

ENERGY TRANSFERS IN CHEMICAL REACTIONS

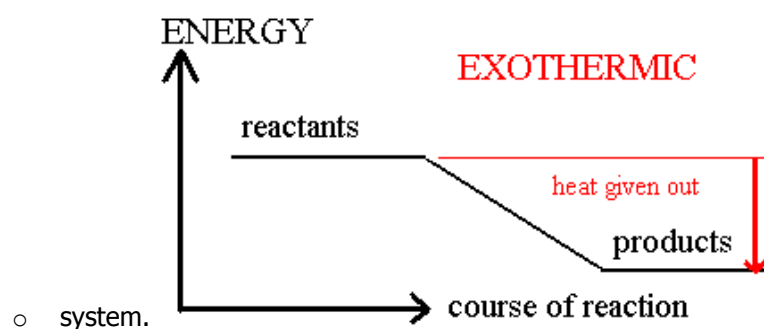


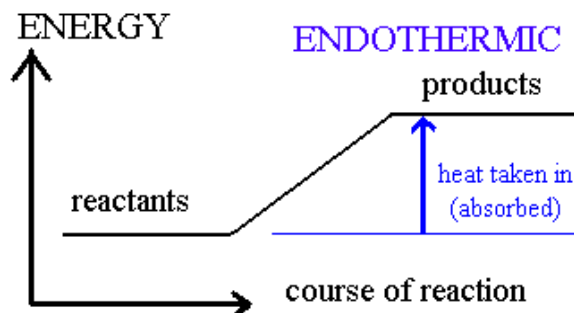
KEYWORDS: [Activation energy](#) ... [Breaking a chemical bond](#) ... [Bond energy explained](#) ... [Bond energy calculations \(theoretical\)](#) ... [calculations \(practical\)](#) ... [Catalyst action](#) ... [Chemical bond](#) ... [Endothermic reaction](#) ... [Energy level diagrams](#) ... [Exothermic reaction](#) ... [Experimental methods for determining energy changes](#) ... [Reaction profiles](#) ... [Making a chemical bond](#)

Heat Changes in Chemical Reactions

- **When chemical reactions occur**, as well as the formation of the products, there is **also a heat energy change** which can often be detected as a temperature change.
- This means **the products have a different energy content than the original reactants** (**see the reaction profile diagrams below**).
- If the products contain less energy than the reactants, heat is **given out** to the surroundings and the change is called **exothermic**. The temperature of the system will be observed to rise in an exothermic change.
 - **Examples:**
 - the burning or combustion of hydrocarbon fuels
 - the burning of magnesium, reaction of magnesium and acid or reaction of sodium on water
 - the neutralisation of acids and alkalis
 - using hydrogen as a fuel in fuel cells
- If the products contain more energy than the reactants, heat is **taken in (absorbed)** from the surroundings and the change is called **endothermic**. If the change can take place spontaneously, the temperature of the reacting system will fall but in some cases the reactants must be heated to speed up the reaction and provide the absorbed heat.
 - **Examples:**
 - the thermal decomposition of limestone)
 - the cracking of oil fractions
- The **difference between the energy levels of the reactants and products gives the overall energy change** for the reaction.
- At a more advanced level the heat change is called the **enthalpy change** is denoted by delta H, ΔH .
 - If ΔH is negative (-ve) for exothermic ie heat energy is being lost from the system,
 - an ΔH is positive (+ve) for endothermic ie heat energy is being gained by the SYSTEM

<i>EXOTHERMIC</i>	<i>ENDOTHERMIC</i>
Combustion $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ $\Delta H = -822kJ/mole$	Decomposition of Limestone $CaCO_3 \rightarrow CaO + CO_2$ $\Delta H = 222kJ/mole$
Haber Process (Formation of Ammonia) $N_2 + 3H_2 \leftrightarrow 2NH_3$ $\Delta H = -184kJ/mole$	Decomposition of Silver Chloride by light $2AgCl \rightarrow 2Ag + Cl_2$ $\Delta H = 254kJ/mole$
Contact Process; Industrial Prep. of Sulphuric Acid $2SO_2 + O_2 \leftrightarrow 2SO_3$ $\Delta H = -189kJ/mole$	Photosynthesis $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$ $\Delta H = 2816kJ/mole$
Reduction of Iron III oxide in Blast Furnace $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$ $\Delta H = -27kJ/mole$	





