



5 Energy from chemicals

Content

- 5.1 Enthalpy
- 5.2 Hydrogen fuel cell

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 (see also 6.1(c), 6.1(d))
- (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)

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5.1 Enthalpy

Enthalpy

Enthalpy (H) is defined as a thermodynamic property of a system.

- ✎ Enthalpy is defined by the following formula:

$$H = U + pV$$

where H : enthalpy
 U : internal energy of the system
 p : pressure
 V : volume

Enthalpy change

Enthalpy change or heat of reaction is the amount of heat released or absorbed when a chemical reaction occurs at constant pressure.

- ✎ Enthalpy change is shown by the symbol ΔH (delta H):

$$\Delta H = \Delta U + p\Delta V$$

$$\text{where } \Delta H = H_{\text{products}} - H_{\text{reactants}}$$

- ✎ ΔH is specified per **mole** of substance as in the balanced chemical equation for the reaction.
- ✎ The units are usually given as **kJ mol⁻¹** (kJ/mol) or sometimes as kcal mol⁻¹ (kcal/mol) (1 cal = 4.184 J).
- ✎ Energy changes are measured under **standard** laboratory conditions at 25°C (298K) and 101.3kPa (1 atmosphere).
- ✎ In terms of energy (or enthalpy changes), there are two types of chemical reactions.
- Exothermic reaction
 - Endothermic reaction
- ✎ Enthalpy changes in a reaction can be determined by using the formula:
- $$\begin{aligned}\Delta H &= \text{solution mass} \times \text{specific heat capacity} \times \text{temperature change} \\ &= mc\theta\end{aligned}$$
- where m : molar mass of solution (g mol⁻¹)
 c : energy to raise temperature of 1g by 1°C (kJ g⁻¹ °C⁻¹)
 θ : temperature change given by $T_{\text{final}} - T_{\text{initial}}$ (°C)



Exothermic reactions

Exothermic reactions liberate heat energy to the surroundings and results in a general increase in the temperature of the surroundings.

- ☞ Energy is **released**.
- ☞ Energy is a product of the reaction.
- ☞ Reaction vessel **becomes warmer**. Temperature inside the reaction vessel increases.
- ☞ It has a **negative (-) ΔH** , which implies that the energy of the reactants is greater than the energy of the products.

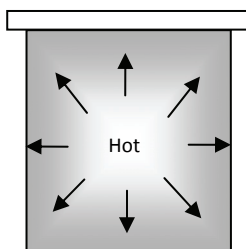
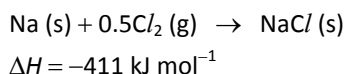


Figure 5–1: Exothermic reaction giving out heat

Examples

- 1 An example of an exothermic reaction is the mixture of sodium and chlorine to yield table salt. This reaction produces 411 kJ of energy for each mole of salt that is produced.



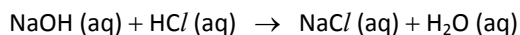
- 2 When a strip of magnesium is dropped into excess hydrochloric acid, there is a noticeable increase in the rate of exothermic reaction during the first few seconds, because the heat produced during the exothermic reaction increases the rate of effective collision between the reactant molecules.

(Examined in 2002.p1.17)

- 3 In a volumetric experiment, hydrochloric acid is added to 25.0 cm³ of aqueous sodium hydroxide.

∴ Deducing the instrument that needs to detect the end–point of reaction process,

Hydrochloric acid and aqueous sodium hydroxide react in a neutralization reaction. The equation describing the neutralisation reaction between hydrochloric acid and aqueous sodium hydroxide is as follows:



The above reaction is exothermic and for every one mole of NaOH and HCl reacted, a standard amount of heat energy will be released. Thus, a **thermometer** can be used to determine the end–point of the reaction.

(Examined in 2006.p1.2)

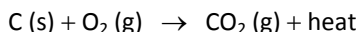


Heat of combustion

- ✍ All combustion reactions are exothermic.
- ✍ The **heat of combustion** is the heat released when 1 mole of substance burns completely in excess oxygen.

Examples

- ① One mole of carbon burns completely in excess oxygen to release 393.5 kJ of heat.

