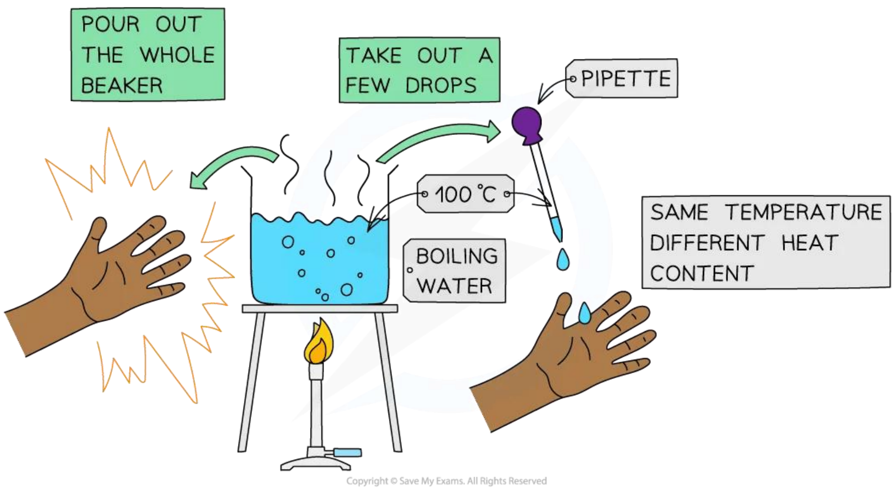
Difference between heat and temperature

What is the difference between heat and temperature?

This can be illustrated using a beaker of boiling water and a pipette:

Diagram to demonstrate the difference between heat and temperature

This can be illustrated using a beaker of boiling water and a pipette:



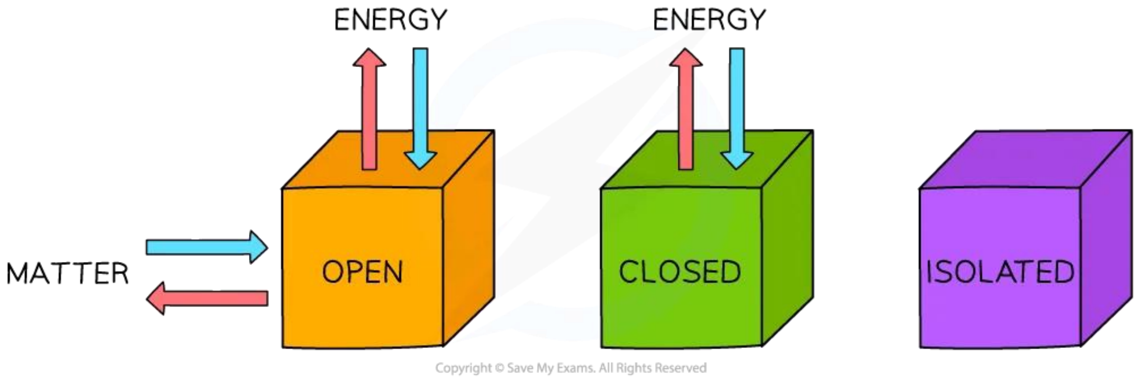
The effects of boiling water can be quite different depending on the quantity of water involved!

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

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

Diagram to show energy and matter transfer in three types of system



Open systems are the most common for chemical reactions

Most chemical reactions take place in open systems in which energy and matter can be exchanged with the surroundings

In a closed system, energy can be exchanged with the surroundings but matter cannot

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

An isolated system cannot exchange matter or energy with the surrounding and are rare

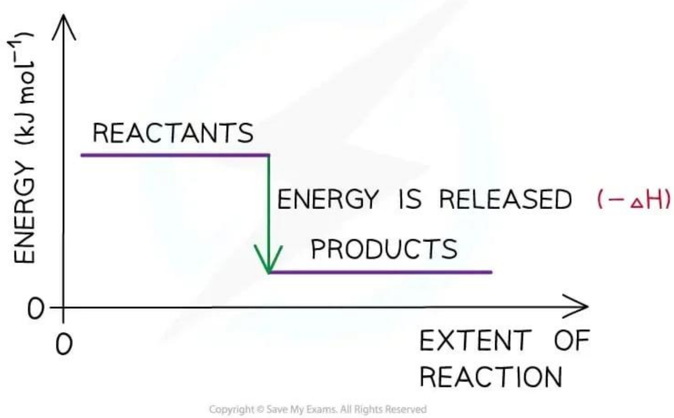
Exothermic & Endothermic Reactions

- 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 ΔH (Δ= 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 ΔH 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

Energy level diagram for an exothermic reaction

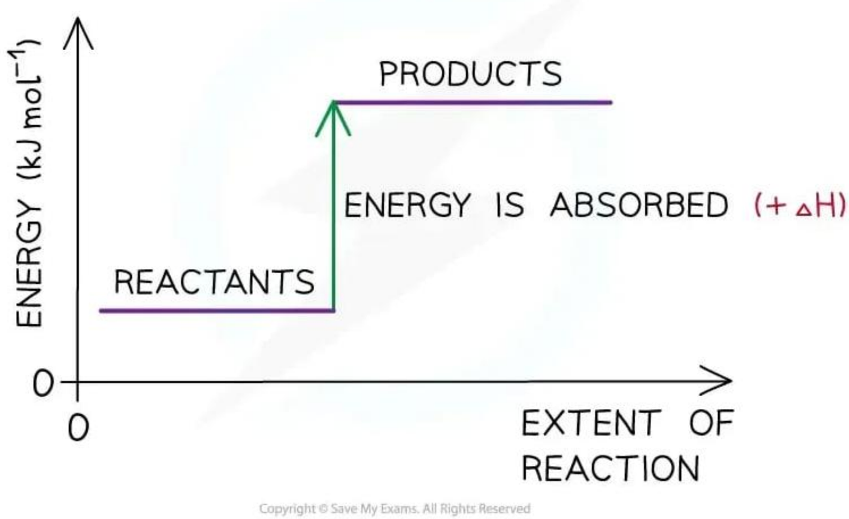


The enthalpy change during an exothermic reaction is negative

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 ΔH is positive

Energy level diagram for an endothermic reaction



The enthalpy change during an endothermic reaction is positive

Examiner Tips and Tricks

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).

