

# IB Chemistry DP

YOUR NOTES



## 5. Energetics / Thermochemistry

### CONTENTS

#### 5.1 Energetics

5.1.1 Energy Changes in Reactions

5.1.2 Standard Enthalpy Change

5.1.3 Calorimetry

5.1.4 Calorimetry Experiments

#### 5.2 Hess's Law

5.2.1 Hess's Law

5.2.2 Using Hess's Law - Cycles

5.2.3 Using Hess's Law - Equations

5.2.4 Using  $\Delta H_f^\circ$  to Find Enthalpy Changes

#### 5.3 Bond Enthalpy

5.3.1 Bond Enthalpy

5.3.2 Bond Enthalpy Calculations

5.3.3 Energy Profiles

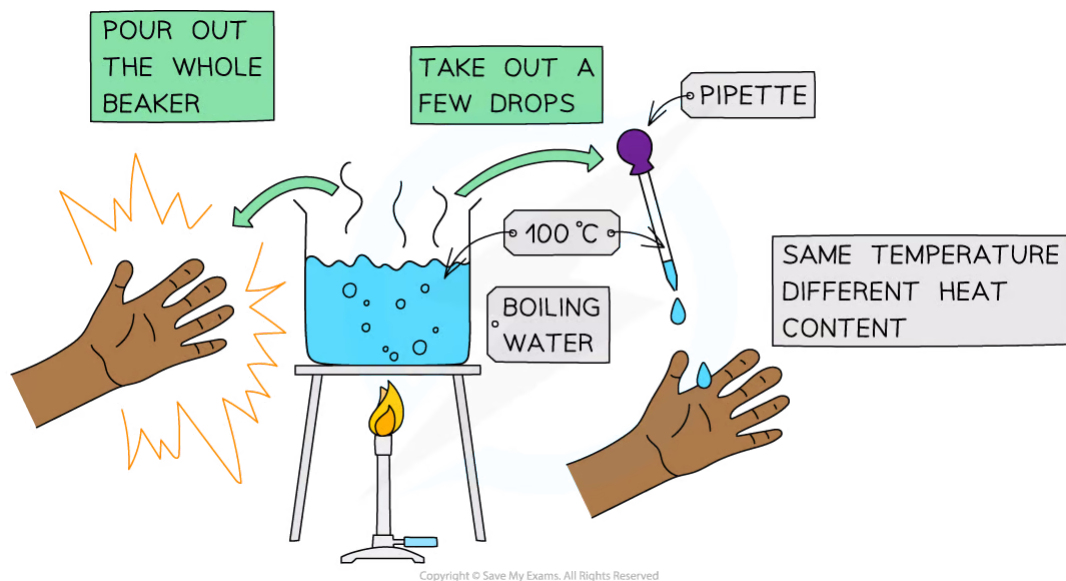
5.3.4 Case Study: Ozone

## 5.1 Energetics

### 5.1.1 Energy Changes in Reactions

#### Temperature & Kinetic Energy

- What is the difference between heat and temperature?
- This can be illustrated using a beaker of boiling water and a pipette:



***The effects of boiling water can be quite different depending on the quantity of water involved!***

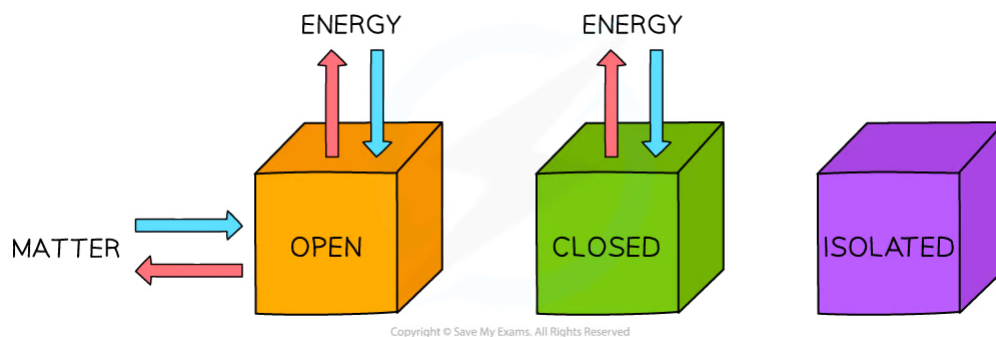
- You would get a very nasty burn if a whole beaker of boiling water spilled onto to your hand, but a drop of boiling water would cause little problem
- The water is at the **same temperature** in the pipette as in the beaker, but the beaker has a much **higher heat content**
- We say that temperature is a measure of the **average kinetic energy** of the particles whereas heat is a measure of the **energy content** of a substance
- The particles have **kinetic energy** because they are moving
  - The **faster** they move the **more energy** they have and the higher the temperature of the substance

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## Conservation of Energy

- **Energy** is a measure of the ability to do **work**
- There are many different types of **energy** and **heat** is only one of them
- During chemical reactions **energy** flows in and out of the reaction vessels
  - Inside the reaction vessel is known as the **system**
  - Outside the reaction vessel is known as the **surroundings**
- Systems come in three types: **open, closed** and **isolated**:



**Three types of systems**

- Isolated systems are very rare; most chemical reactions are open systems
- Open systems are very important when thinking about chemical equilibrium which is covered in Topic 7
- Although energy can be exchanged between open and closed systems and the surroundings, the total energy of the process cannot change
- This is known as the **Law of Conservation of Energy** and is a cornerstone to understanding how chemical changes affect the energy flow in and out of systems

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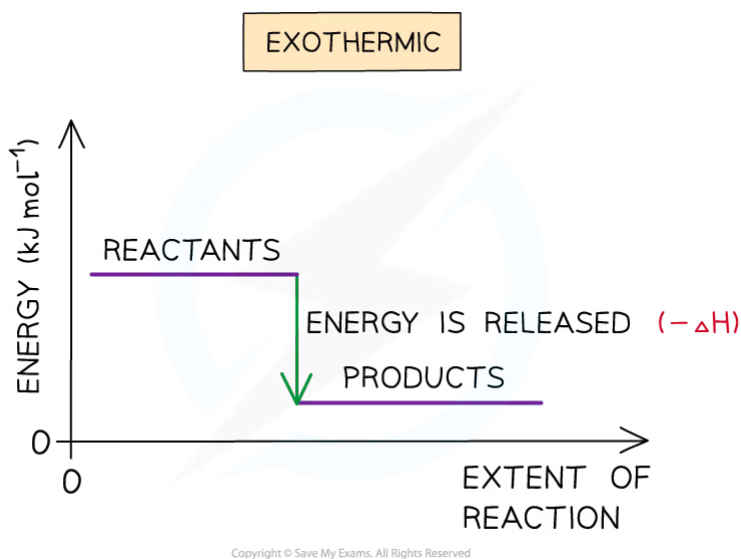


## Exothermic & Endothermic

- The total chemical energy inside a substance is called the **enthalpy** (or heat content)
- When chemical reactions take place, changes in chemical energy take place and therefore the **enthalpy** changes
- An **enthalpy** change is represented by the symbol  $\Delta H$  ( $\Delta$  = change;  $H$  = enthalpy)
- An **enthalpy change** can be positive or negative

### Exothermic reactions

- A reaction is **exothermic** when the products have less **enthalpy** than the reactants
- Heat energy is given off **by** the system **to** the surroundings
  - The **temperature** of the **surroundings increases**
  - The **temperature** of the **system decreases**
- There is an **enthalpy** decrease during the reaction so  $\Delta H$  is **negative**
- **Exothermic** reactions are **thermodynamically** possible (because the enthalpy of the reactants is higher than that of the products)
- However, if the rate is too slow, the reaction may not occur. In this case the reaction is **kinetically** controlled