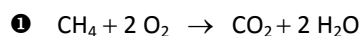


$$\text{Heat of combustion } \Delta H = -393.5 \text{ kJ mol}^{-1}$$

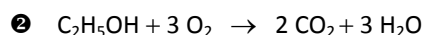
- ② The table below shows the energy value released by some compounds when used as a fuel:

compound	formula	M_r	ΔH in kJ/mol
methane	CH_4	16	- 880
ethanol	$\text{C}_2\text{H}_5\text{OH}$	46	- 1380
propane	C_3H_8	44	- 2200
heptane	C_7H_{16}	100	- 4800

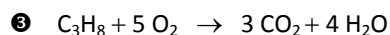
\therefore *Deducing the compound that when 1 g of that fuel is completely burnt would produce the most energy,*



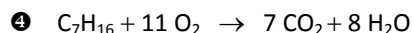
$$\text{Energy released from methane} = 1/16 \times 880 = \underline{55 \text{ kJ}}$$



$$\text{Energy released from ethanol} = 1/46 \times 1380 = \underline{30 \text{ kJ}}$$



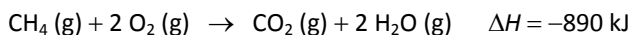
$$\text{Energy released from propane} = 1/44 \times 2200 = \underline{50 \text{ kJ}}$$



$$\text{Energy released from heptanes} = 1/100 \times 4800 = \underline{48 \text{ kJ}}$$

(Examined in 2004.p1.18)

- ③ Fuel methane is set to burn in an exothermic combustion:



Possible choices are:

- ① Molecules release energy when they react.
- ② More bonds are formed than are broken.
- ③ The bonds formed are weaker than the bonds broken.
- ④ The total energy required to break bonds is less than that released in bond formation.

\therefore *Deducing the reason why the combustion of methane is exothermic,*

For a reaction process to be exothermic, the total energy required to break the bonds of reactants must be less than the total energy released during the forming of bonds of the products (④).



Option ❶ is not necessarily true because when molecules react, the overall reaction can be endothermic or exothermic depending on the overall energy gain or energy loss to the environment. If the reaction is exothermic, then the molecules release energy. If the reaction is endothermic, the molecules absorb energy from the surroundings.

Option ❷ is false because the total number of bonds broken in the reactants and the total number of bonds formed in the products is the same, which is 6. The difference in energy loss or energy gain is not a direct consequence of the total number of bonds broken or formed, it is dependent on the bond energy of the bonds in the reactants and products.

Option ❸ is false because it describes an endothermic reaction instead of an exothermic reaction. In an exothermic reaction, the opposite is true, the bonds formed are stronger than the bonds broken.

(Examined in 2006p1.16)

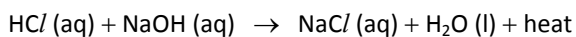


Heat of neutralisation

- When an acid and an alkali react, heat is released.
- The **heat of neutralisation** is the heat released when 1 mole of hydrogen ion (H^+) neutralises 1 mole of hydroxide ion (OH^-), to form 1 mole of water (H_2O).

Example

- One mole of dilute hydrochloric acid reacts with 1 mole of sodium hydroxide to release 57 kJ of heat.



Heat of neutralization $\Delta H = -57 \text{ kJ mol}^{-1}$

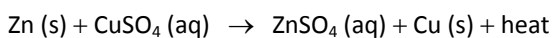


Heat of displacement

- More reactive metals are able to displace less reactive ones from their salts. This reaction is known as displacement.
- The **heat of displacement** is the heat released when 1 mole of metal is displaced from its salt solution by a more electropositive metal.

Example

- One mole of copper is displaced from a copper (II) sulphate solution by zinc to release 190 kJ of heat.



Heat of displacement $\Delta H = -190 \text{ kJ mol}^{-1}$

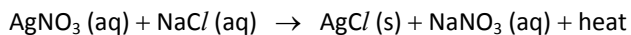


Heat of precipitation

- The **heat of precipitation** is the heat change when 1 mole of precipitate is formed.

Example

- The reaction between silver nitrate (AgNO_3) solution and sodium chloride (NaCl) solution forms the white precipitate silver chloride (AgCl).



Endothermic reaction

Endothermic reactions absorb heat energy from the surroundings and result in a general decrease in the temperature of the surroundings.

