}$ ions into $Mg^{2+}_{(g)}$ ions	$Mg^{+}_{(g)} \rightarrow Mg^{2+}_{(g)} + e^{-}$	IE_{2nd}
Convert $O_{2(g)}$ molecules into $O_{(g)}$ atoms	$\frac{1}{2}O_{2(g)} \rightarrow O_{(g)}$	ΔH^{θ}_{at}
Convert $O_{(g)}$ atoms into $O^{-}_{(g)}$ ions	$O_{(g)} + e^{-} \rightarrow O^{-}_{(g)}$	EA_{1st}
Convert $O^{-}_{(g)}$ ions into $O^{2-}_{(g)}$ ions	$O^{-}_{(g)} + e^{-} \rightarrow O^{2-}_{(g)}$	EA_{2nd}
Add up all values to get ΔH^{θ}_{1}		ΔH^{θ}_{1st}
Apply Hess's Law to find ΔH^{θ}_{latt}		ΔH^{θ}_{latt}

Answer



$$\Delta H_f^{\ominus} = \left(\Delta H_{at}^{\ominus}(Mg)\right) + \left(\Delta H_{at}^{\ominus}(O)\right) + \left(IE_1\right) + \left(IE_2\right) + \left(EA_1\right) + \left(EA_2\right) + \left(\Delta H_{latt}^{\ominus}\right)$$

$$\therefore \Delta H_{latt}^{\ominus} = \left(\Delta H_f^{\ominus}\right) - \underbrace{\left(EA_1\right) - \left(EA_2\right) - \left(IE_1\right) - \left(IE_2\right) - \left(\Delta H_{at}^{\ominus}(Mg)\right) - \left(\Delta H_{at}^{\ominus}(O)\right)}_{\Delta H_1^{\ominus}}$$

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Examiner Tips and Tricks

Your notes

When constructing Born–Haber cycles, the direction of each enthalpy change is important, but the relative size of the steps does not matter. Do not worry if the steps do not reflect the actual magnitudes of the energy changes.

You do not need to include an energy axis on a Born–Haber cycle. However, you must show the electron(s) in the ionisation step, as omitting them may result in the loss of marks.



Your notes

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Your notes

Calculations Using Born-Haber Cycles

- Once a Born-Haber cycle has been constructed, it is possible to calculate the lattice energy ($\Delta H_{latt}^{\ominus}$) by applying Hess's law and rearranging:

$$\Delta H_f^{\ominus} = \Delta H_{at}^{\ominus} + \Delta H_{at}^{\ominus} + IE + EA + \Delta H_{latt}^{\ominus}$$

- If we simplify this into three terms, this makes the equation easier to see:
  - $\Delta H_{latt}^{\ominus}$
  - $\Delta H_f^{\ominus}$
  - $\Delta H_1^{\ominus}$ (the sum of all of the various enthalpy changes necessary to convert the elements in their standard states to gaseous ions)
- The simplified equation becomes

$$\Delta H_f^{\ominus} = \Delta H_1^{\ominus} + \Delta H_{latt}^{\ominus}$$

So, if we rearrange to calculate the lattice energy, the equation becomes

$$\Delta H_{latt}^{\ominus} = \Delta H_f^{\ominus} - \Delta H_1^{\ominus}$$

- When calculating the $\Delta H_{latt}^{\ominus}$, all other necessary values will be given in the question
- A Born-Haber cycle could be used to calculate any stage in the cycle
  - For example, you could be given the lattice energy and asked to calculate the enthalpy change of formation of the ionic compound
  - The principle would be exactly the same
  - Work out the **direct** and **indirect route** of the cycle (the stage that you are being asked to calculate will always be the direct route)
  - Write out the equation in terms of enthalpy changes and rearrange if necessary to calculate the required value
- **Remember:** sometimes a value may need to be doubled or halved, depending on the ionic solid involved
  - For example, with $MgCl_2$ the value for the first electron affinity of chlorine would need to be doubled in the calculation, because there are two moles of chlorine atoms
  - Therefore, you are adding **2 moles** of electrons to **2 moles** of chlorine atoms, to form **2 moles** of Cl^- ions

Worked Example

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Calculating the lattice energy of KCl Given the data below, calculate the $\Delta H_{latt}^{\ominus}$ of potassium chloride (KCl)

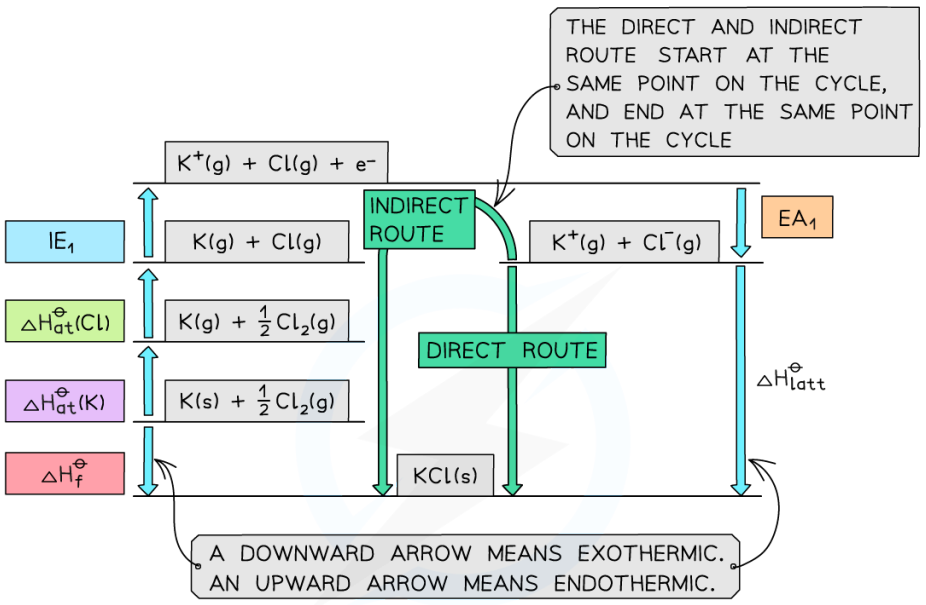
Your notes

	$\Delta H_{at}^{\ominus}$ (kJ mol^{-1})	IE/EA (kJ mol^{-1})
K	+90	+418
Cl	+122	−349
$\Delta H_{f}^{\ominus}$ (kJ mol^{-1})		
KCl	−437	

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Answer

Step 1: The corresponding Born-Haber cycle is:



$$\Delta H_f^{\ominus} = \left(\Delta H_{at}^{\ominus}(K)\right) + \left(\Delta H_{at}^{\ominus}(Cl)\right) + \left(IE_1\right) + \left(EA_1\right) + \left(\Delta H_{latt}^{\ominus}\right)$$

$$\therefore \Delta H_{latt}^{\ominus} = \left(\Delta H_f^{\ominus}\right) - \left(EA_1\right) - \left(IE_1\right) - \left(\Delta H_{at}^{\ominus}(Cl)\right) - \left(\Delta H_{at}^{\ominus}(K)\right)$$

$$\Delta H_1^{\ominus}$$

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Step 2: Applying Hess' law, the lattice energy of KCl is:

$$\Delta H_{latt}^{\ominus} = \Delta H_f^{\ominus} - \Delta H_1^{\ominus}$$

$$\Delta H_{latt}^{\ominus} = \Delta H_f^{\ominus} - [(\Delta H_{at}^{\ominus}\,K) + (\Delta H_{at}^{\ominus}\,Cl) + (IE_1\,K) + (EA_1\,Cl)]$$

Step 3: Substitute in the numbers:

$$\Delta H_{latt}^{\ominus} = (-437) - [(+90) + (+122) + (+418) + (-349)] = -718\ kJ\ mol^{-1}$$