Note on Reversible Reactions

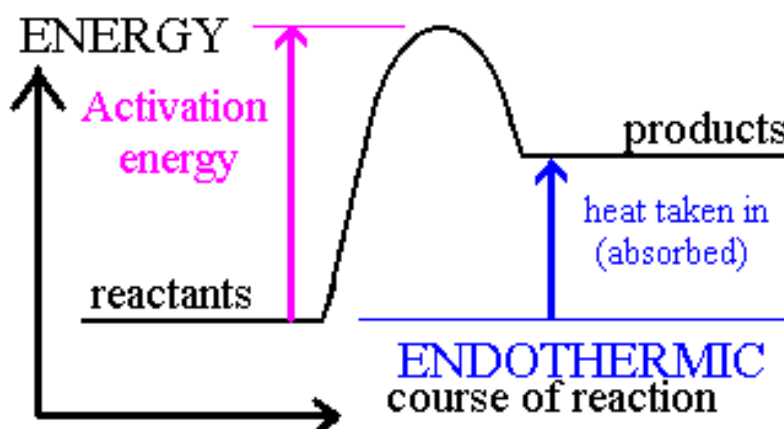
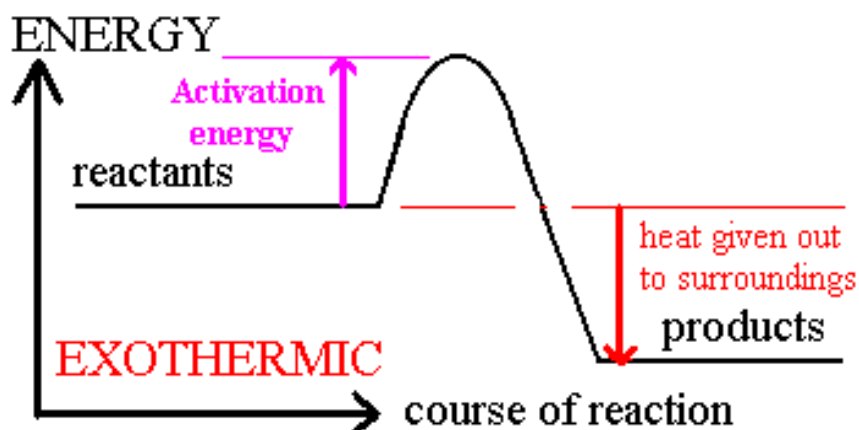
- If the direction of a reversible reaction is changed, the energy change is also reversed.
- For **example**: the **thermal decomposition of hydrated copper(II) sulphate**.
- On **heating** the blue solid, hydrated copper(II) sulphate, steam is given off and the white solid of anhydrous copper(II) sulphate is formed.
 - This a **thermal decomposition** and is **endothermic** as **heat is absorbed (taken in)**
 - The energy is needed to break down the crystal structure and drive off the water.
- When the **white solid is cooled** and water added, blue hydrated copper(II) sulphate is reformed.
 - The reverse reaction is **exothermic** as **heat is given out**.
 - ie on adding water to white anhydrous copper(II) sulphate the mixture heats up as the blue crystals reform.