- Energy is **absorbed**.
- Energy is a reactant of the reaction.
- Reaction vessel **becomes cooler**. Temperature inside the reaction vessel decreases.
- It has a **positive (+) ΔH** , which implies that energy of the reactants is less than the energy of the products.

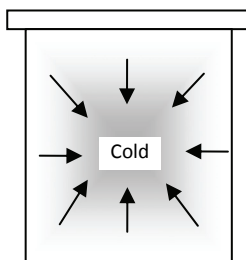
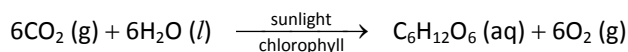


Figure 5–2: Endothermic reaction taking in heat

Example

- Photosynthesis is an example of an endothermic chemical reaction. In this process, plants use the energy from the sun to convert carbon dioxide and water into glucose and oxygen. This reaction requires 15 MJ of energy (sunlight) for every kilogram of glucose that is produced.



$$\Delta H = +15\text{MJ kg}^{-1}$$



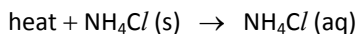


Dissolution of salts

- When some salts dissolve in water, there is temperature change.

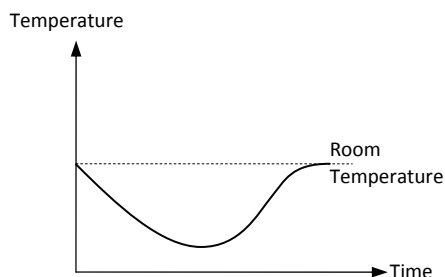
Example

- 1 Ammonium chloride absorbs heat when it dissolves in water. Thus, the solution becomes cold.



- 2 Ammonium nitrate is added to water and the solution is subsequently left to stand.

When dissolving ammonium nitrate in water, the process is *endothermic*. The heat loss will cause the temperature of the solution to drop below room temperature and when the solution is left to stand, it will regain heat and the temperature of the solution will gradually increase back to room temperature.



(Examined in 2002.p1.16, 2010.p1.11)

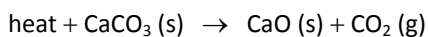


Decomposition of compounds

- Many compounds require heat to decompose. Thus, they undergo reactions when heated.

Example

- 1 Calcium carbonate decomposes to calcium oxide and carbon dioxide when heated.

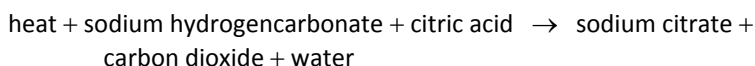


Reaction between acids and hydrogencarbonates

- Acids can release carbon dioxide from hydrogencarbonates. The reaction is always endothermic.

Example

- 1 When a tablet containing sodium hydrogencarbonate and citric acid is dissolved in water, the temperature of the solution drops.



Activation energy

Activation energy (E_a) is the **minimum** energy required for a chemical reaction to take place.

- ✍ The reactants must overcome the activation energy level in order to become products. The activation energy is the minimum energy required to change the chemical bonds within the reactants.
 - The activation energy is like a barrier to the start of a reaction.
- ✍ The activation energy may be provided by the kinetic energy of particle collision. However, in most cases, extra energy from an external heat source such as a spark or a burning splint is needed.

Bond energy

Bond energy is the amount of energy associated with a bond in a chemical compound.

- ✍ Since different bonds have different **bond dissociation energies**, there is often a significant overall energy change in the course of a reaction.
- ✍ The energy absorbed in breaking a bond is the **same** as the energy given out in forming the bond.
- ✍ Overall energy change = Energy given out when bonds are made + Energy taken in when bonds are broken.

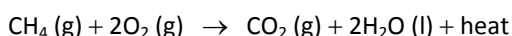
$$\Delta H = \text{Heat released in bond making} + \text{Heat absorbed in bond breaking}$$

- ✍ The bond energies of some common covalent bonds are shown in the table.

Covalent Bond	Average Bond Energy (kJ/mol)
H – H	436
Cl – Cl	242
H – Cl	431
O – H	463
O = O	496
N \equiv N	945

Example

- 1 In the combustion of methane, all six bonds in the reactant molecules are broken and six new bonds are formed in the product molecules.