Your notes

Worked Example

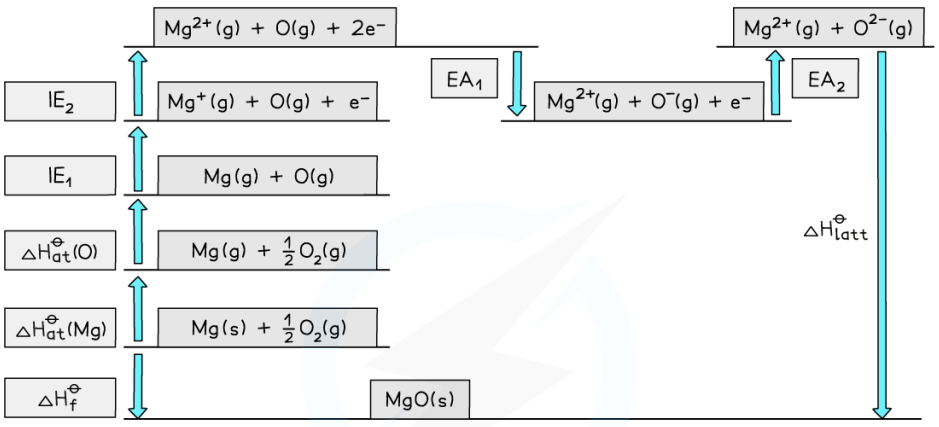
Calculating the lattice energy of MgO Given the data below, calculate the of $\Delta H_{latt}^{\ominus}$ magnesium oxide of magnesium oxide (MgO)

	$\Delta H_{at}^{\ominus}$ (kJ mol^{-1})	IE_1 / EA_1 (kJ mol^{-1})	IE_2 / EA_2 (kJ mol^{-1})
Mg	+148	+736	+1450
O	+248	−142	+770
	$\Delta H_f^{\ominus}$ (kJ mol^{-1})		
MgO	−602		

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Answer

Step 1: The corresponding Born-Haber cycle is:



$$\Delta H_f^{\ominus} = \left(\Delta H_{at}^{\ominus}(Mg)\right) + \left(\Delta H_{at}^{\ominus}(O)\right) + \left(IE_1\right) + \left(IE_2\right) + \left(EA_1\right) + \left(EA_2\right) + \left(\Delta H_{latt}^{\ominus}\right)$$

$$\therefore \Delta H_{latt}^{\ominus} = \left(\Delta H_f^{\ominus}\right) - \underbrace{\left(EA_1\right) - \left(EA_2\right) - \left(IE_1\right) - \left(IE_2\right) - \left(\Delta H_{at}^{\ominus}(Mg)\right) - \left(\Delta H_{at}^{\ominus}(O)\right)}_{\Delta H_1^{\ominus}}$$

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Step 2: Applying Hess' law, the lattice energy of MgO is:

$$\Delta H_{latt}^{\ominus} = \Delta H_f^{\ominus} - \Delta H_1^{\ominus}$$

$$\Delta H_{latt}^{\ominus} = \Delta H_f^{\ominus} - [(\Delta H_{at}^{\ominus}\,\text{Mg}) + (\Delta H_{at}^{\ominus}\,\text{O}) + (\text{IE}_1\,\text{Mg}) + (IE_2\,\text{Mg}) + (EA_1\,\text{O}) + (EA_2\,\text{O})]$$

Step 3: Substitute in the numbers:

$$\Delta H_{latt}^{\ominus} = (-602) - [(+148) + (+248) + (+736) + (+1450) + (-142) + (+770)]$$

$$= -3812\ \text{kJ mol}^{-1}$$

Examiner Tips and Tricks

Make sure you use brackets when carrying out calculations using Born-Haber cycles as you may forget a +/- sign which will affect your final answer!

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Comparing Lattice Enthalpies

How accurate are lattice enthalpies?

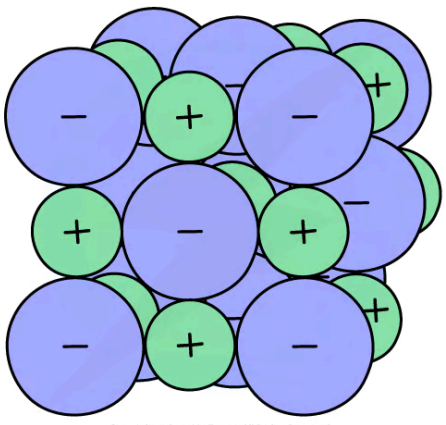
- It is possible to calculate a theoretical value for the lattice enthalpy of an ionic solid. To do this you need to know
  - the **geometry** of the ionic solid
  - the **charge** on the ions
  - the **distance** between the ions
- This has been calculated for a number of ionic solids and allows a comparison between theoretical lattice enthalpies and experimental lattice enthalpies obtained from Born-Haber cycles

Table comparing theoretical and experimental lattice enthalpies

Substance	Theoretical lattice enthalpy/kJ mol^{-1}	Experimental lattice enthalpy/kJmol^{-1}	% difference
NaCl	769	790	2.7
ZnS	3427	3615	5.5

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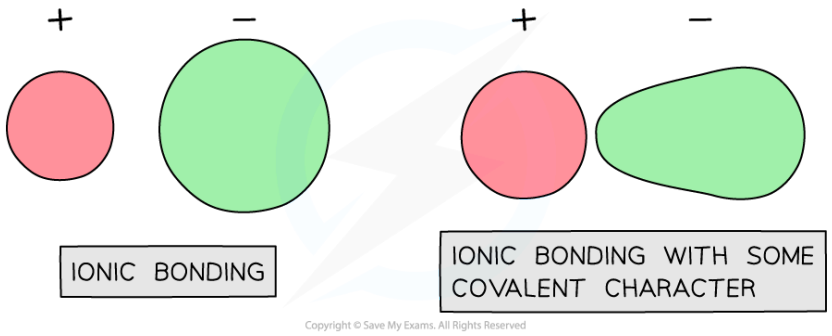
- You can see from the table that there is quite **close agreement** between the two values for the lattice enthalpy of **sodium chloride**
- The calculation of the theoretical value is based on an assumption that the substance is a highly ionic compound with only **electrostatic attraction** between **cations** and **anions**



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The ionic model for sodium chloride

- However, the difference between theoretical and experimental lattice enthalpy increases for zinc sulfide
- This suggests that the bonding is not purely ionic and some **covalent character** is present
- This can be explained as follows:
  - Zinc is a **smaller ion** with a **greater charge**(+2) than sodium(+1)
  - Zinc ions attract electron density towards themselves, distorting the electron cloud and making the bonding slightly covalent
  - Sulfide ions are **larger ions** than chloride ions(-1) with a **greater negative charge**(-2)
  - The electron cloud around sulfide ions is more easily distorted than in chloride ions leading to further covalent character



Covalent character in ionic compounds

- As you move left to right across the period table the lattices become **less ionic** and **more covalent l**eading to a discrepancy in the lattice enthalpy values
- The result of these analyses provides strong evidence that supports the **ionic model** for some compounds like sodium chloride

Examiner Tips and Tricks

The distortion of the electron clouds is known as polarisation and illustrates that bonding is not either pure ionic or covalent, but rather a continuum between the two extremes.

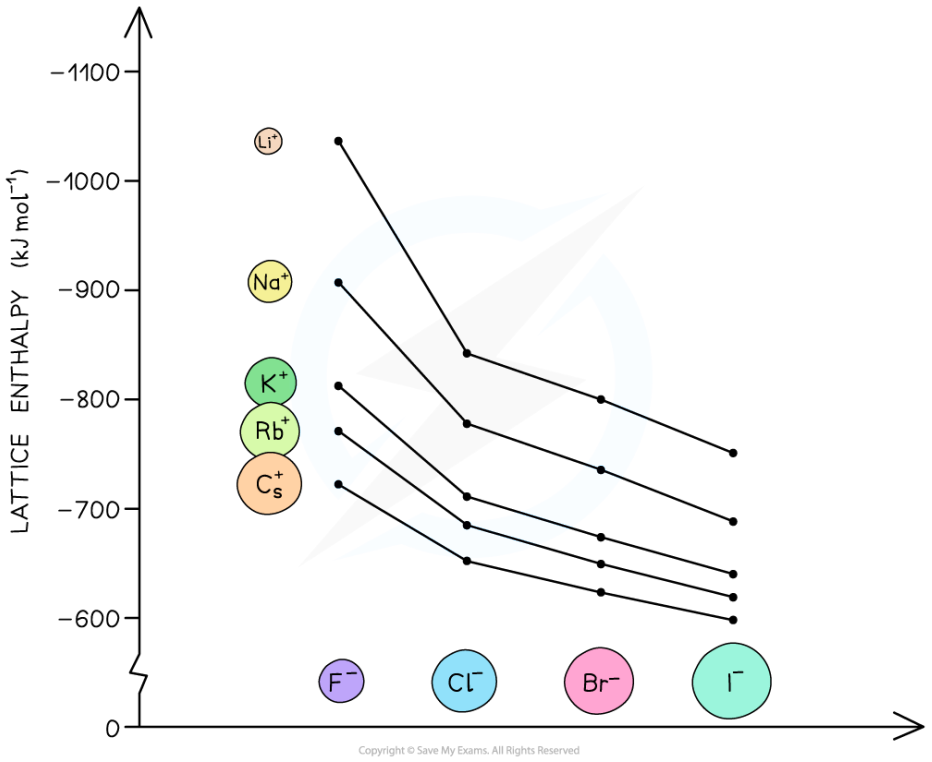
Factors affecting lattice enthalpy

- The two key factors which affect lattice energy, $\Delta H_{latt}^{\ominus}$, are the **charge** and **radius** of the ions that make up the **crystalline lattice**