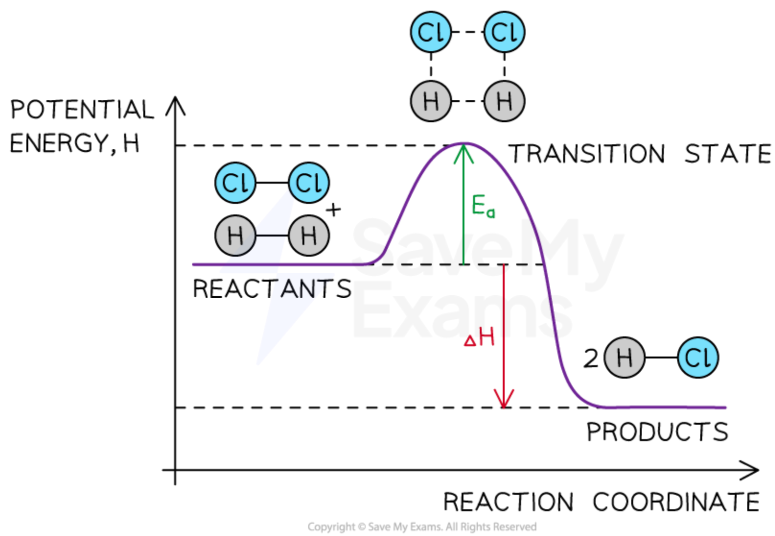
Energy Profiles

- An energy profile 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 (Ea) 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'

Energy profile diagram

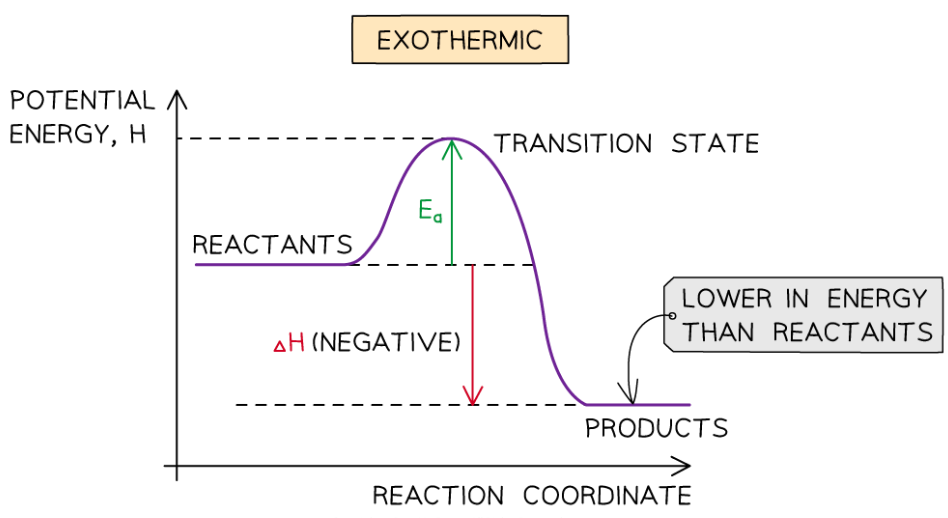


The energy profile for the reaction of hydrogen with chlorine to form hydrogen chloride gas

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

Diagram to show an energy profile for an exothermic reaction



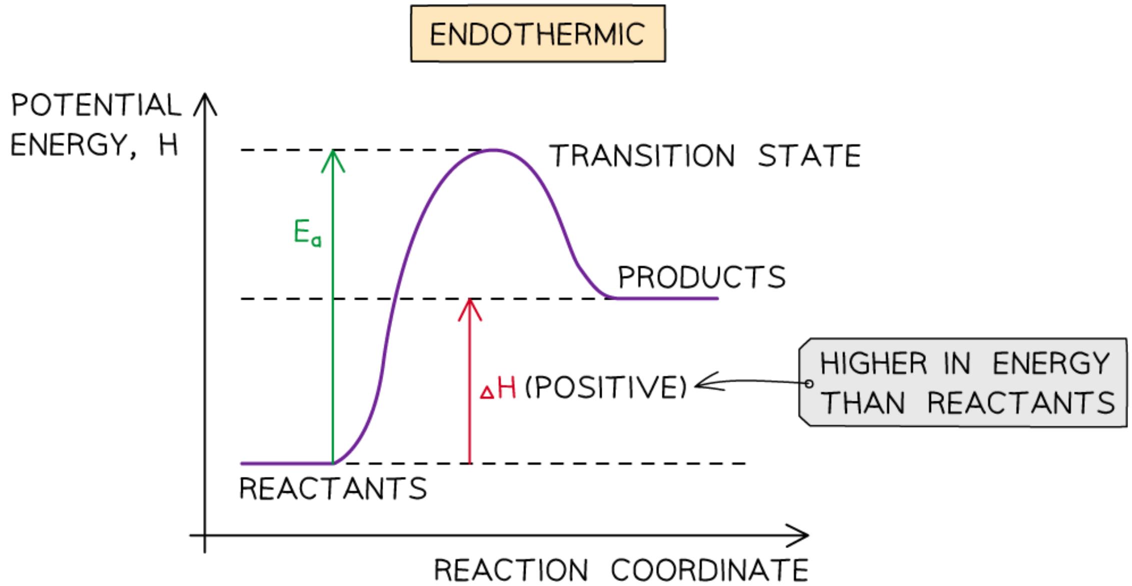
The potential energy of the products is lower than the reactants

