Energy from Chemicals



Bombardier Beetle

adding and the



Energy from Chemicals – Enthalpy Changes Bombardier Beetle



 This is an exothermic reaction that releases approximately 400 kJ of energy for every mole of hydroquinone that reacts.



Energy from Chemicals – Enthalpy Changes Bombardier Beetle



 Result? Whatever is attacking the bombardier beetle is sprayed with a *hot* and *corrosive liquid*.



Chemical reactions are always accompanied by a *change* in *energy*.

 What are some generalisations about change?



• Some examples of generalisations that can be made:

• Change:

 \rightarrow Change is inevitable (unavoidable).

→ Change can have positive consequences or negative consequences.

 \rightarrow Change can be reversible or irreversible.

 \rightarrow Change can be steady, cyclic, random or chaotic.



• Enduring Understandings:

- Chemical reactions (change) can be spontaneous or non-spontaneous.
 - Spontaneous reactions (changes) release energy which can be used to do work. Non-spontaneous reactions (changes) require energy in order to take place.



• Essential Questions:

- How are matter and energy related?
- Why are some chemical reactions exothermic and others endothermic?
- Why do some chemical reactions occur spontaneously, while others do not?
 - Where does the heat and light that is given off by an exothermic reaction originate from, and where does it go to?



Energy from Chemicals – Enthalpy Changes What must I know and understand about energy from chemicals?



Learning Outcomes

Candidates should be able to:

- a) Describe the meaning of enthalpy change in terms of exothermic (ΔH negative) and endothermic (ΔH positive) reactions.
- b) Represent energy changes by energy profile diagrams, including reaction enthalpy changes and activation energies.
- c) Describe bond breaking as an endothermic process and bond making as an exothermic process.
- d) Explain overall enthalpy changes in terms of the energy changes associated with the breaking and making of covalent bonds.
- e) Describe hydrogen, derived from water or hydrocarbons, as a potential fuel, reacting with oxygen to generate electricity directly in a fuel cell (details of the construction and operation of a fuel cell are not required).
 - Singapore Examinations and Assessment
 - Board University of Cambridge International Examinations
 - Ministry of Education Singapore





 Chemists use thermodynamics to keep track of individual changes in energy, and to assess the net change that takes place in a reaction. For this purpose, they use an assessment of the quantity of energy available from a reaction as heat that is called the enthalpy. The name comes from the Greek words for "*heat inside*". There are good technical grounds for distinguishing *enthalpy* from *energy*, but essentially, enthalpy can be considered as just another name for energy trapped in chemicals and available as heat.



What different enthalpy changes can take place in Chemistry?

• Exothermic: Releases energy into the surroundings.

• Endothermic: Absorbs energy from the surroundings.



Energy from Chemicals – Exothermic

Exo is Greek for "outside." Thermasi is Greek for "to heat." The literal meaning of exothermic is therefore "to heat outside."

Exo is a common term used throughout science. For example, insects are described as having an exoskeleton, which literally means "outside skeleton." This accurately describes the animal's hard outer casing.



Energy from Chemicals – Endothermic



Endo is Greek for "inside." Thermasi is Greek for "to heat." The literal meaning of endothermic is therefore "to heat inside."

Endo is a common term used throughout science. For example, mammals are described as having an endoskeleton, which literally means "inside skeleton."



I remember from kinetic particle theory that *changes in state* also involve changes in energy.









Remember: energy $H_2O(g) > energy H_2O(l) > energy H_2O(s)$







Phase changes involve a change in energy content of the system. Alcohol feels cold on the skin because the vaporisation of a liquid is an *exothermic / endothermic* process. As the liquid alcohol evaporates to form alcohol vapour, its energy content *increases / decreases i.e.* energy flows *into / out of* the system. Energy is *taken from / given to* the surroundings (the immediate surroundings is the skin), whose temperature therefore *increases / decreases.*

Steam at 100 °C is said to cause a worse burn than boiling water at the same temperature because the condensation of a vapour to a liquid is an *exothermic / endothermic* process and energy flows *into / out of* the system *from / into* the surroundings. Once again the immediate surroundings include the skin whose temperature is therefore *decreased / increased*.



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Energy Profile for an Exothermic Reaction

Important Things to Note...

• ΔH means change in enthalpy.

 An exothermic change releases energy into the surroundings. Numerical values of ∆H are negative.

 During an exothermic reaction, the temperature of the surroundings increases.



Energy Profile for an Exothermic Reaction



























Energy Profile for an Exothermic Reaction



Energy Profile for an Exothermic Reaction

 All combustion reactions (where a fuel reacts with oxygen) are exothermic.

• For example, the combustion of methane: $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ $\Delta H = -890 \text{ kJ mol}^{-1}$

• For example, the combustion of ethanol: $C_2H_5OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$ $\Delta H = -1371 \text{ kJ mol}^{-1}$



 It is very important to remember that the thermometer is part of the surroundings and not part of the reaction!

• As a consequence, the thermometer measures the *temperature* (or *energy*) of the *surroundings* and not the *temperature* (or *energy*) of the *reaction*!


- The particles in a reaction do not all react at once.
- People running a marathon run at different speeds and cross the finishing line at different times.
- It is the same for the particles in a reaction. The particles move at different speeds, with different amounts of kinetic energy, and will collide and react at different times.





Activation Energy



 Activation energy is the minimum amount of energy that must be supplied to a chemical in order for a reaction to take place.



Activation Energy



 For example, the phosphorus and sulfur in a match head will not react with the oxygen in the air until the match is struck against the sandpaper on the side of the match box.



Activation Energy



 Friction between the match head and sandpaper generates heat energy, which is used to break chemical bonds in the molecules of phosphorus, sulfur and oxygen, thus allowing them to react.









Important Things to Note...

• ΔH means change in enthalpy.

 An endothermic change absorbs energy from the surroundings. Numerical values of ∆H are positive.

During an endothermic reaction, the temperature of the surroundings decreases.









































 $Ba(OH)_{2}(s) + 2NH_{4}Cl(s) \rightarrow BaCl_{2}(aq) + 2NH_{3}(g) + 2H_{2}O(l)$ $\Delta H = +105.1 \text{ kJ mol}^{-1}$

• A few drops of water placed between the flask and wooden block freeze, 'sticking' the flask and block together.





Energy Profile for an Endothermic Reaction • Photosynthesis: carbon dioxide + water \rightarrow glucose + oxygen $6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(s) + 6O_2(g)$ • Thermal Decomposition: calcium carbonate \rightarrow calcium oxide + carbon dioxide $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ Cracking Alkanes: decane \rightarrow octane + ethene $C_{10}H_{22}(l) \rightarrow C_8H_{18}(l) + C_2H_4(g)$ • Electrolysis: sodium chloride \rightarrow sodium + chlorine $NaCl(l) \rightarrow Na(l) + Cl_2(g)$

Chemical reactions are accompanied by energy changes. When the energy content of a chemical system decreases during a reaction, the energy content of the products is *greater / less* than that of the reactants. The reaction is said to be *exothermic / endothermic* and a *rise / fall* in temperature is observed. The value of the enthalpy change of the reaction (Δ H) is *positive / negative*.

When the temperature falls during a reaction, the reaction is said to be **exothermic / endothermic**. The energy content of the products is **greater / less** than that of the reactants *i.e.* the energy content of the system has *increased / decreased* during the reaction. ΔH for the reaction is **positive / negative**.



