HL IB Chemistry

Energy Cycles in Reactions

Contents

Bond Enthalpy Calculations

Bond Enthalpy Calculations

- When bonds are broken or made **enthalpy changes** take place
  - A chemical bond is a force of attraction between two atoms
  - Breaking the bond requires the input of energy it is therefore an **endothermic** process

- The energy change required to break the bond depends on the atoms that form the bond
  - The energy required to break a particular bond is called the **bond dissociation enthalpy**
  - This is usually just shortened to **bond enthalpy** or **bond energy**

- Bond formation is the opposite of bond breaking and so energy is released when bonds are formed
  - It is therefore an **exothermic** process

Diagram to show bond breaking and bond making
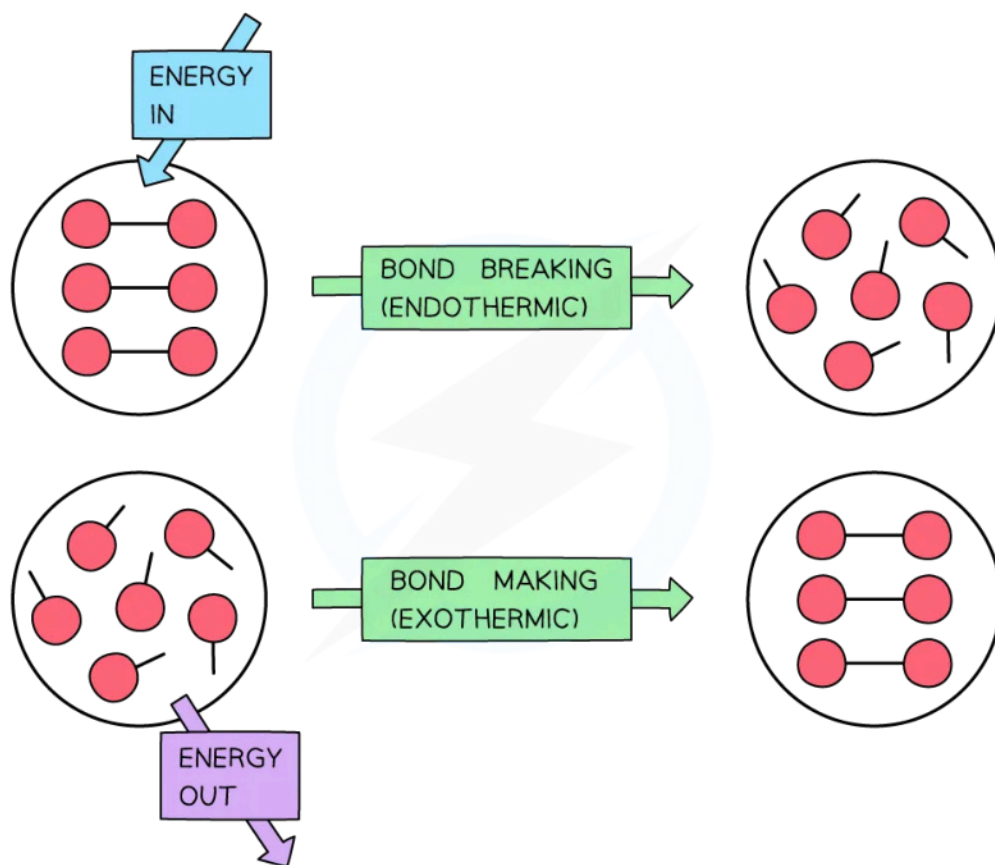
To break bonds energy is required from the surroundings and to make new bonds energy is released from the reaction to the surroundings

Your notes

- The amount of energy released when a particular bond is formed has the same magnitude as the energy taken in when the bond is broken but has the opposite sign

Overall enthalpy changes

- If more energy is released when new bonds are formed than energy is required to break bonds, the reaction is **exothermic**
  - The products are **more stable** than the reactants

- If more energy is required to break bonds than energy is released when new bonds are formed, the reaction is **endothermic**
  - The products are **less stable** than the reactants

- The relationship between bond breaking and bond making can be shown graphically like this:
 **Diagram to show the energy profiles of both exothermic and endothermic reactions**
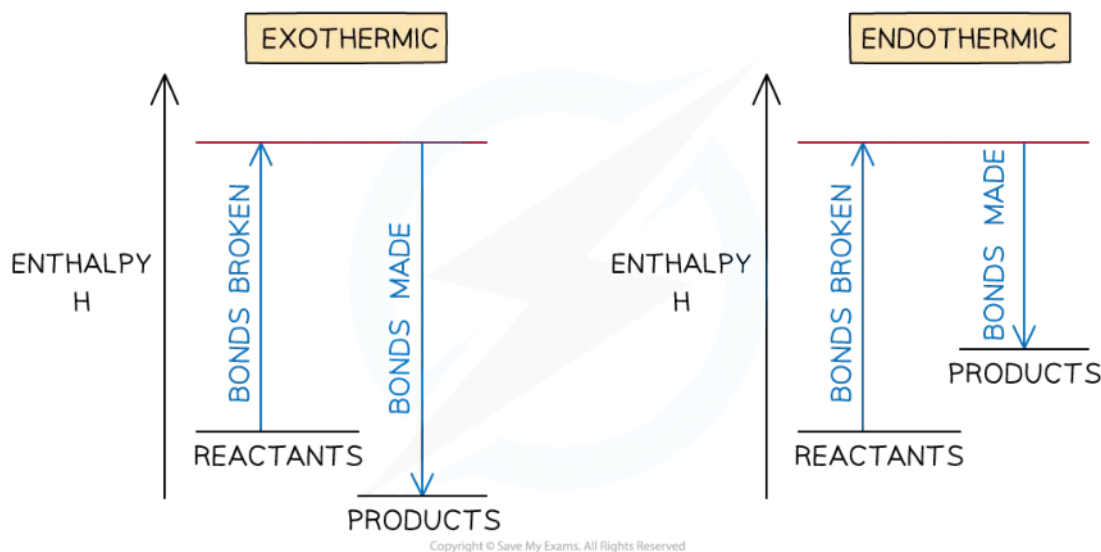
Bond enthalpy profiles

Average bond energy

- Bond energies are affected by other atoms in the molecule (the environment)
- Therefore, an average of a number of the **same type of bond** but in different environments is calculated
- This bond energy is known as the **average bond energy** and is defined as

- 'The energy needed to break one mole of bonds in a gaseous molecule averaged over similar compounds
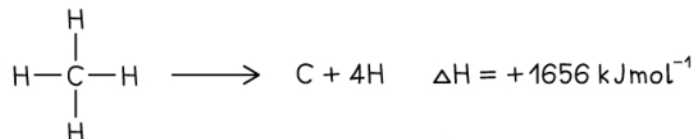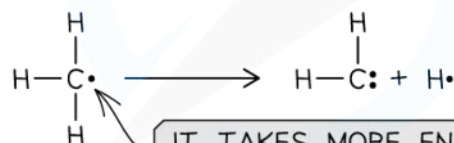

Average bond enthalpy of C–H in methane

- The **average bond enthalpy** of C-H is found by taking the **bond dissociation enthalpy** for the whole molecule and dividing it by the number of C-H bonds
- The first C-H bond is easier to break than the second as the remaining hydrogens are pulled more closely to the carbon
- However, since it is impossible to measure the energy of each C-H bond an average is taken
- This value is also compared with a range of similar compounds to obtain an accepted value for the **average bond enthalpy**

Bond enthalpy calculations

- Bond energies are used to find the $\Delta H^{\ominus}_r$ of a reaction when this cannot be done experimentally
- The process is a step-by-step summation of the bond enthalpies of the all the molecules present finishing with this formula:

$$\Delta H^{\ominus}_r = \text{ENTHALPY CHANGE FOR BONDS BROKEN} + \text{ENTHALPY CHANGE FOR BONDS FORMED}$$

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Formula for calculating the standard enthalpy change of reaction using bond energies

- These two worked examples show how to lay out your calculation
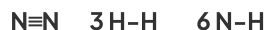
✏️ Worked example

Calculate the enthalpy of reaction for the Haber process reaction.