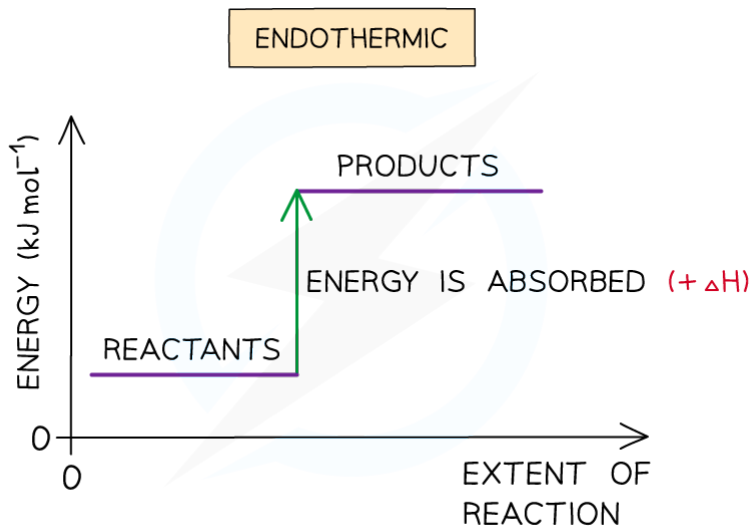
*The enthalpy change during an exothermic reaction*

### Endothermic reactions

- A reaction is **endothermic** when the products have more **enthalpy** than the reactants
- Heat energy is absorbed **by** the system **from** the **surroundings**
  - The **temperature** of the **surroundings decreases**
  - The **temperature** of the **system increases**
- There is an **enthalpy** increase during the reaction so  $\Delta H$  is **positive**

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**The enthalpy change during an endothermic reaction**



**Exam Tip**

It is important to specify the physical states of each species in an equation when dealing with enthalpy changes as any changes in state can cause very large changes of enthalpy. For example:



Also, remember that the **system** is the **substances** that are reacting (ie. the reaction itself) and the **surroundings** is everything else (eg. the flask the reaction is taking place in)

## 5.1.2 Standard Enthalpy Change

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### Standard Enthalpy Change

#### Standard conditions

- To compare the changes in enthalpy between reactions, all thermodynamic measurements are made under **standard conditions**
- These **standard conditions** are:
  - A **pressure** of 100 kPa
  - A **concentration** of  $1 \text{ mol dm}^{-3}$  for all solutions
  - Each substance involved in the reaction is in its **standard state** (solid, gas or liquid)
- Temperature is not part of the definition of **standard state**, but a temperature of **298 K** (25 °C) is usually given as the specified temperature
- To show that a reaction has been carried out under standard conditions, the symbol  $\ominus$  is used
  - Eg.  $\Delta H^\ominus$  = the standard enthalpy change

#### Standard Enthalpies

- There are a few **Standard Enthalpy** changes which are used commonly in energy calculations and they are summarised below:



Standard Enthalpy Change of ...	Definition	Symbol	Exothermic / Endothermic
<b>Reaction</b>	The enthalpy change when the reactants in the <b>stoichiometric equation</b> react to give the products under standard conditions	$\Delta H_r^\ominus$	Both
<b>Formation</b>	The enthalpy change when <b>one mole</b> of a compound is <b>formed</b> from its <b>elements</b> under standard conditions	$\Delta H_f^\ominus$	Both
<b>Combustion</b>	The enthalpy change when <b>one mole</b> of a substance is <b>burnt</b> in excess oxygen under standard conditions	$\Delta H_c^\ominus$	Exothermic
<b>Neutralisation</b>	The enthalpy change when <b>one mole of water</b> is <b>formed</b> by reacting an acid and alkali under standard conditions	$\Delta H_{neut}^\ominus$	Exothermic

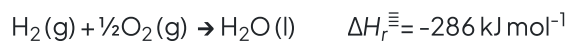
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- Practice your understanding of enthalpy changes on the following worked examples:

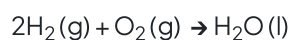


### Worked Example

One mole of water is formed from hydrogen and oxygen releasing 286 kJ



Calculate  $\Delta H_r$  for the reaction below:



#### Answer:

- Since two moles of water molecules are formed in the question above, the energy released is simply:

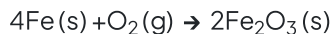
$$\Delta H_r = 2 \text{ mol} \times (-286 \text{ kJ mol}^{-1})$$

$$= -572 \text{ kJ}$$



### Worked Example

Calculate  $\Delta H_r$  for the reaction below



given that  $\Delta H_f^\ominus[\text{Fe}_2\text{O}_3(\text{s})] = -824 \text{ kJ mol}^{-1}$

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#### Answer:

- Since two moles of  $\text{Fe}_2\text{O}_3(\text{s})$  are formed the total change in enthalpy for the reaction above is:

$$\Delta H_r = 2 \text{ mol} \times (-824 \text{ kJ mol}^{-1})$$

$$= -1648 \text{ kJ}$$



### Worked Example

Identify each of the following as  $\Delta H_f^\ominus$ ,  $\Delta H_c^\ominus$ ,  $\Delta H_{\text{neut}}^\ominus$  or  $\Delta H_r^\ominus$

- $\text{MgCO}_3(\text{s}) \rightarrow \text{MgO}(\text{s}) + \text{CO}_2(\text{g})$
- $\text{C}(\text{graphite}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
- $\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$

#### Answer:

**Answer 1:**  $\Delta H_r^\ominus$

**Answer 2:**  $\Delta H_c^\ominus$  as one mole of  $\text{CO}_2$  is formed from its elements in standard state and  $\Delta H_c^\ominus$  as one mole of carbon is burnt in oxygen

**Answer 3:**  $\Delta H_{\text{neut}}^\ominus$  as one mole of water is formed from the reaction of an acid and alkali



### Exam Tip

You need to learn well the Standard Enthalpy change definitions as they are frequently tested in exam papers



5.1.3 Calorimetry

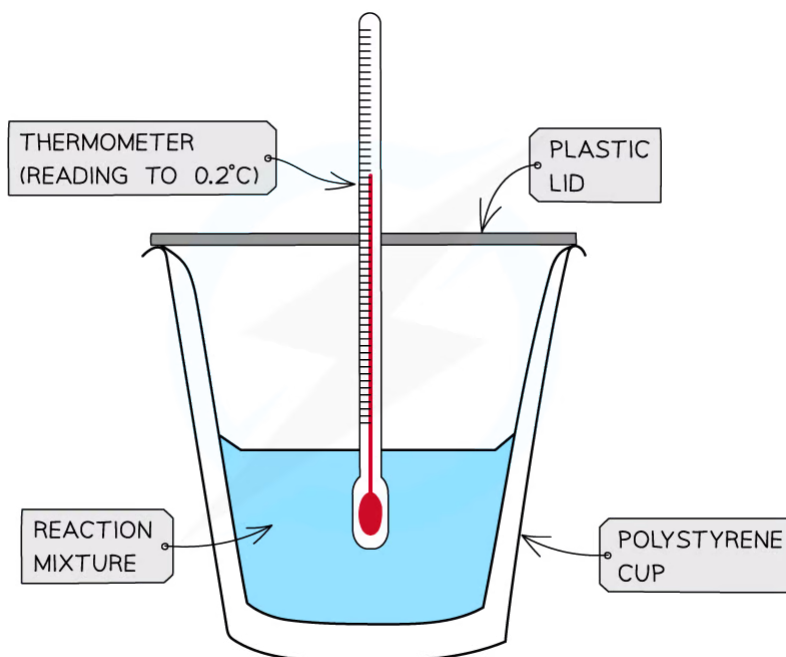
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Calorimetry