Chemical reactions are accompanied by energy changes. When the energy content of a chemical system decreases during a reaction, the energy content of the products is *greater* / *less* than that of the reactants. The reaction is said to be *exothermic* / *endothermic* and a *rise* / *fall* in temperature is observed. The value of the enthalpy change of the reaction (Δ H) is *positive* / *negative*.

When the temperature falls during a reaction, the reaction is said to be **exothermic / endothermic**. The energy content of the products is **greater / less** than that of the reactants *i.e.* the energy content of the system has **increased / decreased** during the reaction. ΔH for the reaction is **positive / negative**.



Why do *endothermic* reactions take place? I thought that chemicals reacted in order to *lose* energy!

 In addition to *enthalpy*, we need to consider the system's *entropy* – how random and chaotic is it?



 Considering Enthalpy: It is true that chemical reactions take place for higher energy and relatively unstable reactants to form lower energy and relatively stable products. This process is exothermic and will release energy into the surroundings.

Considering Entropy: It is also true that nature tends to favour systems that are random and chaotic. This explains why liquids tend to evaporate – even though the particles are gaining energy, they are also becoming more random and chaotic when they change from a liquid into a gas. *Entropy* is used to describe how random and chaotic a system is – the more chaotic the system, the higher its entropy.



high energy, ordered reactants \rightarrow low energy chaotic products

This reaction is very *favourable* and will take place quite easily – it is said to be *spontaneous*.



high energy, ordered reactants \rightarrow low energy chaotic products

This reaction is very *favourable* and will take place quite easily – it is said to be *spontaneous*.

low energy chaotic reactants \rightarrow high energy, ordered products This reaction is *unfavourable* and will take place with difficulty – it is said to be *non-spontaneous*.



high energy, ordered reactants \rightarrow low energy chaotic products

This reaction is very *favourable* and will take place quite easily – it is said to be *spontaneous*.

low energy chaotic reactants \rightarrow high energy, ordered products

This reaction is *unfavourable* and will take place with difficulty – it is said to be *non-spontaneous*.

low energy ordered reactants \rightarrow high energy, chaotic products

Although this reaction is *unfavourable* due to the increase in energy, it could still be *spontaneous* if there is a large *increase in entropy* (*i.e.* there is a relatively *small* increase in *energy*, but the system becomes *very chaotic*). This change is *endothermic*.



 Gibbs free energy gives Chemists an idea as to whether a chemical change will be either spontaneous or non-spontaneous.

• Gibbs free energy is defined by the equation:

$\Delta \mathbf{G} = \Delta \mathbf{H} - \mathbf{T} \Delta \mathbf{S}$

Where:

- ΔG = change in Gibbs free energy / J
- ΔH = enthalpy change of the system / J

T = temperature of the system / K

 ΔS = entropy change of the system / J·K⁻¹

• If ΔG is *negative*, then the chemical change is *spontaneous*.



Advance Concepts – Entropy Gibbs free energy is defined by the equation: $\Delta G = \Delta H - T \Delta S$ $\Delta H > 0$ $\Delta H < 0$ spontaneous at all spontaneous at high $\Delta S > 0$ temperatures temperatures (when $T\Delta S$ is large) $(\Delta G < 0)$ spontaneous at low non-spontaneous at $\Delta S < 0$ temperatures all temperatures (when $T\Delta S$ is small) $(\Delta G > 0)$



Which reaction is more common, *exothermic* or *endothermic*?



 Chemical reactions take place in order for chemicals to reduce their energy and become more stable.

 It is natural for chemicals to go from a state of high energy to a state of low energy, just as it is natural for a ball to roll down a hill.



- In an exothermic reaction, high energy reactants form low energy products, with energy given off to the surroundings.
- In an endothermic reaction, low energy reactants form high energy products, with energy absorbed from the surroundings.





- In terms of energy changes, exothermic reactions are more favorable than endothermic reactions.
- Exothermic reactions are therefore more common than endothermic reactions.



 Question: How do these diagrams illustrate the concept of activation energy?

 Answer: The person must use a specific amount of energy to roll the ball from the left-hand-side to the top of the hill. Only then is the ball free to roll down the opposite side.


































 Analogy for activation energy. Less energy is required to push the boulders around the side of the hill compared to the energy that is required to push the boulders over the hill.

 Using the same amount of energy, more boulders can be pushed around the side of the hill compared to the number that can be pushed over the hill.







Assessment for Learning

Can I please have a short question to check my current understanding?



Assessment for Learning





Assessment for Learning



A Activation energy of the forward reaction.
B Activation energy of the forward reaction with a catalyst.
C Enthalpy change (ΔH) of the forward reaction.
D Activation energy of the backward reaction.





- Imagine that you were given \$50 (+50).
 - You spend \$30 (-30).
- You will be in *credit* by \$20
 (+50) + (-30) = +20.
- Overall, you have "gained money from the surroundings".



- Imagine that you were given \$50 (+50).
 - You spend \$80 (-80).
- You will in *debt* by \$30 (+50) + (-80) = -30.
- Overall, you have *"lost money to the surroundings"*.



Reactions can be considered to take place in two stages:

1) Bonds between atoms in the reactants are *broken*.

 2) New bonds between atoms are *formed* to produce the products.



Enthalpy Change Calculations Important Things to Note...

- Bond breaking absorbs energy and is therefore endothermic. Numerical values of ∆H for bond breaking are positive.
- Bond formation releases energy and is therefore exothermic.
 Numerical values of ∆H for bond formation are negative.











nitrogen + hydrogen \rightleftharpoons ammonia N₂(g) + 3H₂(g) \rightleftharpoons 2NH₃(g)



 Bond breaking absorbs energy.
∆H is positive.



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 Bond breaking absorbs energy.
∆H is positive.





























Enthalpy Change Calculations Important Things to Note... Total Total **Overall** amount amount of energy of energy enthalpy absorbed released change of a to break when new chemical existing chemical chemical bonds are reaction bonds (ΔH) formed (**+**∆**H**) $(-\Delta H)$



lf....

Total amount of energy absorbed to break existing chemical bonds (**+**∆**H**)



Total amount of energy released when new chemical bonds are formed $(-\Delta H)$

Overall, energy is absorbed and the reaction will be endothermic, *i.e.* ∆H will be positive.



 Energy absorbed to break bonds in the reactants is greater than the energy released when new bonds are formed in the products.

 Overall, the reaction absorbs energy from the surroundings. The reaction is therefore endothermic.



lf....

Total amount of energy absorbed to break existing chemical bonds (**+**∆**H**)



Total amount of energy released when new chemical bonds are formed $(-\Delta H)$

Overall, energy is released and the reaction will be exothermic, *i.e.* ∆H will be negative.



 Energy absorbed to break bonds in the reactants is less than the energy released when new bonds are formed in the products.

 Overall, the reaction releases energy into the surroundings. The reaction is therefore exothermic.



Overview of the Reaction:









 $1 \times N \equiv N$ bond is broken forming $2 \times N$ atoms.



Bond breaking is *endothermic*: ΔH for this change is *positive*.

 $N \equiv N = 944 \text{ kJ mol}^{-1}$ $H = 436 \text{ kJ mol}^{-1}$ $N-H = 388 \text{ kJ mol}^{-1}$ $2N_{(g)} + 6H_{(g)}$ $2N_{(g)} + 3H_{2(g)}$ Energy (kJ)N_{2(g)} + 3H H

 $3 \times H$ –H bonds are broken forming $6 \times H$ atoms.