The relevant bond energies are given in the table below:

Bond	Average Bond Energy (kJ mol^{-1})
N $\equiv$ N	945
H — H	436
N — H	391

Answer:

- **Step 1:** The chemical equation for the Haber process is:

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

    N≡N   3 H–H   6 N–H

- **Step 2:** Set out the calculation as a balance sheet as shown below:

Bonds broken (kJ mol^{-1})	Bonds formed (kJ mol^{-1})
1 x N $\equiv$ N = 1 x 945 = 945	6 N–H = 6 x 391
3 x H — H = 3 x 436 = 1308	
Total = +2253	Total = –2346

Note! Values for bonds broken are positive (endothermic) and values for bonds formed are negative (exothermic)

- **Step 3:** Calculate the standard enthalpy of reaction

$\Delta H_r^{\ominus}$ = **enthalpy change for bonds broken + enthalpy change for bonds formed**

    = (+2253 kJ mol^{-1}) + (–2346 kJ mol^{-1})

    = –93 kJ mol^{-1}

✏️ **Worked example**

The complete combustion of ethyne, C_2H_2, is shown in the equation below:

$2C_2H_2$ (g) $+ 5 O_2$ (g) $\rightarrow$ $2H_2O$ (g) $+ 4CO_2$ (g)
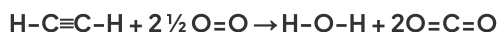
Using the average bond enthalpies given in the table, what is the enthalpy of combustion of ethyne?

Bond	Average Bond Energy (kJ mol^{-1})
C — H	414
C ≡ C	839
O = O	498
C = O	804
O — H	463
O — C	358

Answer:

- **Step 1:** The enthalpy of combustion is the enthalpy change when **one mole** of a substance reacts in excess oxygen to produce water and carbon dioxide

The chemical reaction should be therefore simplified such that only **one mole** of **ethyne** reacts in excess oxygen:

$$H–C≡C–H + 2½ O=O \rightarrow H–O–H + 2O=C=O$$

- **Step 2:** Set out the calculation as a balance sheet as shown below:

Bonds broken (kJ mol^{-1})	Bonds formed (kJ mol^{-1})
2 x CH = 2 x 414= 828 1 x CC= 1 x 839= 839 2½ OO = 2½ x 498 = 1245	2 x OH= 2 x 463 = 926 4 x CO = 4 x 804 = 3216
Total = +2912	**Total= –4142**

$\Delta H^{\ominus}_r$ = enthalpy change for bonds broken + enthalpy change for bonds formed

Your notes

$= (+2912 \text{ kJ mol}^{-1}) + (-4142 \text{ kJ mol}^{-1})$

$= \mathbf{-1230 \text{ kJ mol}^{-1}}$

💡 Examiner Tip

The key to success in bond enthalpy calculations is to be very careful when accounting for every bond present. Always draw out the full displayed structures of the molecules so you don't miss any of the bonds.

Watch out for coefficients in the balanced equations as students often miss those, forget to multiply them by the bond enthalpies and get the answer wrong!

It is super important to show your steps because bond enthalpy calculations often carry 3 marks, 2 of which could be for workings if you get the final answer wrong

Hess's Law

Hess's Law

- In 1840, the Russian chemist Germain Hess formulated a law which went on to be known as **Hess's Law**
- This went on to form the basis of one of the laws of thermodynamics. The first law of thermodynamics relates to the **Law of Conservation of Energy**
- It is sometimes expressed in the following form:

   Energy cannot be created or destroyed, it can only change form

- This means that in a closed system, the total amount of energy present is always constant
- Hess's law can be used to calculate the standard enthalpy change of a reaction from known standard enthalpy changes
- **Hess's Law** states that:

   "The total enthalpy change in a chemical reaction is independent of the route by which the chemical reaction takes place as long as the initial and final conditions are the same."

- This means that whether the reaction takes place in one or two steps, the total enthalpy change of the reaction will still be the same

Diagram to show Hess's Law
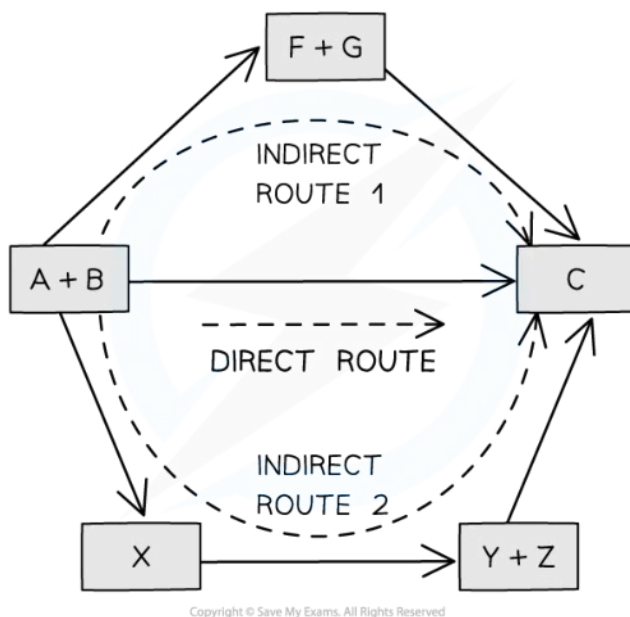
The diagram above illustrates Hess' Law: the enthalpy change of the direct route, going from reactants (A+B) to product (C) is equal to the enthalpy change of the indirect routes

Your notes

- Hess' Law is used to calculate enthalpy changes which can't be found experimentally using **calorimetry**, eg:
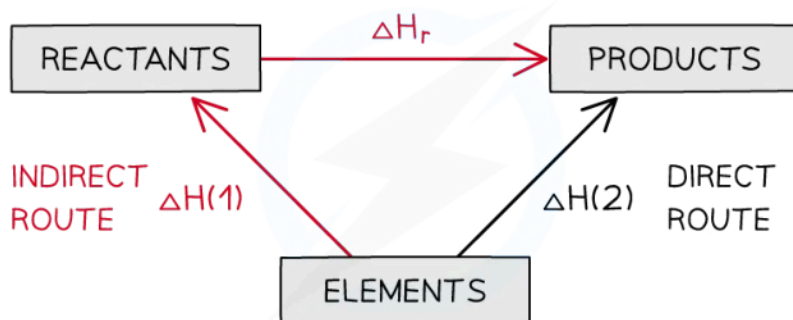
$$3C\,(s) + 4H_2\,(g) \rightarrow C_3H_8(g)$$

- ΔH_f (propane) can't be found experimentally as hydrogen and carbon don't react under standard conditions

Calculating ΔH_r from ΔH_f using Hess's Law energy cycles

- You can see the relationships on the following diagram:

Diagram to show Hess's Law

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The enthalpy change from elements to products (direct route) is equal to the enthalpy change of elements forming reactants and then products (indirect route)

- The products can be directly formed from the elements = **ΔH_2**

    OR

- The products can be indirectly formed from the elements = **$\Delta H_1 + \Delta H_r$**
- **Equation**

$$\Delta H_2 = \Delta H_1 + \Delta H_r$$

Therefore for energy to be conserved,

$$\Delta H_r = \Delta H_2 - \Delta H_1$$

💡 Examiner Tip

You do not need to learn Hess's Law word for word as it is not a syllabus requirement, but you do need to understand the principle as it provides the foundation for all the problem solving in Chemical Energetics