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

Diagram to show an energy profile for an endothermic reaction

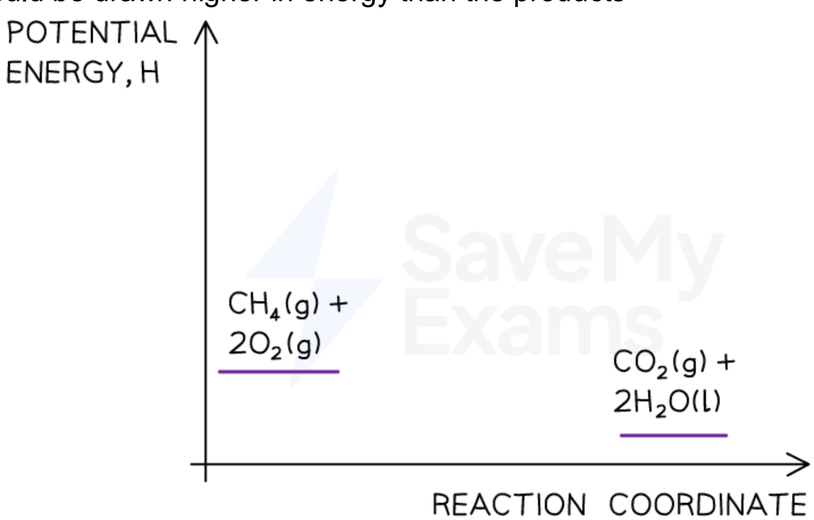


The potential energy of the products is lower than the reactants

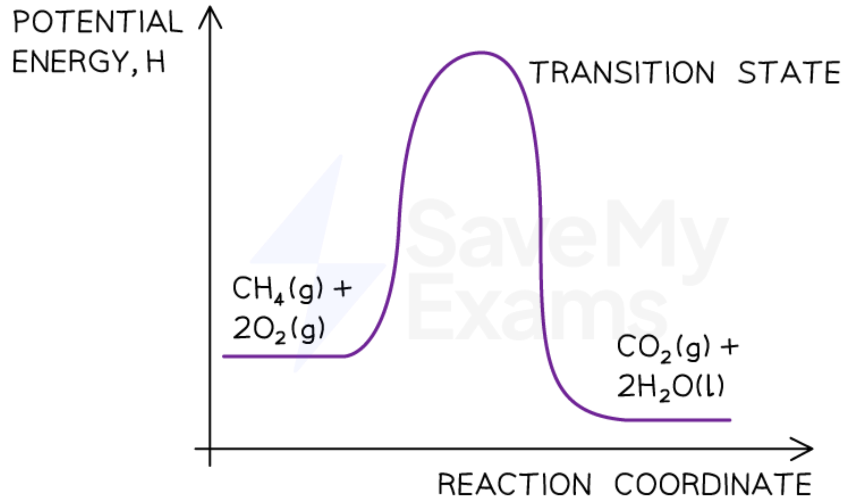
Worked Example

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

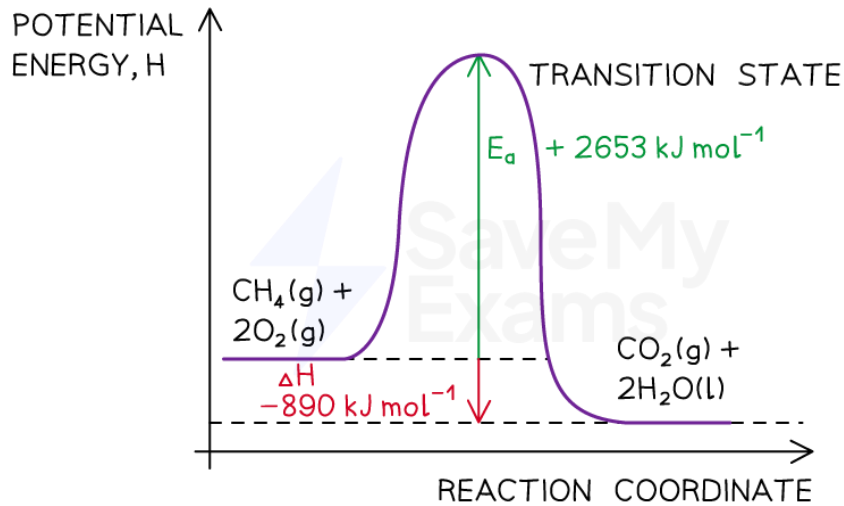
- Step 1: The chemical equation for the complete combustion of methane is:
  $$CH_4\ (g) + 2O_2\ (g) \rightarrow CO_2\ (g) + 2H_2O\ (l)$$
- Step 2: Combustion reactions are always exothermic (ΔH is negative) so the reactants should be drawn higher in energy than the products



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

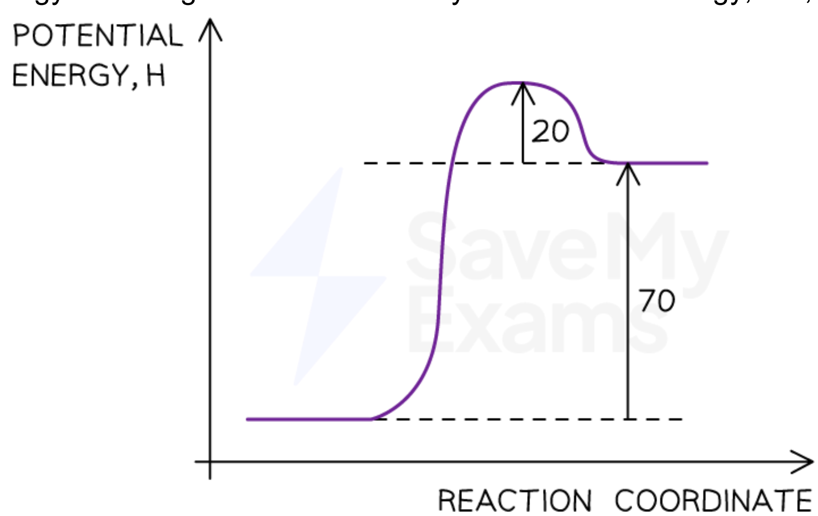


- Step 4: Draw arrows to show the Ea and ΔH including their values



Worked Example

Use the energy level diagram below to identify the activation energy, Ea , 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 kJ mol^{-1}) + (+ 20 kJ mol^{-1}) = +90 kJ mol^{-1}

Examiner Tips and Tricks

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!

Standard Enthalpy Change

- The standard enthalpy change for a chemical reaction, $\Delta H^{\ominus}$, refers to the heat transferred at constant pressure under standard conditions and states
- These standard conditions are:
  - A pressure of 100 kPa
  - A concentration of 1 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 oC) 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
Reaction	The enthalpy change when the reactants in the stoichiometric equation react to give the products under standard conditions	$\Delta H^{\ominus}_r$	Both
Formation	The enthalpy change when one mole of a compound is formed from its elements under standard conditions	$\Delta H^{\ominus}_f$	Both
Combustion	The enthalpy change when one mole of a substance is burnt in excess oxygen under standard conditions	$\Delta H^{\ominus}_c$	Exothermic

Neutralisation	The enthalpy change when one mole of water is formed by reacting an acid and alkali under standard conditions	$\Delta H^{\ominus}_{neut}$	Exothermic

- 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

H_2 (g) + ½O_2 (g) → H_2O (l) $\Delta H^{\ominus}_r$= -286 kJ mol^{-1}

Calculate ΔH_r for the reaction below:

2H_2 (g) + O_2 (g) → 2H_2O (l)

Answer:

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

ΔH_r = 2 mol x (-286 kJ mol^{-1})

= - 572 kJ

Worked Example

Calculate ΔHr for the reaction below

4Fe (s) +O_2 (g) → 2Fe_2O_3 (s)

given that $\Delta H^{\ominus}_f$ [Fe_2O_3 (s)] = - 824 kJ mol^{-1}

Answer:

- Since two moles of Fe_2O_3 (s) are formed the total change in enthalpy for the reaction above is:

ΔH_f = 2 mol x (-824 kJ mol^{-1})

= - 1648 kJ

Worked Example

Identify each of the following as $\Delta H^{\ominus}_r$, $\Delta H^{\ominus}_f$, $\Delta H^{\ominus}_c$ or $\Delta H^{\ominus}_{neut}$

1. $MgCO_3$ (s) → MgO (s) + CO_2 (g)
2. C (graphite) + O_2 (g) → CO_2 (g)
3. HCl (aq) + NaOH (aq) → NaCl (aq) + H_2O (l)

Answers:

- Answer 1: $\Delta H^{\ominus}_r$
- Answer 2: $\Delta H^{\ominus}_f$ as one mole of CO_2 is formed from its elements in standard state and $\Delta H^{\ominus}_c$ as one mole of carbon is burnt in oxygen
- Answer 3: $\Delta H^{\ominus}_{neut}$ as one mole of water is formed from the reaction of an acid and alkali