Ionic radius

Your notes

- The lattice energy becomes **less exothermic** as the **ionic radius** of the ions **increases**
- This is because the charge on the ions is more **spread out** over the ion when the ions are **larger**
- The ions are also **further apart** from each other in the lattice
  - The attraction between ions is between the centres of the ions involved, so the bigger the ions the bigger the distance between the centre of the ions
- Therefore, the **electrostatic forces of attraction** between the oppositely charged ions in the lattice are **weaker**
- For example, the lattice energy of caesium fluoride (CsF) is **less exothermic** than the lattice energy of potassium fluoride (KF)
  - Since both compounds contain a fluoride (F^-) ion, the difference in lattice energy must be due to the caesium (Cs^+) ion in CsF and potassium (K^+) ion in KF
  - Potassium is a Group 1 and Period 4 element
  - Caesium is a Group 1 and Period 6 element
  - This means that the Cs^+ ion is **larger** than the K^+ ion
  - There are **weaker** electrostatic forces of attraction between the Cs^+ and F^- ions compared to K^+ and F^- ions
  - As a result, the **lattice energy** of CsF is **less exothermic** than that of KF



The lattice energies get less exothermic as the ionic radius of the ions increases

Your notes

Ionic charge



Your notes

- The lattice energy gets **more exothermic** as the **ionic charge** of the ions **increases**
- The greater the ionic charge, the **higher the charge density**
- This results in **stronger electrostatic attraction** between the oppositely charged ions in the lattice
- As a result, the lattice energy is **more exothermic**
- For example, the lattice energy of calcium oxide (CaO) is **more exothermic** than the lattice energy of potassium chloride (KCl)
  - Calcium oxide is an ionic compound which consists of calcium (Ca^{2+}) and oxide (O^{2-}) ions
  - Potassium chloride is formed from potassium (K^{+}) and chloride (Cl^{-}) ions
  - The ions in calcium oxide have a **greater ionic charge** than the ions in potassium chloride
  - This means that the electrostatic forces of attraction are **stronger** between the Ca^{2+} and O^{2-} compared to the forces between K^{+} and Cl^{-}
  - Therefore, the lattice energy of calcium oxide is **more exothermic,** as more energy is released upon its formation from its gaseous ions
  - Ca^{2+} and O^{2-} are also smaller ions than K^{+} and Cl^{-}, so this also adds to the value for the lattice energy being more exothermic

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Your notes

Solution & Hydration

Enthalpy of solution

- The **standard enthalpy change of solution** (ΔH_{sol}^{θ}) is the enthalpy change that occurs when **one mole** of an ionic substance dissolves in sufficient water to form an **infinitely dilute solution**
- The symbol **(aq)** is used to show that the substance is dissolved in a large excess of water
- For example, the enthalpy change of solution for potassium chloride can be represented by either of the following equations:

$$KCl(s) + aq \rightarrow KCl(aq)$$

OR

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

- The standard enthalpy change of solution can be **exothermic** (negative) or **endothermic** (positive)

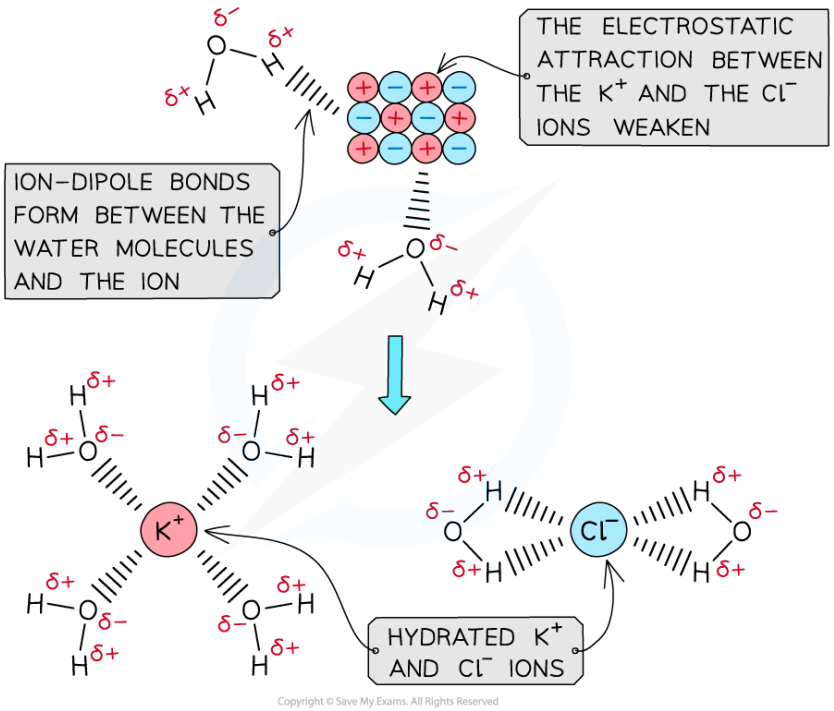
Enthalpy of hydration

- The **standard enthalpy change of hydration** (ΔH_{hyd}^{θ}) is the enthalpy change when **one mole** of a specified gaseous ion dissolves in sufficient water to form an **infinitely dilute solution**
  - For example, the enthalpy change of hydration for magnesium ions is represented by the equation:

$$Mg^{2+}(g) + aq \rightarrow Mg^{2+}(aq)$$

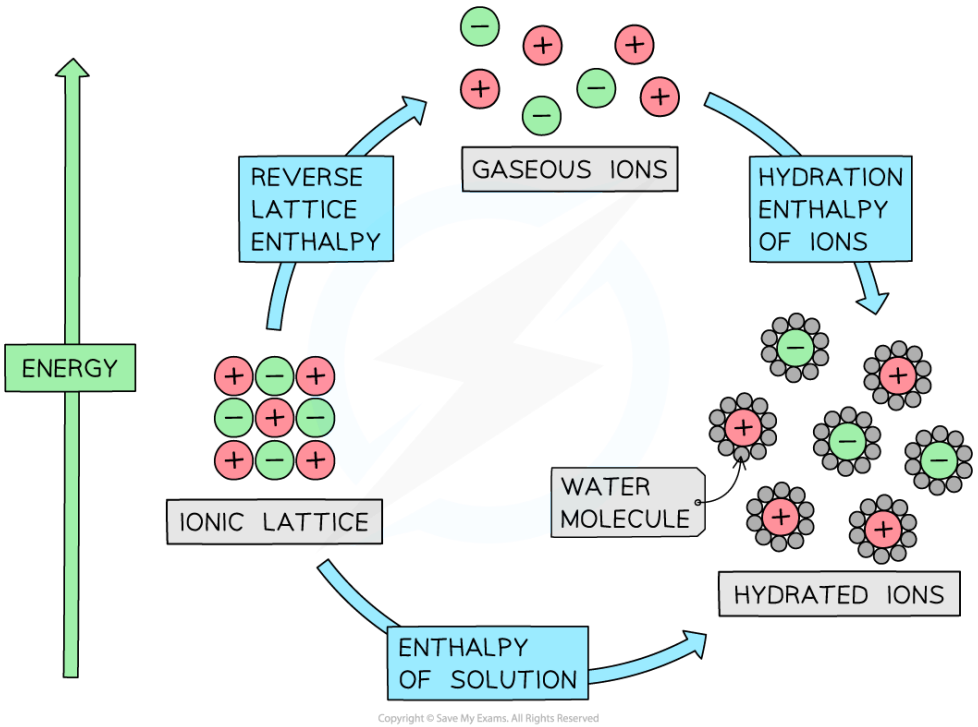
- Hydration enthalpies measure the energy released when attractions form between ions and water molecules
  - These enthalpy changes are always **exothermic**
- When an **ionic solid** dissolves in water, positive and negative ions are formed
- Water is a polar molecule, with a δ^- oxygen atom and δ^+ hydrogen atoms, which form **ion–dipole attractions** with the ions in solution.
- The oxygen atoms are attracted t**o positive ions**, while the hydrogen atoms are attracted to **negative ions**

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The polar water molecules will form ion–dipole bonds

How are the enthalpies of solution and hydration related?