Hess's Law Calculations

Your notes

Hess's Law Calculations

- There are two common methods to solving Hess's Law problems, using cycles and using equations
- To be successful in using cycles you need to follow carefully a step-by-step plan using the information in the question to construct a cycle and add the given information
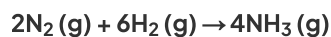- The following example shows one way to lay out your solution:

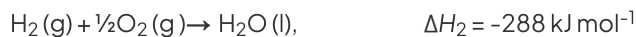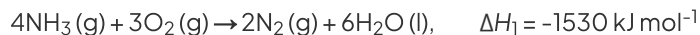### Solving Hess's Law problems using cycles:

✏️ Worked example

Calculate the enthalpy of reaction for:

$$2N_2 \text{ (g)} + 6H_2 \text{ (g)} \rightarrow 4NH_3 \text{ (g)}$$

Given the data:

$4NH_3 \text{ (g)} + 3O_2 \text{ (g)} \rightarrow 2N_2 \text{ (g)} + 6H_2O \text{ (l)}, \qquad \Delta H_1 = -1530 \text{ kJ mol}^{-1}$

$H_2 \text{ (g)} + \frac{1}{2}O_2 \text{ (g)} \rightarrow H_2O \text{ (l)}, \qquad\qquad \Delta H_2 = -288 \text{ kJ mol}^{-1}$

Answer:

- **Step 1:** Begin by writing the target enthalpy change at the top of your diagram from left to right:
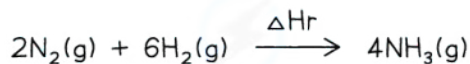
- **Step 2:** Next, write the alternative route at the bottom of your cycle and connect the top and bottom with arrows pointing in the correct directions:
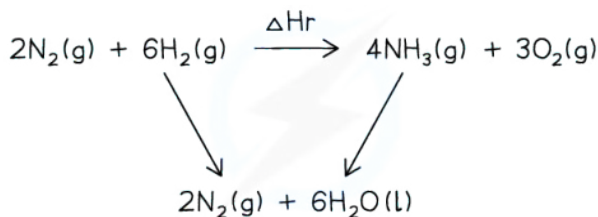
- **Step 3:** Add the enthalpy data and adjust, as necessary, for different molar amounts
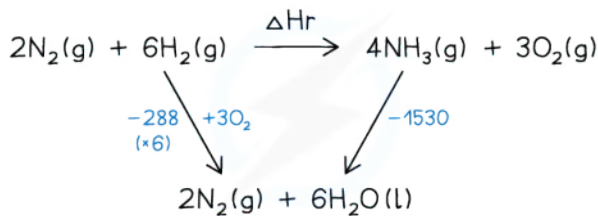
- **Step 4:** Write the Hess's Law calculation out:

$$\Delta H_r = +6\Delta H_2 - \Delta H_1 = + (-288 \times 6) - (-1530) = -198 \text{ kJ}$$

    - Two important rules:
        - If you <u>follow the direction of the arrow</u> you **ADD** the quantity
        - If you go <u>against the arrow</u> you **SUBTRACT** the quantity

✏️ Worked example

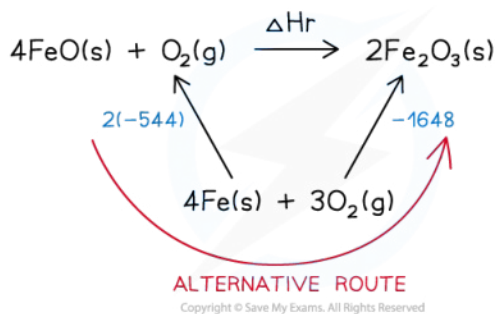What is the enthalpy change, in kJ, for the reaction below?

$$4FeO \text{ (s)} + O_2 \text{ (g)} \rightarrow 2Fe_2O_3 \text{ (s)}$$

Given the data:

$$2Fe(s) + O_2 \text{ (g)} \rightarrow 2FeO \text{ (s)} \qquad \Delta H = -544 \text{ kJ}$$

$$4Fe \text{ (s)} + 3O_2 \text{ (g)} \rightarrow 2Fe_2O_3 \text{ (s)} \qquad \Delta H = -1648 \text{ kJ}$$

Answer:

- **Step 1:** Draw the Hess cycle and add the known values

- **Step 2:** Write the Hess's Law calculation out:

  Follow the alternative route and the process the calculation

  $$\Delta H_r = -(-544 \times 2) + (-1648) = -560 \text{ kJ}$$

💡 Examiner Tip

It is very important you get the arrows in the right direction and that you separate the mathematical operation from the sign of the enthalpy change. Many students get these problems wrong because they confuse the signs with the operations. To avoid this always put brackets around the values and add the mathematical operator in front
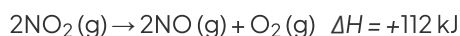
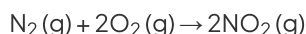## Solving Hess's Law problems using equations step-by-step:
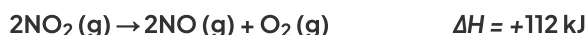
✏️ Worked example

Consider the following reactions.

$N_2 (g) + O_2 (g) \rightarrow 2NO (g)$ $\Delta H = +180$ kJ

$2NO_2 (g) \rightarrow 2NO (g) + O_2 (g)$ $\Delta H = +112$ kJ

What is the ΔH value, in kJ, for the following reaction?
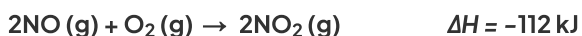
$N_2 (g) + 2O_2 (g) \rightarrow 2NO_2 (g)$

Answer:

- **Step 1**: Identify which given equation contains the product you want
This equation contains the desired product on the left side:

$$2NO_2 (g) \rightarrow 2NO (g) + O_2 (g) \qquad \Delta H = +112 \text{ kJ}$$

- **Step 2:** Adjust the equation if necessary, to give the same product. If you reverse it, **reverse the ∆H value**
Reverse it and reverse the sign

$$2NO (g) + O_2 (g) \rightarrow 2NO_2 (g) \qquad \Delta H = -112 \text{ kJ}$$

- **Step 3:** Adjust the equation if necessary, to give the same number of moles of product
The equation contains the same number of moles as in the question, so no need to adjust the moles

- **Step 4:** Identify which given equation contains your reactant
This equation contains the reactant

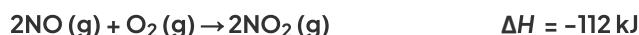$$N_2 (g) + O_2 (g) \rightarrow 2NO (g) \qquad \Delta H = +180 \text{ kJ}$$

- **Step 5:** Adjust the equation if necessary, to give the same reactant. If you reverse it, reverse the ∆H value
No need to reverse it as the reactant is already on the left side

- **Step 6:** Adjust the equation if necessary, to give the same number of moles of reactant

- **Step 7:** Add the two equations together

$$N_2 (g) + O_2 (g) \rightarrow 2NO (g) \qquad \Delta H = +180 \text{ kJ}$$

$$2NO (g) + O_2 (g) \rightarrow 2NO_2 (g) \qquad \Delta H = -112 \text{ kJ}$$

- **Step 8:** Cancel the common items

$$N_2 (g) + O_2 (g) + 2NO (g) + O_2 (g) \rightarrow 2NO (g) + 2NO_2 (g)$$

- **Step 9:** Add the two ΔH values together to get the one you want

$$N_2 (g) + 2O_2 (g) \rightarrow 2NO_2 (g) \qquad \Delta H = +180 - 112 = +68 \text{ kJ}$$

Your notes

✏️ Worked example

The enthalpy changes for two reactions are given.