Measuring enthalpy changes

- **Calorimetry** is a technique used to measure changes in enthalpy of chemical reactions
- A **calorimeter** can be made up of a **polystyrene drinking cup**, a **vacuum flask** or **metal can**



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**A polystyrene cup can act as a calorimeter to find enthalpy changes in a chemical reaction**

- The energy needed to raise the temperature of 1 g of a substance by 1 K is called the **specific heat capacity** (*c*) of the liquid
- The **specific heat capacity** of water is 4.18 J g<sup>-1</sup> K<sup>-1</sup>
- The energy transferred as heat can be calculated by:

$$q = m \times c \times \Delta T$$

*q* = THE HEAT TRANSFERRED, J  
*m* = THE MASS OF WATER, g  
*c* = THE SPECIFIC HEAT CAPACITY, J g<sup>-1</sup> K<sup>-1</sup>  
 $\Delta T$  = THE TEMPERATURE CHANGE, K

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**Equation for calculating energy transferred in a calorimeter**



### Worked Example

The energy from 0.01 mol of propan-1-ol was used to heat up 250 g of water. The temperature of the water rose from 298 K to 310 K (the specific heat capacity of water is  $4.18 \text{ J g}^{-1} \text{ K}^{-1}$ ). Calculate the enthalpy of combustion.

**Answer:**

**Step 1:**  $q = m \times c \times \Delta T$

$$m \text{ (of water)} = 250 \text{ g}$$

$$c \text{ (of water)} = 4.18 \text{ J g}^{-1} \text{ K}^{-1}$$

$$\Delta T \text{ (of water)} = 310 - 298 \text{ K}$$

$$= 12 \text{ K}$$

**Step 2:**  $q = 250 \times 4.18 \times 12$

$$= 12540 \text{ J}$$

**Step 3:** This is the energy released by 0.01 mol of propan-1-ol

$$\text{Total energy } \Delta H = q \div n = 12540 \text{ J} \div 0.01 \text{ mol} = 1254000 \text{ J mol}^{-1}$$

$$\text{Total energy} = -1254 \text{ kJ mol}^{-1}$$



### Exam Tip

There's no need to convert the temperature units in calorimetry as the change in temperature in  $^{\circ}\text{C}$  is equal to the change in temperature in K

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## 5.1.4 Calorimetry Experiments

### Calorimetry Experiments

- There are two types of calorimetry experiments you need to know for IB Chemistry:
  - **Enthalpy** changes of **reactions in solution**
  - **Enthalpy** changes of **combustion**
- In both cases you should be able to give an outline of the experiment and be able to process experimental data using calculations or graphical methods

#### Enthalpy changes for reactions in solution

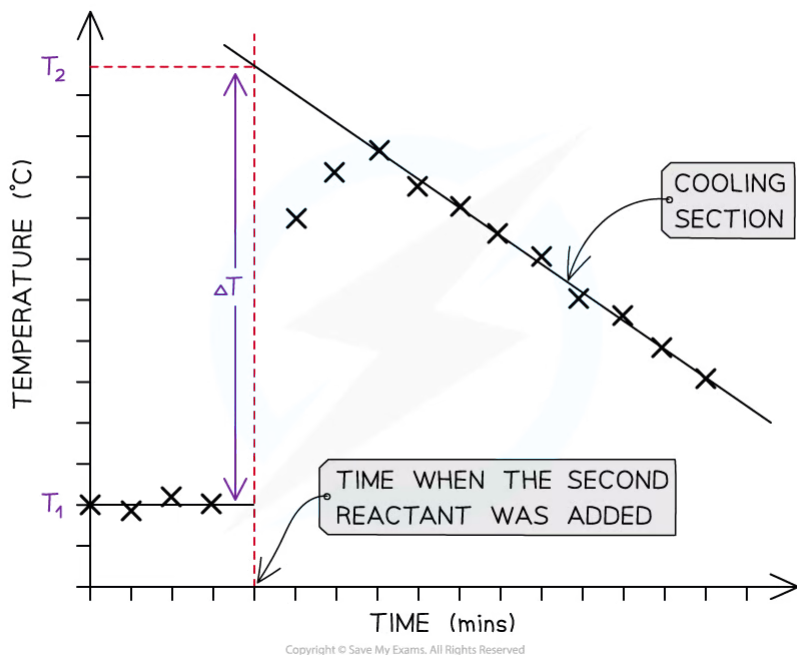
- The principle of these calorimetry experiments is to carry out the reaction with an excess of one reagent and measure the temperature change over the course of a few minutes
- The apparatus needed to carry out an enthalpy of reaction in solution calorimetry experiment is shown in the previous section **5.1.3 Calorimetry**
- For the purposes of the calculations, some assumptions are made about the experiment:
  - That the specific heat capacity of the solution is the same as pure water, i.e.  **$4.18 \text{ J g}^{-1} \text{ K}^{-1}$**
  - That the density of the solution is the same as pure water, i.e.  **$1 \text{ g cm}^{-3}$**
  - The specific heat capacity of the container is ignored
  - The reaction is complete
  - There are negligible heat losses

#### Temperature correction graphs

- For reactions which are not instantaneous there may be a delay before the maximum temperature is reached
- During that delay the substances themselves may be losing heat to the surroundings, so that the true maximum temperature is never actually reached
- To overcome this problem we can use graphical analysis to determine the maximum enthalpy change

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**A temperature correction graph for a metal displacement reaction between zinc and copper sulfate solution. The zinc is added after 4 minutes**

The steps to make a temperature correction graph are:

1. Take a temperature reading before adding the reactants for a few minutes to get a steady value
2. Add the second reactant and continue recording the temperature and time
3. Plot the graph and **extrapolate** the cooling part of the graph until you intersect the time at which the second reactant was added

- An assumption made here is that the rate of cooling is constant
- The analysis can also be used for endothermic reactions, but this time there will be a 'warming' section as the substances return to room temperature

### ? Worked Example

Excess iron powder was added to 100.0 cm<sup>3</sup> of 0.200 mol dm<sup>-3</sup> copper(II)sulfate solution in a calorimeter. The reaction equation was as follows



The maximum temperature rise was 7.5 °C. Determine the enthalpy of reaction, in kJ

**Answer:**

**Step 1:** Calculate q

$$q = m \times c \times \Delta T$$

$$q = 100 \text{ g} \times 4.18 \text{ J g}^{-1} \text{ K}^{-1} \times 7.5 \text{ K} = -3135 \text{ J}$$