Examiner Tips and Tricks

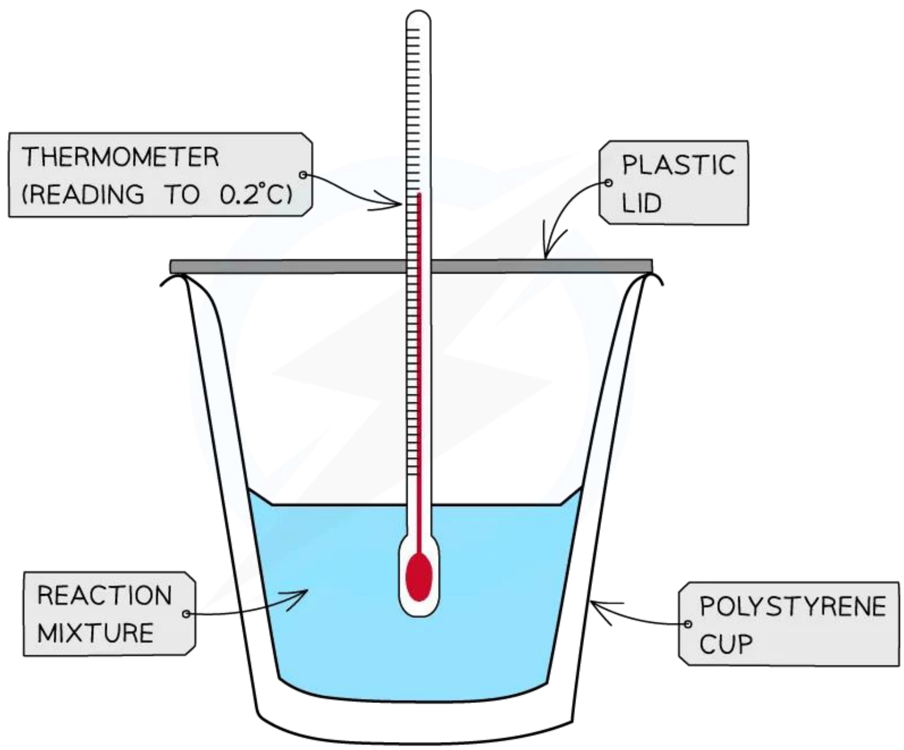
You need to learn well the Standard Enthalpy change definitions as they are frequently tested in exam papers

Calorimetry Experiments

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

Diagram to show how to set up a simple calorimeter



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^{-1} K^{-1}
- 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 $g^{-1}K^{-1}$
ΔT = THE TEMPERATURE CHANGE, K

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 298K to 310K (the specific heat capacity of water is 4.18 J g^{-1} K^{-1}.Calculate the enthalpy of combustion.

Answer:

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

m (of water) = 250 g
c (of water) = 4.18 J g^{-1} K^{-1}
ΔT (of water) = 310 - 298 K
= 12 K

- Step 2: q = 250 x 4.18 x 12

= 12 540 J

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

Total energy $\Delta H = q \div n$ = 12 540 J ÷ 0.01 mol = 1 254 000 J mol^{-1}
Total energy = - 1254 kJ mol^{-1}

Examiner Tips and Tricks

There's no need to convert the temperature units in calorimetry as the change in temperature in oC is equal to the change in temperature in K

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

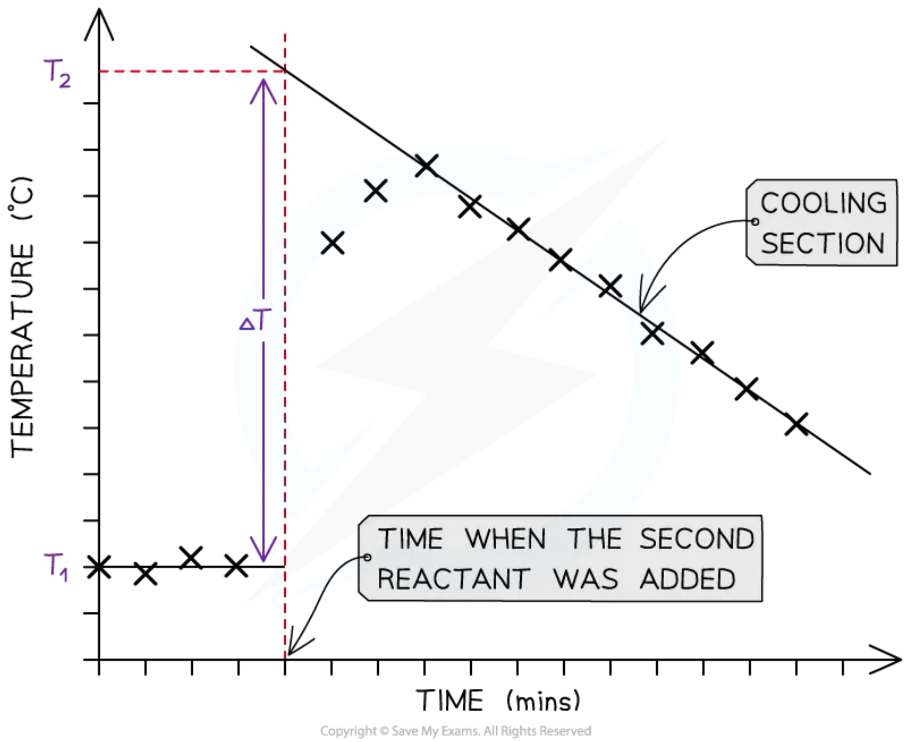
Enthalpy changes for reactions in solution

- 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
- 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 J g^{-1} K^{-1}
  - That the density of the solution is the same as pure water, i.e. 1 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

A temperature correction graph for a metal displacement reaction between zinc and copper sulfate solution



The cooling section of the graph is extrapolated back to the time when the reaction started to allow for heat loss

- 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^3 of 0.200 mol dm^{-3} copper(II) sulfate solution in a calorimeter. The reaction equation was as follows

$Fe (s) + CuSO_4 (aq) \rightarrow FeSO_4 (aq) + Cu (s)$

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

Answer:

