

SL IB Chemistry



Your notes

Energy Cycles in Reactions

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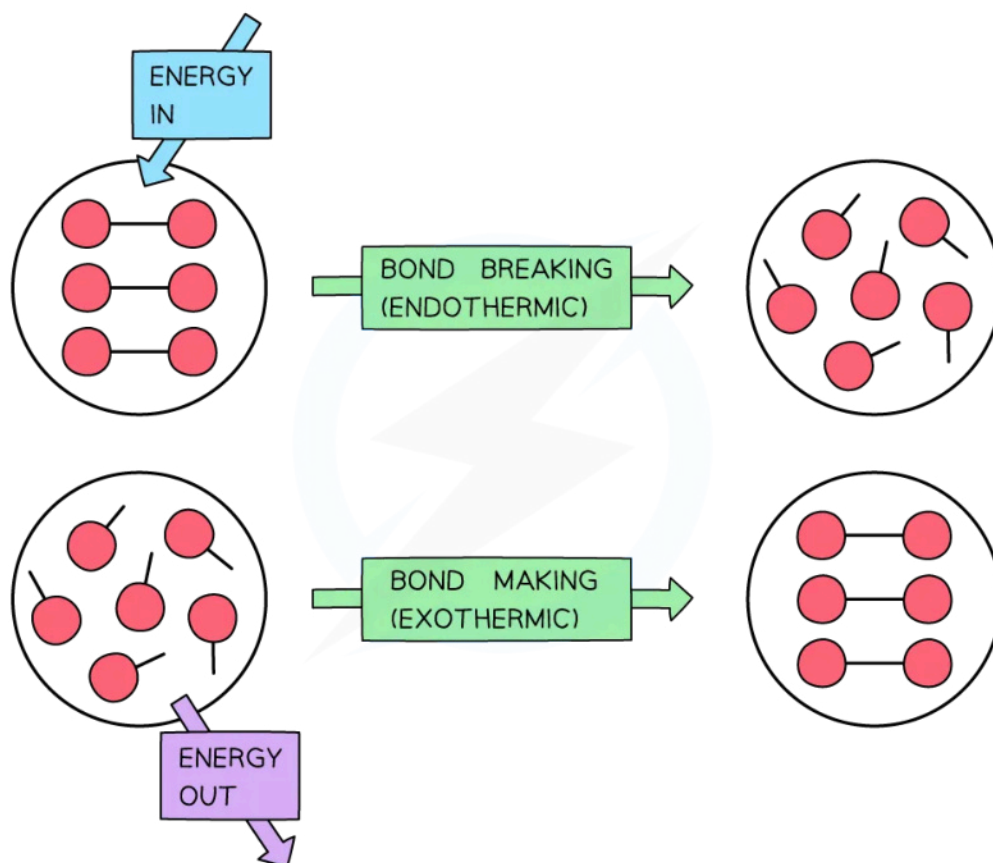
Your notes

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



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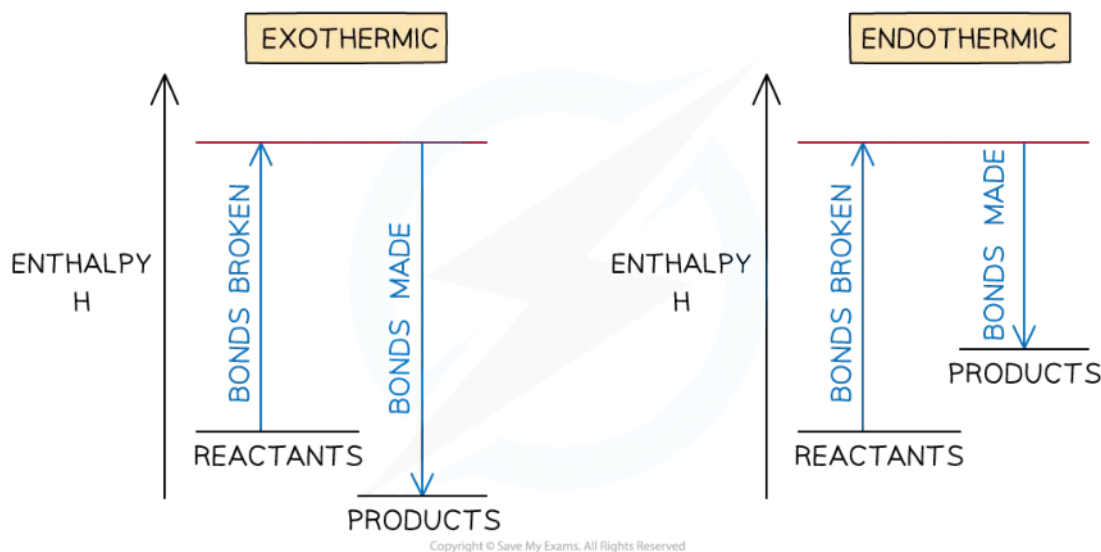
To break bonds energy is required from the surroundings and to make new bonds energy is released from the reaction to the surroundings