**Step 2:** Calculate the amount of  $\text{CuSO}_4(\text{aq})$

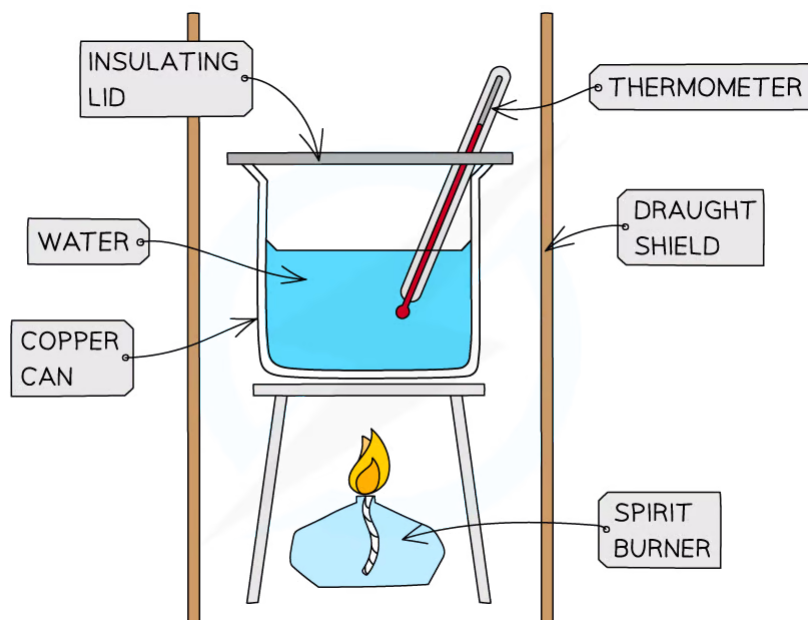
$$\text{moles} = \text{volume in dm}^3 \times \text{concentration} = 0.1 \times 0.2 = 0.02 \text{ mol}$$

**Step 3:** Calculate  $\Delta H$

$$\Delta H = q \div n = -3135 \text{ J} \div 0.02 \text{ mol} = -156750 \text{ J} = -156.75 \text{ kJ} = \mathbf{-160 \text{ kJ}} \text{ (2 sig figs)}$$

## Enthalpy of Combustion Experiments

- The principle here is to use the heat released by a combustion reaction to increase the heat content of water
- A typical simple calorimeter is used to measure the temperature changes to the water



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### *A simple combustion calorimeter*

- Not all the heat produced by the combustion reaction is transferred to the water
  - Some heat is lost to the surroundings
  - Some heat is absorbed by the calorimeter
- To minimise the heat losses the copper calorimeter should not be placed too far above the flame and a lid placed over the calorimeter
- Shielding can be used to reduce draughts
- In this experiment the main sources of error are
  - Heat losses**
  - Incomplete combustion**

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### Worked Example

1.023 g of propan-1-ol ( $M = 60.11 \text{ g mol}^{-1}$ ) was burned in a spirit burner and used to heat 200 g of water in a copper calorimeter. The temperature of the water rose by  $30^\circ\text{C}$ . Calculate the enthalpy of combustion of propan-1-ol using this data.

**Answer:**

**Step 1:** Calculate  $q$

$$q = m \times c \times \Delta T$$

$$q = 200 \text{ g} \times 4.18 \text{ J g}^{-1} \text{ K}^{-1} \times 30 \text{ K} = -25\,080 \text{ J}$$

**Step 2:** Calculate the amount of propan-1-ol burned

$$\text{moles} = \text{mass} \div \text{molar mass} = 1.023 \text{ g} \div 60.11 \text{ g mol}^{-1} = 0.01702 \text{ mol}$$

**Step 3:** Calculate  $\Delta H$

$$\Delta H = q \div n = -25\,080 \text{ J} \div 0.01702 \text{ mol} = -1\,473\,560 \text{ J} = -1\,474 \text{ kJ} = \mathbf{-1.5 \times 10^3 \text{ kJ}}$$



### Exam Tip

There are many potential sources of error in calorimetry experiments, both quantitative and qualitative. Determining % errors and comparing  $\Delta H$  results to data book values is an important part of this topic and is covered in more detail in **Topic 11 Measurement and Data Processing**

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## 5.2 Hess's Law

### 5.2.1 Hess's Law

#### Hess's Law

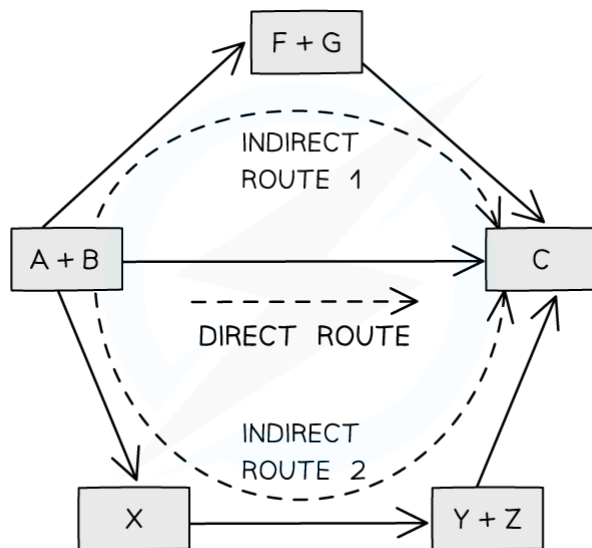
- In 1840, the Russian chemist Germain Hess formulated a law which went on to be known as **Hess's Law**
- This went on to form the basis of one of the laws of thermodynamics. The first law of thermodynamics relates to the **Law of Conservation of Energy**
- It is sometimes expressed in the following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



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**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:

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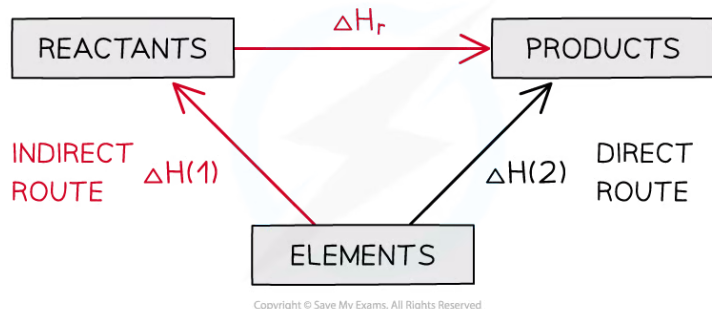




- [popover id="dGQI3oDiqUIQrR1A" label="ΔH<sub>f</sub>"], ΔH<sub>f</sub> (propane) can't be found experimentally as hydrogen and carbon don't react under standard conditions

### Calculating ΔH<sub>r</sub> from ΔH<sub>f</sub> using Hess's Law energy cycles

- You can see the relationships on the following diagram:



*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<sub>2</sub>
- OR
- The products can be indirectly formed from the elements = ΔH<sub>1</sub> + ΔH<sub>r</sub>
- **Equation**

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

Therefore for energy to be conserved,

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



#### Exam 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

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## 5.2.2 Using Hess's Law - Cycles

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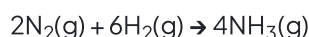


## Hess's Law using Cycles

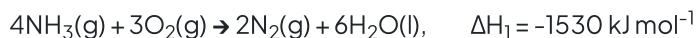
- There are two common methods to solving Hess's Law problems, using cycles and using equations
- To be successful in using cycles you need to follow carefully a step-by-step plan using the information in the question to construct a cycle and add the given information
- The following example shows one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

### ? Worked Example

Calculate the enthalpy of reaction for

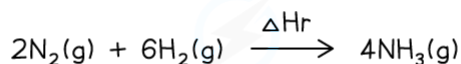


Given the data:

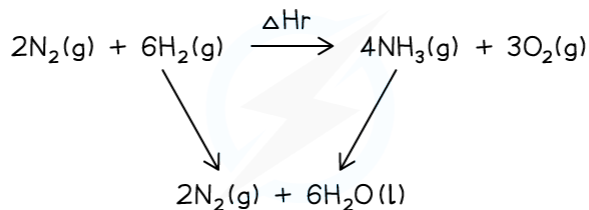


#### Answer:

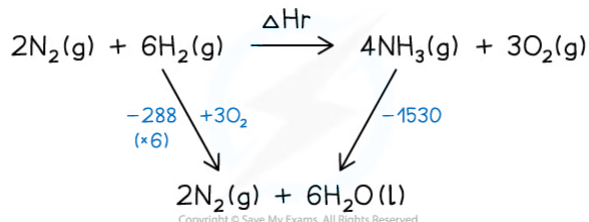
- Begin by writing the target enthalpy change at the top of your diagram from left to right:


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


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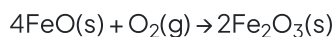
- Write the Hess's Law calculation out:

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

- 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

### ? Worked Example

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

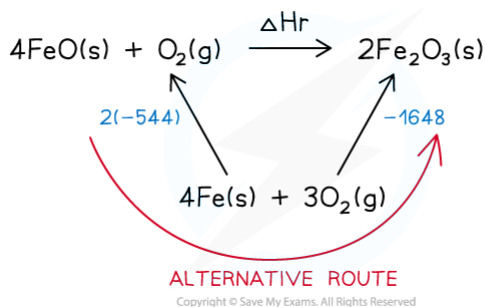


Given the data:



**Answer:**

- Draw the Hess cycle and add the known values



- Write the Hess's Law calculation out:

Follow the alternative route and the process the calculation

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



### Exam 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

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## 5.2.3 Using Hess's Law - Equations

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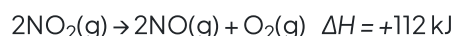

**Hess's Law using Equations**

- We can use Hess's Law to solve unknown enthalpy changes by combining equations
- This requires a methodical step-by-step approach
- It is necessary to identify how the given equations relate to the target equation as the following example illustrates

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


**Worked Example**

Consider the following reactions.


 What is the  $\Delta H$  value, in kJ, for the following reaction?

**Answer:**

1. Identify which given equation contains the product you want

**This equation contains the desired product on the left side:**

 2. Adjust the equation if necessary, to give the same product. If you reverse it, **reverse the  $\Delta H$  value**
**Reverse it and reverse the sign**


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**
**Next steps**

4. Identify which given equation contains your reactant

**This equation contains the reactant**



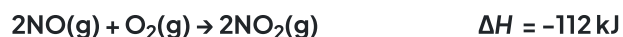

5. Adjust the equation if necessary, to give the same reactant. If you reverse it, reverse the  $\Delta H$  value

**No need to reverse it as the reactant is already on the left side**

6. Adjust the equation if necessary, to give the same number of moles of reactant

### Final steps

7. Add the two equations together



8. Cancel the common items

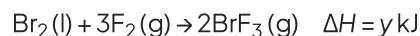


9. Add the two  $\Delta H$  values together to get the one you want



### ? Worked Example

The enthalpy changes for two reactions are given.



What is the enthalpy change for the following reaction?

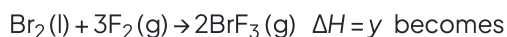


- A.  $x - y$
- B.  $y - x$
- C.  $\frac{1}{2}(-x + y)$
- D.  $\frac{1}{2}(x - y)$

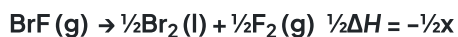
### Answer:

The correct option is **C**.

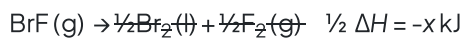
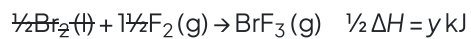
- The second equation contains the desired product, but it needs to be halved to make 1 mole



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



- Combine the two equations and cancel the common terms:



### Exam 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

YOUR NOTES



5.2.4 Using  $\Delta H_f^\circ$  to Find Enthalpy Changes

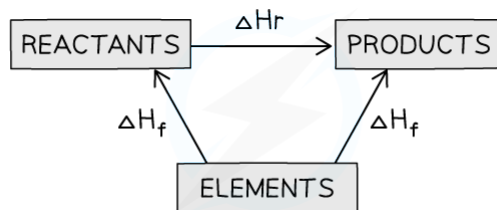
YOUR NOTES


**Using  $\Delta H_f^\circ$  to Find Enthalpy Changes**

- 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



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**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  $\Delta H$  will always be in the same arrangement

$$\Delta H_r = \sum \Delta H_f \text{ products} - \sum \Delta H_f \text{ reactants}$$

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- Try the following worked example:


**Worked Example**

Given the data:

Substance	$B_2H_6(g)$	$B_2O_3(g)$	$H_2O(g)$
$\Delta H_f / kJ mol^{-1}$	+31.4	-1270	-242

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


**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  $\Delta H_f$  of elements by definition is zero

**Step 3:** Calculate the enthalpy change

$$\Delta H = \Delta H_{f \text{ products}} - \Delta H_{f \text{ reactants}} = -1996 - (+31.4) = \mathbf{-2027.4 \text{ kJ}}$$



### Exam Tip

In Paper 1, Enthalpy of Formation data will be given in the question. For Paper 2, you may need to refer to Section 12 of the Data Booklet where you will find Thermodynamic Data for Selected Compounds

YOUR NOTES

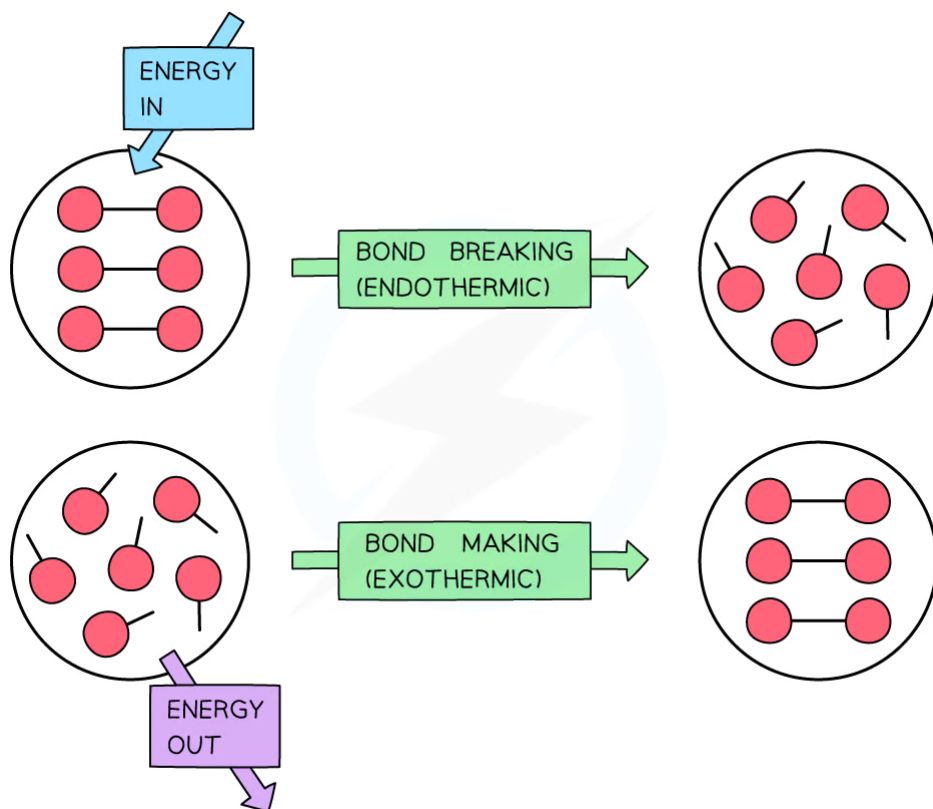


## 5.3 Bond Enthalpy

### 5.3.1 Bond Enthalpy

#### Bonds & Energy

- 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



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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**