$$Br_2(l) + F_2(g) \rightarrow 2BrF(g) \qquad \Delta H = x \text{ kJ}$$
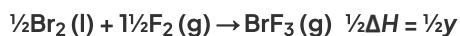
$$Br_2(l) + 3F_2(g) \rightarrow 2BrF_3(g) \qquad \Delta H = y \text{ kJ}$$

What is the enthalpy change for the following reaction?

$$BrF(g) + F_2(g) \rightarrow BrF_3(g)$$
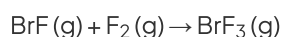
    A. $x - y$

    B. $y - x$

    C. $\frac{1}{2}(-x + y)$

    D. $\frac{1}{2}(x - y)$

Answer:

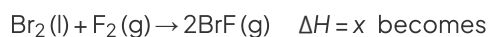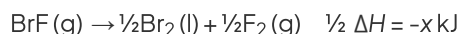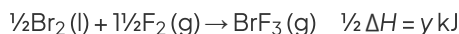- The correct option is **C**.
  - The second equation contains the desired product, but it needs to be halved to make 1 mole

    $$Br_2(l) + 3F_2(g) \rightarrow 2BrF_3(g) \quad \Delta H = y \quad \text{becomes}$$

    $$\tfrac{1}{2}Br_2(l) + 1\tfrac{1}{2}F_2(g) \rightarrow BrF_3(g) \quad \tfrac{1}{2}\Delta H = \tfrac{1}{2}y$$
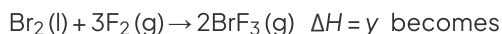
  - The first equation contains the reactant, but it needs to be reversed and halved:

    $$Br_2(l) + F_2(g) \rightarrow 2BrF(g) \quad \Delta H = x \quad \text{becomes}$$

    $$BrF(g) \rightarrow \tfrac{1}{2}Br_2(l) + \tfrac{1}{2}F_2(g) \quad \tfrac{1}{2}\Delta H = -\tfrac{1}{2}x$$
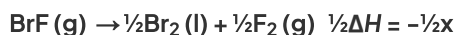
  - Combine the two equations and cancel the common terms:

    $$\tfrac{1}{2}Br_2(l) + 1\tfrac{1}{2}F_2(g) \rightarrow BrF_3(g) \quad \tfrac{1}{2}\Delta H = y \text{ kJ}$$

    $$BrF(g) \rightarrow \tfrac{1}{2}Br_2(l) + \tfrac{1}{2}F_2(g) \quad \tfrac{1}{2}\Delta H = -x \text{ kJ}$$

    $$BrF(g) + F_2(g) \rightarrow BrF_3(g) \quad \Delta H = \tfrac{1}{2}y + -\tfrac{1}{2}x = \tfrac{1}{2}(-x + y)$$

💡 Examiner Tip

If doesn't matter whether you use equations or cycles to solve Hess's Law problems, but you should be familiar with both methods and sometimes one is easier than another

Calculate Enthalpy Changes Using ΔHf⊖ (HL)

Calculate Enthalpy Changes Using ΔHf⊖

- Standard Enthalpy of Formation is defined as

  "The enthalpy change when one mole of a compound is formed from its elements under standard conditions"

- We can use enthalpy of formation of substances to find an unknown enthalpy change using a Hess cycle
- In this type of cycle the elements are always placed at the bottom of the diagram:
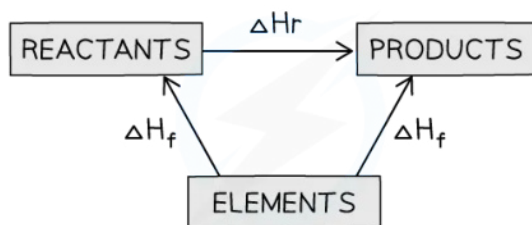
Enthalpy changes using enthalpy of formation

- In this cycle the arrows will always be pointing upwards because the definition of the enthalpy of formation must go from elements to compounds
- This means the Hess's Law calculation of ΔH will always be in the same arrangement

$$\Delta H_r = \Sigma \Delta H_{f\,products} - \Sigma \Delta H_{f\,reactants}$$

- Try the following worked example:

Your notes

✏️ Worked example

Given the data:

Substance	B_2H_6 (g)	B_2O_3 (g)	H_2O (g)
ΔH_f /kJmol^{-1}	+31.4	–1270	–242

Calculate the enthalpy of combustion of gaseous diborane given that it burns according to the following equation:

$$B_2H_6 \,(g) + 3O_2 \,(g) \rightarrow B_2O_3 \,(s) + 3H_2O \,(g)$$
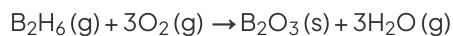
Answer:

- **Step 1:** Find the sum of the enthalpies of combustion of the products
    $\Delta H_f = + (\,–1270) + (\,–242 \times 3) = \,–1996 \text{ kJ}$

- **Step 2:** Find the sum of the enthalpies of combustion of the reactants
    $\Delta H_f = + (+31.4) + 0 \ = + 31.4 \text{ kJ}$

    There is no enthalpy of formation for oxygen as ΔH_f of elements by definition is zero

- **Step 3:** Calculate the enthalpy change
    $\Delta H = \Delta H_{f \, products} \ – \Delta H_{f \, reactants} \ = \,– 1996 – (+ 31.4) = $ **–2027.4 kJ**

💡 Examiner Tip

Enthalpy of formation data are given to you in the data booklet.

Calculate Enthalpy Changes Using ΔHc⊖ (HL)

Calculate Enthalpy Changes Using $\Delta Hc^{\ominus}$

- The standard enthalpy change of combustion is
The enthalpy change that occurs when one mole of the substance burns completely under standard conditions

- We can use enthalpy of combustion to find an unknown enthalpy change using a Hess cycle
- In this type of cycle, the combustion products are always placed at the bottom of the diagram and the arrows should be pointing downwards

Energy cycle including combustion products

The combustion products of both reactants and products should be placed at the bottom of the cycle

- The general expression for $\Delta H^{\ominus}$ is therefore:

$$\Delta H^{\ominus} = \sum \Delta H_c^{\ominus}(\text{reactants}) - \sum \Delta H_c^{\ominus}(\text{products})$$

✏️ Worked example

Calculate ΔH_f [ethane].

The relevant change in standard enthalpy of combustion (ΔH_c) values are shown in the table below:
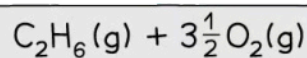
Reaction	ΔH_c (kJ mol^{-1})
C (graphite) + O_2 (g) $\rightarrow$ CO_2 (g)	-393.5
H_2 (g) + ½O_2(g) $\rightarrow$ H_2O (l)	-285.8
C_2H_6 (g) + 3½ O_2 (g) $\rightarrow$ 2CO_2 (g) + 3H_2O (l)	-1559.7

Answer:

- **Step 1:** Write the equation for enthalpy change of formation at the top and add oxygen on both side

$$2C \text{ (GRAPHITE)} + 3H_2(g) + 3\tfrac{1}{2}O_2(g) \qquad C_2H_6(g) + 3\tfrac{1}{2}O_2(g)$$
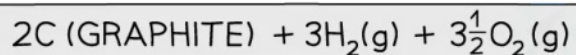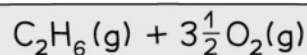
- **Step 2:** Draw the cycle with the combustion products at the bottom

$$2C \text{ (GRAPHITE)} + 3H_2(g) + 3\tfrac{1}{2}O_2(g) \qquad C_2H_6(g) + 3\tfrac{1}{2}O_2(g)$$

$$2CO_2(g) + 3H_2O \text{ (l)}$$
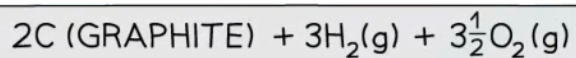
- **Step 3:** Draw all arrows in the correct direction