- Step 1: Calculate q

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

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

- Step 2: Calculate the amount of $CuSO_4$ (aq)

  moles = volume in dm^3 x concentration = 0.1 x 0.2 = 0.02 mol

- Step 3: Calculate ΔH

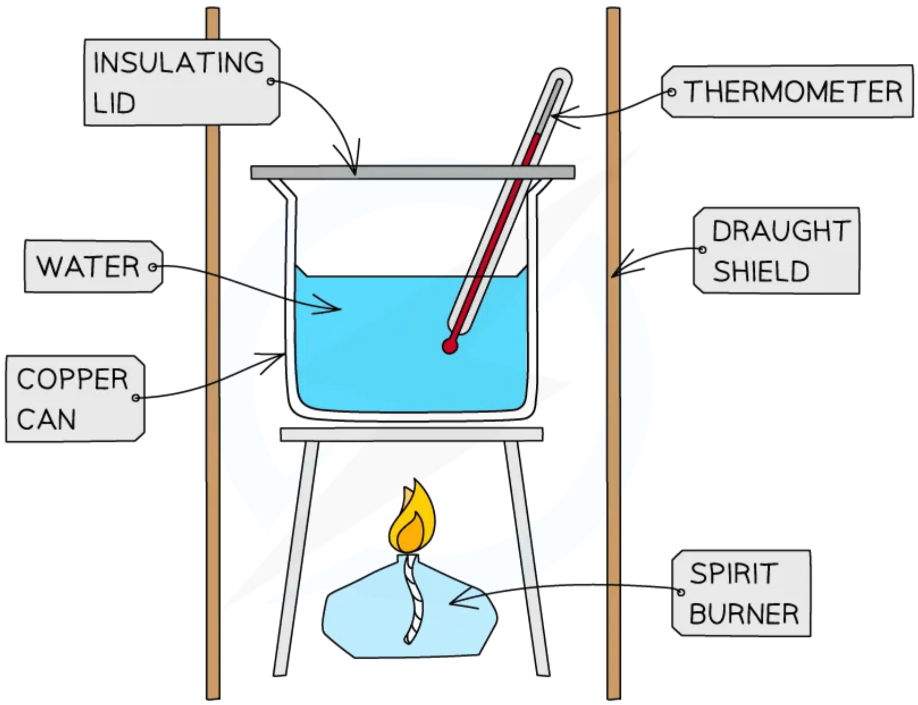
  $\Delta H = q \div n = -3135\ J \div 0.02\ mol = -\ 156\ 750\ J = -156.75\ kJ$

  = -160 kJ (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

Diagram to show the set up of a typical 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

Worked Example

1.023 g of propan-1-ol (M = 60.11 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 °C. Calculate the enthalpy of combustion of propan-1-ol using this data.

Answer:

- Step 1: Calculate q

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

  $q = 200\ g \times 4.18\ J\ g^{-1}\ K^{-1} \times 30\ K = -\ 25\ 080\ J$
- Step 2: Calculate the amount of propan-1-ol burned

  moles = mass ÷ molar mass = 1.023 g ÷ 60.11 g mol^{-1} = 0.01702 mol
- Step 3: Calculate ΔH

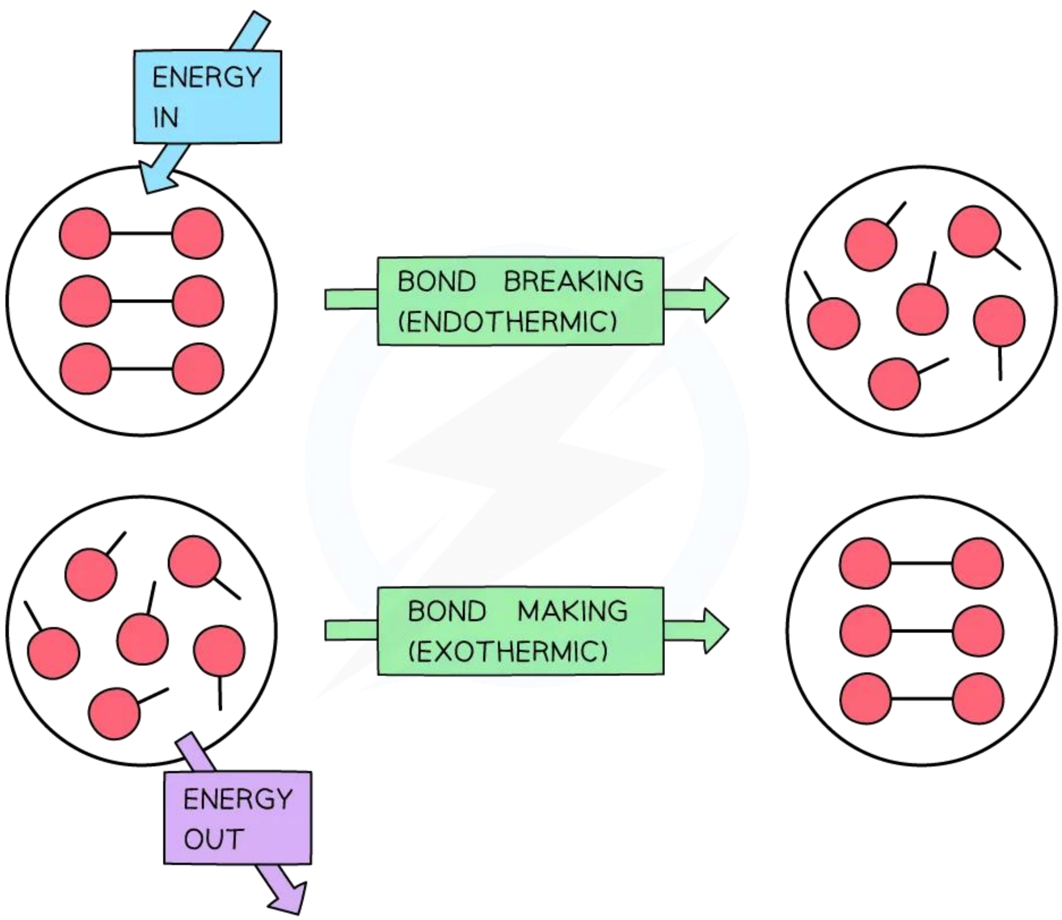
  $\Delta H = q \div n = -25\ 080\ J \div 0.01702\ mol = -\ 1\ 473\ 560\ J = -1\ 474\ kJ$

  $= -1.5 \times 10^{3}\ kJ$

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

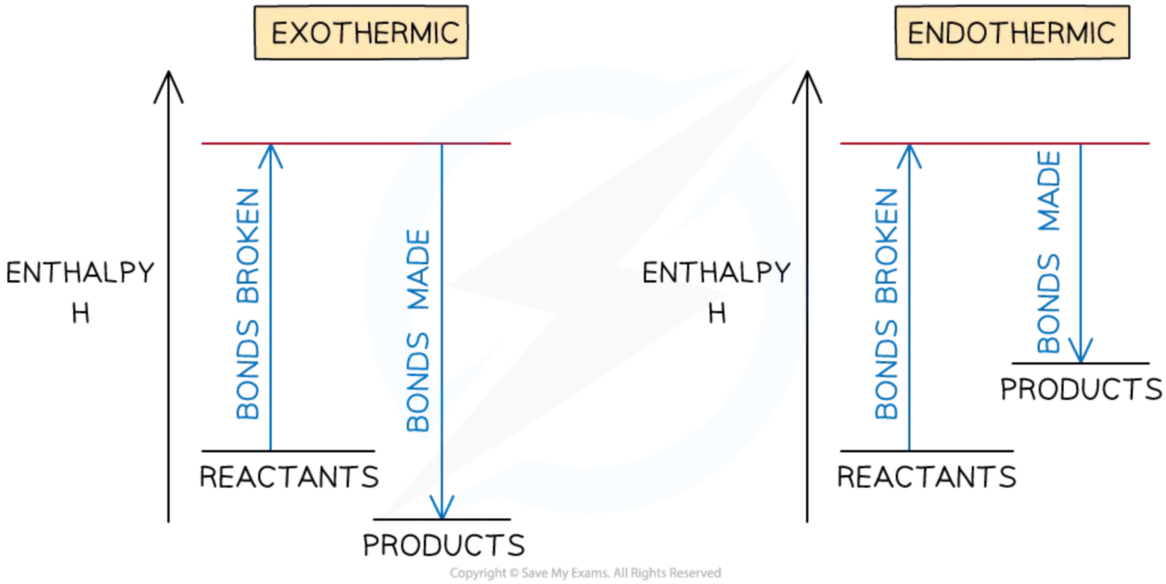
- The amount of energy released when a particular bond is formed has the same magnitude as the energy taken in when the bond is broken but has the opposite sign