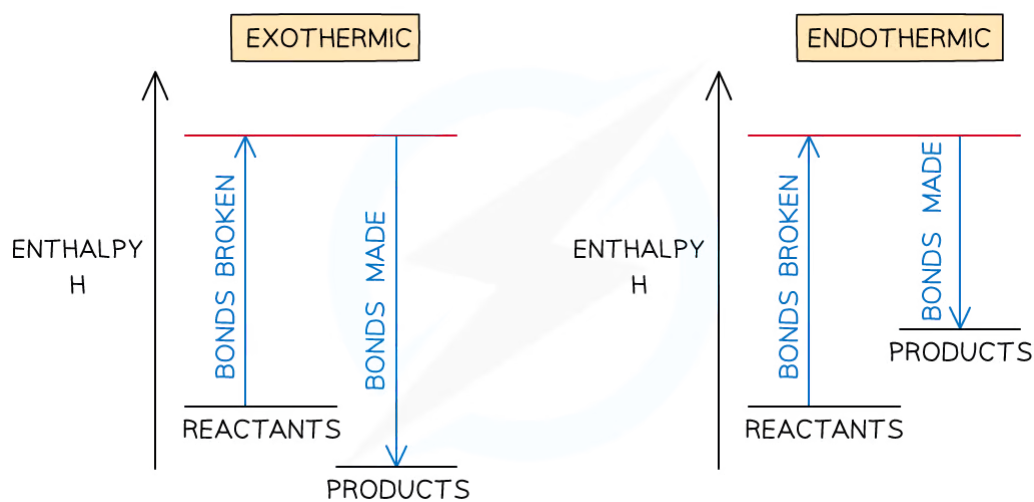
- The amount of energy released when a particular bond is formed has the same magnitude as the energy taken in when the bond is broken but has the opposite sign





## 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:



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**Bond enthalpy profiles**

YOUR NOTES



## Bond Enthalpy

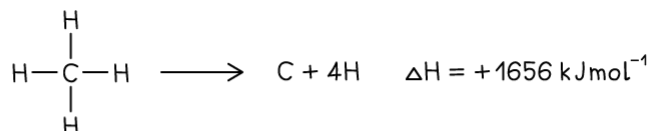
YOUR NOTES



### 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

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

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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**



### Exam Tip

A lot of students mix up endothermic / exothermic and bond breaking / bond making.

An easy way to remember is that **ENDOTHERMIC** leads to the poetic phrase the '**end o' the bond**'

YOUR NOTES



## 5.3.2 Bond Enthalpy Calculations

YOUR NOTES


**Bond Enthalpy Calculations**

- Bond energies are used to find the  $\Delta H_r^\ominus$  of a reaction when this cannot be done experimentally
- The process is a step-by-step summation of the bond enthalpies of 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

### ? Worked Example

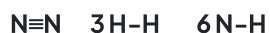
Calculate the enthalpy of reaction for the Haber process reaction. The relevant bond energies are given in the table below:

Bond	Average Bond Energy (kJ mol <sup>-1</sup> )
N ≡ N	945
H - H	436
N - H	391

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**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 ( $\text{kJ mol}^{-1}$ )	Bonds formed ( $\text{kJ mol}^{-1}$ )
$1 \times \text{N} \equiv \text{N} = 1 \times 945 = 945$ $3 \times \text{H} - \text{H} = 3 \times 436 = 1308$	$6 \times \text{N} - \text{H} = 6 \times 391$
Total = +2253	Total = -2346

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

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

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

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

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



### Worked Example

The complete combustion of ethyne,  $\text{C}_2\text{H}_2$ , 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 ( $\text{kJ mol}^{-1}$ )
C - H	414
C $\equiv$ C	839
O = O	498
C = O	804
O - H	463
O - C	358

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**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 ( $\text{kJ mol}^{-1}$ )	Bonds Formed ( $\text{kJ mol}^{-1}$ )
$1 \times \text{C} \equiv \text{C} = 1 \times 839 = 839$	$2 \times \text{O}-\text{H} = 2 \times 463 = 926$
$2 \times \text{C}-\text{H} = 2 \times 414 = 828$	$4 \times \text{C}=\text{O} = 4 \times 804 = 3216$
$2\frac{1}{2} \times \text{O}=\text{O} = 2\frac{1}{2} \times 498 = 1245$	
Total = +2912	Total = -4142

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

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

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



### Exam 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!

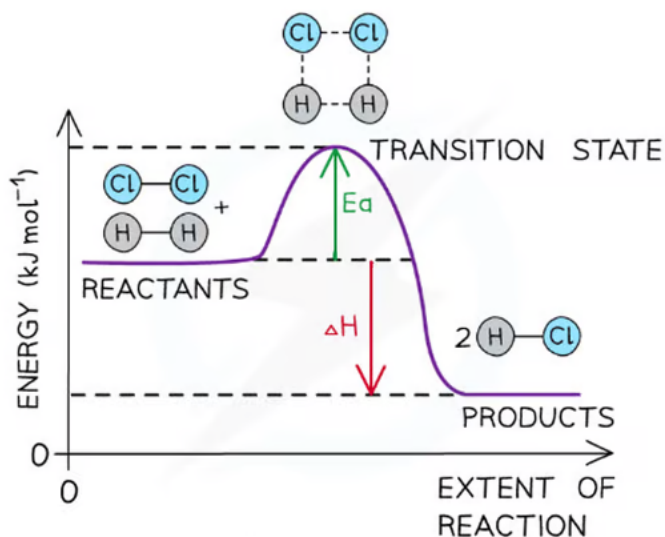
It is super important to show your steps because bond enthalpy calculations often carry 3 marks, 2 of which could be for workings if you get the final answer wrong

### 5.3.3 Energy Profiles

## Energy Profiles

- An energy profile or energy level diagram is a diagram that shows the energies of the reactants, the **transition state(s)** and the products of the reaction with time
  - The **transition state** is a stage during the reaction at which chemical bonds are partially broken and formed
  - The **transition state** is very unstable – it cannot be isolated and is higher in energy than the reactants and products
- The **activation energy** ( $E_a$ ) is the energy needed to reach the **transition state**
- We can define the **activation energy** as

**'the minimum amount of energy needed for reactant molecules to have a successful collision and start the reaction'**



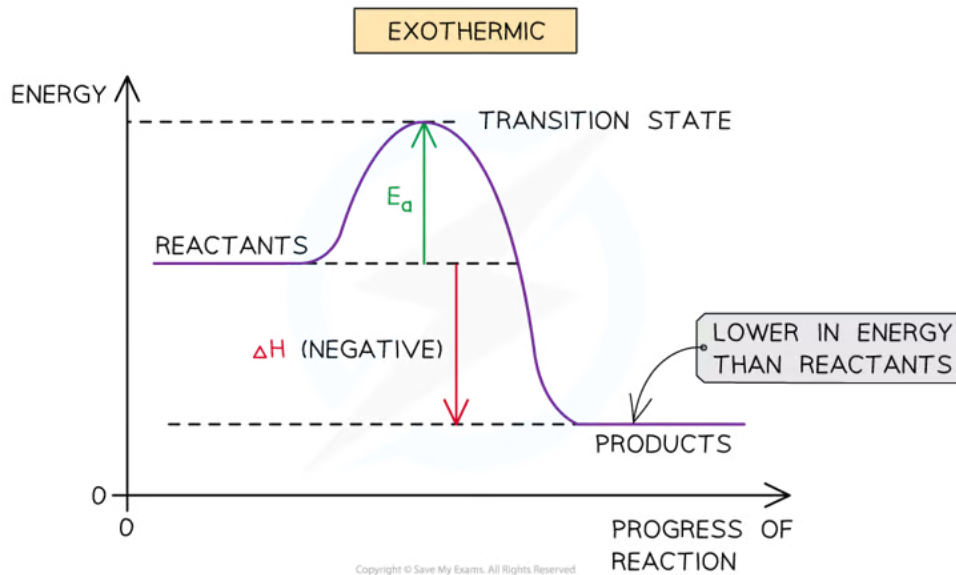
*The energy level diagram for the reaction of hydrogen with chlorine to form hydrogen chloride gas*