Your notes

$$2C \text{ (GRAPHITE)} + 3H_2(g) + 3\tfrac{1}{2}O_2(g) \xrightarrow{\Delta H_f} C_2H_6(g) + 3\tfrac{1}{2}O_2(g)$$

$2\Delta Hc \text{ [C(GRAPHITE)]} +$
$3\Delta Hc \text{ [H}_2(g)]$ ΔH_1 ΔH_2 $\Delta Hc \text{ [C}_2H_6 (g)]$

$$2CO_2(g) + 3H_2O (l)$$
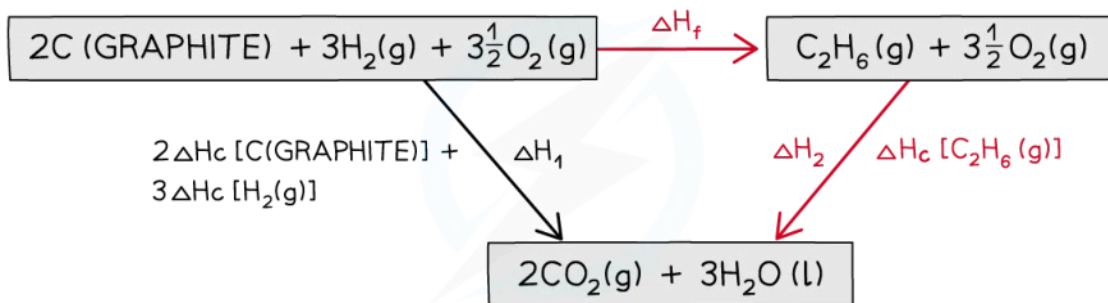
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- **Step 4:** Apply Hess's Law
  - $\Delta H_f = \Delta H_1 - \Delta H_2$
  - $\Delta H_f = 2(-393.5) + 3(-285.8) - (-1559.7)$
  - $\Delta H_f = \textbf{-84.7 kJ mol}^{-1}$

🔘 Examiner Tip

Don't forget to make sure the number of atoms of each element is balanced when drawing your cycle

Using Hess's Law to Solve ΔHc⊖ & ΔHf⊖ Problems

Using Hess's Law to solve ΔH^{θ}_f problems

- Standard enthalpy changes of formation, ΔH^{θ}_f can also be used to calculate standard enthalpy changes of reactions, ΔH^{θ}
- The overall equation will be:

$$\Delta H^{\theta}_f \text{ (reactants)} + \Delta H^{\theta} = \Delta H^{\theta}_f \text{ (products)}$$

- Which rearranges to:

$$\Delta H^{\theta} = \Delta H^{\theta}_f \text{ (products)} - \Delta H^{\theta}_f \text{ (reactants)}$$

- Be careful to count up all the atoms you need to use, and make sure they are written as they occur in the elements in their standard state

Diagram to show the Hess's Law cycle for calculating ΔH^{θ} from ΔH^{θ}_f data
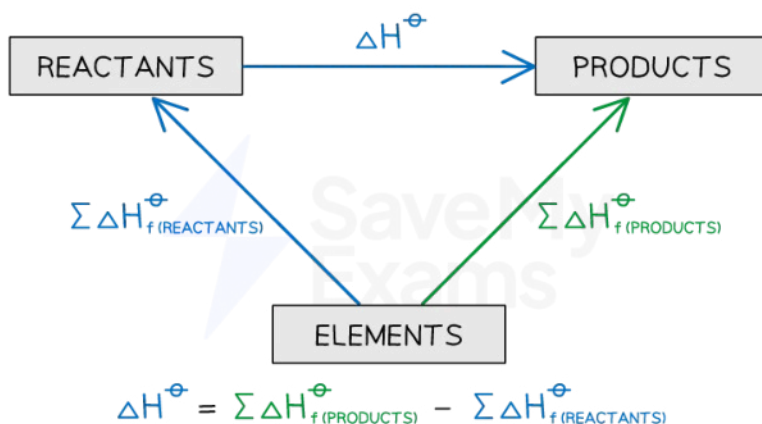
Elements should be in their standard state and balanced when written in a Hess's Law cycle

Using Hess's Law to solve ΔH^{θ}_c problems

- Standard enthalpy changes of combustion, ΔH^{θ}_c can also be used to calculate standard enthalpy changes of reactions, ΔH^{θ}
- The overall equation will be:

$$\Delta H^{\theta}_c \text{ (products)} + \Delta H^{\theta} = \Delta H^{\theta}_c \text{ (reactants)}$$

- Which rearranges to:

$$\Delta H^{\theta} = \Delta H^{\theta}_c \text{ (reactants)} - \Delta H^{\theta}_c \text{ (products)}$$

Diagram to show the Hess's Law cycle for calculating ΔH^{θ} from ΔH^{θ}_c data

Your notes

$$\Delta H^{\ominus} = \Sigma \Delta H^{\ominus}_{c\ (REACTANTS)} - \Sigma \Delta H^{\ominus}_{c\ (PRODUCTS)}$$
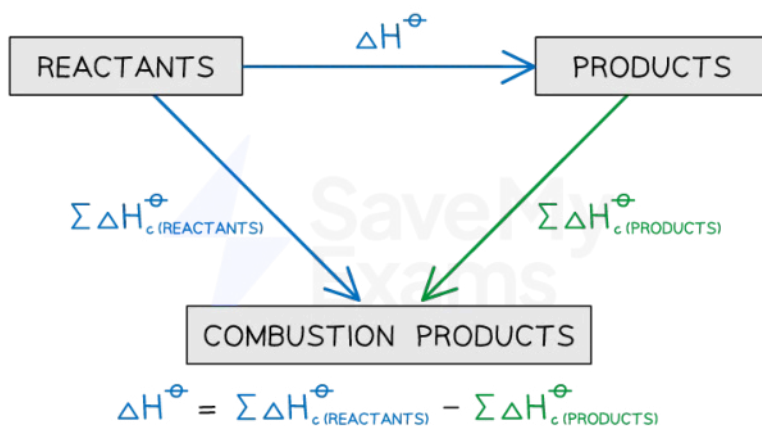
*Hess's Law says that the enthalpy changes on the two routes are the same*

Born-Haber Cycles (HL)

Born-Haber Cycles

- A **Born-Haber cycle** is a specific application of **Hess's Law** for ionic compounds and enables us to calculate lattice enthalpy, which cannot be found by experiment
- The basic principle of drawing the cycle is to construct a diagram in which energy increases going up the diagram
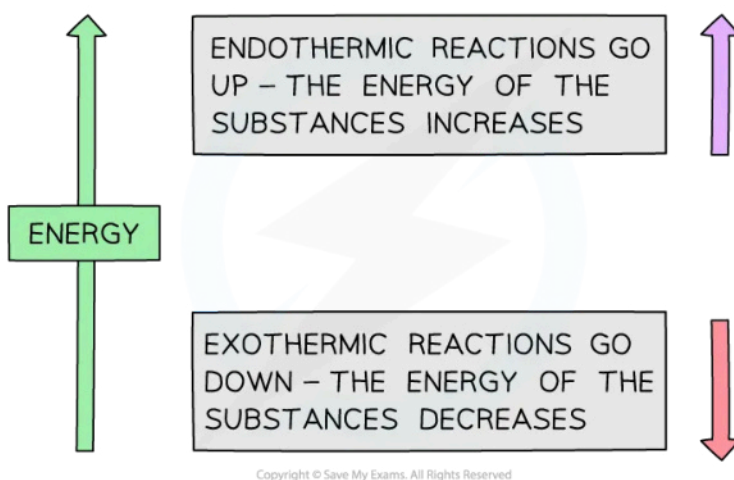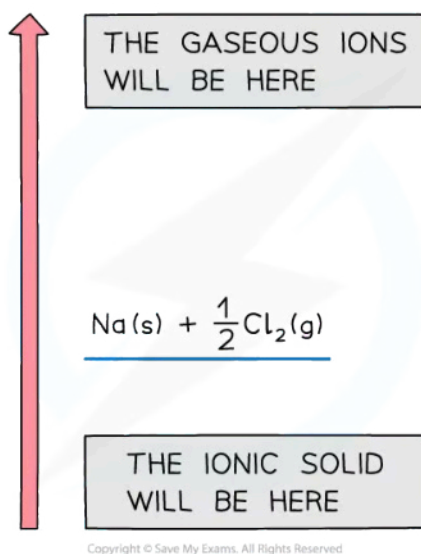