The relationship between lattice enthalpy, hydration enthalpies and enthalpy of solution

- From the diagram, we can see that the relationship is

Your notes

Enthalpy of solution = reverse lattice enthalpy* + hydration enthalpy

- The hydration enthalpy is the **sum** of the hydration enthalpies of each ion
- If there is more than one cation or anion, such as in $MgCl_2$, then you must multiply by the appropriate coefficient for that ion



Examiner Tips and Tricks

* This exam board uses the term 'lattice energy' for formation and dissolution in equal measure, so the term reverse lattice enthalpy here means the reverse of lattice *formation* enthalpy. It could also be termed lattice dissociation enthalpy here.

Calculating Enthalpy Changes

- Questions on this topic often require you to calculate the hydration enthalpy of one ion, given the lattice enthalpy, the enthalpy of solution, and the hydration enthalpy of the other ion
- This can be done by constructing an appropriate energy cycle and applying Hess's Law to determine the unknown enthalpy change
- The energy cycle above shows that there are two possible routes from gaseous ions to ions in aqueous solution
  - **Route 1 (indirect route):** gaseous ions → ionic solid → ions in aqueous solution
  - **Route 2 (direct route):** gaseous ions → ions in aqueous solution
- According to Hess's Law, the total enthalpy change for both routes is the same, so:

$$\Delta H_{hyd}^{\theta} = \Delta H_{latt}^{\theta} + \Delta H_{sol}^{\theta}$$

- Each ion will have its own enthalpy change of hydration, ΔH_{hyd}^{θ}, which will need to be taken into account during calculations
  - The total ΔH_{hyd}^{θ} is found by adding the ΔH_{hyd}^{θ} values of both anions and cations together



Worked Example

Calculate the enthalpy of hydration of the chloride ion, given the following data:

ΔH_{latt}^{θ} [KCl] = -711 kJ mol^{-1}

ΔH_{sol}^{θ} [KCl] = +26 kJ mol^{-1}

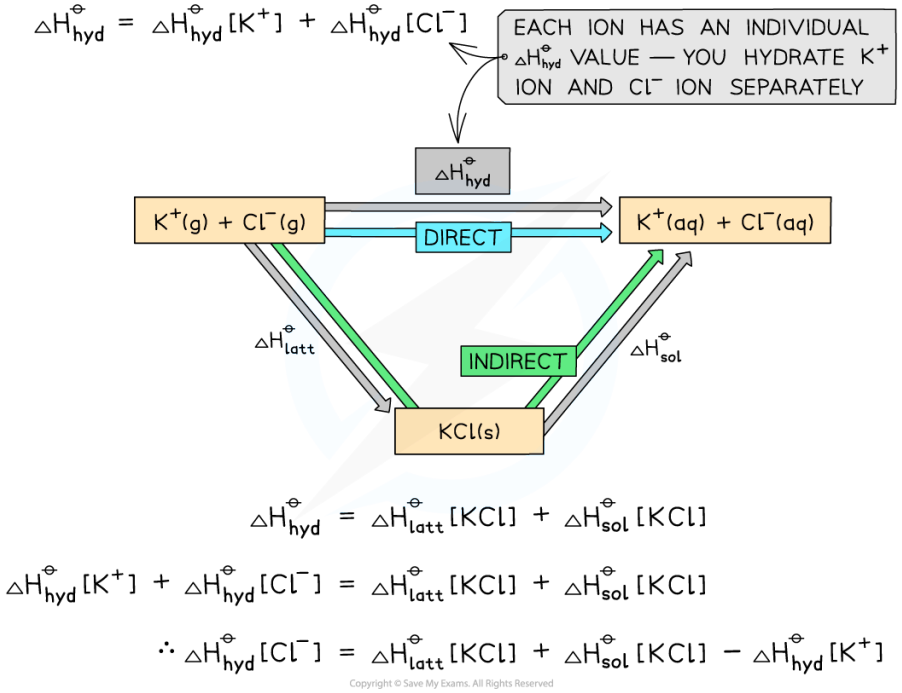
Your notes

$\Delta H_{hyd}^{\theta}[K^+] = -322\ kJ\ mol^{-1}$

Your notes

Answer

Step 1: Draw the energy cycle and make $\Delta H_{hyd}^{\ominus}[Cl^-]$ the subject of the formula:



$$\triangle H^{\ominus}_{hyd} = \triangle H^{\ominus}_{latt}[KCl] + \triangle H^{\ominus}_{sol}[KCl]$$

$$\triangle H^{\ominus}_{hyd}[K^+] + \triangle H^{\ominus}_{hyd}[Cl^-] = \triangle H^{\ominus}_{latt}[KCl] + \triangle H^{\ominus}_{sol}[KCl]$$

$$\therefore \triangle H^{\ominus}_{hyd}[Cl^-] = \triangle H^{\ominus}_{latt}[KCl] + \triangle H^{\ominus}_{sol}[KCl] - \triangle H^{\ominus}_{hyd}[K^+]$$

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Step 2: Substitute the values to find $\Delta H_{hyd}^{\theta}[Cl^-]$

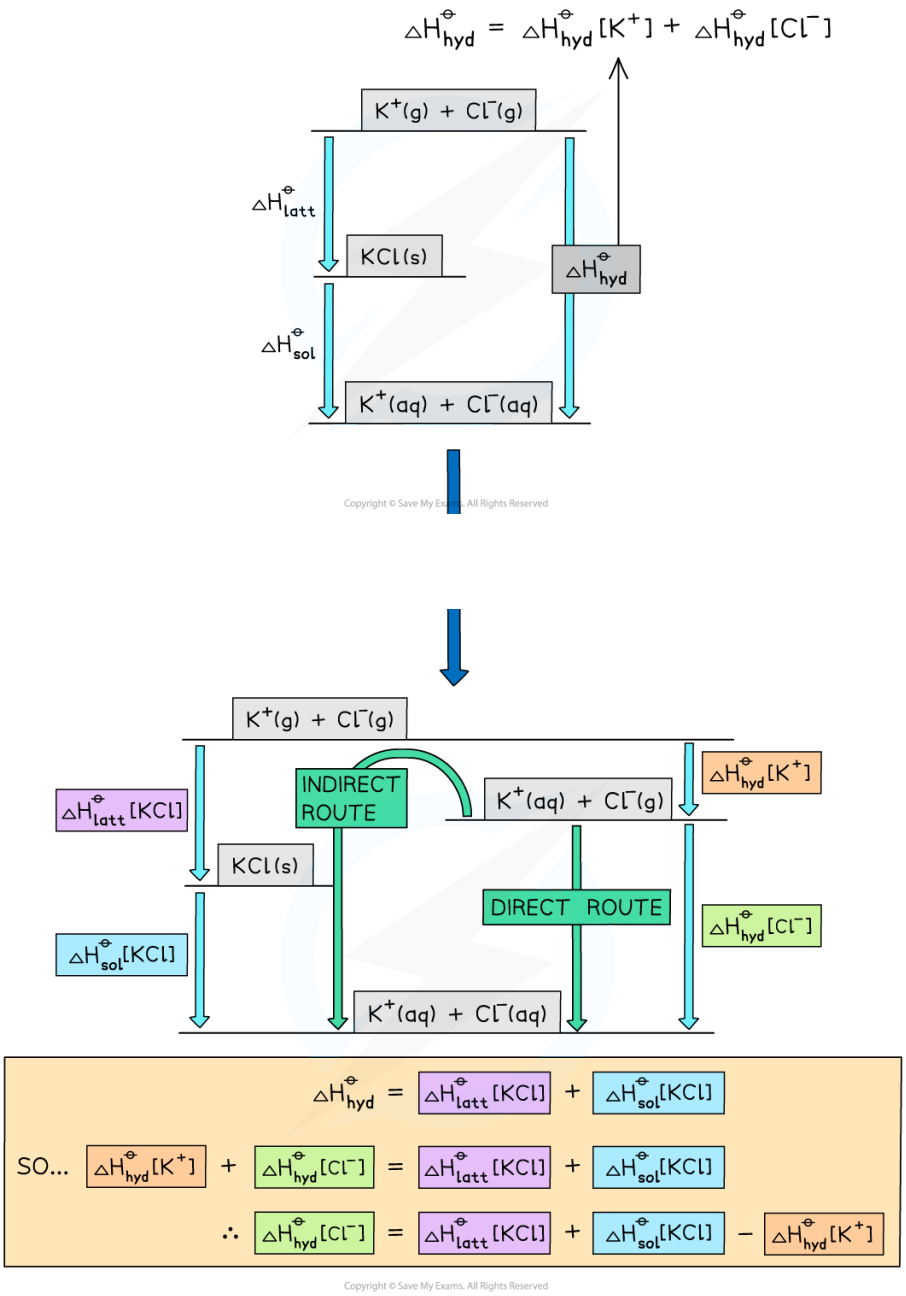
$$\Delta H_{hyd}^{\theta}[Cl^-] = (-711) + (+26) - (-322) = \mathbf{-363\ kJ\ mol^{-1}}$$