 $N \equiv N = 944 \text{ kJ mol}^{-1}$ $H = 436 \text{ kJ mol}^{-1}$ $N-H = 388 \text{ kJ mol}^{-1}$ $2N_{(g)} + 6H_{(g)}$ energy level diagram $3 \times +436$ = +1308 kJ $2N_{(g)} + 3H_{2(g)}$ Energy (kJ)Н Н N_{2(g)} + 3⊢ Η H

Bond breaking is *endothermic*: ΔH for this change is *positive*.
N≡N = 944 kJ mol⁻¹

 $H-H = 436 \text{ kJ mol}^{-1}$

 $N-H = 388 \text{ kJ mol}^{-1}$







 $6 \times N-H$ bonds are formed creating $2 \times NH_3$ molecules.



Bond formation is *exothermic*: ΔH for this change is *negative*.

 $N \equiv N = 944 \text{ kJ mol}^{-1}$ $H = 436 \text{ kJ mol}^{-1}$ $N-H = 388 \text{ kJ mol}^{-1}$ $2N_{(q)} + 6H_{(g)}$ Ν Н Н $= 3 \times +436$ = +1308 kJ $2N_{(g)} + 3H_{2(g)}$ H Energy $= 6 \times -388$ $1 \times +944$ (kJ)= +944 kJ= -2328 kJ N_{2(g)} + 3H_{2(g)} Ν = (+944) + (+1308)Η Н +(-2328)= -76 kJ 2NH_{3(g)} Η

 $(+944) + (+1308) + (-2328) = -76 kJ mol^{-1}$



(+944) + (+1308) + (-2328) = -76 kJ mol⁻¹

energy level diagram

Overview of the Reaction:





 $O-O = 146 \text{ kJ mol}^{-1}$

 $O-H = 463 \text{ kJ mol}^{-1}$

 $O=O = 496 \text{ kJ mol}^{-1}$



 $O-O = 146 \text{ kJ mol}^{-1}$

 $O-H = 463 \text{ kJ mol}^{-1}$

 $O=O = 496 \text{ kJ mol}^{-1}$



 $2 \times O-O$ bond are broken forming $4 \times OH$ molecules.

 $O-O = 146 \text{ kJ mol}^{-1}$

 $O-H = 463 \text{ kJ mol}^{-1}$

 $O=O = 496 \text{ kJ mol}^{-1}$



Bond breaking is *endothermic*: ΔH for this change is *positive*.

 $O-O = 146 \text{ kJ mol}^{-1}$

O–H = 463 kJ mol^{−1}

 $O=O = 496 \text{ kJ mol}^{-1}$



 $4 \times O$ -H bonds are broken forming $4 \times O$ and $4 \times H$ atoms.

 $O-O = 146 \text{ kJ mol}^{-1}$

O–H = 463 kJ mol^{−1}

 $O=O = 496 \text{ kJ mol}^{-1}$



Bond breaking is *endothermic*: ΔH for this change is *positive*.

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 $O-O = 146 \text{ kJ mol}^{-1}$

O–H = 463 kJ mol^{−1}

 $O=O = 496 \text{ kJ mol}^{-1}$



 $1 \times O=O$ bond is formed creating $1 \times O_2$ molecule.

 $O-O = 146 \text{ kJ mol}^{-1}$

 $O-H = 463 \text{ kJ mol}^{-1}$

 $O=O = 496 \text{ kJ mol}^{-1}$



Bond formation is *exothermic*: ΔH for this change is *negative*.

 $O-O = 146 \text{ kJ mol}^{-1}$

O–H = 463 kJ mol^{−1}

 $O=O = 496 \text{ kJ mol}^{-1}$



 $4 \times O-H$ bonds are formed creating $2 \times H_2O$ molecules.

 $O-O = 146 \text{ kJ mol}^{-1}$

 $O-H = 463 \text{ kJ mol}^{-1}$

 $O=O = 496 \text{ kJ mol}^{-1}$



Bond formation is *exothermic*: ΔH for this change is *negative*.

 $O-O = 146 \text{ kJ mol}^{-1}$

O–H = 463 kJ mol^{−1}

O=O = 496 kJ mol⁻¹



 $(+292) + (+1852) + (-496) + (-1852) = -204 \text{ kJ mol}^{-1}$

 $O-O = 146 \text{ kJ mol}^{-1}$

O–H = 463 kJ mol^{−1}

 $O=O = 496 \text{ kJ mol}^{-1}$



(+292) + (+1852) + (-496) + (-1852) = -204 kJ mol⁻¹

Overview of the Reaction:





 $C-H = 412 \text{ kJ mol}^{-1}$ $O=O = 496 \text{ kJ mol}^{-1}$ $C=O = 743 \text{ kJ mol}^{-1}$ $O-H = 463 \text{ kJ mol}^{-1}$



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 $4 \times C$ –H bonds are broken forming $1 \times C$ atom and $4 \times H$ atoms.

 $C-H = 412 \text{ kJ mol}^{-1}$ $O=O = 496 \text{ kJ mol}^{-1}$ $C=O = 743 \text{ kJ mol}^{-1}$ $O-H = 463 \text{ kJ mol}^{-1}$



Bond breaking is *endothermic*: ΔH for this change is *positive*.

 $C-H = 412 \text{ kJ mol}^{-1}$ $O=O = 496 \text{ kJ mol}^{-1}$ $C=O = 743 \text{ kJ mol}^{-1}$ $O-H = 463 \text{ kJ mol}^{-1}$



 $2 \times O=O$ bonds are broken forming $4 \times O$ atoms

 $C-H = 412 \text{ kJ mol}^{-1}$ $O=O = 496 \text{ kJ mol}^{-1}$ $C=O = 743 \text{ kJ mol}^{-1}$ $O-H = 463 \text{ kJ mol}^{-1}$



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 $2 \times C=O$ bonds are formed creating $1 \times CO_2$ molecule.

 $C-H = 412 \text{ kJ mol}^{-1}$ $O=O = 496 \text{ kJ mol}^{-1}$ $C=O = 743 \text{ kJ mol}^{-1}$ $O-H = 463 \text{ kJ mol}^{-1}$



Bond formation is *exothermic*: ΔH for this change is *negative*.

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 $4 \times O-H$ bonds are formed creating $2 \times H_2O$ molecules.

 $C-H = 412 \text{ kJ mol}^{-1}$ $O=O = 496 \text{ kJ mol}^{-1}$ $C=O = 743 \text{ kJ mol}^{-1}$ $O-H = 463 \text{ kJ mol}^{-1}$



Bond formation is *exothermic*: ΔH for this change is *negative*.

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(+1648) + (+992) + (-1486) + (-1852) = -698 kJ mol⁻¹

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(+1648) + (+992) + (-1486) + (-1852) = -698 kJ mol⁻¹

Overview of the Reaction:





 $O-H = 463 \text{ kJ mol}^{-1}$ $O=O = 496 \text{ kJ mol}^{-1}$ $H-H = 436 \text{ kJ mol}^{-1}$



 $O-H = 463 \text{ kJ mol}^{-1}$ $O=O = 496 \text{ kJ mol}^{-1}$ $H-H = 436 \text{ kJ mol}^{-1}$



 $4 \times O-H$ bonds are broken forming $2 \times O$ and $4 \times H$ atoms.