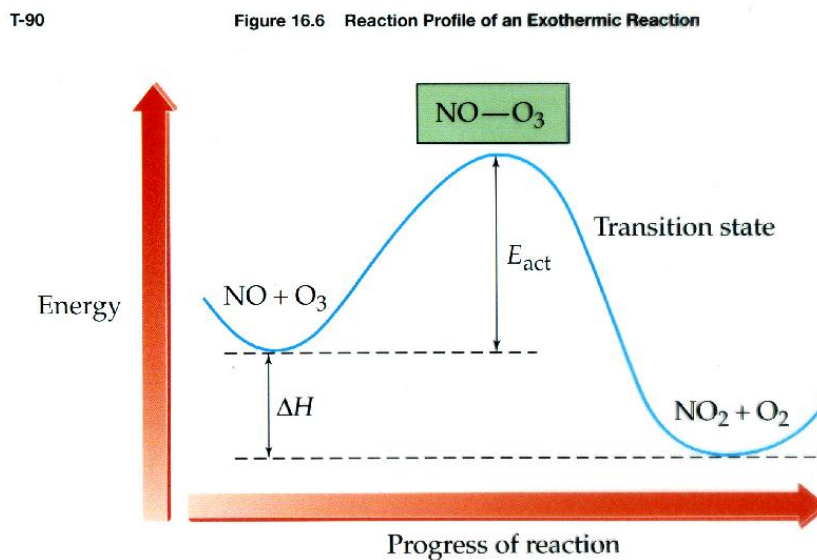
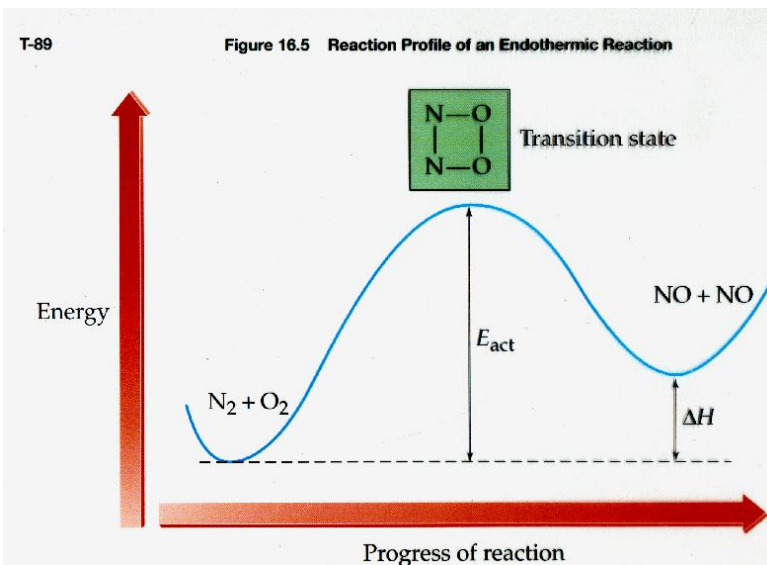


Activation Energy and Reaction Profiles

- When gases or liquids are heated the particles gain kinetic energy and move faster increasing the chance of collision between reactant molecules.
- However this is **not** the main reason for the increased reaction speed because most molecular collisions do not result in chemical change.
- Before any change takes place on collision, the colliding molecules must have a minimum kinetic energy called the **Activation Energy**. Do not confuse it with the overall energy change also shown in the diagrams below.

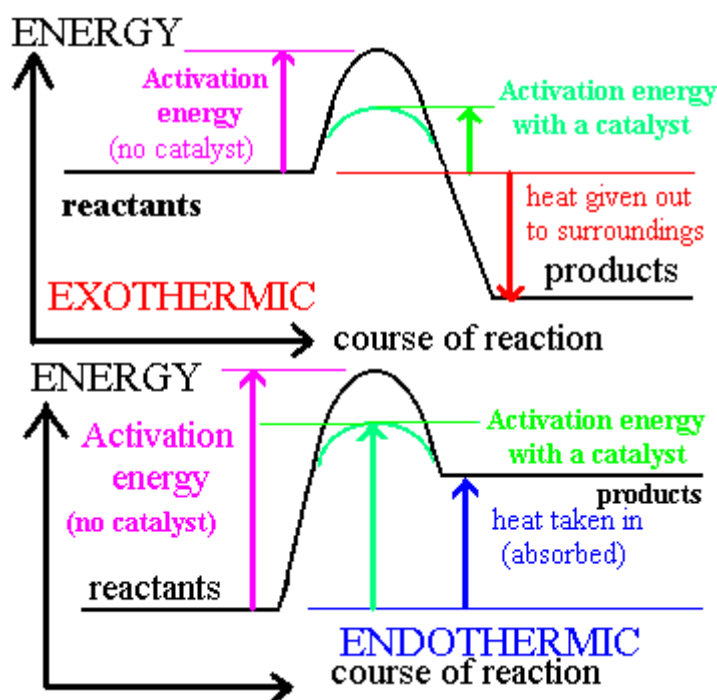
- It does not matter whether the reaction is an exothermic or an endothermic energy change. Heated molecules have a greater kinetic energy and more of them will then have the required activation energy to react.
- **The increased chance of higher energy collisions greatly increases the speed of the reaction.**
- The **activation energy 'hump'** can be related to the **bond breaking and making processes**.
 - Up the hump is endothermic, representing breaking bonds (energy absorbed, needed to pull atoms apart),
 - down the other side of the hump is exothermic, representing bond formation (energy released, as atoms become electronically more stable).