Alternative Diagram

- You can also draw a Born-Haber cycle as an alternative approach to the same problem

Energy level diagram:

Your notes



Worked Example

Construct an energy cycle to calculate the ΔH_{hyd}^{θ} of magnesium ions in magnesium chloride, given the following data:

ΔH_{latt}^{θ} [$MgCl_2$] = -2592 kJ mol^{-1}

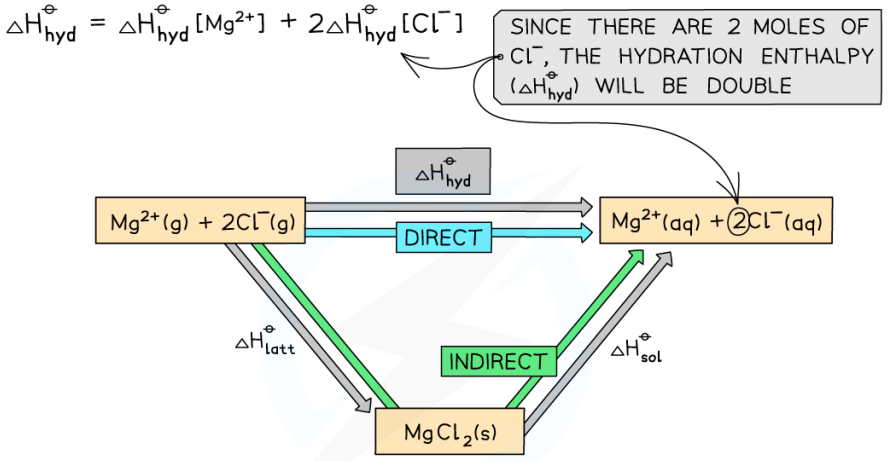
ΔH_{sol}^{θ} [$MgCl_2$] = -55 kJ mol^{-1}

ΔH_{hyd}^{θ} [Cl^-] = -363 kJ mol^{-1}

Your notes

Answer

Step 1: Draw an energy cycle:



$$\triangle H_{hyd}^{\ominus} = \triangle H_{latt}^{\ominus}[MgCl_2] + \triangle H_{sol}^{\ominus}[MgCl_2]$$

$$\triangle H_{hyd}^{\ominus}[Mg^{2+}] + 2\triangle H_{hyd}^{\ominus}[Cl^-] = \triangle H_{latt}^{\ominus}[MgCl_2] + \triangle H_{sol}^{\ominus}[MgCl_2]$$

$$\therefore \triangle H_{hyd}^{\ominus}[Mg^{2+}] = \triangle H_{latt}^{\ominus}[MgCl_2] + \triangle H_{sol}^{\ominus}[MgCl_2] - 2\triangle H_{hyd}^{\ominus}[Cl^-]$$

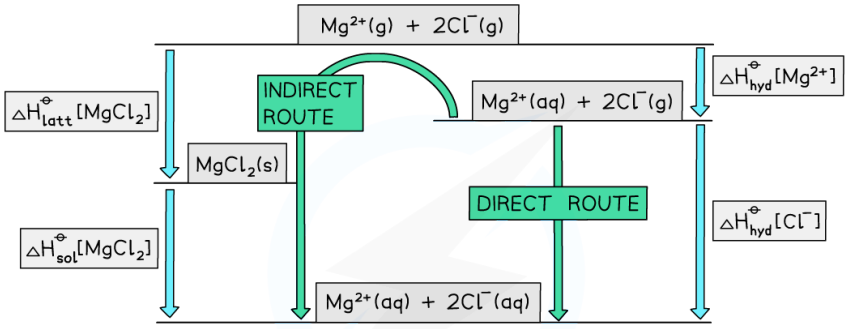
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Step 2: Substitute the values to find ΔH_{hyd}^{θ} [Mg^{2+}]

$$\Delta H_{hyd}^{\theta}[Mg^{2+}] = (-2592) + (-55) - (2 \times -363) = \mathbf{-1921\ kJ\ mol^{-1}}$$

Alternative solution

- Here is the same solution using a Born-Haber cycle



$$\triangle H_{hyd}^{\ominus} = \triangle H_{latt}^{\ominus}[MgCl_2] + \triangle H_{sol}^{\ominus}[MgCl_2]$$

$$\triangle H_{hyd}^{\ominus}[Mg^{2+}] + 2\triangle H_{hyd}^{\ominus}[Cl^-] = \triangle H_{latt}^{\ominus}[MgCl_2] + \triangle H_{sol}^{\ominus}[MgCl_2]$$

$$\triangle H_{hyd}^{\ominus}[Mg^{2+}] = \triangle H_{latt}^{\ominus}[MgCl_2] + \triangle H_{sol}^{\ominus}[MgCl_2] - 2\triangle H_{hyd}^{\ominus}[Cl^-]$$

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Examiner Tips and Tricks

It does not matter whether you use Hess cycles or Born–Haber style cycles to solve these problems, as long as the information is correctly labelled and the arrow directions match the definitions.

Exam questions in this topic often include diagrams with missing labels, which you must complete before calculating unknown values.

The key to success in energy cycle calculations is to stay calm and work step by step: label each enthalpy change carefully, show your working clearly, and use brackets to separate mathematical operations from the enthalpy changes.

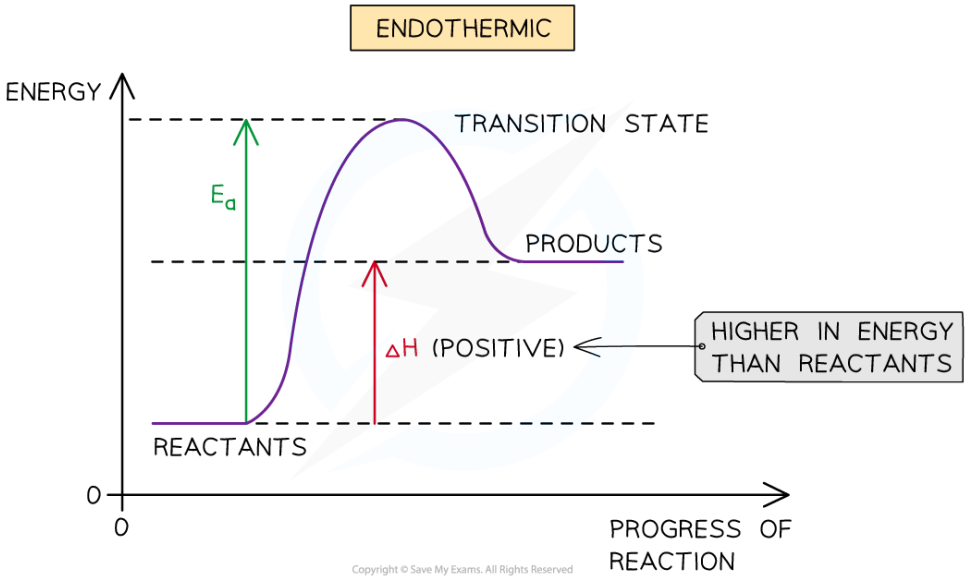
Your notes

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Your notes

Entropy

- You may have wondered why it is that **endothermic** reactions occur at all, after all, what can be the driving force behind endothermic reactions if the products end up in a less stable, higher energy state?
- Although the majority of chemical reactions we experience everyday are **exothermic**, $\Delta H^{\ominus}$ alone is not enough to explain why endothermic reactions occur