Reactants: 4 C–H bonds, 2 O=O bonds

Products: 2 C=O bond, 4 O–H bonds



Bond breaking

- ✍ All chemical reactions involve the **breaking** of old bonds followed by the **making** of new bonds.
- ✍ The heat **absorbed** in a reaction is used in the **breaking** of chemical bonds.
- ✍ Bond breaking is **endothermic** (absorbs energy).

(Examined in 2012p1.18)

Example

- ① During electrolysis, compounds (usually water) are separated by running an electric current through it. Heat is absorbed in the process.

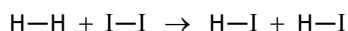


Bond making

- ✍ The heat **given out** in a reaction comes from the chemical bonds being **formed**.
- ✍ Bond making is **exothermic** (releases energy).

Examples

- ① During the burning of a wooden splint, heat and light energy and gases like CO₂ and H₂O are given off while carbon is left behind.
- ② The reaction between hydrogen and iodine to produce hydrogen iodide is endothermic.



(Examined in 2003p1.16)

- ①: The number of bonds broken is the same as the number of bonds formed. The bonds broken in the reaction are the two covalent bonds between two hydrogen atoms and two iodine atoms. The bonds formed in the reaction are two covalent bonds between a hydrogen atom and an iodine atom.
- ②: The formation of bonds is an exothermic reaction which means that bond formation releases energy, instead of absorbing energy.
- ③: In an endothermic reaction, the products will possess more energy than the reactants because the enthalpy change of reaction is positive. This also means that the products are less stable as compared to the reactants.
- ④: The bond formation releases energy so it is exothermic while bond breaking takes in energy so it is endothermic. Since the overall reaction is endothermic, the total energy change in bond formation must be less than that in bond breaking.

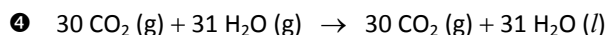
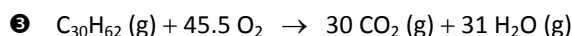
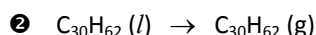
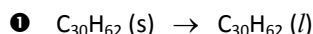


Overall enthalpy changes in a reaction

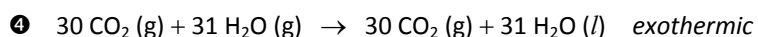
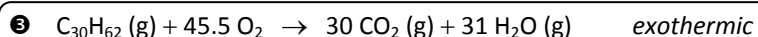
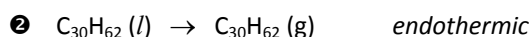
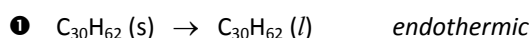
- ✍ Whether the overall reaction is exothermic or endothermic depends on which of the two energy values (absorbed or released) is greater.
 - The reaction is **exothermic** when the energy absorbed for **bond breaking** is **less** than that released during bond forming.
 - The reaction is **endothermic** when the energy absorbed for **bond breaking** is **more** than that released during bond forming.
- ✍ Most spontaneous chemical reactions are exothermic, which means the energy released in bond formation is greater than that absorbed by bond breaking.
 - The products have less energy than the reactants.
- ✍ In chemical reactions, some (or even all) of the bonds that hold together the atoms of reactant and product molecules may be broken while other bonds are formed.

Example

- ① Four stages, ① to ④, in the conversion of solid candlewax, $C_{30}H_{62}$, are explained below. Carbon dioxide and water are produced in the final stage.



\therefore *Deducing the energy-releasing (exothermic) stages,*



- ① and ② are *endothermic* processes because during melting and boiling respectively, energy is absorbed to increase the internal energy of the substance, so that it can change from one state to the other.

- ③ is an *exothermic* process. ④ is a combustion reaction, and combustion is always exothermic. In this reaction, there are bonds broken (endothermic) and bonds formed (exothermic). Overall, the energy required to form the bonds is much greater than the energy required to break the necessary bonds. As a result, this causes the reaction to be exothermic.

Note: 62 C–H bonds and 45.5 O=O bonds are broken, while 60 C=O bonds and 62 O–H bonds are formed. By sheer number, the number of bonds formed is already suggestive of the exothermic reaction. C=O happens to be a very strong bond which requires a lot of energy to form.



- ④ is an *exothermic* reaction because the water vapour condensed to become liquid, which also means that the vapour loses energy. This is opposite to boiling.