Catalysts and Activation Energy

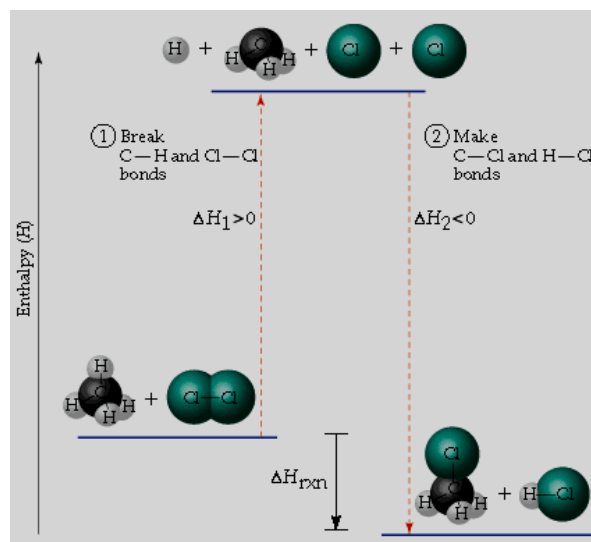
- **Catalysts** increase the rate of a reaction **by helping break chemical bonds** in reactant molecules.
- This effectively means the **Activation Energy is reduced** (see diagram 'humps' below).
- Therefore at the same temperature, more reactant molecules have enough kinetic energy to react compared to the uncatalysed situation and so the reaction speeds up with the greater chance of a 'fruitful' collision.
- Although a true catalyst does take part in the reaction, **it does not get used up and can be reused** with more reactants.
- However a solid catalyst might change physically by becoming more finely divided, especially if the reaction is exothermic.
- Also note from the diagram that although the activation energy is reduced, the overall exothermic or endothermic energy change is the same for both the catalysed or uncatalysed reaction. The catalyst might help break the bonds BUT it cannot change the actual bond energy



Calculation of heat transfer using bond energies

- Atoms in molecules are held together by **chemical bonds** which are the electrical attractive forces between the atoms.
- **The bond energy** is the energy involved in making or breaking bonds and is usually quoted **in kJ per mole of the particular bond involved**.

- To **break a chemical bond** requires the molecule to **take in energy** to pull atoms apart, which is an **endothermic** change. The atoms of the bond vibrate more until they spring apart.
- To **make a chemical bond**, the atoms must **give out energy** to become combined and electronically more stable in the molecule, this is an **exothermic** change.
- The energy to make or break a chemical bond is called the **bond energy** and is quoted in **kJ/mol** of bonds.
 - Each bond has a typical value eg to break 1 mole of C-H bonds is on average about 413kJ,
 - the C=O takes on average 743 kJ/mol, and note the stronger the bond, the more energy is needed,
 - and not surprisingly, a typical double bond needs more energy to break than a typical single bond.
- During a chemical reaction, energy must be supplied to **break chemical bonds** in the molecules, this is the **endothermic 'upward' slope** on the [reaction profile on diagrams above](#).
- When the new molecules are formed, **new bonds must be made** in the process, this is the **exothermic 'downward' slope** on the [reaction profile on diagrams above](#).
- If we know all the bond energies of the molecules involved in a reaction, we can theoretically calculate what the net energy change is for that reaction and determine whether the reaction is exothermic or endothermic.
- We do this by calculating the energy taken in to break the bonds in the reactant molecules. We then calculate the energy given out when the new bonds are formed. The difference between these two gives us the net energy change.
 - In a reaction energy must be supplied to break bonds (energy absorbed, taken in, endothermic).
 - Energy is released when new bonds are formed (energy given out, releases, exothermic).
 - If more energy is needed to break the original existing bonds of the reactant molecules, than is given out when the new bonds are formed in the product molecules, the reaction is endothermic.
 - If less energy is needed to break the original existing bonds of the reactant molecules, than is given out when the new bonds are formed in the product molecules, the reaction is exothermic.
 - So the overall energy change for a reaction (ΔH) is the overall energy net change from the bond making and bond forming processes. These ideas are illustrated in the calculations below.