The driving force behind chemical reactions cannot be explained by enthalpy changes alone as it makes not sense for chemical to end up in a less stable higher energy state in endothermic reactions

- The answer is **entropy**

Chaos in the universe

- The **entropy (S)** of a given system is the number of possible arrangements of the particles and their energy in a given system
  - In other words, it is a measure of how **disordered** or **chaotic** a system is
- When a system becomes **more disordered**, its entropy will **increase**
- An increase in entropy means that the system becomes **energetically more stable**
- For example, during the thermal decomposition of calcium carbonate ($CaCO_3$) the entropy of the system increases:

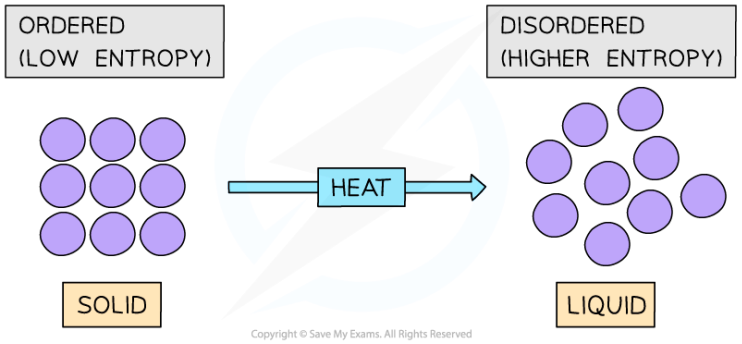
$$\mathbf{CaCO_3(s) \rightarrow CaO(s) + CO_2(g)}$$

- In this decomposition reaction, a gas molecule (CO_2) is formed

- The CO_2 gas molecule is more disordered than the solid reactant ($CaCO_3$), as it is constantly moving around
- As a result, the system has become more **disordered** and there is an **increase** in **entropy**
- Another typical example of a system that becomes more disordered is when a solid is **melted**
- For example, melting ice to form liquid water:

$$H_2O(s) \rightarrow H_2O(l)$$

- The water molecules in ice are in fixed positions and can only vibrate about those positions
- In the liquid state, the particles are still quite close together but are arranged more randomly, in that they can move around each other
- Water molecules in the liquid state are therefore more **disordered**
- Thus, for a given substance, the **entropy increases** when its solid form melts into a liquid
- In both examples, the system with the **higher entropy** will be **energetically favourable** (as the energy of the system is more spread out when it is in a disordered state)



Melting a solid will cause the particles to become more disordered resulting in a higher entropy state

Feasible or spontaneous reactions

- Chemists talk about reactions being **feasible** or **spontaneous**
- What they mean is that reactions take place of their own accord, in other words, they are energetically favourable
- This is an outcome of the **second law of thermodynamics** which broadly states the the entropy of the universe is always increasing
- We can see examples of this all around us:
  - cups fall off tables and spontaneously break into many pieces, never the other way around

Your notes

- hot objects always cool and spread their heat into the surroundings, never the other way around
- Earthquakes destroy buildings and create chaos and disorder
- When living things die they decompose and change from complex ordered systems into disordered simple molecules

- However, **feasibility** takes no account of the **rate of reaction** and states only what is possible, not what actually happens. A feasible reaction might be incredibly slow, such as the rusting of iron.



Examiner Tips and Tricks

Make sure you don't confuse the system with your surroundings!The system consists of the molecules that are reacting in a chemical reaction.The surroundings are everything else such as the solvent, the air around the reaction, test-tube, etc.

Calculating Entropy Changes

- Entropy changes are an order of magnitude smaller than enthalpy changes, so entropy is measured in joules rather than kilojoules. The full unit for entropy is $\mathbf{J\,K^{-1}\,mol^{-1}}$
- The standard entropy change ($\Delta S_{system}^{\ominus}$) for a given reaction can be calculated using the standard entropies ($S^{\ominus}$) of the reactants and products
- The equation to calculate the standard entropy change of a system is:

$$\Delta S_{system}^{\ominus} = \Sigma \Delta S_{products}^{\ominus} - \Sigma \Delta S_{reactants}^{\ominus}$$

(where Σ = sum of)

- For example, the standard entropy change for the formation of ammonia (NH_3) from nitrogen (N_2) and hydrogen (H_2) can be calculated using this equation

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$\Delta S_{system}^{\ominus} = (2 \times \Delta S^{\ominus}(NH_3)) - (\Delta S^{\ominus}(N_2) + 3 \times \Delta S^{\ominus}(H_2))$$

- Notice that, unlike enthalpy of formation for elements, entropy for elements is **not** zero and you can find entropy values for elements and compounds in data books



Worked Example

Calculating entropy changes Calculate the entropy change of the system for the following reaction:

$\mathbf{2Mg\,(s) + O_2\,(g) \rightarrow 2MgO\,(s)}$

$S^{\ominus}[Mg(s)] = 32.60\ J\,K^{-1}\,mol^{-1}$

$S^{\ominus}[O_2(g)] = 205.0\ J\,K^{-1}\,mol^{-1}$

Your notes

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$S^{\ominus}[MgO(s)] = 38.20\ J\ K^{-1}\ mol^{-1}$

Answer

$\Delta S_{system}^{\ominus} = \Sigma \Delta S_{products}^{\ominus} - \Sigma \Delta S_{reactants}^{\ominus}$

$\Delta S_{system}^{\ominus} = (2 \times 38.20) - (2 \times 32.60 + 205.0)$

$= \mathbf{-193.8\ J\ K^{-1}\ mol^{-1}}$



Examiner Tips and Tricks

Use the **stoichiometry** of the equation and the correct state of the compounds when calculating the entropy change of a reaction.



Your notes

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Your notes

Gibbs Free Energy

- The thermodynamic feasibility of a reaction depends on two factors: the enthalpy change (ΔH) and the entropy change (ΔS)
- These factors are combined in the Gibbs free energy change, ΔG, which determines whether a reaction is thermodynamically feasible under standard conditions
- The Gibbs equation is:

$$\Delta G^{\ominus} = \Delta H_{reaction}^{\ominus} - T\Delta S_{system}^{\ominus}$$

Where:

$\Delta G^{\ominus}$ is the standard Gibbs free energy change (kJ mol^{-1})

$\Delta H_{reaction}^{\ominus}$ is the standard enthalpy change (kJ mol^{-1})

T is the temperature in kelvin (K)

$\Delta S_{system}^{\ominus}$ is the standard entropy change (J K^{-1} mol^{-1})

- Because ΔH° is given in kJ mol^{-1} and ΔS° is usually given in J K^{-1} mol^{-1}, the entropy value must be converted to kJ K^{-1} mol^{-1} (by dividing by 1000) before substituting into the equation

Calculating $\Delta G^{\ominus}$

- There are two ways you can calculate the value of $\Delta G^{\ominus}$
  - From $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ values
  - From the $\Delta G^{\ominus}$ values of all the substances present

Worked Example

Calculate the free energy change for the following reaction:

$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(l) + CO_2(g)$

$\Delta H^{\ominus} = +135\ kJ\ mol^{-1}$ $\Delta S^{\ominus} = +344\ J\ K^{-1}\ mol^{-1}$

Answer

Step 1: Convert the entropy value in kilojoules

$\Delta S^{\ominus} = +344\ J\ K^{-1}\ mol^{-1} \div 1000 = +0.344\ kJ\ K^{-1}\ mol^{-1}$

Step 2: Substitute the terms into the Gibbs Equation

$\Delta G^{\ominus} = \Delta H_{reaction}^{\ominus} - T\Delta S_{system}^{\ominus}$

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= +135 - (298 x 0.344)

= **+32.49 kJ mol^{-1}**

The temperature is 298 K since standard values are quoted in the question



Worked Example

What is the standard free energy change, $\Delta G^{\ominus}$, for the following reaction?