- 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

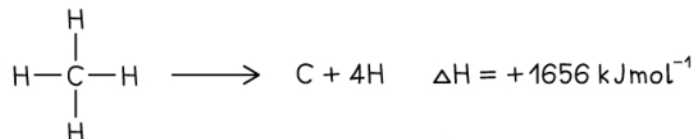


Bond enthalpy profiles

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

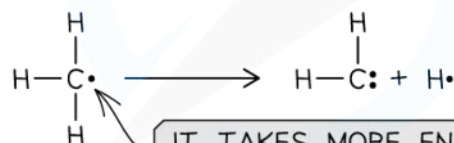


FIRST STEP



THE REMAINING Hs ARE HELD MORE STRONGLY

SECOND STEP



IT TAKES MORE ENERGY TO REMOVE MORE H ATOMS

$$\text{AVERAGE BOND ENTHALPY} \quad \Delta H = \frac{+1656}{4} = +414 \text{ kJmol}^{-1}$$

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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 ΔH_r^\ominus 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:

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

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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



Your notes



Your notes

Worked example

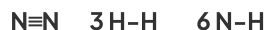
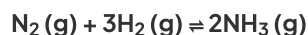
Calculate the enthalpy of reaction for the Haber process reaction.

The relevant bond energies are given in the table below:

Bond	Average Bond Energy (kJ mol ⁻¹)
N ≡ N	945
H - H	436
N - H	391

Answer:

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



- **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 ≡ 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

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

$$= (+2253 \text{ kJ mol}^{-1}) + (-2346 \text{ kJ mol}^{-1})$$

$$= -93 \text{ kJ mol}^{-1}$$



Your notes

Worked example

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



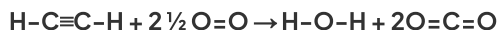
Using the average bond enthalpies given in the table, what is the enthalpy of combustion of ethyne?

Bond	Average Bond Energy (kJ mol^{-1})
C—H	414
C \equiv 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:



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

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

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

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

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



Your notes

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



Your notes

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:

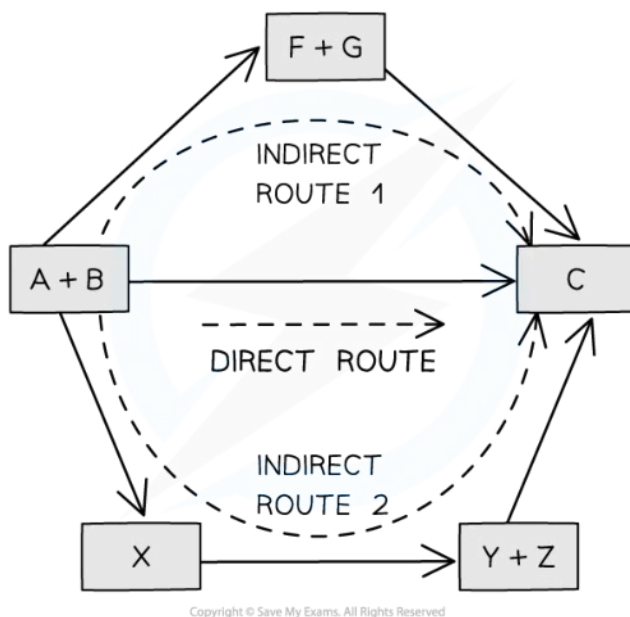
Energy cannot be created or destroyed, it can only change form

- 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

- Hess' Law is used to calculate enthalpy changes which can't be found experimentally using **calorimetry**, eg:

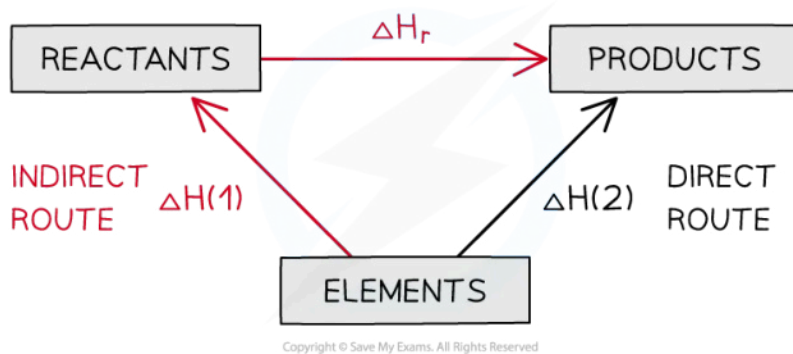


- ΔH_f (propane) can't be found experimentally as hydrogen and carbon don't react under standard conditions