The basic principle of a Born-Haber cycle

- The cycle shows all the steps needed to turn atoms into gaseous ions and from gaseous ions into the ionic lattice
- The alternative route to the ionic lattice begins from the enthalpy of formation of the 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 a third of the way up the diagram
- This is shown as the left hand side of the equation for the process indicated
- The location is marked by drawing a horizontal bar or line which represents the starting energy level

Drawing a Born-Haber cycle- Step 1

Your notes

THE GASEOUS IONS
WILL BE HERE

$$Na\,(s) \; + \; \frac{1}{2}Cl_2\,(g)$$

THE IONIC SOLID
WILL BE HERE

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Start with your ionic solid

- Next, we need to create the gaseous ions
- This is a two step process of first creating the gaseous atoms and then turning them into ions
- Creating gaseous atoms is a bond breaking process, so arrows must be drawn upwards
- It doesn't matter whether you start with sodium or chlorine
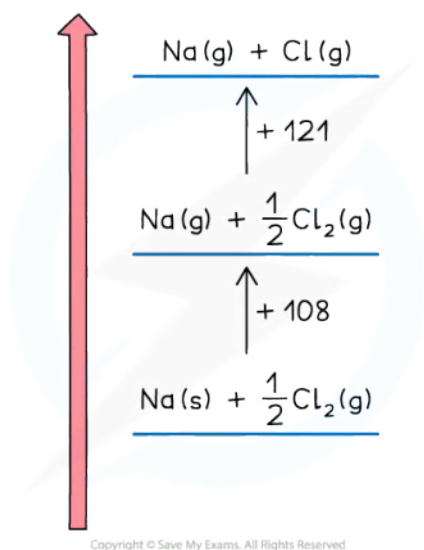- The enthalpy of atomisation of sodium is

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

- The enthalpy of atomisation of chlorine is

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

- We can show the products of the process on the horizontal lines and the energy value against a vertical arrow connecting the energy levels

Drawing a Born–Haber cycle– Step 2

Create the gaseous atoms

- Now that the ions are created:
- The sodium ion loses an electron, so this energy change is the first ionisation energy for sodium
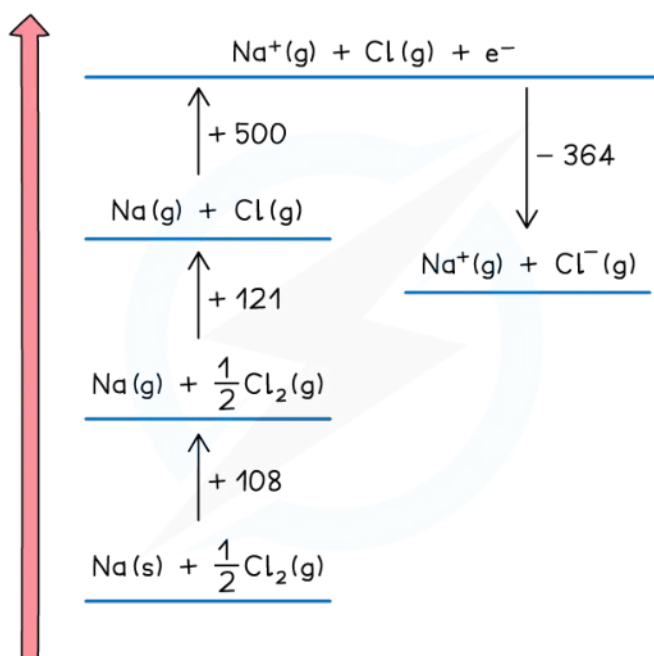
$$Na \text{ (g)} \rightarrow Na^+ \text{ (g)} + e^- \qquad \Delta H^{\ominus}_{IE} = +500 \text{ kJ mol}^{-1}$$

- The change is endothermic so the direction continues upwards
- The chlorine atom gains an electron, so this is electron affinity

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

- The exothermic change means this is downwards
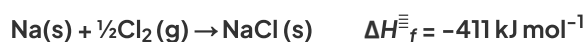- The change is displaced to the right to make the diagram easier to read

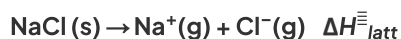**Drawing a Born–Haber cycle– Step 3**

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Create 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

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

- This is an exothermic change for sodium chloride so the arrow points downwards
- Enthalpy of formation can be exothermic or endothermic, so you may need to show it above the elements (and displaced to the right) for a endothermic change
- The final change is lattice enthalpy, which is shown as the change from solid to gaseous ions. This means the arrow must point upwards. For sodium chloride, the equation is

$$NaCl(s) \rightarrow Na^+(g) + Cl^-(g) \quad \Delta H^{\ominus}_{latt}$$

Drawing a Born-Haber cycle- Step 4
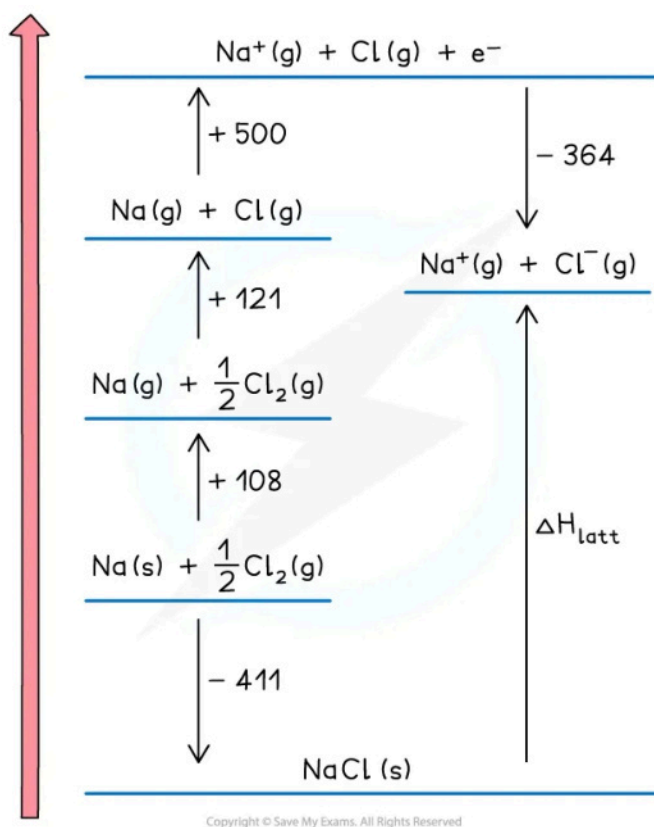
Complete the cycle