### Exothermic reaction

- In an **exothermic** reaction, the reactants are higher in energy than the products
- The reactants are therefore closer in energy to the **transition state**
- This means that **exothermic** reactions have a lower **activation energy** compared to **endothermic** reactions

YOUR NOTES

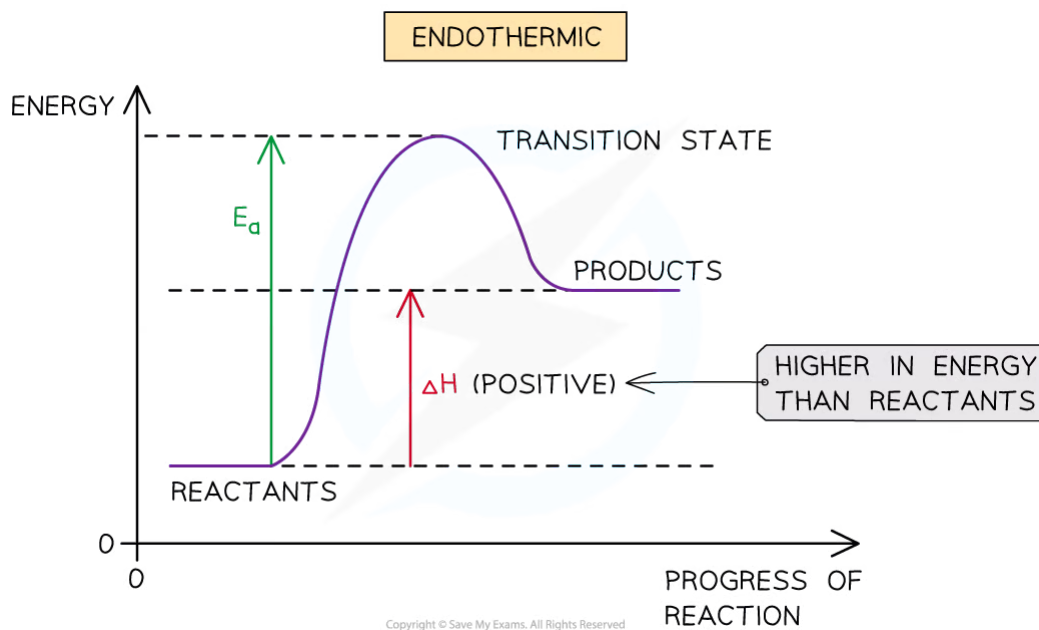




*The energy level diagram for exothermic reactions*

### Endothermic reaction

- In an **endothermic** reaction, the reactants are lower in energy than the products
- The reactants are therefore further away in energy to the **transition state**
- This means that **endothermic** reactions have a higher **activation energy** compared to **exothermic** reactions



*The energy level diagram for endothermic reactions*



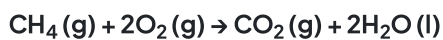


**? Worked Example**

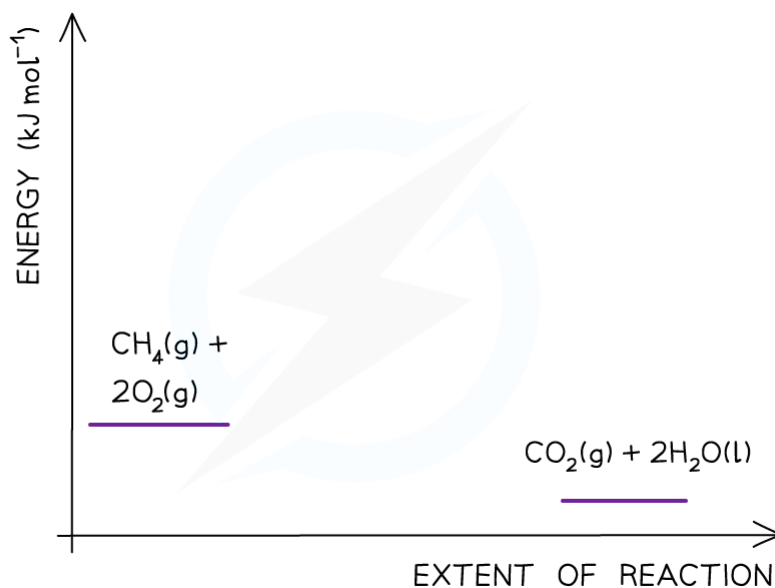
The enthalpy of combustion for methane is  $-890 \text{ kJ mol}^{-1}$  and the activation energy is  $+2653 \text{ kJ mol}^{-1}$ . Draw a labelled energy level diagram for this reaction.

**Answer:**

**Step 1:** The chemical equation for the complete combustion of methane is:

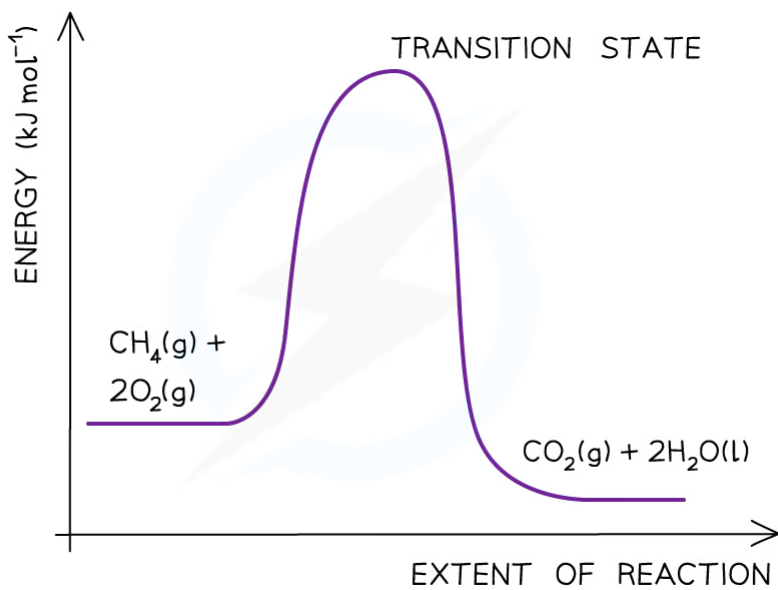


**Step 2:** Combustion reactions are always exothermic ( $\Delta H$  is negative) so the reactants should be drawn higher in energy than the products