$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$

Substance	$\Delta G^{\ominus}$ in kJ mol^{-1}
C_2H_5OH (l)	-175
O_2 (g)	0
CO_2 (g)	-394
H_2O (g)	-229

Answer

$\Delta G^{\ominus} = \Sigma \Delta G_{products}^{\ominus} - \Sigma \Delta G_{reactants}^{\ominus}$

$\Delta G^{\ominus} = [(2 \times CO_2) + (3 \times H_2O)] - [(C_2H_5OH) + (3 \times O_2)]$

$\Delta G^{\ominus} = [(2 \times -394) + (3 \times -229)] - [-175 + 0]$

$\Delta G^{\ominus} =$ **-1300 kJ mol^{-1}**



Examiner Tips and Tricks

The idea of free energy is what's left over to do useful work when you've carried out the reaction. The enthalpy change is the difference between the energy you put in to break the chemical bonds and the energy out when making new bonds; the entropy change is the 'cost' of carrying out the reaction, so free energy is what you are left with!



Your notes

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Your notes

Reaction Feasibility

- The Gibbs equation can be used to calculate whether a reaction is **feasible** or not

$$\Delta G^{\ominus} = \Delta H_{reaction}^{\ominus} - T\Delta S_{system}^{\ominus}$$

- When $\Delta G^{\ominus}$ is **negative**, the reaction is **feasible** and likely to occur
- When $\Delta G^{\ominus}$ is **positive**, the reaction is **not feasible** and unlikely to occur
- **Feasible** and **spontaneous** are fairly similar terms to describe reactions
  - Feasible tends to be used to describe reactions which are energetically favourable, so *reactions that should go*
  - Spontaneous tends to be used to describe *reactions that go of their own accord*

Summary for temperature and Gibbs free energy

If ΔH...	And if ΔS...	Then ΔG is...	Spontaneous...	Because
Is negative < 0 exothermic	Is positive > 0 More disorder	Always negative < 0	Always	Forward reaction spontaneous at any T
Is positive > 0 endothermic	Is negative < 0 More order	Always positive > 0	Never	Reverse reaction spontaneous at any T
Is negative < 0 exothermic	Is negative < 0 More order	Negative at low T Positive at high T	Depending on T	Spontaneous only at low T TΔS < H
Is positive > 0 endothermic	Is positive > 0 More disorder	Negative at high T Positive at low T	Depending on T	Spontaneous only at high T TΔS > H

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Worked Example

Determining the feasibility of a reaction Calculate the Gibbs free energy change for the following reaction at 298 K and determine whether the reaction is feasible.

$2Ca\,(s) + O_2\,(g) \rightarrow 2CaO\,(s)$ $\Delta H = -635.5\ kJ\ mol^{-1}$

$S^{\ominus}[Ca(s)] = 41.00\ J\ K^{-1}\ mol^{-1}$

$S^{\ominus}[O_2(g)] = 205.0\ J\ K^{-1}\ mol^{-1}$

$S^{\ominus}[CaO(s)] = 40.00\ J\ K^{-1}\ mol^{-1}$

Answer

Step 1: Calculate $\Delta S_{system}^{\ominus}$

$\Delta S_{system}^{\ominus} = \Sigma \Delta S_{products}^{\ominus} - \Sigma \Delta S_{reactants}^{\ominus}$

$\Delta S_{system}^{\ominus} = (2 \times \Delta S^{\ominus}[CaO(s)]) - (2 \times \Delta S^{\ominus}[Ca(s)] + \Delta S^{\ominus}[O_2(g)])$

$= (2 \times 40.00) - (2 \times 41.00 + 205.0)$

$= -207.0\ J\ K^{-1}\ mol^{-1}$

Step 2: Convert $\Delta S^{\ominus}$ to $kJ\ K^{-1}\ mol^{-1}$

$= -207.0\ J\ K^{-1}\ mol^{-1} \div 1000 = -0.207\ kJ\ mol^{-1}$

Step 3: Calculate $\Delta G^{\ominus}$

$\Delta G^{\ominus} = \Delta H_{reaction}^{\ominus} - T\Delta S_{system}^{\ominus}$

$= -635.5 - (298 \times -0.207)$

$= \mathbf{-573.8\ kJ\ mol^{-1}}$

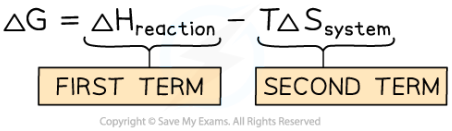
Step 4: Determine whether the reaction is feasible

Since the $\Delta G^{\ominus}$ is **negative** the reaction is **feasible**

Your notes

Reaction Feasibility: Temperature Changes

- The **feasibility** of a reaction can be affected by the **temperature**
- The Gibbs equation will be used to explain what will affect the feasibility of a reaction for exothermic and endothermic reactions

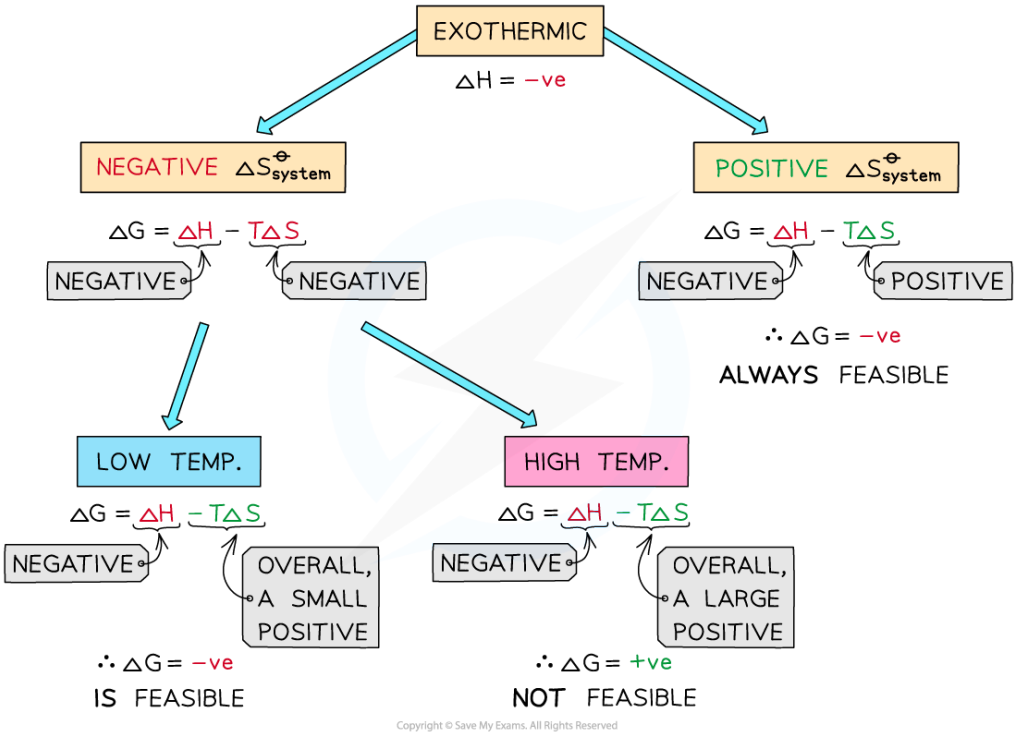


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Exothermic reactions

- In exothermic reactions, $\Delta H_{reaction}^{\ominus}$ is **negative**
- If the $\Delta S_{system}^{\ominus}$ is **positive:**
  - Both the first and second term will be **negative**
  - Resulting in a **negative** $\Delta G^{\ominus}$ so the reaction is **feasible**
  - Therefore, regardless of the temperature, an exothermic reaction with a positive $\Delta S_{system}^{\ominus}$ will **always be feasible**

- If the $\Delta S_{system}^{\ominus}$ is **negative:**
  - The first term is **negative** and the second term is **positive**
  - At very high temperatures, the $-T\Delta S_{system}^{\ominus}$ will be very **large** and **positive** and will overcome $\Delta H_{reaction}^{\ominus}$
  - Therefore, at high temperatures $\Delta G^{\ominus}$ is **positive** and the reaction is **not feasible**
- Since the relative size of an entropy change is much smaller than an enthalpy change, it is unlikely that $T\Delta S > \Delta H$ as temperature increases
- These reactions are therefore usually spontaneous at normal conditions