- The cycle is now complete
- The cycle is usually used to calculate the lattice enthalpy of an ionic solid, but can be used to find other enthalpy changes if you are given the lattice enthalpy
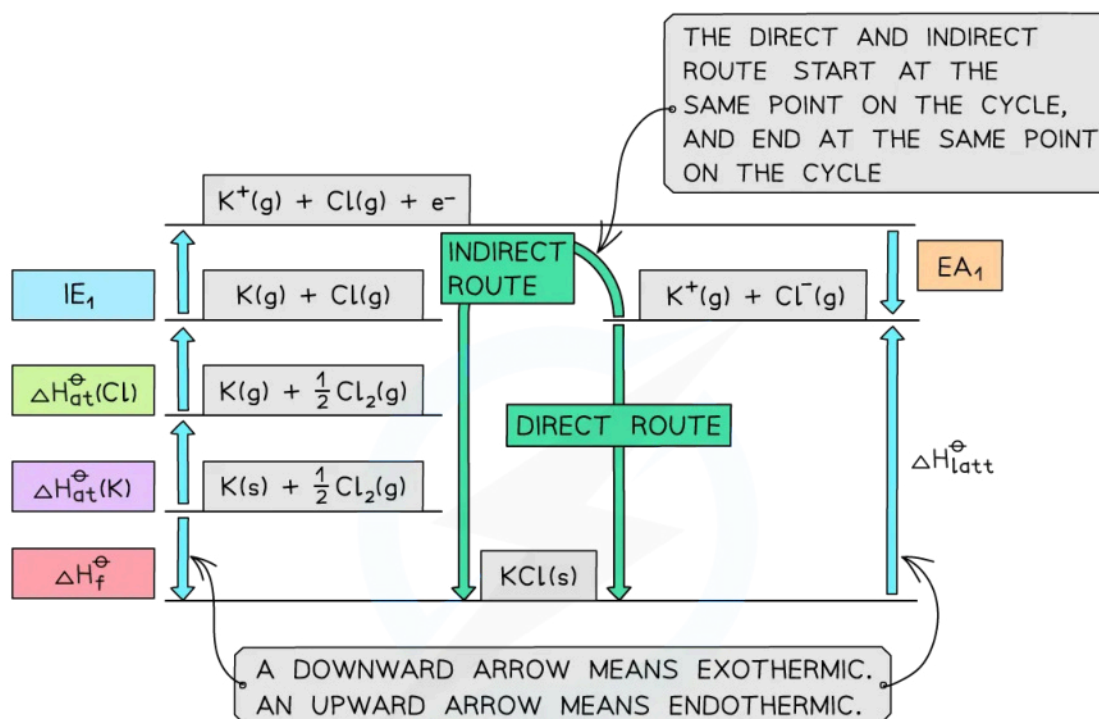
✏️ Worked example

Constructing a Born–Haber cycle for KCl

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	$K(s) \rightarrow K(g)$	$\Delta H^{\ominus}_{at}$
Convert K(g) atoms into K^+ (g) ions	$K(g) \rightarrow K^+(g) + e^-$	IE_1
Convert Cl_2 (g) molecules into Cl (g) atoms	$\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$	$\Delta H^{\ominus}_{at}$
Convert Cl (g) atoms into Cl^- (g) ions	$Cl(g) + e^- \rightarrow Cl^-(g)$	EA_1
Add up all the values to get $\Delta H^{\ominus}_1$		$\Delta H^{\ominus}_1$
Apply to Hess's law to get $\Delta H^{\ominus}_{lat}$		$\Delta H^{\ominus}_{lat}$

Answer:

THE DIRECT AND INDIRECT ROUTE START AT THE SAME POINT ON THE CYCLE, AND END AT THE SAME POINT ON THE CYCLE

$$K^+(g) + Cl(g) + e^-$$

INDIRECT ROUTE

IE_1

$K(g) + Cl(g)$

$K^+(g) + Cl^-(g)$

EA_1

$\Delta H^\ominus_{at}(Cl)$

$K(g) + \frac{1}{2}Cl_2(g)$

DIRECT ROUTE

$\Delta H^\ominus_{latt}$

$\Delta H^\ominus_{at}(K)$

$K(s) + \frac{1}{2}Cl_2(g)$

$\Delta H^\ominus_f$

$KCl(s)$

A DOWNWARD ARROW MEANS EXOTHERMIC.
AN UPWARD ARROW MEANS ENDOTHERMIC.

$$\Delta H^\ominus_f = \left(\Delta H^\ominus_{at}(K)\right) + \left(\Delta H^\ominus_{at}(Cl)\right) + \left(IE_1\right) + \left(EA_1\right) - \left(\Delta H^\ominus_{latt}\right)$$

$$\therefore \Delta H^\ominus_{latt} = -\left(\Delta H^\ominus_f\right) + \underbrace{\left(\Delta H^\ominus_{at}(K)\right) + \left(\Delta H^\ominus_{at}(Cl)\right) + \left(IE_1\right) + \left(EA_1\right)}_{\Delta H^\ominus_1}$$

Your notes

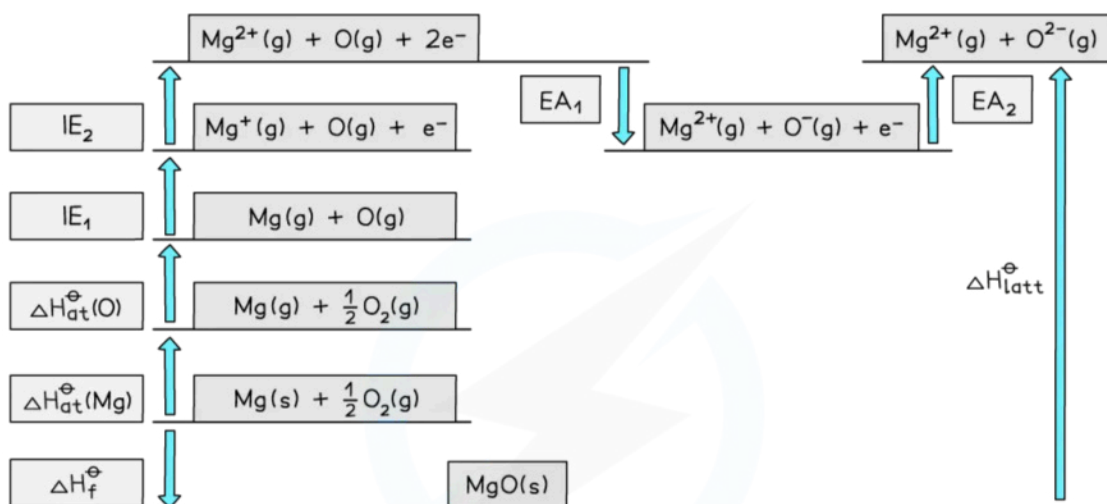## ✏️ Worked example

Constructing a Born–Haber cycle for MgO

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

Step	Equation	Enthalpy Change
Convert Mg (s) atoms into Mg (g) atoms	$Mg\,(s) \rightarrow Mg\,(g)$	$\Delta H^{\ominus}_{at}$
Convert Mg (g) atoms into Mg^{+} (g) ions	$Mg\,(g) \rightarrow Mg^{+}\,(g) + e^{-}$	IE_1
Convert Mg^{+} (g) ions into Mg^{2+} (g) ions	$Mg^{+}(g) \rightarrow Mg^{2+} + e^{-}$	IE_2
Convert O_2 (g) molecules into O (g) atoms	$\frac{1}{2}O_2\,(g) \rightarrow O(g)$	$\Delta H^{\ominus}_{at}$
Convert O(g) atoms into O^{-}(g) ions	$O\,(g) + e^{-} \rightarrow O^{-}\,(g)$	EA_1
Convert O^{-}(g) ions into O^{2-}(g) ion	$O^{-}(g) + e^{-} \rightarrow O^{2-}\,(g)$	EA_2
Add up all the values to get $\Delta H^{\ominus}_1$		$\Delta H^{\ominus}_1$
Apply to Hess's law to get $\Delta H^{\ominus}_{lat}$		$\Delta H^{\ominus}_{lat}$