• **Example 1. Hydrogen + Chlorine ==> Hydrogen Chloride**

- The symbol equation is: $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \Rightarrow 2\text{HCl}(\text{g})$
- but think of it as: $\text{H-H} + \text{Cl-Cl} \Rightarrow \text{H-Cl} + \text{H-Cl}$
- (where - represents the chemical bonds to be broken or formed)
- the bond energies in kJ/mol are: H-H 436; Cl-Cl 242; H-Cl 431
- Energy needed to break bonds = $436 + 242 = 678$ kJ taken in
- Energy released on bond formation = $431 + 431 = 862$ kJ given out
- The net difference between them = $862 - 678 = 184$ kJ given out (92 kJ per mole of HCl formed)
- More energy is given out than taken in, so the reaction is **exothermic**.

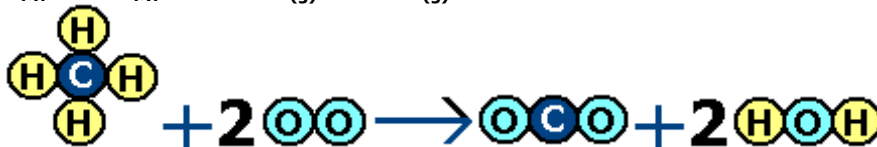
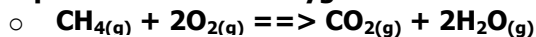
• **Example 2. Hydrogen Bromide ==> Hydrogen + Bromine**

- The symbol equation is: $2\text{HBr}(\text{g}) \Rightarrow \text{H}_2(\text{g}) + \text{Br}_2(\text{g})$
- but think of it as: $\text{H-Br} + \text{H-Br} \Rightarrow \text{H-H} + \text{Br-Br}$
- (where - represents the chemical bonds to be broken or formed)
- the bond energies in kJ/mol are: H-Br 366; H-H 436; Br-Br 193
- Energy needed to break bonds = $366 + 366 = 732$ kJ taken in
- Energy released on bond formation = $436 + 193 = 629$ kJ given out
- The net difference between them = $732 - 629 = 103$ kJ taken in (51.5 kJ per mole of HBr decomposed)
- More energy is taken in than given out, so the reaction is **endothermic**

- **Example 3. hydrogen + oxygen ==> water**
 - $2\text{H}_{2(\text{g})} + \text{O}_{2(\text{g})} \Rightarrow 2\text{H}_2\text{O}_{(\text{g})}$
 - or $2 \text{H-H} + \text{O=O} \Rightarrow 2 \text{H-O-H}$ (where - or = represent the covalent bonds)
 - bond energies in kJ/mol: H-H is 436, O=O is 496 and O-H is 463
 - bonds broken and energy absorbed (taken in):
 - $(2 \times \text{H-H}) + (1 \times \text{O=O}) = (2 \times 436) + (1 \times 496) = 1368 \text{ kJ}$
 - bonds made and energy released (given out):
 - $(4 \times \text{O-H}) = (4 \times 463) = 1852 \text{ kJ}$
 - overall energy change is:
 - $1852 - 1368 = 484 \text{ kJ given out}$ (242 kJ per mole hydrogen burned or water formed)
 - since more energy is given out than taken in, the reaction is **exothermic**.
 - **NOTE: Hydrogen gas can be used as fuel and a long-term possible alternative to fossil fuels (see methane combustion below in example 5..**
 - It burns with a pale blue flame in air reacting with oxygen to be oxidised to form water.
 - **hydrogen + oxygen ==> water** or $2\text{H}_{2(\text{g})} + \text{O}_{2(\text{g})} \Rightarrow 2\text{H}_2\text{O}_{(\text{l})}$
 - It is a non-polluting clean fuel since the only combustion product is water and so its use would not lead to all environmental problems associated with burning fossil fuels.
 - It would be ideal if it could be manufactured by electrolysis of water eg using solar cells.
 - Hydrogen can be used to power [fuel cells](#).

- **Example 4. nitrogen + hydrogen ==> ammonia**
 - $\text{N}_{2(\text{g})} + 3\text{H}_{2(\text{g})} \Rightarrow 2\text{NH}_{3(\text{g})}$
 - or $\text{N}\equiv\text{N} + 3 \text{H-H} \Rightarrow 2$ 
 - bond energies in kJ/mol: $\text{N}\equiv\text{N}$ is 944, H-H is 436 and N-H is 388
 - bonds broken and energy absorbed (taken in):
 - $(1 \times \text{N}\equiv\text{N}) + (3 \times \text{H-H}) = (1 \times 944) + (3 \times 436) = 2252 \text{ kJ}$
 - bonds made and energy released (given out):
 - $2 \times (3 \times \text{N-H}) = 2 \times 3 \times 388 = 2328 \text{ kJ}$
 - overall energy change is:
 - $2328 - 2252 = 76 \text{ kJ given out}$ (38 kJ per mole of ammonia formed)
 - since more energy is given out than taken in, the reaction is **exothermic**.

• **Example 5. methane + oxygen ==> carbon dioxide + water**



○ or

○ bond energies in kJ/mol:

- C-H single bond is 412, O=O double bond is 496, C=O double bond is 743, H-O single bond is 463

○ bonds broken and energy absorbed (taken in from surroundings)

- $(4 \times \text{C-H}) + 2 \times (1 \times \text{O=O}) = (4 \times 412) + 2 \times (1 \times 496) = 1648 + 992 = 2640$ kJ taken in

○ bonds formed and energy released (given out to surroundings)

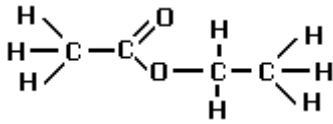
- $(2 \times \text{C=O}) + 2 \times (2 \times \text{O-H}) = (2 \times 743) + 2 \times (2 \times 463) = 1486 + 1852 = 3338$ given out

○ overall energy change is:

- $3338 - 2640 = 698$ kJ/mol given out per mole methane burned,
- since more energy is given out than taken in, the reaction is **exothermic**.

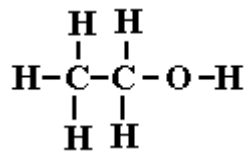
○ **NOTE:** This is the **typical very exothermic combustion chemistry of burning fossil fuels** but has many associated environmental problems

• **Example 6. analysing the bonds in more complex molecules**



ethyl ethanoate

- 2 x C-C single covalent bonds
- 8 x C-H single covalent bonds
- 2 x C-O single covalent bonds
- 1 x C=O double covalent bond



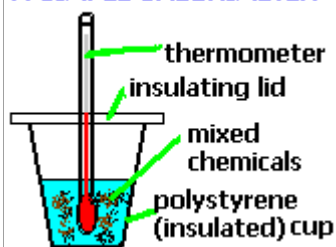
ethanol

- 1 x C-C single covalent bond
- 5 x C-H single covalent bonds
- 1 x C-O single covalent bond
- 1 x O-H single covalent bond

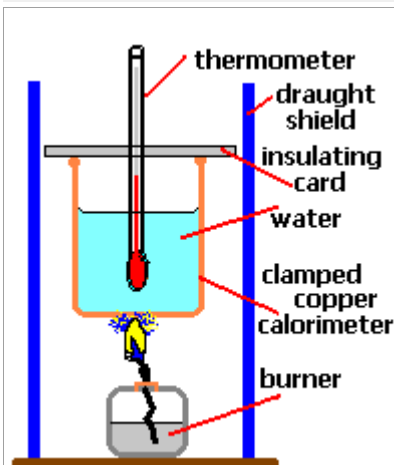
○ Heats of combustion can be theoretically calculated like in example 5.

The experimental determination of energy changes

A SIMPLE CALORIMETER



This **method 1.** can be used for **any non-combustion reaction** that will happen spontaneously at room temperature involving liquids or solid reacting with a liquid. The reactants are weighed in if solid and a known volume of any liquid (usually water or aqueous solution). The mixture could be a salt and water (heat change on dissolving) or an acid and an alkali solution (heat change of neutralisation). It doesn't matter whether the change is exothermic (heat released or given out) or endothermic (heat absorbed or taken in). See [calculations](#) below.



This **method 2.** is specifically for determining the heat energy released (given out) for burning fuels. The burner is weighed before and after combustion to get the mass of fuel burned. The thermometer records the temperature rise of the known mass of water ($1\text{g} = 1\text{cm}^3$).

You can use this system to compare the heat output from burning various fuels. The bigger the temperature rise, the more heat energy is released. See [calculations](#) below for expressing calorific values.

This is a very inaccurate method because of huge losses of heat eg radiation from the flame and calorimeter, conduction through the copper calorimeter, convection from the flame gases passing by the calorimeter etc. BUT, at least using the same burner and set-up, you can do a reasonable comparison of the heat output of different fuels.

Calculations from the experimental results

- The method described below applies to both experimental methods described above.
- You need to know the following:
 - the mass of material reacting in the calorimeter (or their concentrations and volume),
 - the mass of water in the calorimeter,
 - the temperature change (always a rise for method 2. combustion),
 - the specific heat capacity of water, (shorthand is $\text{SHC}_{\text{water}}$), and this is $4.2\text{J/g/}^\circ\text{C}$,
 - this means it takes 4.2 J of heat energy to change the temperature of 1g of water by 1°C (or K).
- Example 1 typical of method 1.
 - 5g of ammonium nitrate (NH_4NO_3) was dissolved in 50cm^3 of water (50g) and the temperature fell from 22°C to 14°C .
 - Temperature change = $22 - 14 = 8^\circ\text{C}$ (endothermic, temperature fall, heat energy absorbed)
 - Heat absorbed by the water = mass of water \times $\text{SHC}_{\text{water}}$ \times temperature
 - = $50 \times 4.2 \times 8 = 1680\text{ J}$ (for 5g)
 - heat energy absorbed on dissolving = $1680 / 5 = 336\text{ J/g}$ of NH_4NO_3
 - this energy change can be also expressed on a molar basis.
 - Relative atomic masses A_r : $\text{N} = 14$, $\text{H} = 1$, $\text{O} = 16$

- $M_r(\text{NH}_4\text{NO}_3) = 14 + (1 \times 4) + 14 + (3 \times 16) = 80$, so 1 mole = 80g
 - Heat absorbed by dissolving 1 mole of $\text{NH}_4\text{NO}_3 = 80 \times 336 = 26880 \text{ J/mole}$
 - At AS level this will be expressed as enthalpy of solution = $\Delta H_{\text{solution}} = +26.88 \text{ kJmol}^{-1}$
 - The data book value is $+26 \text{ kJmol}^{-1}$
 - Example 2 typical of method 2.
 - 100 cm³ of water (100g) was measured into the calorimeter.
 - The spirit burner contained the fuel ethanol $\text{C}_2\text{H}_5\text{OH}$ ('alcohol') and weighed 18.62g at the start.
 - After burning it weighed 17.14g and the temperature of the water rose from 18 to 89°C.
 - The temperature rise = $89 - 18 = 71^\circ\text{C}$ (exothermic, heat energy given out).
 - Mass of fuel burned = $18.62 - 17.14 = 1.48\text{g}$.
 - Heat absorbed by the water = mass of water \times $\text{SHC}_{\text{water}}$ \times temperature
 - = $100 \times 4.2 \times 71 = 29820 \text{ J}$ (for 1.48g)
 - heat energy released per g = energy supplied in J / mass of fuel burned in g
 - heat energy released on burning = $29820 / 1.48 = 20149 \text{ J/g}$ of $\text{C}_2\text{H}_5\text{OH}$
 - this energy change can be also expressed on a molar basis.
 - Relative atomic masses A_r : C = 12, H = 1, O = 16
 - $M_r(\text{C}_2\text{H}_5\text{OH}) = (2 \times 12) + (1 \times 5) + 16 + 16 = 46$, so 1 mole = 46g
 - Heat released (given out) by 1 mole of $\text{C}_2\text{H}_5\text{OH} = 46 \times 20149 = 926854 \text{ J/mole}$
 - At AS level this will be expressed as enthalpy of combustion = $\Delta H_{\text{comb}} = -926.9 \text{ kJmol}^{-1}$
 - The data book value for the heat of combustion of ethanol is -1371 kJmol^{-1} , showing lots of heat loss!
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DONE