 $O-H = 463 \text{ kJ mol}^{-1}$ $O=O = 496 \text{ kJ mol}^{-1}$ $H-H = 436 \text{ kJ mol}^{-1}$



Bond breaking is *endothermic*: ΔH for this change is *positive*.

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 $1 \times O=O$ bond is formed creating $1 \times O_2$ molecule.

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Bond formation is *exothermic*: ΔH for this change is *negative*.

 $O-H = 463 \text{ kJ mol}^{-1}$ $O=O = 496 \text{ kJ mol}^{-1}$ $H-H = 436 \text{ kJ mol}^{-1}$



 $2 \times H$ –H bonds are formed creating $2 \times H_2$ molecules.

 $O-H = 463 \text{ kJ mol}^{-1}$ $O=O = 496 \text{ kJ mol}^{-1}$ $H-H = 436 \text{ kJ mol}^{-1}$



Bond formation is *exothermic*: ΔH for this change is *negative*.

 $O-H = 463 \text{ kJ mol}^{-1}$ $O=O = 496 \text{ kJ mol}^{-1}$ $H-H = 436 \text{ kJ mol}^{-1}$



 $(+1852) + (-496) + (-872) = +484 \text{ kJ mol}^{-1}$

energy level diagram

 $O-H = 463 \text{ kJ mol}^{-1}$ $O=O = 496 \text{ kJ mol}^{-1}$ $H-H = 436 \text{ kJ mol}^{-1}$



(+1852) + (-496) + (-872) = +484 kJ mol⁻¹

Energy from Chemicals – Enthalpy Changes

Is a *double* covalent bond twice as strong as a *single* covalent bond?



Energy from Chemicals – Enthalpy Changes

• Study the bond energies given below:

- C-C = 348 kJ C=C = 612 kJ
- O-O = 146 kJ O=O = 496 kJ
- Is a double covalent bond twice as strong as a single covalent bond?
 - For carbon, 2 × C–C = 2 × 348 = 696 kJ 696 kJ ≠ 612 kJ 696 kJ > 612 kJ

For oxygen, 2 × O–O = 2 × 146 = 292 kJ
 292 kJ ≠ 496 kJ
 292 kJ < 496 kJ



Energy from Chemicals – Enthalpy Changes

Why is a double covalent bond not twice as strong as a single covalent bond?



Because there are different types of covalent bonds called σ-bonds (sigma bonds) and π-bonds (pi bonds).
 σ-bonds and π-bonds have different strengths.



What affects the enthalpy change when a chemical *dissolves in water*?



• The enthalpy change of solution is the enthalpy change associated with dissolving one mole of a chemical in a solvent (usually water) at room temperature and pressure.

• The enthalpy change of solution can be *exothermic*, *e.g.* dissolving *sodium hydroxide* in distilled water:

NaOH(s) \rightarrow Na⁺(aq) + OH⁻(aq) Δ H = -45.0 kJ mol⁻¹

• The enthalpy change of solution can be *endothermic*, *e.g.* dissolving *ammonium nitrate* in distilled water:

 $NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq) \quad \Delta H = +25.0 \text{ kJ mol}^{-1}$



 Dissolving an ionic compound in water can be considered to take place in *two stages*.

 The electrostatic force of attraction between the oppositely charged anions and cations of the solute must be overcome. This process of *bond breaking* will *absorb energy* from the surroundings and is therefore *endothermic*, +∆H. Note: This enthalpy change is sometimes referred to as the *lattice enthalpy*.

2. New bonds are formed between the anions and cations of the solute and the water molecules (solvent). This process of *bond formation* will *release energy* into the surroundings and is therefore *exothermic*, $-\Delta H$. Note: This enthalpy change is sometimes referred to as the *hydration enthalpy*.



• The ionic compound (solute) is added to water (solvent).





1. Energy is *absorbed* from the surroundings to overcome the electrostatic force of attraction between the anions and cations (*endothermic*, $+\Delta H$).



2. Energy is *released* into the surroundings when bonds are formed between the anions and cations of the solute and water molecules (*exothermic*, $-\Delta H$).







 The enthalpy change of solution for NaOH(s) is -45.0 kJ mol⁻¹. Using ideas about bond breaking and bond formation, comment on the significance of this enthalpy change.



 The enthalpy change of solution for NaOH(s) is -45.0 kJ mol⁻¹. Using ideas about bond breaking and bond formation, comment on the significance of this enthalpy change.

The energy that is *released* into the surroundings during bond formation between Na⁺ and H₂O, and OH⁻ and H₂O is *greater* than the energy that is *absorbed* from the surroundings to overcome the electrostatic force of attraction between Na⁺ and OH⁻ of the solute. Overall, energy is *released* into the surroundings and the enthalpy change of solution for NaOH(s) is *exothermic*, –ΔH.







energy level diagram





energy level diagram



 $\Delta H_{solution} = (+867) + (-932) = -45.0 \text{ kJ mol}^{-1}$



 The enthalpy change of solution for NH₄NO₃(s) is +25.0 kJ mol⁻¹. Using ideas about bond breaking and bond formation, comment on the significance of this enthalpy change.



 The enthalpy change of solution for NH₄NO₃(s) is +25.0 kJ mol⁻¹. Using ideas about bond breaking and bond formation, comment on the significance of this enthalpy change.

The energy that is *absorbed* from the surroundings to overcome the electrostatic force of attraction between NH₄⁺ and NO₃⁻ of the solute is *greater* than the energy that is *released* into the surroundings during bond formation between NH₄⁺ and H₂O, and NO₃⁻ and H₂O. Overall, energy is *absorbed* from the surroundings and the enthalpy change of solution for NH₄NO₃(s) is *endothermic*, +ΔH.













 $\Delta H_{solution} = (+646) + (-621) = +25.0 \text{ kJ mol}^{-1}$



 The energy that must be *absorbed* from the surroundings in order to overcome the electrostatic force of attraction between an anion and a cation depends upon their *charge densities**. The *greater* the anion's and cation's charge densities, the *greater* the amount of energy that must be absorbed in order to overcome the electrostatic force of attraction between them.

 The energy that is *released* into the surroundings when anions and cations are hydrated by water depends upon their *charge densities**. The *greater* an anion's and cation's charge densities, the *greater* the energy that will be released when water molecules bond to them.

*The *smaller* the ion's *radius*, and the *greater* the ion's *charge*, then the greater the ion's *charge density*, *e.g.* A*l*³⁺ will have a relatively high charge density while Cs⁺ will have a relatively small charge density.



Advance Concepts – Born-Haber Cycles

How do I calculate the *enthalpy change* of a reaction that has an *ionic product* (binary salt)?



Advance Concepts – Born-Haber Cycles



An Overview of a Born-Haber Cycle

 The Born-Haber cycle takes account of all the enthalpy changes that occur when a metallic element and a non-metallic element react to form one mole of an ionic compound. The metallic and non-metallic elements must be atomised and ionised before they can combine together to form a crystal lattice.

Advance Concepts – Born-Haber Cycles





• Standard Enthalpy Change of Formation – ΔH^{Θ}_{f} :

The standard enthalpy change of formation is the enthalpy change when one mole of a compound is formed from its pure constituent elements, all substances being in their standard states at 1 atmosphere pressure (101.3 kPa) and 25°C (298 K).