Answer:

Your notes

Born-Haber cycle diagram for MgO:

$$Mg^{2+}(g) + O(g) + 2e^-$$
$$Mg^{2+}(g) + O^{2-}(g)$$
IE_2 $Mg^+(g) + O(g) + e^-$ EA_1 $Mg^{2+}(g) + O^-(g) + e^-$ EA_2
IE_1 $Mg(g) + O(g)$
$\Delta H^{\ominus}_{at}(O)$ $Mg(g) + \frac{1}{2}O_2(g)$ $\Delta H^{\ominus}_{latt}$
$\Delta H^{\ominus}_{at}(Mg)$ $Mg(s) + \frac{1}{2}O_2(g)$
$\Delta H^{\ominus}_f$ $MgO(s)$

$$\Delta H^{\ominus}_f = \left(\Delta H^{\ominus}_{at}(Mg)\right) + \left(\Delta H^{\ominus}_{at}(O)\right) + \left(IE_1\right) + \left(IE_2\right) + \left(EA_1\right) + \left(EA_2\right) - \left(\Delta H^{\ominus}_{latt}\right)$$

$$\therefore \ \Delta H^{\ominus}_{latt} = -\left(\Delta H^{\ominus}_f\right) + \underbrace{\left(\Delta H^{\ominus}_{at}(Mg)\right) + \left(\Delta H^{\ominus}_{at}(O)\right) + \left(IE_1\right) + \left(IE_2\right) + \left(EA_1\right) + \left(EA_2\right)}_{\Delta H^{\ominus}_1}$$

💡 Examiner Tip

You will not be asked to drawn an entire Born-Haber cycle from scratch but could be asked to complete a partially drawn one. When constructing Born-Haber cycles, the direction of the changes is important, but the relative size of the steps does not matter so don't worry if the steps don't correspond to the magnitude of the energy changes.

You don't need to show the energy axis in a Born-Haber cycle, but you do need to show the electron(s) in the ionisation step otherwise you might lose marks in an exam.

Born–Haber Cycle Calculations (HL)

Your notes

Born–Haber Cycle Calculations

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

$$\Delta H^{\ominus}_f = \Delta H^{\ominus}_{at} + \Delta H^{\ominus}_{at} + IE + EA - \Delta H^{\ominus}_{lat}$$

- If we simplify this into three terms, this makes the equation easier to see:
  - $\Delta H^{\ominus}_{lat}$
  - $\Delta H^{\ominus}_f$
  - $\Delta H^{\ominus}_1$ (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:

$$\Delta H^{\ominus}_f = \Delta H^{\ominus}_1 - \Delta H^{\ominus}_{lat}$$

- So, if we rearrange to calculate the lattice enthalpy, the equation becomes

$$\Delta H^{\ominus}_{lat} = -\Delta H^{\ominus}_f + \Delta H^{\ominus}_1$$

- When calculating the $\Delta H_{lat}^{\ominus}$, 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 enthalpy 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 chloride ions, i.e. $2Cl^-$
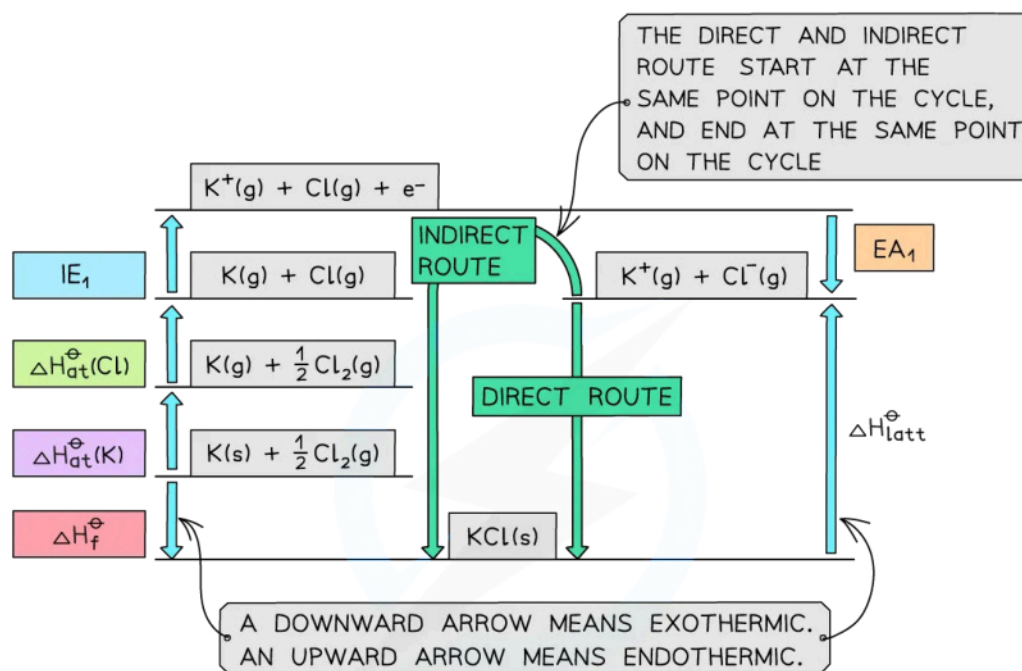
✏️ Worked example

Calculating the lattice enthalpy of KCl

Given the data below, calculate the $\Delta H^{\ominus}_{lat}$ of potassium chloride (KCl).

	$\Delta H^{\ominus}_{at}$ (kJmol^{-1})	*IE / EA* (kJmol^{-1})
K	+90	+418
Cl	+122	-349
$\Delta H^{\ominus}_{f}$ (kJmol^{-1})		
KCl	-437	

Answer:

- **Step 1:** Construct the Born-Haber cycle

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- **Step 2:** Applying Hess' law, the lattice enthalpy of KCl is:

$$\Delta H^{\ominus}_{lat} = -\Delta H^{\ominus}_f + \Delta H^{\ominus}_1$$

$$\Delta H^{\ominus}_{lat} = -\Delta H^{\ominus}_f + [(\Delta H^{\ominus}_{at} K) + (\Delta H^{\ominus}_{at} Cl) + (IE_1 K) + (EA_1 Cl)]$$

- **Step 3:** Substitute in the numbers:

$$\Delta H^{\ominus}_{lat} = -(-437) + [(+90) + (+122) + (+418) + (-349)] = 718 \text{ kJ mol}^{-1}$$

✎ Worked example

Calculating the lattice enthalpy of MgO

Given the data below, calculate the of $\Delta H^{\ominus}_{lat}$ magnesium oxide of magnesium oxide (MgO)

	$\Delta H^{\ominus}_{at}$ (kJmol^{-1})	IE_1 / EA_1(kJmol^{-1})	IE_1 / EA_1(kJmol^{-1})
Mg	+148	+736	+1450
O	+248	-142	+770
$\Delta H^{\ominus}_{f}$ (kJmol^{-1})			
MgO	-602		

Answer:

- **Step 1:** Construct the Born-Haber cycle

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- **Step 2:** Applying Hess' law, the lattice enthalpy of MgO is:

$$\Delta H^{\ominus}_{lat} = -\Delta H^{\ominus}_{f} + \Delta H^{\ominus}_{1}$$

$$\Delta H^{\ominus}_{lat} = -\Delta H^{\ominus}_{f} + [(\Delta H^{\ominus}_{at} Mg) + (\Delta H^{\ominus}_{at} O) + (IE_1 Mg) + (IE_2 Mg) + (EA_1 O) + (EA_2 O)]$$

- **Step 3:** Substitute in the numbers:

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

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