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



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



Your notes

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:



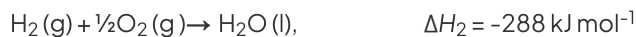
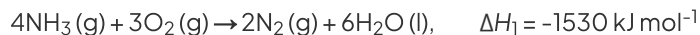
Your notes

Worked example

Calculate the enthalpy of reaction for:

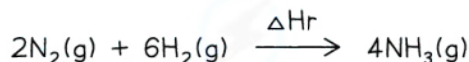


Given the data:



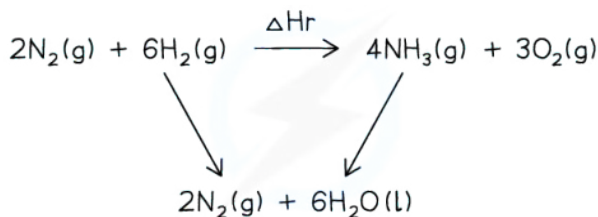
Answer:

- Step 1: Begin by writing the target enthalpy change at the top of your diagram from left to right:



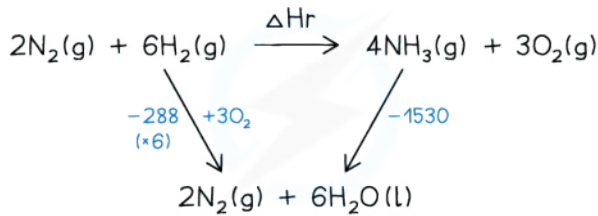
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- Step 2: Next, write the alternative route at the bottom of your cycle and connect the top and bottom with arrows pointing in the correct directions:



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- Step 3: Add the enthalpy data and adjust, as necessary, for different molar amounts



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- 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 follow the direction of the arrow you **ADD** the quantity
 - If you go against the arrow you **SUBTRACT** the quantity



Your notes

Worked example

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

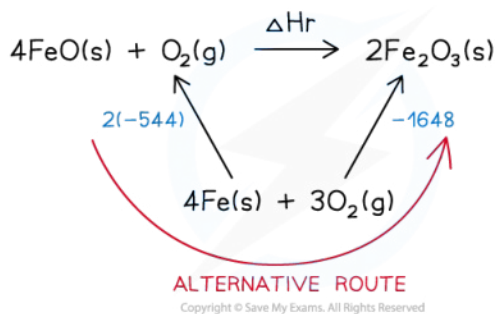


Given the data:



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

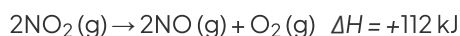
Solving Hess's Law problems using equations step-by-step:



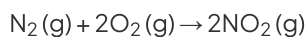
Your notes

Worked example

Consider the following reactions.



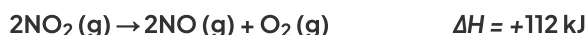
What is the ΔH value, in kJ, for the following reaction?



Answer:

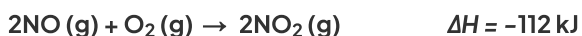
- **Step 1:** Identify which given equation contains the product you want

This equation contains the desired product on the left side:



- **Step 2:** Adjust the equation if necessary, to give the same product. If you reverse it, **reverse the ΔH value**

Reverse it and reverse the sign



- **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

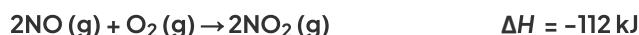


- **Step 5:** Adjust the equation if necessary, to give the same reactant. If you reverse it, reverse the ΔH value

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



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



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





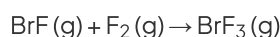
Your notes

Worked example

The enthalpy changes for two reactions are given.



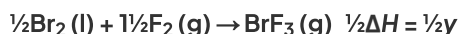
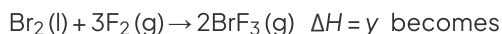
What is the enthalpy change for the following reaction?



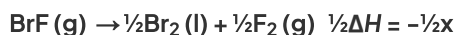
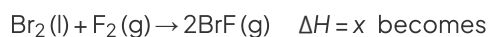
- A. $x - y$
- B. $y - x$
- C. $\frac{1}{2}(-x + y)$
- D. $\frac{1}{2}(x - y)$

Answer:

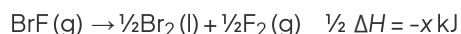
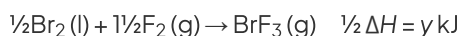
- The correct option is **C**.
 - The second equation contains the desired product, but it needs to be halved to make 1 mole



- The first equation contains the reactant, but it needs to be reversed and halved:



- Combine the two equations and cancel the common terms:



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