• Standard Enthalpy of Atomisation – ΔH^{Θ}_{at} :

The standard enthalpy of atomisation is the enthalpy change when one mole of gaseous atoms is formed from its element in its defined physical state at 1 atmosphere pressure (101.3 kPa) and 25°C (298 K). The general equation for a diatomic element is:

 $^{1}/_{2}X_{2}(g) \rightarrow X(g)$



• Bond Dissociation Enthalpy – ΔH_{bde}^{Θ} :

The bond dissociation enthalpy is the standard enthalpy change when one mole of chemical bonds are cleaved homolytically under standard conditions at 1 atmosphere pressure (101.3 kPa) and 25°C (298 K). The general equation for a diatomic element is:

> $X_2(g) \rightarrow 2X(g)$ $X - X(g) \rightarrow 2X(g)$

Note: For a diatomic element, the value of the bond dissociation enthalpy is *twice* the value of the standard enthalpy of atomisation.



• Lattice Formation Enthalpy – ΔH^{Θ}_{LA} :

Lattice formation enthalpy is the standard enthalpy change when a solid ionic lattice is formed from its separate gaseous anions and cations. It is an exothermic process ($-\Delta H$). For example:

 $Na^+(g) + Cl^-(g) \rightarrow NaCl(s) \Delta H = -787 \text{ kJ mol}^{-1}$



• Lattice Dissociation Enthalpy – ΔH^{Θ}_{LA} :

Lattice dissociation enthalpy is the standard enthalpy change when a solid ionic lattice is dissociated into its component gaseous anions and cations which are separated by an infinite distance from each other. It is an endothermic process (+∆H). For example:

 $NaCl(s) \rightarrow Na^{+}(g) + Cl^{-}(g) \Delta H = +787 \text{ kJ mol}^{-1}$

Note: For the same ionic compound, the lattice formation enthalpy and lattice dissociation enthalpy have the same numerical value, but *opposite sign*.



• First Ionisation Energy – $\Delta H_{1st IE}$:

First ionisation energy is the energy absorbed (endothermic, $+\Delta H$) to convert one mole of gaseous atoms into one mole of gaseous cations, each cation carrying a charge of 1+. It is represented by the general equation:

 $X(g) \rightarrow X^+(g) + e^-$


Advance Concepts – Born-Haber Cycles Definitions of Terms Used

• Second Ionisation Energy – $\Delta H_{2nd IE}$:

Second ionisation energy is the energy absorbed (endothermic, $+\Delta$) to convert one mole of gaseous cations, each carrying a charge of 1+, into one mole of gaseous cations, each carrying a charge of 2+. It is represented by the general equation:

 $X^+(g) \rightarrow X^{2+}(g) + e^-$



Advance Concepts – Born-Haber Cycles Definitions of Terms Used

• First Electron Affinity – $\Delta H_{1st ea}$:

First electron affinity is the energy released (exothermic, $-\Delta H$) when one mole of gaseous atoms is converted into one mole of gaseous anions, each anion carrying a charge of 1–. It is represented by the general equation:

 $X(g) + e^- \rightarrow X^-(g)$



Advance Concepts – Born-Haber Cycles Definitions of Terms Used

• Second Electron Affinity – $\Delta H_{2nd ea}$:

Second electron affinity is the energy absorbed (endothermic, $+\Delta H$) when one mole of gaseous anions, each carrying a charge of 1–, is converted into one mole of gaseous anions, each carrying a charge of 2–. It is represented by the general equation:

 $X^{-}(g) + e^{-} \rightarrow X^{2-}(g)$



Advance Concepts – Born-Haber Cycles

• The following data can be used to construct a Born-Haber cycle to represent the formation of one mole of sodium chloride from the elements sodium and chlorine in their standard states.

$$\begin{split} \mathsf{Na}(\mathsf{s}) \ &+ \ {}^{1}\!/_{2}\mathsf{C}l_{2}(\mathsf{g}) \ \to \ \mathsf{Na}\mathsf{C}l(\mathsf{s}) \ \ \Delta\mathsf{H}_{\textit{formation}} = -410 \ \mathsf{kJ} \ \mathsf{mol}^{-1} \\ & \mathsf{Na}(\mathsf{s}) \ \to \ \mathsf{Na}(\mathsf{g}) \ \ \Delta\mathsf{H}_{atomisation} = +108 \ \mathsf{kJ} \ \mathsf{mol}^{-1} \\ & {}^{1}\!/_{2}\mathsf{C}l_{2}(\mathsf{g}) \ \to \ \mathsf{C}l(\mathsf{g}) \ \ \Delta\mathsf{H}_{atomisation} = +122 \ \mathsf{kJ} \ \mathsf{mol}^{-1} \\ & \mathsf{Na}(\mathsf{g}) \ \to \ \mathsf{Na}^{+}(\mathsf{g}) \ + \ e^{-} \ \ \Delta\mathsf{H}_{\textit{first ionisation}} = +496 \ \mathsf{kJ} \ \mathsf{mol}^{-1} \\ & \mathsf{C}l(\mathsf{g}) \ + \ e^{-} \ \to \ \mathsf{C}l^{-}(\mathsf{g}) \ \ \Delta\mathsf{H}_{\textit{first electron affinity}} = -349 \ \mathsf{kJ} \ \mathsf{mol}^{-1} \\ & \mathsf{Na}^{+}(\mathsf{g}) \ + \ \mathsf{C}l^{-}(\mathsf{g}) \ \to \ \mathsf{Na}\mathsf{C}l(\mathsf{s}) \ \ \Delta\mathsf{H}_{\textit{lattice enthalpy}} = -787 \ \mathsf{kJ} \ \mathsf{mol}^{-1} \end{split}$$



Advance Concepts – Born-Haber Cycles Born-Haber Cycle for Sodium Chloride



CALS' HIGH

Not Drawn to Scale

Not Drawn to Scale

Advance Concepts – Born-Haber Cycles

 Use the data given below to calculate the *enthalpy change of formation* of calcium fluoride from the elements calcium and fluorine in their standard states.

 $Ca(s) + F_2(g) \rightarrow CaF_2(s) \Delta H_{formation} = unknown kJ mol^{-1}$ Ca(s) \rightarrow Ca(g) $\Delta H_{atomisation} = +179 \text{ kJ mol}^{-1}$ $F_2(g) \rightarrow 2F(g) \Delta H_{atomisation} = +69.5 \text{ kJ mol}^{-1}$ $Ca(g) \rightarrow Ca^{+}(g) + e^{-} \Delta H_{first ionisation energy} = +590 \text{ kJ mol}^{-1}$ $Ca^+(g) \rightarrow Ca^{2+}(g) + e^- \Delta H_{second ionisation energy} = +1140 \text{ kJ mol}^{-1}$ $2F(g) + 2e^- \rightarrow 2F^-(g) \Delta H_{first electron affinity} = -656 \text{ kJ mol}^{-1}$ $Ca^{2+}(g) + 2F^{-}(g) \rightarrow CaF_{2}(s) \Delta H_{lattice enthalov} = -2612 \text{ kJ mol}^{-1}$



• Calculate the enthalpy change of formation for $CaF_2(s)$.





• It is not possible to go directly from $Ca(s) + F_2(g)$ to $CaF_2(s)$





- Follow the direction of the blue arrows through the cycle.
- The sum of the enthalpy changes will give the ΔH_f for CaF₂.





 $\Delta H_f(\mathsf{CaF}_2) = (+179) + (+139) + (+590) + (+1140) + (-656) + (-2612)$





 $\Delta H_f (CaF_2) = (+179) + (+139) + (+590) + (+1140) + (-656) + (-2612)$ $\Delta H_f (CaF_2) = -1220 \text{ kJ mol}^{-1}$



Advance Concepts – Born-Haber Cycles

 Use the data given below to calculate the *lattice formation* enthalpy of sodium oxide.