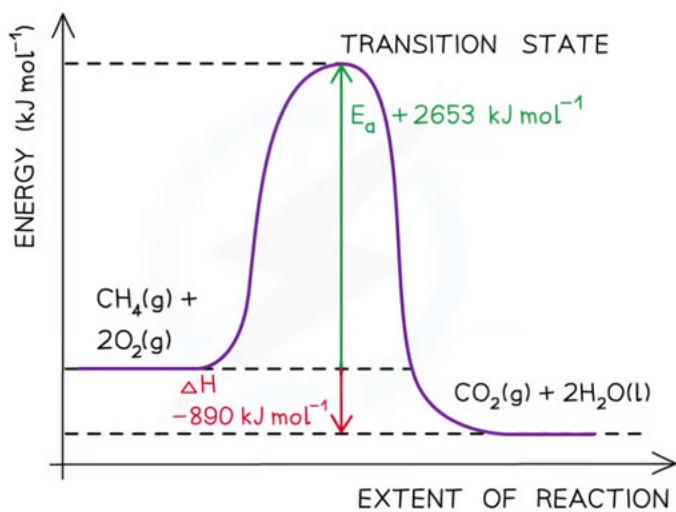
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**Step 3:** Draw the curve in the energy level diagram clearly showing the transition state



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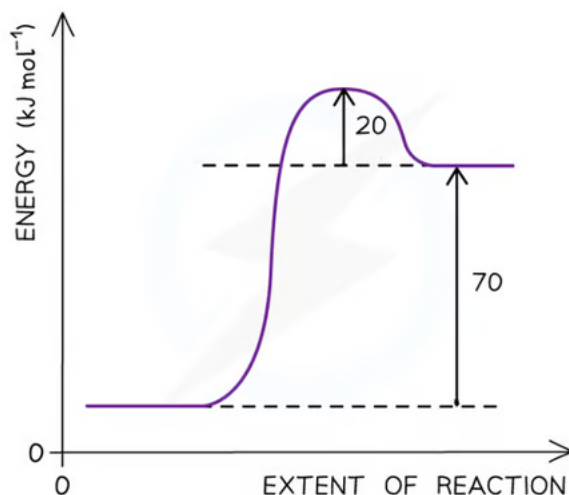
**Step 4:** Draw arrows to show the  $E_a$  and  $\Delta H$  including their values





### Worked Example

Use the energy level diagram below to identify the activation energy,  $E_a$ , for the reaction



The reaction pathway diagram for a reversible reaction

#### Answer:

- The  $E_a$  is the energy difference from the energy level of the reactants to the top of the 'hump'
- $E_a$  (forward reaction) =  $(+70 \text{ kJ mol}^{-1}) + (+20 \text{ kJ mol}^{-1}) = +90 \text{ kJ mol}^{-1}$



#### Exam Tip

The activation energy is the energy difference from **reactants** to **transition state**. The enthalpy change of the reaction is the energy difference from **reactants** to **products**. Remember to label the axis of the energy level diagrams!

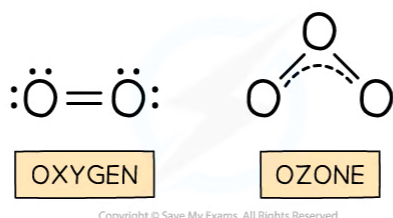
### 5.3.4 Case Study: Ozone

YOUR NOTES



#### Case study: Ozone & Bond Strength

- A study of **bond enthalpy** can explain why ozone and oxygen in the atmosphere play very different roles in the flow of energy
- These processes have a profound effect on the amount of solar radiation reaching ground level
- The structure of oxygen and ozone molecules influences the amount of energy needed to break their bonds:

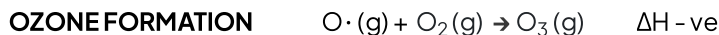


#### The structure of oxygen and ozone

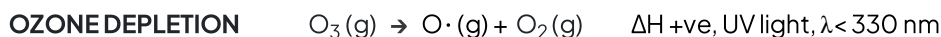
- The double bond in oxygen is stronger than the **delocalised  $\pi$  bonds** in ozone
  - We say the **bond order** of oxygen is **2** and the **bond order** of ozone is **1.5**
  - Both bonds are broken by ultraviolet radiation but the bond in oxygen requires radiation of higher energy and shorter wavelength than the bond in ozone
- High energy UV radiation in the stratosphere breaks the oxygen-oxygen double bond creating oxygen atoms



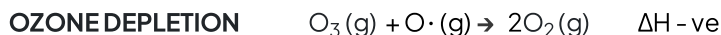
- These oxygen atoms have unpaired electrons- they are known as **free radicals**
- The **free radicals** are highly reactive and quickly attack oxygen molecules forming ozone in an **exothermic** reaction, which raises the temperature of the stratosphere



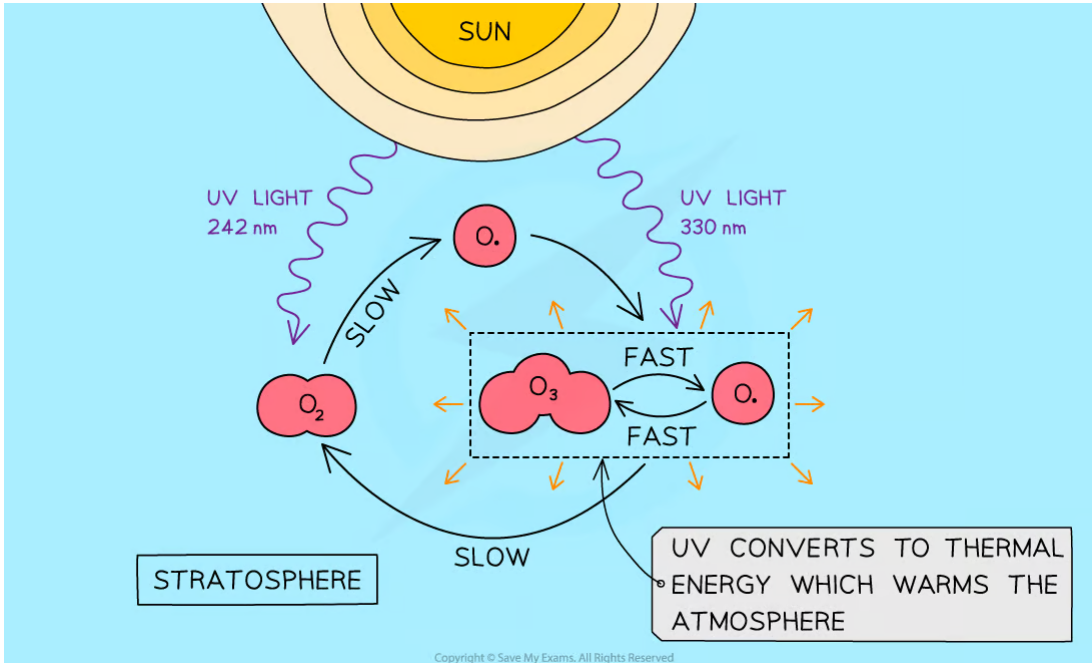
- Ozone requires less energy to break than oxygen
- It produces an oxygen molecule and an oxygen free radical:



- The radical reacts with another ozone molecule making two molecules of oxygen in an **exothermic** reaction



- The temperature in the stratosphere is maintained by the balance of ozone formation and ozone depletion in a process known as the Chapman Cycle
- It is not a closed system as matter and energy flow in and out, but it is what is called a **steady state**



### The Chapman cycle

- Unfortunately, chemicals we have introduced into the atmosphere have interfered with this steady state resulting in ozone depleting at a faster rate than it is replaced
- Amongst these chemicals are **chlorofluorocarbons (CFCs)** found in refrigerants, propellants and solvents
- **CFCs** are greatly damaging to stratospheric ozone and have been largely replaced by safer alternatives following the 1985 Montreal Protocol
- The depletion of ozone has allowed greater amounts of harmful **UV light** to reach the surface of the Earth
- **UV light** has been linked to greater incidence of skin cancer and cataracts as well as the destruction of phytoplankton and reduced plant growth