(Examined in 2008.p1.15)



Energy profile diagrams

Energy profile diagrams are graphs of energy changes against time during chemical reactions.

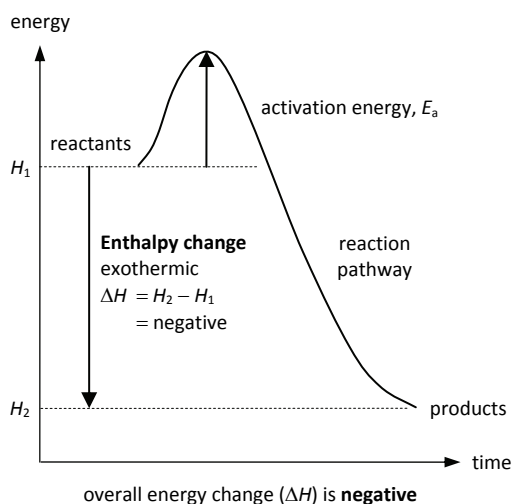


Figure 5-3: Energy profile for exothermic reaction

(Examined in 2010p1.12)

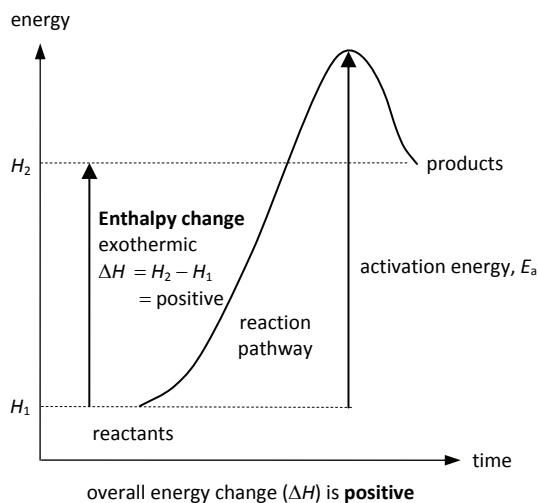
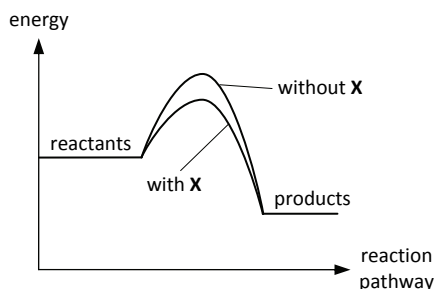


Figure 5-4: Energy profile for endothermic reaction

(Examined in 2006p2.4, 2007p1.13, 2012p2.5b, 2013p1.13)

Example

- ① When substance **X** is added to a reaction mixture, the graph of the changes in the energy output along the reaction pathway is shown below.



∴ Since the addition of substance **X** to the reaction mixture lowers the activation energy of the reaction, therefore substance **X** must be a catalyst to the reaction. Consequently, when the substance **X** is added to the reaction mixture, *the speed of the reaction must increase*. This is because, by lowering the activation energy of the reaction, the catalyst increases the number of reactant particles possessing energy greater than the activation energy of the reaction. Subsequently, the rate of reaction increases.

It is wrong to say that *the reaction becomes less exothermic* because the catalyst does not increase the amount of heat energy produced during the reaction. The amount of heat energy produced during the reaction is dependent on the number of moles of reactant molecules and product molecules, thus it is dependent on the concentration of reactants and products.

(Examined in 2002p1.18, 2003p2.3, 2008p2.2)



Worked Examples

Example 1

If bond energy of C–H is 412 kJ/mol, how much energy is required to break all the C–H bonds in CH₄?

Solution:

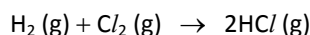
CH₄ has 4 C–H bonds.

Energy involved in the reaction = $+(4 \times 412) = +1648$ kJ.