The diagram shows under which conditions exothermic reactions are feasible

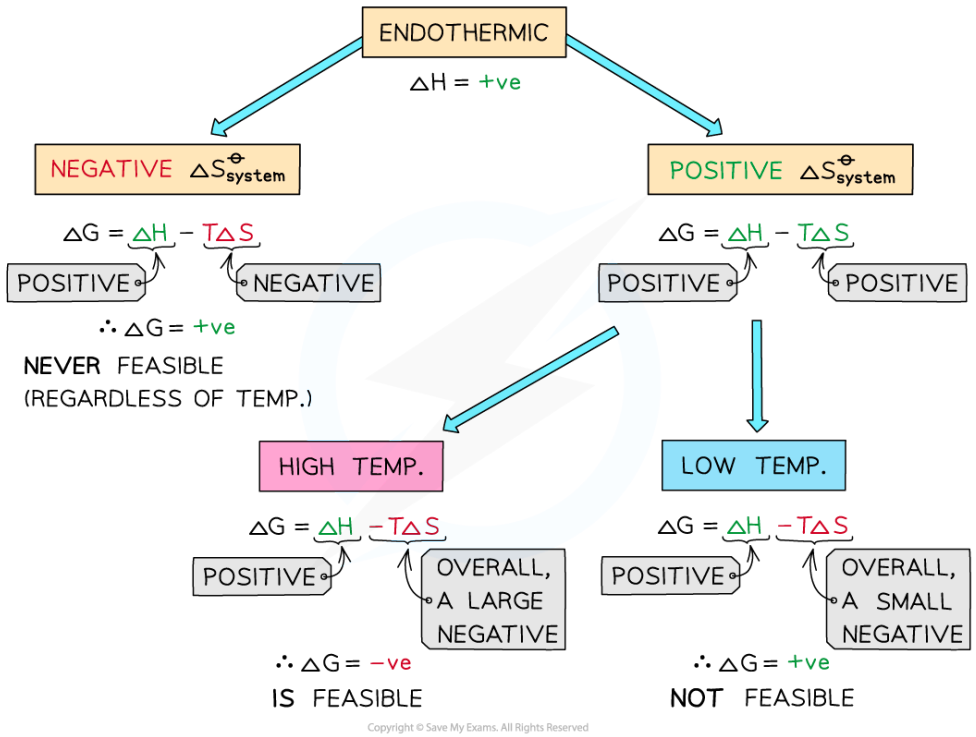
Endothermic reactions

- In endothermic reactions, $\Delta H_{reaction}^{\ominus}$ is **positive**
- If the $\Delta S_{system}^{\ominus}$ is **negative:**
  - Both the first and second term will be **positive**
  - Resulting in a **positive** $\Delta G^{\ominus}$ so the reaction is **not feasible**
  - Therefore, regardless of the temperature, endothermic with a negative $\Delta S_{system}^{\ominus}$ will **never be feasible**
- If the $\Delta S_{system}^{\ominus}$ is **positive:**
  - The first term is **positive** and the second term is **negative**

Your notes

- At low temperatures, the $-T\Delta S_{system}^{\ominus}$ will be **small** and **negative** and will not overcome the larger $\Delta H_{reaction}^{\ominus}$
- Therefore, at low temperatures $\Delta G^{\ominus}$ is **positive** and the reaction is not feasible
- The reaction is **more feasible** at **high temperatures** as the second term will become negative enough to overcome the $\Delta H_{reaction}^{\ominus}$ resulting in a negative $\Delta G^{\ominus}$

- This tells us that for certain reactions which are not feasible at room temperature, they can become feasible at higher temperatures
  - An example of this is found in metal extractions, such as the extraction if iron in the blast furnace, which will be unsuccessful at low temperatures but can occur at higher temperatures (~1500 °C in the case of iron)



The diagram shows under which conditions endothermic reactions are feasible

A summary table of free energy conditions

ΔH	ΔS	As temperature increases	Spontaneous?
negative	positive	makes ΔG more negative	always
negative	negative	unlikely to make TΔS >ΔH	usually
positive	positive	makes TΔS >ΔH	yes, above a certain temperature
positive	negative	no effect: ΔG always positive	never

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Your notes

Free Energy Vs Temperature Graphs



Your notes

- Rearranging the Gibbs equation allows you to determine the temperature at which a non-spontaneous reaction become feasible

$$\Delta G^{\ominus} = \Delta H_{reaction}^{\ominus} - T\Delta S_{system}^{\ominus}$$

- For a reaction to be feasible $\Delta G^{\ominus}$ must be zero or negative

$$0 = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

$$\Delta H^{\ominus} = T\Delta S^{\ominus}$$

$$T = \Delta H^{\ominus} / \Delta S^{\ominus}$$



Worked Example

At what temperature will the reduction of aluminium oxide with carbon become spontaneous?

$Al_2O_3(s) + 3C(s) \rightarrow 2Al(s) + 3CO(g)$ $\quad \Delta H^{\ominus} = +1336\ kJ\ mol^{-1}$ $\quad \Delta S^{\ominus} = +581\ J\ K^{-1}mol^{-1}$

Answer:

If $\Delta G = 0$ then , $T = \Delta H^{\ominus} / \Delta S^{\ominus}$

$T = 1336 \div (581/1000)$

$T = 2299\ K$

Graphing the Gibbs Equation

- The Gibbs equation can be expressed as the equation for a straight line

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

$$\Delta G^{\ominus} = -\Delta S^{\ominus} T + \Delta H^{\ominus}$$

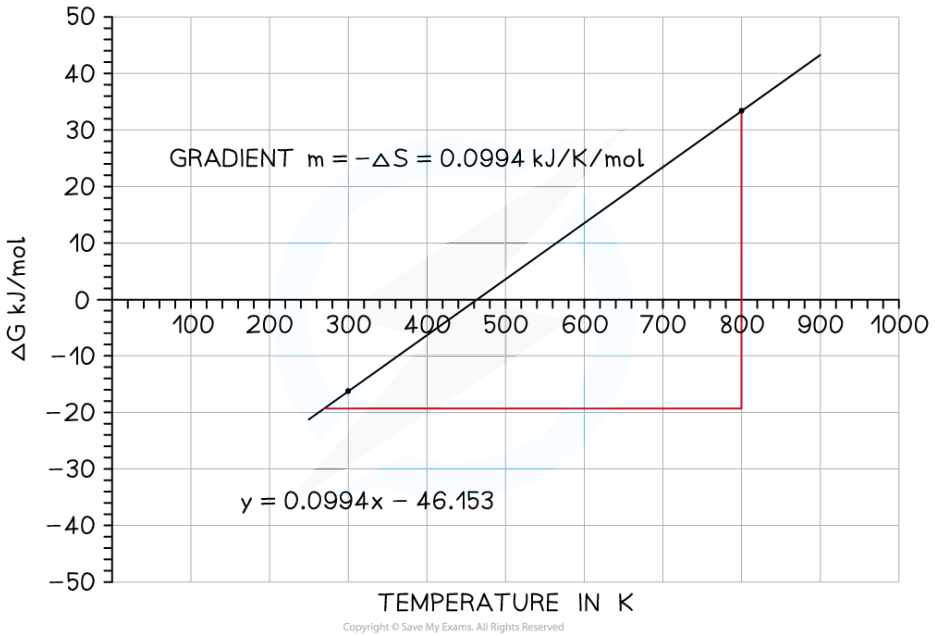
$$y = mx + c$$

- A graph of free energy versus temperature (in K) will give a straight line, with slope $-\Delta S^{\ominus}$ and y-intercept, $\Delta H^{\ominus}$.

- The variation of $\Delta G^{\ominus}$ against T for the synthesis of ammonia has been plotted below:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

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Graph of free energy versus temperature for the synthesis of ammonia

- From this graph you should be able to see some key features:
  - The x-intercept shows you where the reaction ceases to be spontaneous, in this case at 460 K (187 °C)
  - Above this temperature $\Delta G^{\ominus}$ is positive so the reaction is not feasible
    - However, you may recall that the operating conditions of the Haber process are higher than this temperature, but this graph takes no account of the use of a catalyst which affects the energetics of the system, nor does it take into account anything about the rate of reaction or the fact that it is an equilibrium and removal of the ammonia as soon as it is formed also tips the balance in favour of the product
  - The y-intercept shows you reaction is exothermic which you can see from the enthalpy of formation; the value is approximately -46 kJ mol^{-1}
  - An exothermic equilibrium reaction would be favoured by lower temperatures - this is seen by the value of $\Delta G^{\ominus}$ becoming increasingly negative as the temperature falls

Examiner Tips and Tricks

You will notice that the line on the graph does not continue below 240 K. The simple reason for this is that at this point the ammonia will have reached it boiling point and so the gradient would change because it is now liquid ammonia.

Your notes