 $2Na(s) + \frac{1}{2}O_2(g) \rightarrow Na_2O(s) \Delta H_{formation} = +414 \text{ kJ mol}^{-1}$ $2Na(s) \rightarrow 2Na(g) \Delta H_{atomisation} = +216 \text{ kJ mol}^{-1}$ $\frac{1}{2}O_2(g) \rightarrow O(g) \quad \Delta H_{atomisation} = +249 \text{ kJ mol}^{-1}$ $Na(g) \rightarrow Na^{+}(g) + e^{-} \Delta H_{first ionisation} = +992 \text{ kJ mol}^{-1}$ $O(g) + e^- \rightarrow O^-(g) \Delta H_{first electron affinity} = -141 \text{ kJ mol}^{-1}$ $O^{-}(g) + e^{-} \rightarrow O^{2-}(g) \Delta H_{second \ electron \ affinity} = +798 \ kJ \ mol^{-1}$ $2Na^{+}(g) + O^{2-}(g) \rightarrow Na_2O(s) \Delta H_{lattice enthalpy} = unknown kJ mol^{-1}$





• Calculate the lattice formation enthalpy for Na₂O(s).





• It is not possible to go directly from $2Na^+(g) + O^{2-}(g)$ to $Na_2O(s)$.





Follow the direction of the blue arrows through the cycle.
Some arrows have to be reversed. Reversing an arrow changes the sign (+ to – and – to +) of the enthalpy change that is associated with it.





 $\Delta H_{LE} (\mathrm{Na_2O}) = (-798) + (+141) + (-992) + (-249) + (-216) + (-414)$





 $\Delta H_{LE} (Na_2O) = (-798) + (+141) + (-992) + (-249) + (-216) + (-414)$ $\Delta H_{LE} (Na_2O) = -2528 \text{ kJ mol}^{-1}$



Advance Concepts – Born-Haber Cycles

• Use the data given below to calculate the second ionization energy of magnesium.

Mg(s) + $\frac{1}{2}O_2(g) \rightarrow MgO(s) \Delta H_{formation} = -602 \text{ kJ mol}^{-1}$ $Mg(s) \rightarrow Mg(g) \Delta H_{atomisation} = +148 \text{ kJ mol}^{-1}$ $^{1}/_{2}O_{2}(g) \rightarrow O(g) \quad \Delta H_{atomisation} = +249 \text{ kJ mol}^{-1}$ $Mg(g) \rightarrow Mg^+(g) + e^- \Delta H_{first ionisation} = +738 \text{ kJ mol}^{-1}$ $Mg^+(g) \rightarrow Mg^{2+}(g) + e^- \Delta H_{second ionisation} = unknown kJ mol^{-1}$ $O(g) + e^- \rightarrow O^-(g) \Delta H_{first electron affinity} = -141 \text{ kJ mol}^{-1}$ $O^{-}(g) + e^{-} \rightarrow O^{2-}(g) \Delta H_{second \ electron \ affinity} = +798 \ kJ \ mol^{-1}$ $Mg^{2+}(g) + O^{2-}(g) \rightarrow MgO(s) \Delta H_{lattice enthalpy} = -3845 \text{ kJ mol}^{-1}$





Calculate the second ionization energy for Mg(s).





• It is not possible to go directly from Mg⁺(g) to Mg²⁺(g).





Follow the direction of the blue arrows through the cycle.
Some arrows have to be reversed. Reversing an arrow changes the sign (+ to – and – to +) of the enthalpy change that is associated with it.















 Hess's Law states that the total enthalpy change during the complete course of a chemical reaction is the same, whether the reaction takes place in one step, or it takes place in several steps.





 Hess's Law states that the total enthalpy change during the complete course of a chemical reaction is the same, whether the reaction takes place in one step, or it takes place in several steps.



 Hess's Law maybe rephrased to say that the enthalpy change of a chemical reaction is *independent* of the path taken from the reactants to the products.



 Hess's Law is based upon the principle that energy must be conserved during a chemical reaction (energy can not be created or destroyed, it can only be converted from one form to another).



- Hess's Law allows the enthalpy change (∆H) of a chemical reaction to be calculated, even when it cannot be measured directly by experiment.
- This is achieved by performing simple calculations for related reactions, the enthalpy changes for which are known.



 The enthalpy change of formation, ∆H_f, for butane, C₄H₁₀, is the enthalpy change when 1 mole of butane is formed from carbon (as graphite) and hydrogen in their standard states at room temperature and pressure.

 The enthalpy change of formation for butane cannot be measured directly in the laboratory, but it can be calculated using a Hess Cycle.

• Use the following enthalpy changes of combustion, ΔH_c , to construct an appropriate Hess Cycle, and hence calculate the enthalpy change of formation for butane:

> ΔH_c for graphite = -394 kJ mol⁻¹ ΔH_c for hydrogen = -286 kJ mol⁻¹ ΔH_c for butane = -2877 kJ mol⁻¹























 Reverse the direction of the arrow between C₄H₁₀ and CO₂ / H₂O to ensure that the Hess Cycle moves in the correct direction, from reactants to products: 4C(s) + 5H₂(g) → 4CO₂(g) + 5H₂O(g) → C₄H₁₀(g)

Note: If the direction of an arrow is reversed, then the sign of the enthalpy change associated with the arrow is also changed (what was once an exothermic reaction is now an endothermic reaction).

• The enthalpy change of formation for butane is then the sum of the enthalpy changes leading from $4C(s) + 5H_2(g)$ to $C_4H_{10}(g)$.


Advance Concepts – Hess Cycles





Advance Concepts – Hess Cycles





Advance Concepts – Hess Cycles





Alkane Combustion Spreadsheet Can enthalpy change calculations be automated in a spreadsheet?

Alkanes are hydrocarbons with the general formula C_nH_{2n + 2}.
Alkanes react with oxygen to produce carbon dioxide and water.
Design a spreadsheet that will, when the number of carbon

atoms in the molecule is keyed in, automatically calculate the energy change for the combustion of one mole of an alkane.

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	Definition: The enthalpy change of combustion is the energy change produced when																					
one mole of a chemical completely reacts with oxygen under standard conditions.																						
						Instru	ctions:															
	1) Choose an	alkane I	ov tvning a	whole nur	nber inte	the cell th	hat is high	lighted in h	lue and	nress "Re	sturn"	on your ke	vhoard									
	2) The spread	disheet w	ill generat	te the bala	nced ch	emical equ	uation for t	the comple	te comb	ustion of o	one n	nole of the	alkane									
	3) Using average bond energies, the spreadsheet will calculate the enthalpy change of combustion for one mole of the alkane											e.										
	-,,							,														
	Average Bond Energies:									Na	Names of the First Ten Straight Chain Alkanes											
	C-C = 348 kJ mol ⁻¹ C-H = 412 kJ mol ⁻¹ O=O = 496 kJ mol ⁻¹								CH ₄ = Methane													
		$C=0 = 743 \text{ kJ} \text{ mol}^{-1}$ $O-H = 463 \text{ kJ} \text{ mol}^{-1}$							$C_2H_6 = Ethane$													
																	C.H. =	Propane				
					Balar	ced Che	mical Equ	uation.									C.H.	= Butane				
	C .		4 .		2	0		1	co	+	2	н.0			C-H= Pentane							
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				Energy	Chang	During	Covalent	Bona Bre	eaking:								C7H16	= Heptane				
		0	×	C-C	=	0	×	+348	=	0							C ₈ H ₁₈	= Octane				
		4	×	C-H	=	4	×	+412	=	+1648			_				C ₉ H ₂₀	= Nonane				
		2	×	0=0	=	2	×	+496	=	+992							C ₁₀ H ₂₂	= Decane				
								Tota	=	+2640			1									
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		4	×	U-H	=	4	×	-403	=	-1002												
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					=	+2640	+	-3338														
					=	-698	kJ mol ⁻¹															





- Consider the combustion of methane and the combustion of ethane shown on the left.
 - Let the number of carbon atoms = n.
- In relation to n, how many C–C bonds break?
- In relation to n, how many C–H bonds break?
- In relation to n, how many O=O bonds break?
- In relation to n, how many C=O bonds form?
- In relation to n, how many O–H bonds form?





 Consider the combustion of methane and the combustion of ethane shown on the left. Let the number of carbon atoms = n. In relation to n, how many C–C bonds break? n - 1 In relation to n, how many C–H bonds break? 2n + 2 • In relation to n, how many O=O bonds break? 1.5n + 0.5 In relation to n, how many C=O bonds form? 2n In relation to n, how many O–H bonds form? 2n + 2



- In summary, for an alkane with the general formula C_nH_{2n+2} :
 - The number of C–C bonds broken = n 1.
 - The number of C–H bonds broken = 2n + 2.
 - The number of O=O bonds broken = 1.5n + 0.5.
 - The number of C=O bonds formed = 2n.
 - The number of O-H bonds formed = 2n + 2.
 - Average C–C bond energy = 348 kJ mol^{-1} .
 - Average C–H bond energy = 411 kJ mol^{-1} .
 - Average O=O bond energy = 498 kJ mol⁻¹.
 - Average C=O bond energy = 804 kJ mol⁻¹.
 - Average O–H bond energy = 463 kJ mol^{-1} .
- Remember, bond breaking is endothermic, ΔH is positive, while bond formation is exothermic, Δ is negative.



• How do your results compare to the experimental data?

Name of Straight Alkane	Formula of Straight Chain Alkane	Physical State at Room Temperature and Pressure	Standard Molar Enthalpy Change of Combustion at 298 K / kJ mol ⁻¹			
Methane	CH ₄	Gas	-890			
Ethane	C_2H_6	Gas	-1560			
Propane	C ₃ H ₈	Gas	-2220			
Butane	C_4H_{10}	Gas	-2877			
Pentane	C_5H_{12}	Liquid	-3509			
Hexane	C ₆ H ₁₄	Liquid	-4163			

• Identify any possible sources of error in the calculations.



Higher Order Thinking Skills

In what ways are exothermic and endothermic reactions **a)** similar **b)** different?



Higher Order Thinking Skills Compare and Contrast Exothermic and Endothermic Reactions





Higher Order Thinking Skills Compare and Contrast Exothermic and Endothermic Reactions Reaction involves Reaction involves bond formation. bond breaking. Exothermic Endothermic Reaction Reaction

Reaction has an activation energy.
A catalyst will lower the activation energy.



Higher Order Thinking Skills Compare and Contrast Exothermic and Endothermic Reactions







What is a *hydrogen fuel cell*? Do they really generate electricity without causing pollution?



• A hydrogen fuel cell car.



 The Toyota Mirai – the world's first commercial hydrogen fuel cell car – went on sale in Japan on 15th December 2014.









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Hydrogen

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TIT

 When hydrogen reacts with oxygen, an exothermic reaction takes place that produces water as the only reaction product.

 $2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \quad \Delta H = -572 \text{ kJ mol}^{-1}$

 In a hydrogen fuel cell, the hydrogen reacts with oxygen to produce water and energy in the form of electricity. The electrical energy can be used to do useful work, such as driving an electric motor to move a car.





Reaction pathway



 In the hydrogen fuel cell, a catalyst causes molecular hydrogen to break-down into hydrogen ions and electrons.
 H₂(g) → 2H⁺(aq) + 2e⁻

• The electrons pass through metal wires in an external circuit where they are made to do useful work, such as drive an electric motor. The hydrogen ions pass through a special membrane.

On the other side of the membrane, the hydrogen ions, electrons and oxygen combine together to form water.
 4H⁺(aq) + 4e⁻ + O₂(g) → 2H₂O(l)







• Hydrogen required for the hydrogen fuel cell is obtained by *cracking* long-chain hydrocarbons from crude oil, *e.g.* $C_{20}H_{42}(s) \rightarrow C_8H_{16}(l) + C_{12}H_{24}(l) + H_2(g)$

 Hydrogen can also be obtained from the *electrolysis* of water (the decomposition of water by electricity): 2H₂O(*l*) → 2H₂(g) + O₂(g)

 Remember, the hydrogen that is produced by cracking long-chain hydrocarbons is also used in the manufacture of ammonia – NH₃.

 The hydrogen must be stored with the hydrogen fuel cell. The large scale storage of hydrogen is hazardous because it is a highly flammable gas.





Reaction pathway

• The electrolysis of water is an endothermic process.



 Oxygen required for the hydrogen fuel cell is taken directly from the Earth's atmosphere, which is 21% oxygen.



The only chemical product of the reaction is H₂O, which is not considered to be a pollutant.
 Compare this to the chemicals that are produce by the internal combustion engine, *e.g.* CO, CO₂, NO₂ and SO₂.

Why is the

hydrogen fuel cell

considered to be a

source of *clean*

energy?



Are hydrogen fuel cells really the solution to our *environmental problems*?

 Hydrogen is obtained by cracking of long-chain hydrocarbons and electrolysis of water, both of which require energy. If this energy is provided by *burning fossil fuels*, then the hydrogen fuel cell is not as clean as it may seem.



Experimental Design

How do I *plan an experiment* to measure the enthalpy change of a reaction?



Experimental Design

• The combustion of an alcohol is an exothermic reaction. For example: methanol $2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(g)$ ethanol $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$ propan-1-ol $2C_3H_7OH(l) + 9O_2(g) \rightarrow 6CO_2(g) + 8H_2O(g)$

 Design an experiment to determine which alcohol, methanol, ethanol or propan-1-ol, releases the greatest amount of energy when one gram of the alcohol is completely burned in air.





• Experiments should be designed using critical thinking skills.





 What is the reason for performing the experiment?

 What hypothesis is being proved / disproved by performing the experiment?





 Clearly state exactly what the experiment is being designed to do.

What is the problem
 statement for the experiment?





• What essential information needs to be collected by the experiment?

 What observations need to be made?

 What are the different variables (independent, dependent and control)?




 How must the data from the experiment be manipulated and presented?

 What calculations (if any) need to be done?

 What graphs (if any) need to be plotted?





 What essential concept / law does the design of the experiment rely on? For example, the concept of energy and the law that energy can not be created or destroyed, but only converted from one form into another.





 What assumptions are being made when designing the experiment?

 Is it reasonable to make these assumptions?

 Identifying assumptions can help to identify errors.





 What are the implications and consequences if the results
 obtained from the experiment prove / disprove a specific hypothesis?





 Is there more than just one way of doing this experiment?

 If there is more than one way, which way is the most valid and reliable?



Experimental Design

• What is your hypothesis or problem statement?

• What are the variables? Which variables must be kept constant? What is your independent (input) variable? What is your dependent (output) variable?

- What is the big idea? Provide a general overview of the method.
 - What apparatus is required to perform the experiment?
- How is the apparatus set-up? Provide a clear, labelled diagram.

• How will you perform the experiment? Provide step-by-step instructions, including how variables will be controlled and what measurements will be taken.

- How will data from the experiment will be recorded? Provide an example results table that includes clear headings and units.
- How will the experimental data be manipulation? What graphs need to be plotted? What calculations need to be performed?
- What errors are associated with the experiment? What effect do these errors have on your results?



Experimental Design

Problem Statement

 Does the alcohol containing the greater number of carbon atoms per molecule release more energy when one gram of it is burned?

Variables

• Mass of water in the copper calorimeter (constant).

 Mass of alcohol burned during the experiment (independent variable).

• Temperature change of the water in the copper calorimeter (dependent variable).



Experimental Design General Overview of the Method

A known mass of alcohol is burned and used to heat a known mass of water, causing its temperature to increase by a known amount. Using the equation $E = m \times c \times \Delta T$, the heat energy absorbed by the water is calculated. It is assumed that the energy used to heat the water originated from combustion of the alcohol, therefore the energy released per unit mass of the alcohol can be calculated.



Experimental Design

Apparatus and Reagents

Diagram





Experimental Design Method

1) Weigh the copper calorimeter on the digital weighing machine. Record the data in the results table.

2) Use the measuring cylinder to pour 80 cm³ of water into the copper calorimeter.

3) Re-weigh the copper calorimeter and water and hence calculate the mass of water present in the calorimeter. Record the data in the results table.

4) Support the copper calorimeter in the retort stand and clamp.

5) Place a thermometer in the copper calorimeter and measure the initial temperature of the water. Record the data in the results table.

6) Weigh the spirit burner and lid containing the methanol on the digital weighing machine. Record the data in the results table.



Experimental Design Method

7) Place the spirit burner under the copper calorimeter. Adjust the height of the calorimeter so that it is 2 – 3 cm above the spirit burner.

8) Remove the lid from the spirit burner and, using the matches, immediately light the spirit burner. Adjust the height of the copper calorimeter once more so that the flame of the burning methanol covers the base of the calorimeter.

9) Using the glass rod, gently stir the water in the copper calorimeter. Ensure that no water spills out of the calorimeter.

10) When the temperature of the water in the copper calorimeter has increased by 20 °C, place the lid back on the spirit burner to extinguish the flame.



Experimental Design Method

11) Measure the temperature of the water in the copper calorimeter at the end of the experiment. Record the data in the results table.

12) Calculate the change in temperature of the water in the calorimeter. Record the data in the results table.

13) Re-weigh the spirit burner on the digital weighing machine at the end of the experiment. Record the data in the results table.

- 14) Calculate the mass of methanol burned during the experiment. Record the data in the results table.
- 15) Repeat the experiment for the other two alcohols, ethanol and propan-1-ol.

16) Repeat the entire experiment at least once more.



Experimental Design

Results

Measured and Derived Quantities	Methanol	Ethanol	Propan-1-ol
Mass of the copper calorimeter / g	X	X	X
Mass of the copper calorimeter + water / g	X	X	X
Mass of water in the copper calorimeter / g	X	X	X
Mass of spirit burner + lid + alcohol at the start of the reaction / g	Х	X	X
Mass of spirit burner + lid + alcohol at the end of the reaction / g	X	X	X
Mass of alcohol burned during the reaction / g	X	X	X
Temperature of the water in the copper calorimeter at the start of the reaction / g	X	X	X
Temperature of the water in the copper calorimeter at the end of the reaction / g	Х	Х	Х
Temperature increase of the water in the copper calorimeter during the reaction / g	X	X	X



Experimental Design Calculation

 It is assumed that all of the energy released during combustion of the alcohol is absorbed by the water in the copper calorimeter, *i.e.*

energy produced by combustion of alcohol = energy gained by water

```
    Energy gained by water = m<sub>w</sub> × c × ΔT
where:
    m<sub>w</sub> = mass of water / g
    c = specific heat capacity of water = 4.20 j / g / °C
ΔT = change in temperature of the water / °C
```

• Energy released by burning 1 g of alcohol = $(m_w \times c \times \Delta T) \div m_a$ where: $m_a = mass of alcohol / g$



Experimental Design Source of Error

The alcohol undergoes incomplete combustion.
 Incomplete combustion of the alcohol releases less energy than complete combustion. This will reduce the amount by which the water in the calorimeter increases in temperature, resulting in a smaller value for the calculated energy change.

2) Heat energy is lost to the surroundings.

Heat energy from combustion of the alcohol is lost to the surroundings rather than being transferred into the water. This will reduce the amount by which the water in the calorimeter increases in temperature, resulting in a smaller value for the calculated energy change.



Experimental Design Source of Error

3) Heat energy is absorbed by the copper calorimeter. Heat energy from combustion of the alcohol is absorbed by the copper calorimeter rather than being transferred into the water. This will reduce the amount by which the water in the calorimeter increases in temperature, resulting in a smaller value for the calculated energy change.



Experimental Design

 When ammonium chloride dissolves in water, an endothermic energy change takes place: NH₄Cl(s) → NH₄Cl(aq) +ΔH

 Design an experiment to determine the energy change when one mole of ammonium chloride dissolves completely in water.



Experimental Design



• The apparatus that could be used for conducting this experiment is shown in the diagram on the left.

 Refer to the diagram to help you design the experiment.



Assessment for Learning

Could I pleas have some questions to *check my understanding*?



Assessment for Learning Question 1:

 Dissolving ammonium nitrate in water is endothermic. Which graph shows how the temperature alters as the ammonium nitrate is added to water and the solution is left to stand?





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Assessment for Learning Question 2:

- The formation of hydrogen iodide from hydrogen and iodine is an endothermic reaction.
 H–H + I–I → H–I + H–I
 What may be deduced from this information?
- A The number of bonds broken is greater than the number of bonds formed.
- **B** The formation of H–I bonds absorbs energy.
- **C** The products possess less energy than the reactants.
- D The total energy change in bond formation is less than that in bond breaking.



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Assessment for Learning Question 3:

• The table below shows the energy released by the complete combustion of some compounds used as fuels.

Compound	Formula	<i>M</i> _r	∆H in kJ mol ⁻¹
methane	CH ₄	16	-880
ethanol	C ₂ H ₅ OH	46	-1380
propane	C ₃ H ₈	44	-2200
heptane	C ₇ H ₁₆	100	-4800

Which fuel produces the most energy when 1 g of the compound is completely burned?

A EthanolC MethaneD Propane



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Assessment for Learning Question 4:

• The enthalpy diagram shows an uncatalysed, exothermic reaction.



The reaction was repeated in the presence of a catalyst. What effect does the catalyst have on the activation energy , E_a , and the enthalpy change, ΔH ?

- **A** E_a decreases and Δ H decreases.
- **B** E_{a} decreases and Δ H unchanged.
- **C** E_{a} increases and ΔH increases.
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Assessment for Learning Question 5:

The scheme shows four stages, I to IV, in the conversion of solid candlewax, $C_{30}H_{62}$, into carbon dioxide and water.

Which stages are exothermic?

- A I and II.
- B II and III.
- C III and IV.
- **D** I and IV.



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- **D** I and IV.



Energy from Chemicals – Enthalpy Changes



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