Example 2

Estimate the change in enthalpy, ΔH , for the following reaction:



Solution:

Bond breaking in reactants:

1 mol H₂ contains 1 H–H bond, bond energy = +436 kJ/mol

1 mol Cl₂ contains 1 Cl–Cl bond, bond energy = +242 kJ/mol

$\Delta H_1 = +436 \text{ kJ} + 242 \text{ kJ} = +678 \text{ kJ}$ (endothermic)



Bond making in products:

2 mol HCl contains 2 H-Cl bonds, bond energy = +431 kJ/mol

$$\Delta H_2 = -(2 \times 431) \text{ kJ} = -862 \text{ kJ (exothermic)}$$

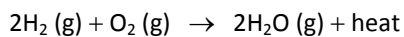
$$\begin{aligned}\Delta H &= \Delta H_1 + \Delta H_2 \\ &= +678 - 862 \\ &= -184 \text{ kJ}\end{aligned}$$



Example 3

How much heat is produced when hydrogen gas is burnt in oxygen to form water vapour?

Solution:



$$\begin{aligned}\Delta H &= \text{Heat released in bond making} + \text{Heat absorbed in bond breaking} \\ &= -(2 \times 2 (\text{O-H})) + (2 \times (\text{H-H}) + \text{O=O}) \\ &= -(4 \times 463) + (2 \times 436 + 496) \\ &= -1852 + 1368 \\ &= -484 \text{ kJ/mol}\end{aligned}$$

Heat produced = 484 kJ/mol



5.2 Hydrogen fuel cells

Hydrogen

- ✍ Hydrogen burns cleanly in air to form steam. *(Examined in 2009p2.3, 2013p2.5b)*
- ✍ It is a very clean fuel and produces at least twice as much heat than other fuels. Thus, it is used as a fuel in space shuttles and rockets.
- ✍ Hydrogen is a potential alternative to petrol. Experiments are ongoing to use hydrogen to power vehicles, run turbines, produce electricity and generate heat and electricity for buildings.

Production of hydrogen

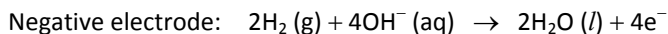
- ✍ Most hydrogen is manufactured on a large scale from petroleum and natural gas.
 - Methane from natural gas and steam are passed over a nickel catalyst.
$$\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \xrightarrow{\text{catalyst}} \text{CO}(\text{g}) + 3\text{H}_2(\text{g})$$
(Examined in 2006p1.22)
 - The carbon monoxide is reacted with more steam to form carbon dioxide, which can be removed by passing the gases through an alkali.
$$\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$$
- ✍ Another way to produce hydrogen is by the electrolysis of water, but this is a much more expensive process.
- ✍ Scientists are also investigating ways to use solar energy to perform decomposition of water.

Fuel cells

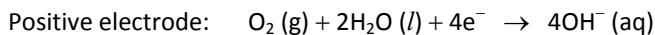
- ✍ A fuel cell works like a battery but does not run down or need recharging. It produces electricity as long as fuel is supplied and the energy conversion is very efficient.
- ✍ A fuel cell is a chemical cell. It consists of two electrodes, a negative electrode and a positive electrode, sandwiched around an electrolyte.
- ✍ Hydrogen and oxygen can be pumped into a fuel cell to produce electricity. The voltage obtained is 1.2V.
 - Hydrogen is fed to the **negative electrode**, where it is oxidised to form water.



- Oxygen is fed to the **positive electrode**, where it is reduced to form hydroxide ions.
- Hydrogen reacts with hydroxide ions on the platinum electrode (catalyst) to release electrons, thus make the electrode negative.

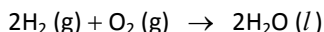


- Oxygen reacts with water on the platinum electrode to remove electrons, thus make the electrode positive.



- The electrons go through an **external circuit**, creating an electric current flow.

- The overall reaction is:



(Examined in 2013p2.5a)

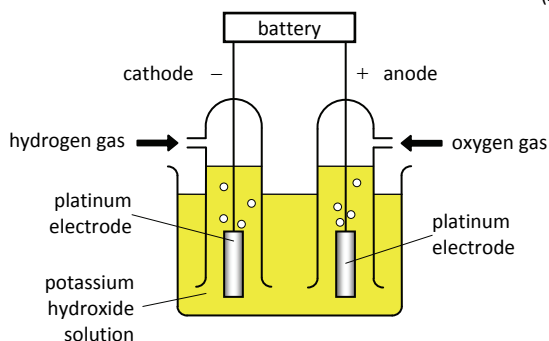


Figure 5-5: A simple hydrogen fuel cell

(Examined in 2010p2.10e)

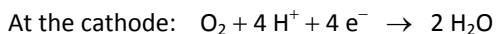
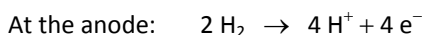
Example

- ① Given:

- ① electricity is generated directly
- ② electricity is used to produce water
- ③ hydrogen is burned to form steam
- ④ hydrogen reacts to form a hydrocarbon fuel

\therefore Deducing what happens when hydrogen and oxygen are used in a fuel cell,

A fuel cell is a device that converts the chemical energy from a fuel, such as hydrogen, into electricity through a chemical reaction with oxygen or another oxidizing agent.