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:

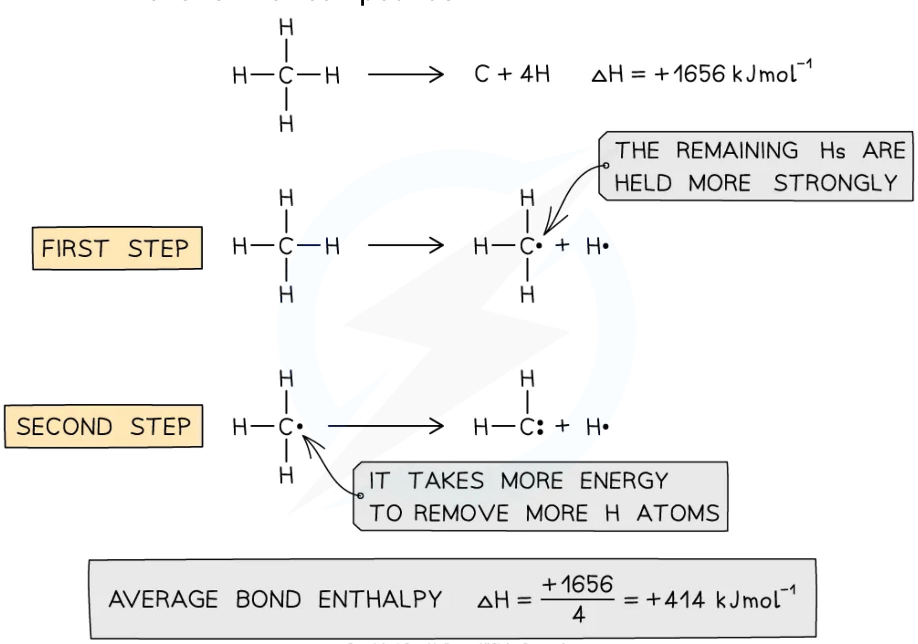
Diagram to show the energy profiles of both exothermic and endothermic reactions



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:

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

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≡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) ⇌ $2NH_3$ (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≡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

$\Delta Hr^{\ominus}$ = 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) + $5O_2$ (g) → $2H_2O$ (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 + 2 ½ O=O → 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 C–H = 2 x 414= 828
1 x C–C= 1 x 839= 839

2½ O═O = 2½ x 498 = 1245

Total = +2912

2 x O–H = 2 x 463 = 926

4 x C═O = 4 x 804 = 3216

Total= -4142

ΔH~~o~~r = enthalpy change for bonds broken + enthalpy change for bonds formed

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

= -1230 kJ mol-1

Examiner Tips and Tricks

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

- 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:

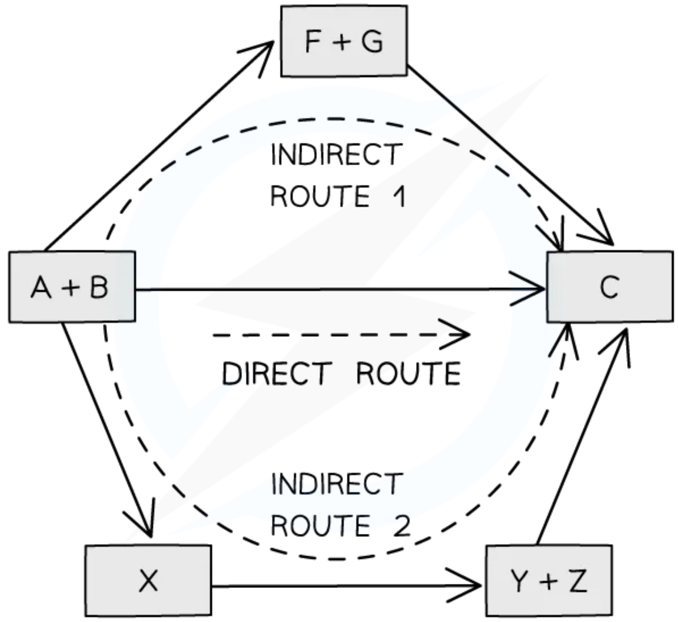
Energy cannot be created or destroyed, it can only change form

- 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:

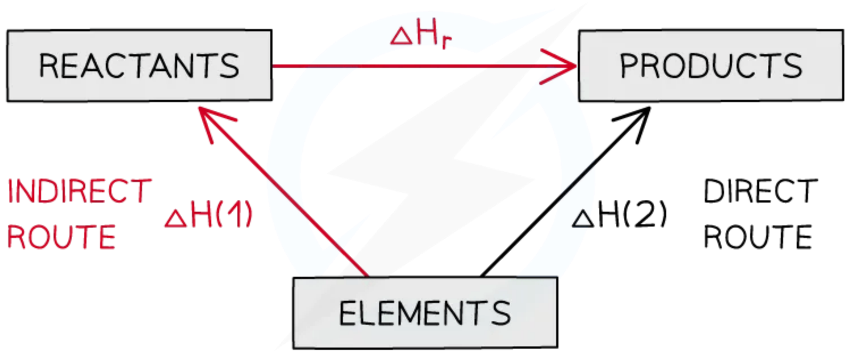
$3C\ (s) + 4H_2\ (g) \rightarrow C_3H_8(g)$

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

Calculating ΔHr from ΔHf 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,
$\Delta Hr = \Delta H_2 - \Delta H_1$

Examiner Tips and Tricks

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

- 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:

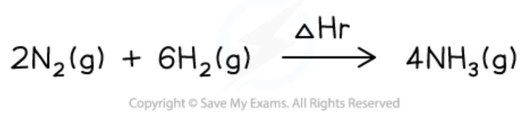
Solving Hess's Law problems using cycles:

Worked Example

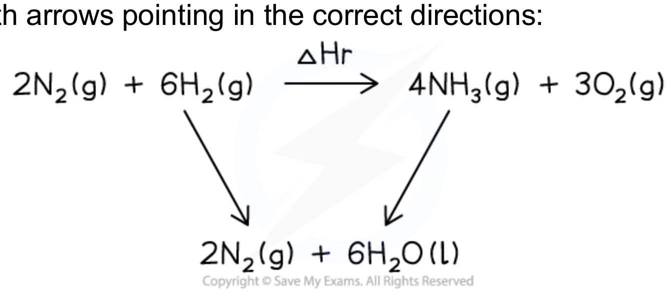
Calculate the enthalpy of reaction for:
$2N_2\ (g) + 6H_2\ (g) \rightarrow 4NH_3\ (g)$
Given the data:
$4NH_3\ (g) + 3O_2\ (g) \rightarrow 2N_2\ (g) + 6H_2O\ (l)$, $\Delta H_1 = -1530$ kJ mol^{-1}
$H_2\ (g) + ½O_2\ (g) \rightarrow H_2O\ (l)$, $\Delta H_2 = -288$ kJ mol^{-1}

Answer:

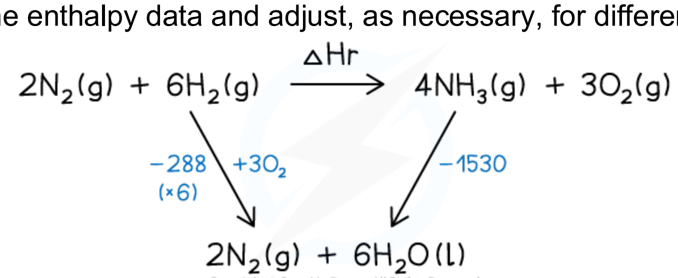
- Step 1: Begin by writing the target enthalpy change at the top of your diagram from left to right:



- 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:

$\Delta H_r = +6\Delta H_2 - \Delta H_1 = + (-288 \times 6) - (-1530) = -198$ 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?

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

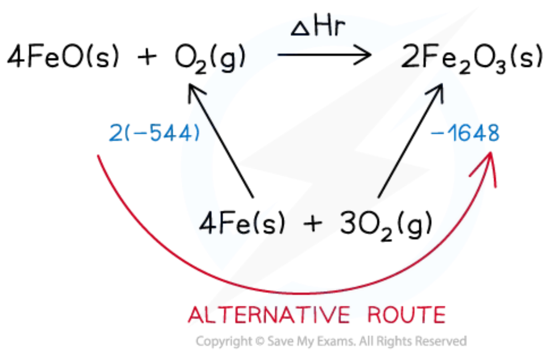
Given the data:

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

$4Fe (s) + 3O_2 (g) \rightarrow 2Fe_2O_3 (s)$ $\Delta H = -1648$ 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

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

Examiner Tips and Tricks

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:

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

- 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

$2NO (g) + O_2 (g) \rightarrow 2NO_2 (g)$ $\Delta H = -112$ 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) → 2NO (g)   ΔH = +180 kJ

- 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

N_2 (g) + O_2 (g) → 2NO (g)   ΔH = +180 kJ

2NO (g) + O_2 (g) → 2NO_2 (g)   ΔH = -112 kJ

- Step 8: Cancel the common items

N_2 (g) + O_2 (g) + 2NO (g) + O_2 (g) → 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) → 2NO_2 (g)   ΔH = +180-112 = +68 kJ

Worked Example

The enthalpy changes for two reactions are given.

Br_2 (l) + F_2 (g) → 2BrF (g)   ΔH = x kJ

Br_2 (l) + 3F_2 (g) → 2BrF_3 (g)   ΔH = y kJ

What is the enthalpy change for the following reaction?

BrF (g) + F_2 (g) → BrF_3 (g)

A. x – y

B. y - x

C. ½ (–x + y)

D. ½ (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) → 2BrF_3 (g)   ΔH = y   becomes

½Br_2 (l) + 1½F_2 (g) → BrF_3 (g)   ½ΔH = ½y

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

Br_2 (l) + F_2 (g) → 2BrF (g)   ΔH = x   becomes

BrF (g) → ½Br_2 (l) + ½F_2 (g)   ½ΔH = -½x

- Combine the two equations and cancel the common terms:

½Br_2 (l) + 1½F_2 (g) → BrF_3 (g)   ½ ΔH = y kJ

BrF (g) → ½Br_2 (l) + ½F_2 (g)   ½ ΔH = -x kJ

BrF (g) + F_2 (g) → BrF_3 (g)   ΔH = ½y + -½x = ½(-x + y)

Examiner Tips and Tricks

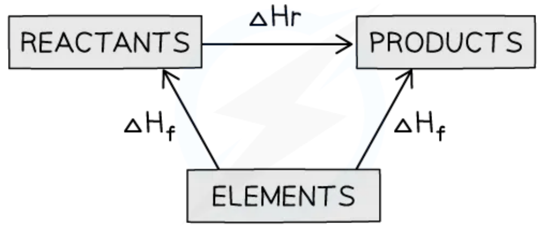
If doesn't matter whether you use equations or cycles to solve Hess's Law problems, but you should be familiar with both methods and sometimes one is easier than another.

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

- 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:

Worked Example

Given the data:

Substance	B_2H_6 (g)	B_2O_3 (g)	H_2O (g)
ΔHf /$kJmol^{-1}$	+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) → B_2O_3 (s) + $3H_2O$ (g)

Answer:

- Step 1: Find the sum of the enthalpies of combustion of the products

ΔH_f = + (-1270) + (- 242 x 3) = - 1996 kJ

- Step 2: Find the sum of the enthalpies of combustion of the reactants

ΔH_f = + (+31.4) + 0 = + 31.4 kJ

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

- Step 3: Calculate the enthalpy change

ΔH = ΔH_f products - ΔH_f reactants = - 1996 - (+ 31.4) = -2027.4 kJ

Examiner Tips and Tricks

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

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

- 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:

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

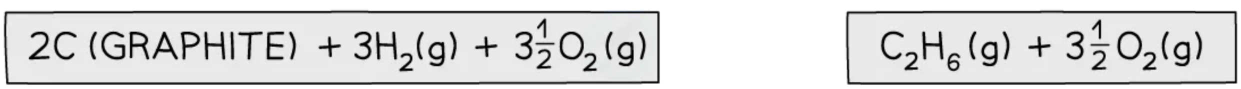
Worked Example

Calculate ΔH_f [ethane].
The relevant change in standard enthalpy of combustion (ΔHc) values are shown in the table below:

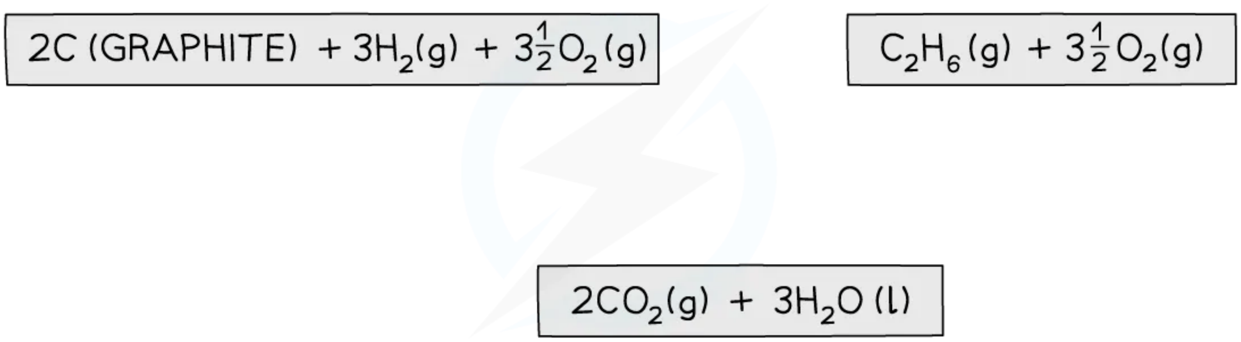
Reaction	ΔH_c (kJ mol^{-1})
C (graphite) + O_2 (g) → CO_2 (g)	-393.5
H_2 (g) + ½O_2(g) → H_2O (l)	-285.8
C_2H_6 (g) + 3 ½ O_2 (g) → $2CO_2$ (g) + $3H_2O$ (l)	-1559.7

Answer:

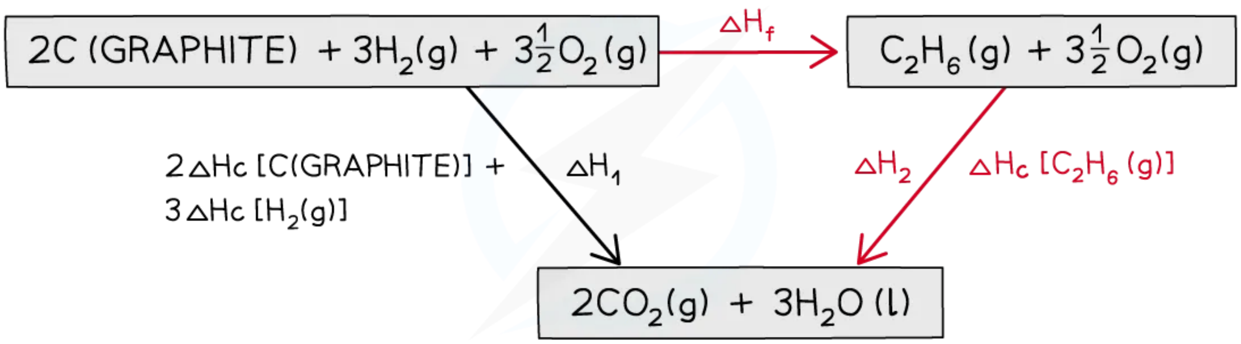
- Step 1: Write the equation for enthalpy change of formation at the top and add oxygen on both side



- Step 2: Draw the cycle with the combustion products at the bottom



- Step 3: Draw all arrows in the correct direction



- Step 4: Apply Hess's Law
  - $\Delta H_f = \Delta H_1 - \Delta H_2$
  - $\Delta H_f = 2(-393.5) + 3(-285.8) - (-1559.7)$
  - $\Delta H_f = -84.7$ kJ mol-1

Examiner Tips and Tricks

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 $\Delta H_c^{\ominus}$ & $\Delta H_f^{\ominus}$ 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:

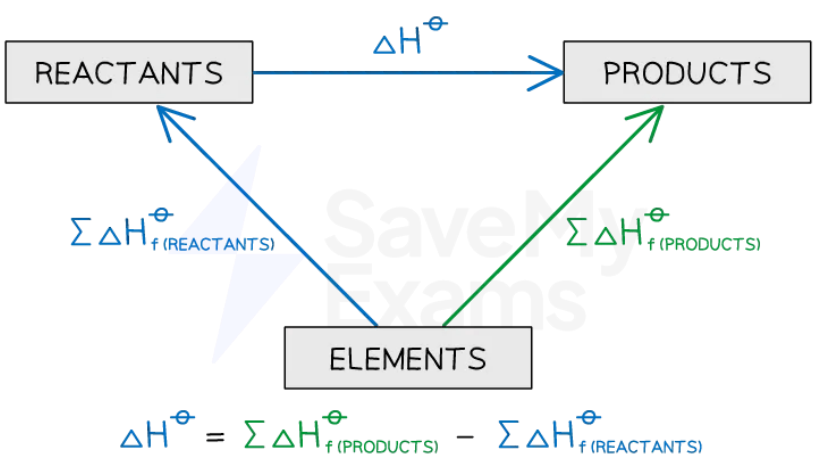
$\Delta H\theta f$ (reactants) + ΔH^{θ} = ΔH^{θ}_f (products)

- Which rearranges to:

ΔH^{θ} = ΔH^{θ}_f (products) - ΔH^{θ}_f (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 ΔHθ from ΔHθf 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

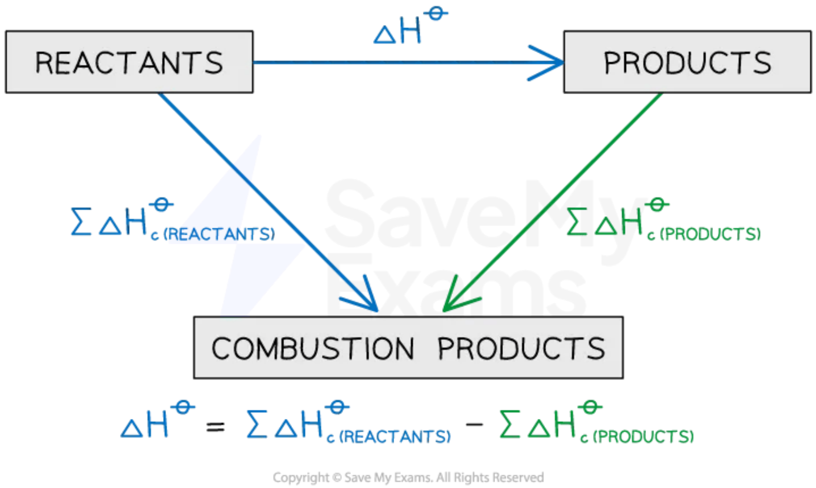
- Standard enthalpy changes of combustion, ΔH^{θ}_{c} can also be used to calculate standard enthalpy changes of reactions, ΔH^{θ}
- The overall equation will be:

ΔH^{θ}_{c} (products) + ΔH^{θ} = ΔH^{θ}_{c} (reactants)

- Which rearranges to:

ΔH^{θ} = ΔH^{θ}_{c} (reactants) - ΔH^{θ}_{c} (products)

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



Hess's Law says that the enthalpy changes on the two routes are the same.