(Examined in 2009p1.15)



Worked Problems

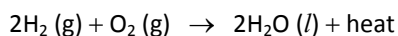
Example 1

Explain the following when hydrogen burns in oxygen.

- The forming and breaking of bonds.
- The heat changes involved.

Solution:

- The reactants H_2 and O_2 contain H–H and O=O bonds. The products contain O–H bonds. The H–H and O=O bonds in the reactants must be broken before new O–H bonds can be formed in the product.
- Heat is absorbed to break the bonds in the reactants. Then when the new bonds form, heat is released. The heat released during O–H bond formation in water is more than is the heat required to break the bonds in the hydrogen and oxygen gases. Thus, the overall process is exothermic.



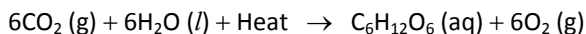
Example 2

Explain whether photosynthesis is an exothermic or endothermic reaction.

Solution:

Photosynthesis is an endothermic chemical reaction. In this process, plants use the energy from the sun to convert carbon dioxide and water into glucose and oxygen.

This reaction requires 15MJ of energy (sunlight) for every kilogram of glucose produced

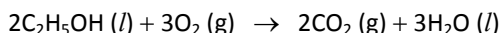


$$\Delta H = +15\text{MJ kg}^{-1}$$



Example 3

Ethanol burns in air according to the following reaction.



- What type of enthalpy change occurs during the reaction?
- The combustion of 1g of ethanol produces 30kJ of heat. Calculate the heat of reaction for the equation.

Solution:

- The enthalpy change is actually the heat of combustion, which is endothermic.



(b) Molecular mass of ethanol = $2 \times 12 + 6 + 16 = 46$

$$\text{No. of moles of ethanol} = \frac{1}{46} = 0.0217 \text{ mol}$$

$$\text{Heat of reaction} = \frac{30}{0.0217}$$

$$= 1380 \text{ kJ/mol (ans)}$$



Example 4

Calculate the heat change when 50 cm^3 of sodium hydroxide (NaOH) solution is reacted with 100 cm^3 of dilute hydrochloric acid (HCl). In this reaction, the temperature of the mixture rises from 30°C to 50°C .

The specific heat capacity of the solution is $4.2 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$. Density of the solution is 1 g cm^{-3} .

Solution:

$$\begin{aligned} \text{Mass of solution} &= (50 + 100) \times 1 \\ &= 150 \text{ g} \end{aligned}$$

$$\begin{aligned} \text{Heat change } \Delta H &= mc\theta \\ &= 150 \times 4.2 \times (50 - 30) \\ &= 12.6 \text{ kJ (ans)} \end{aligned}$$



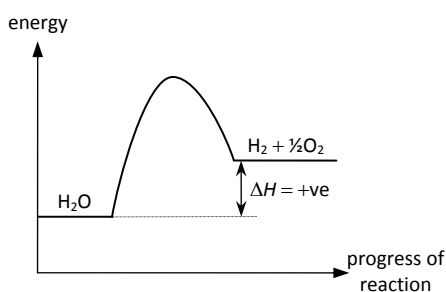
Example 5

Draw the energy profile diagram for the electrolysis of water.

Explain why hydrogen is not a completely non-polluting fuel.

(Examined in 2013p2.5cd)

Solution:



The combustion of hydrogen gives water, which is non-polluting. However, the production of hydrogen from fossil fuel gives off CO_2 as by-products. CO_2 is a greenhouse gas that causes global warming. Burning of fossil fuel also releases SO_2 and oxides of nitrogen which are causes of acid rain.

Production of hydrogen by electrolysis of water will require electricity generated from fossil fuel burning, which will similarly produce polluting gases.



Notes: