CHEMISTRY MATTERS

INTRODUCTION

'Chemistry Matters' is a program of study based on two premises: learning ideas and concepts is is best achieved through repeated practice, over the period of a chemistry course students develop their abilities to use ideas and concepts to account for chemical phenomena.

Repeated practice, in a context in which chemical theories and models are presented sequentially, is the best strategy to ensure students leave a chemistry course with ability and knowledge. By developing the theoretical foundations of energetics, bonding models and kinetics at increasing levels of complexity, the text ensures that students practice the ideas they are introduced to throughout their course. An idea or concept met on a single occasion is unlikely to have a lasting effect.

Mastering any skill or ability takes time and practice and this includes the frequently counter intuitive ideas used to account for chemical phenomena. Relating composition, structure and change to the behavior of atoms, ions and molecules is not common to everyday experience. The models and concepts used to explain chemical phenomena are not part of our everyday experience of the world. Atoms, ions and molecules behave very differently to the objects we see, feel and handle every day. The theories and models constructed to make sense of their behavior do not connect with the way we make sense of the world around us.

By developing and integrating concepts in a range of situations; environmental systems, biochemistry, industry, analysis, medicine and physiology, students explore and use chemistry in situations that matter to themselves and to society as a whole.

Recurring concepts, models and themes are the threads which integrate the text. Energetics threads through the text in contexts ranging from respiration and photosynthesis to nuclear power plants and batteries, to end with predictions based in the Second Law of thermodynamics. Water, together with carbon and its compounds, are the threads around which bonding models and the relationships between composition, structure and change are explored. Water's omnipresent role in chemistry is also explored in acid base and redox reactions. The Periodic Table is an ever present backcloth to relate reactions met in descriptive chemistry. Kinetics, initially introduced as collision theory to rationalize experimental data, is the thread that runs through reaction mechanisms and the role of enzymes in biological systems.

TABLE OF CONTENTS

Chapter 14
MOLECULES IN MOTION 171 - 190

Chapter 15
ELECTRON TRANSFER REACTIONS 191 -212

Chapter 16
REACTION RATES 213 - 230

Chapter 20
CARBON TOOLS 293 - 324

Chapter 21
THE HIDDEN COST OF LIVING 325 - 344

Chapter 22
HOW DOES CARBON DO IT 345 - 364

Chapter 23
THERMODYNAMICS: ENERGY FLOWS AND CHANGE 365 - 386

Chapter 24
POWERFUL REACTIONS 387 - 412

Chapter 25
EQUILIBRIA IN AQUEOUS SOLUTIONS 413 - 444

Chapter 26

PATHWAYS IN ORGANIC REACTIONS 445 - 472

Chapter 27

ORGANIC FAMILIES 473 - 528

Chapter 28

PERIODIC PATTERNS 529 - 580

Chapter 29

DIRECTING CHANGE 581 - 608

Chapter 30

CONTROLLING CHANGE 609 - 632

1

ENERGY FLOWS IN REACTIONS

RESPIRATION

Energy for muscles comes from 'burning up' glucose in respiration.

Chemists study **reactions**. The changes that take place when atoms rearrange. Atomic **rearrangements** always involve a change in energy. Most reactions produce heat energy. Some reactions, however, will only take place if energy is supplied to the rearranging atoms. When reactions take place **energy** either **flows into** or **out of** the **rearranging atoms**.

REACTIONS WE DEPEND ON

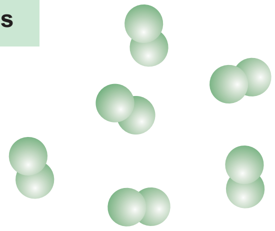
Photosynthesis, respiration and combustion are three reactions we depend on. Photosynthesis in plants makes our food, respiration powers the processes that take place in our cells and combustion drives our machines.

What produces the energy changes when these reactions take place? Why does energy flow out of the rearranging atoms in respiration and combustion? Why is sunlight needed to power the atomic rearrangements that make up photosynthesis?

REACTION EQUATION: $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

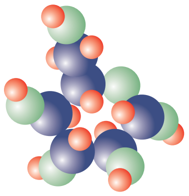
The reaction equation for respiration shows the number of oxygen molecules (O_2) needed to supply the oxygen atoms (O) to 'burn up' a single glucose molecule ($C_6H_{12}O_6$). The carbon (C), hydrogen (H) and oxygen (O) atoms in the reactants are rearranged into carbon dioxide (CO_2) and water (H_2O) molecules.
The mitochondria, found in all cells, provide the molecular machinery to carry out this re-arrangement and ensure that the energy 'locked up' in glucose molecules is released in a form the cell can use, to work muscles for example.

O_2 molecules



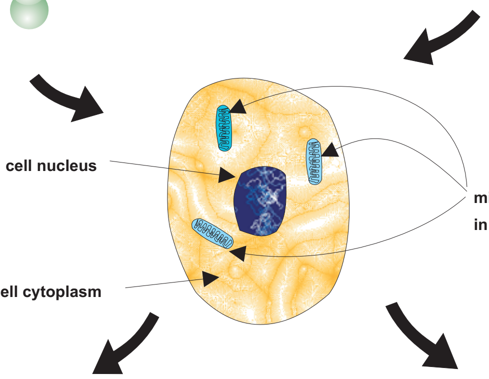
Living cells need a continual supply of energy to keep alive. The 'power stations' which generate this energy are located in the mitochondria.

$C_6H_{12}O_6$ molecule



A GLUCOSE MOLECULE $C_6H_{12}O_6$
Glucose molecules are made up of 6 carbon atoms (linked in a chain), 12 hydrogen atoms and 6 oxygen atoms bonded together.

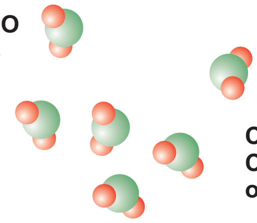
OXYGEN MOLECULES O_2
Oxygen molecules are made up of 2 oxygen atoms bonded together.

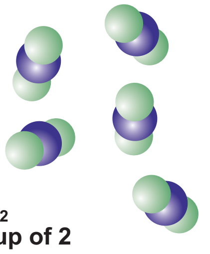


mitochondria
in the cytoplasm

H_2O molecules

WATER MOLECULES H_2O
Water molecules are made up of 2 hydrogen atoms bonded to an oxygen atom.

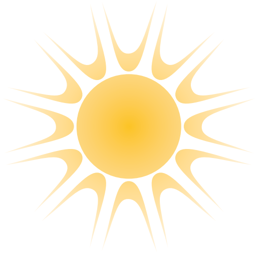




CO_2 molecules

CARBON DIOXIDE MOLECULES CO_2
Carbon dioxide molecules are made up of 2 oxygen atoms bonded to a carbon atom.

PHOTOSYNTHESIS



The cell machinery which builds the carbon chains in glucose molecules is powered by solar radiation.

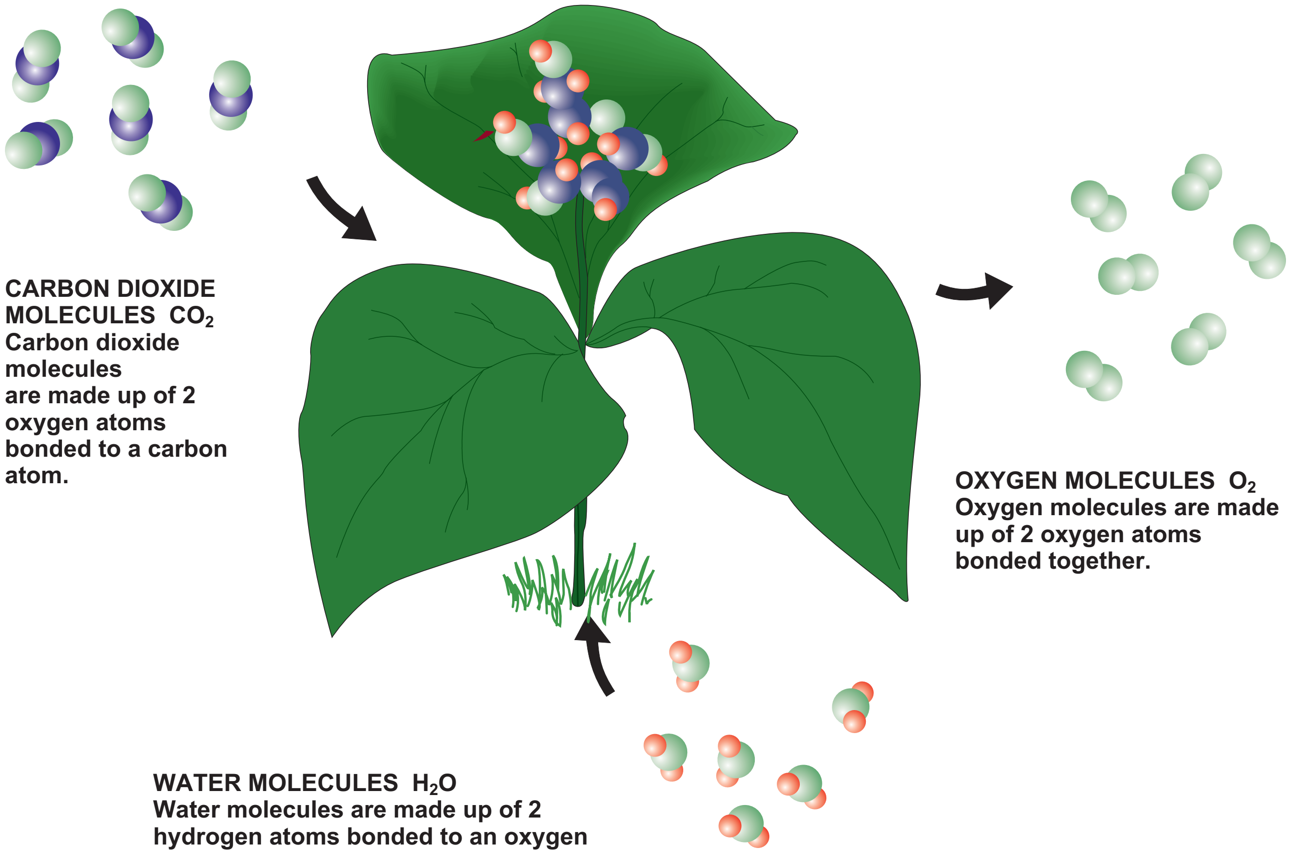
TRAPPING SOLAR ENERGY

Photosynthesizing plants use solar energy to **rearrange** the carbon (**C**), hydrogen (**H**) and oxygen (**O**) atoms in carbon dioxide (**CO_2**) and water (**H_2O**) molecules to make glucose molecules (**$C_6H_{12}O_6$**). Oxygen molecules (**O_2**) are also produced as a by product.
In photosynthesis, less energy is released making new bonds than is used up breaking bonds. Pulling carbon dioxide (CO_2) and water (H_2O) molecules apart uses up more energy than is released when carbon (C), hydrogen (H) and oxygen (O) atoms come together to make glucose ($C_6H_{12}O_6$) and oxygen (O_2) molecules. Plants therefore need an **energy input** to **manufacture glucose** molecules.

Plants can only **photosynthesize** in **daylight**. They depend on the Sun to meet the energy deficit involved in **rearranging** carbon (**C**), hydrogen (**H**) and oxygen (**O**) atoms into glucose (**$C_6H_{12}O_6$**) and oxygen (**O_2**) molecules.

REACTION EQUATION: $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$
The reaction equation for photosynthesis shows the number of carbon dioxide (CO_2) and water (H_2O) molecules needed to supply the carbon (C), oxygen (O) and hydrogen (H) atoms needed to manufacture a glucose molecule ($C_6H_{12}O_6$). The 6 carbon atoms in glucose make a chain which forms the molecule's backbone.

A GLUCOSE MOLECULE $C_6H_{12}O_6$
Glucose molecules are made up of 6 carbon atoms (linked in a chain), 12 hydrogen atoms and 6 oxygen atoms bonded together.

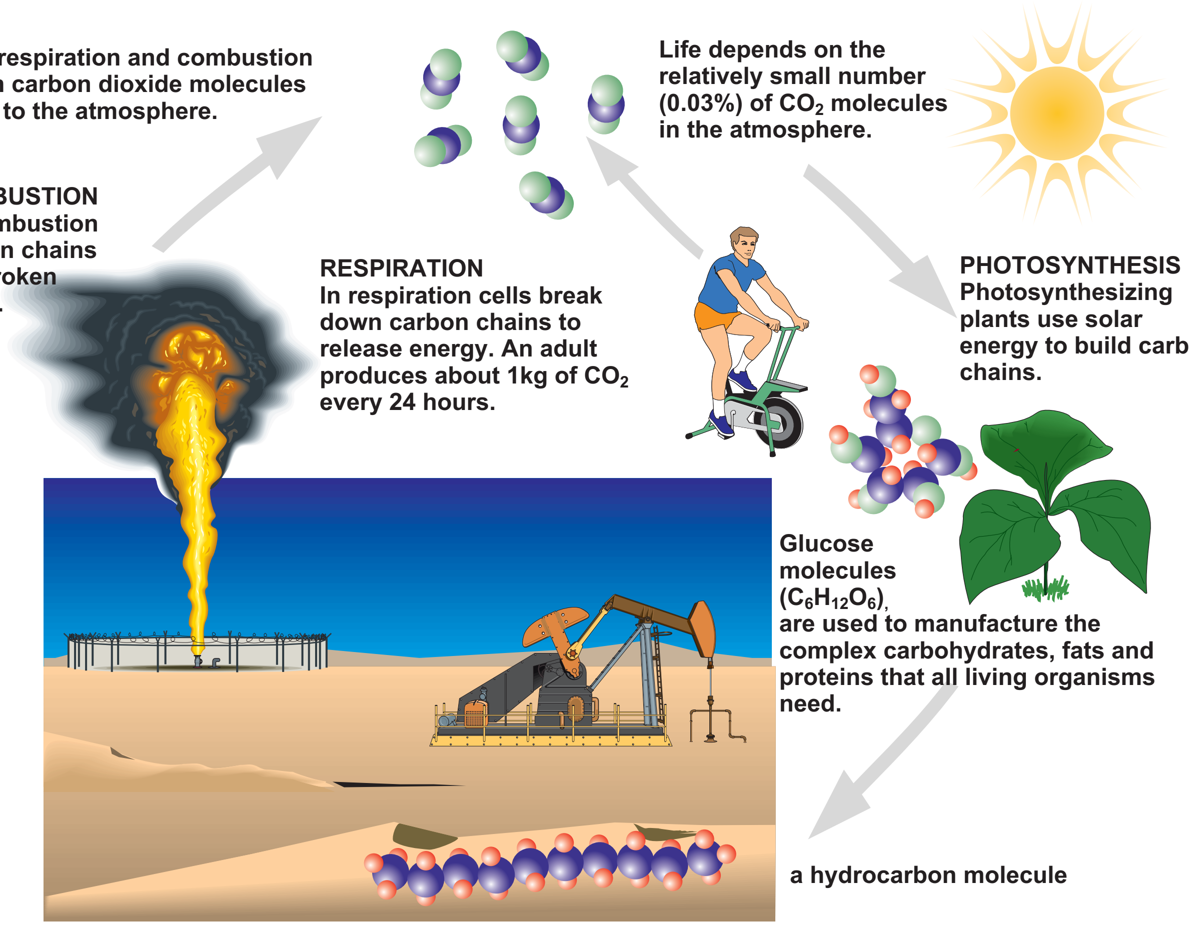


CARBON DIOXIDE MOLECULES CO_2
Carbon dioxide molecules are made up of 2 oxygen atoms bonded to a carbon atom.

OXYGEN MOLECULES O_2
Oxygen molecules are made up of 2 oxygen atoms bonded together.

WATER MOLECULES H_2O
Water molecules are made up of 2 hydrogen atoms bonded to an oxygen atom.

BUILDING UP AND BREAKING DOWN CARBON CHAINS



Both respiration and combustion return carbon dioxide molecules (CO_2) to the atmosphere.

Life depends on the relatively small number (0.03%) of CO_2 molecules in the atmosphere.

COMBUSTION
In combustion carbon chains are broken down.

RESPIRATION
In respiration cells break down carbon chains to release energy. An adult produces about 1kg of CO_2 every 24 hours.

PHOTOSYNTHESIS
Photosynthesizing plants use solar energy to build carbon chains.

Glucose molecules ($C_6H_{12}O_6$), are used to manufacture the complex carbohydrates, fats and proteins that all living organisms need.

a hydrocarbon molecule

PETROLEUM OIL
Some of the carbon chains made by photosynthesizing plants, during the carboniferous period 200 to 300 million years ago, have ended up in the hydrocarbon molecules which make up in petroleum oil.

THE CARBON CYCLE

Carbon atoms are constantly being swapped between living organisms and the atmosphere. As carbon chains in carbohydrates, fats and proteins are broken down in respiration and combustion, more are being made from the glucose molecules produced in photosynthesis.
The former returns carbon (in CO_2 molecules) to the atmosphere; the latter takes carbon (in CO_2 molecules) from the atmosphere.

Carbon (**C**) atoms, taken from simple carbon dioxide (**CO_2**) molecules, are **built up** by photosynthesizing plants into carbon chains. The backbone of the glucose (**$C_6H_{12}O_6$**) molecule is a chain of six carbon atoms. All of the complex carbohydrates, fats and proteins that living cells need are built out of carbon chains manufactured in photosynthesis.

The carbon dioxide taken from the atmosphere, by plants, must be replaced. If not supplies for photosynthesis would run out and plants, and the animals which feed off plants, would soon die. Carbon dioxide is returned to the atmosphere when living cells breakdown carbon chains in respiration. The combustion of fuels also breaks down carbon chains and puts carbon dioxide back into the atmosphere.

The amount of carbon dioxide in the atmosphere will remain constant as long as the rate at which it is removed matches the rate that it is replaced. If reactions put carbon dioxide into the atmosphere faster than it is taken out this balance, or equilibrium, will be disturbed.

SUMMARY

- Atomic rearrangements always involve a change in energy.
- Breaking bonds absorbs energy; making bonds releases energy.
- In exothermic reactions, like respiration and combustion, more energy is released making bonds than is absorbed breaking bonds.
- In endothermic reactions, like photosynthesis, more energy is absorbed breaking bonds than is released making bonds.
- The energy change in a reaction depends on the relative energies of the reactants and products.
- Energy profiles which break down a reaction into two steps, breaking bonds and making bonds, summarize the energy changes from reactants to products. This is equivalent in energy terms to the actual pathway a reaction takes.
- Our energy needs; for transport, heating and generating electricity, are largely met by burning the hydrocarbons found in petroleum oil.
- Traffic smog is part of the price we pay for the energy we consume.

Study Questions
Chapter 1: ENERGY FLOWS IN REACTIONS

1 Photosynthesizing plants manufacture glucose in an endothermic reaction using carbon dioxide and water as raw materials.

- a Write the formulae for water, carbon dioxide and glucose molecules.

- b Photosynthesizing plants produce a waste product when they manufacture glucose. Name and write the molecular formula of this waste product.

- c Describe, using chemical symbols. how the carbon (C), hydrogen (H) and oxygen (O) atoms in carbon dioxide (CO_2) and water molecules (H_2O) are rearranged in photosynthesis. Explain, from a consideration of the bonds broken and the bonds formed, why the overall atomic rearrangement that takes place in photosynthesis is an endothermic process. Draw an energy profile of the reaction to illustrate your answer.

- d The accepted theory for the origin of the chains of carbon atoms found in hydrocarbon fuels is that they were manufactured by photosynthesizing plants. Explain the basis of this theory.

2 Powering machines consumes energy. Man made machines generally depend either, directly or indirectly, on burning hydrocarbon fuels to meet their energy needs; molecular machines, in living cells, on burning glucose. Both combustion and respiration are exothermic processes.

- a Write the formulae for following hydrocarbon fuels, methane, ethane, propane, butane and octane. Draw a structural formula for glucose using symbols to represent the carbon (C) hydrogen (H) and oxygen (O) atoms in its molecules.

- b Describe, in general terms, how the carbon (C) and hydrogen (H) atoms in hydrocarbons are rearranged in combustion. Explain from a consideration of the bonds broken and the bonds formed why the atomic rearrangements that take place in combustion are exothermic reactions. Draw an energy profile of the combustion of one of these fuels. Repeat for respiration.

- c Determine the ratio of hydrocarbon to oxygen molecules when the following burn completely; methane, ethane, propane, butane and octane. Repeat for the ratio of water and carbon dioxide molecules produced.

- d Petroleum or crude oil is a mixture of hydrocarbons. Describe, with the help of a diagram, how hydrocarbon fuels are obtained from crude oil. This separation process is based on differences in which physical property?.

Study Questions
Chapter 1: ENERGY FLOWS IN REACTIONS

Question 2 continued

e There are two main reasons why burning hydrocarbons causes pollution, one is due to the nature of the fuel itself, the other is a consequence of the engines that burn it. Explain the basis for these reasons.

f Gaseous hydrocarbons, like methane and propane, are cleaner fuels than liquid gasoline. If this is the case why are they not more widely used to power vehicles?.

3 Carbon atoms exist in carbon dioxide molecules in the atmosphere: in carbon chains in complex carbohydrates in the walls of plant cells, in complex proteins in animal muscles and in chains in hydrocarbons. Describe the processes that have, and continue to, cycle carbon between these different molecules.

4 A student was asked to measure the heat energy produced when 1 gram of ethanol was completely burnt. He decided to trap the heat produced in a measured quantity of water in a can calorimeter.

  a Design a table listing the measurements he would take in the experiment.

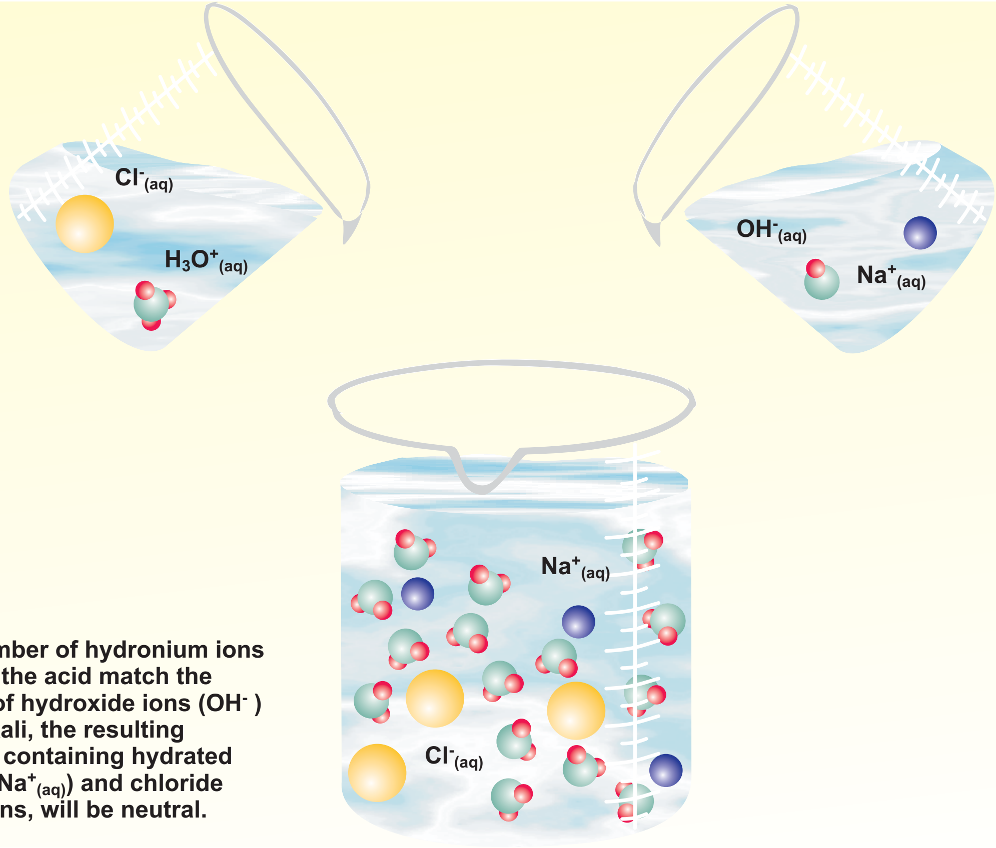
  b Explain how he would use these measurements to calculate a value for the heat of combustion of ethanol (joules per gram of ethanol burnt).

  c In comparing his result with the value found in a chemistry data book he found that his value for the heat of combustion was significantly lower. Suggest possible reasons for the discrepancy in results. How could he redesign the experiment to get a better correlation between his result and the accepted value for the heat of combustion of ethanol?

Notes

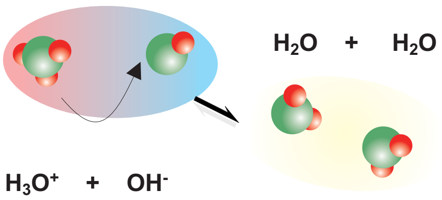
10

REACTING ACIDS AND BASES



If the number of hydronium ions (H_3O^+) in the acid match the number of hydroxide ions (OH^-) in the alkali, the resulting solution, containing hydrated sodium ($Na^+_{(aq)}$) and chloride ($Cl^-_{(aq)}$) ions, will be neutral.

PROTON TRANSFER



Protons (H^+) readily transfer from hydronium ions (H_3O^+) onto hydroxide ions (OH^-). The reverse reaction, protons being knocked out of water molecules to reform charged ions, has little tendency to take place.

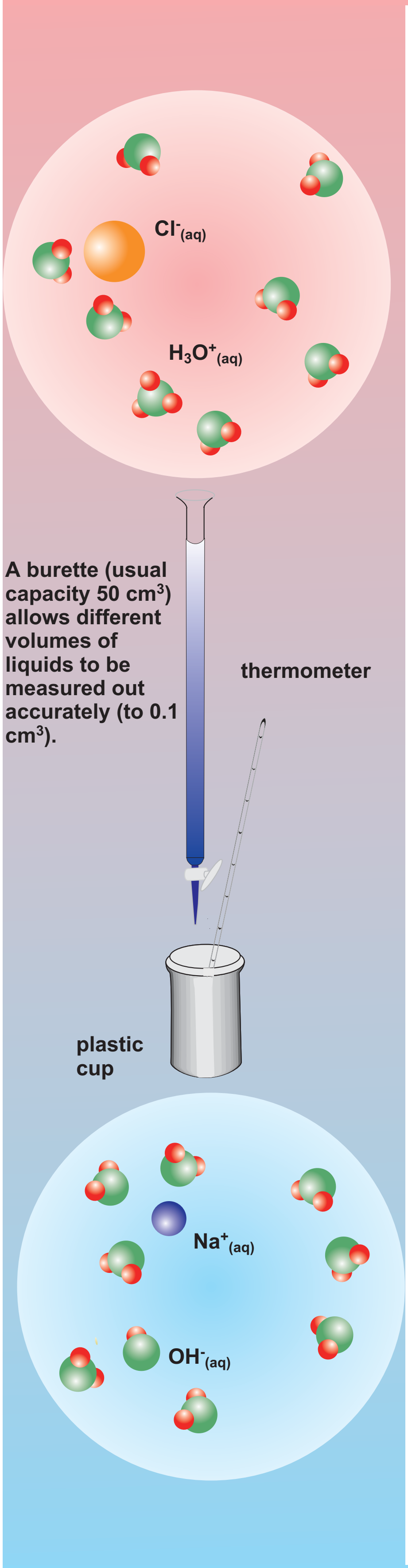
When a **strong acid** reacts with a **strong alkali**, the proton (**H^+**) traffic is predominately one way. Hydronium ions (**H_3O^+**) in **acids** are willing **proton donors**; the hydroxide ions (**OH^-**) in **alkalis** willing **proton acceptors**. The reverse reaction, water molecules exchanging protons to reform hydronium and hydroxide ions, has little tendency to take place.

If the numbers of protons donated by hydronium ions (H_3O^+) equals the number accepted by hydroxide ions (OH^-), the resulting solution will be neutral. It will contain neither hydronium ions nor hydroxide ions in excess. Donating protons (H^+) will have changed all the hydronium ions (H_3O^+) into water molecules (H_2O); accepting protons (H^+) will also have changed all the hydroxide ions (OH^-) into water molecules (H_2O). Reacting a strong acid with a strong alkali ensures that there are no basic ions from a weak acid, nor acidic ions from a weak base, to complicate the picture of what takes place during the neutralization reaction.

How can the endpoint of a neutralization reaction, when the solution is neither acidic nor alkaline, be determined? Ions are too small for the fate of individuals to be easily monitored. What can be followed, however, are the effects produced by large numbers of ions during a reaction.

Following such a change, and using it to determine the volumes of acid and alkali at a reaction's endpoint, is known as a titration.

HYDROCHLORIC ACID contains hydronium ions ($H_3O^+_{(aq)}$) and chloride ions ($Cl^-_{(aq)}$).



A burette (usual capacity 50 cm^3) allows different volumes of liquids to be measured out accurately (to 0.1 cm^3).

A THERMOMETRIC TITRATION

Like all reactions the transfer of protons, that takes place during neutralization, involves the making and breaking of bonds. **Energy** is **absorbed** pulling protons (**H^+**) out of hydronium ions (**H_3O^+**). When protons (**H^+**) bond to hydroxide ions (**OH^-**) **energy** is **released**.

Bonding protons to hydroxide ions releases more energy than is absorbed pulling protons out of hydronium ions. Since more energy is released than absorbed, the reaction overall is exothermic ($-\Delta H$).

The heat released in a proton transfer reaction causes the temperature of the reaction mixture to rise. Following the change in temperature during a titration can therefore be used to determine the reaction's endpoint.

The results shown are from a titration in which a burette was used to add 2 cm^3 portions of a hydrochloric acid solution to 20 cm^3 of a sodium hydroxide solution in a plastic cup (plastic is a better insulator than glass, so using a plastic cup reduces heat 'losses' to the surroundings). After each addition of acid, the temperature of the reaction mixture was measured. The results were plotted on a graph, with temperature on the vertical axis and the volume of acid on the horizontal axis.

At first, each addition of acid caused the temperature of the reaction mixture to rise. The proton transfer reaction between the hydronium ions (**$H_3O^+_{(aq)}$**) in the acid and hydroxide ions (**$OH^-_{(aq)}$**) in the alkali **released** the **heat** energy responsible for this temperature rise.

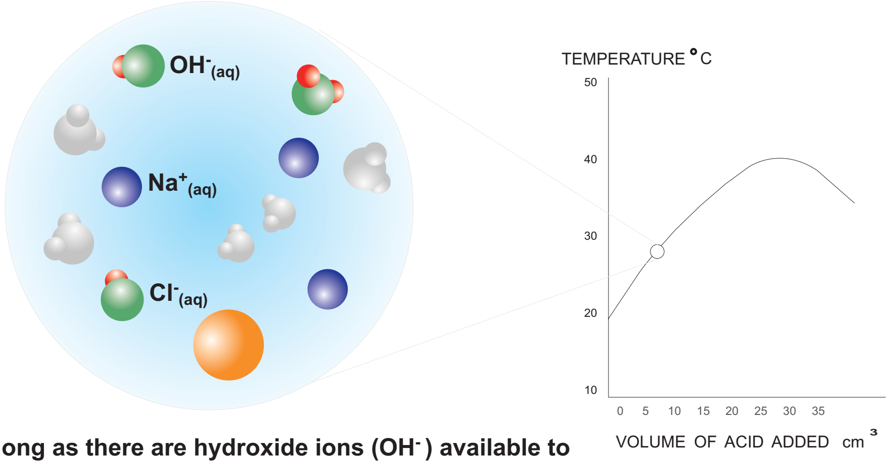
Eventually a point was reached when further additions of acid caused no further increase in temperature. With no more hydroxide ions left to react, the supply of heat energy was cut off. Turning off the burner under a pan of hot water has the same effect. With no heat input, the temperature stops rising and starts to slowly fall back to room temperature.

At the maximum temperature reached by the reaction mixture, all the hydroxide ions in the alkali had reacted. Since excess acid had not yet been added, hydronium ions were also absent from the reaction mixture. The **maximum temperature** therefore marked the **reaction's endpoint**.

The sodium ions (**$Na^+_{(aq)}$**) and chloride ions (**$Cl^-_{(aq)}$**) from the alkali and acid played no part in the reaction. For this reason they are often referred to as 'spectator' ions. Evaporating the water, from the solution at the endpoint, would produce crystals of sodium chloride ($Na^+Cl^-_{(s)}$).

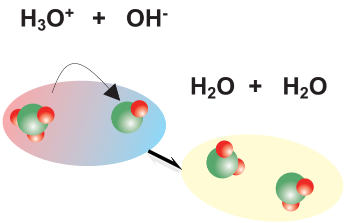
SODIUM HYDROXIDE contains sodium ions ($Na^+_{(aq)}$) and hydroxide ions ($OH^-_{(aq)}$).

In the beginning as the temperature rises ......



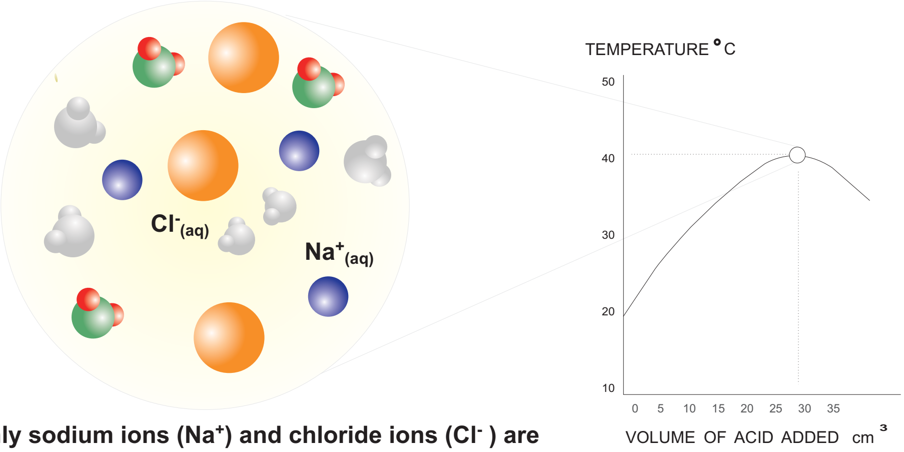
Protons (H^+) are pulled out of hydronium ions (H_3O^+) onto hydroxide ions (OH^-) in an exothermic reaction. The energy released in this reaction is responsible for the temperature rise observed when hydrochloric acid is added to sodium hydroxide.

As long as there are hydroxide ions (OH^-) available to accept the protons (H^+) from the added hydronium ions (H_3O^+) the temperature continues to rise.



H_3O^+ and OH^- ions react in a 1:1 ratio

... at the highest temperature

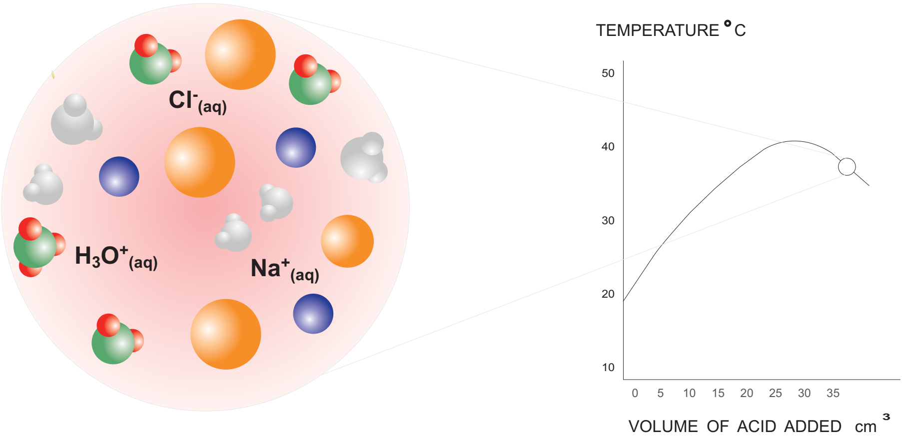


The maximum temperature is reached when all the hydroxide ions (OH^-) in the alkali have reacted. At this point the reaction mixture is neither acidic nor alkaline, the only ions it contains are sodium ions (Na^+) and chloride ions (Cl^-). This marks the reaction's endpoint.

Only sodium ions (Na^+) and chloride ions (Cl^-) are present at the reaction endpoint.

In this titration experiment approximately 28 cm^3 of acid contained enough hydronium ions (H_3O^+) to neutralize the hydroxide ions (OH^-) in the alkali. Since hydronium ions (H_3O^+) and hydroxide ions (OH^-) react in a 1:1 ratio, the number of hydronium ions reacted equals the number of hydroxide ions in the original 20 cm^3 of sodium hydroxide solution.

.... and as the temperature falls



Further additions of hydronium ions (H_3O^+), after the endpoint has been reached, cause no further increase in temperature. With all the hydroxide ions (OH^-) reacted no more proton transfers can take place and hence no more heat is released.

SUMMARY

- The proton traffic in neutralization reactions is predominately one way. Acidic hydronium (H_3O^+) ions donate protons (H^+) to basic hydroxide (OH^-) ions to produce neutral water (H_2O) molecules.

- The reverse of neutralization, water molecules exchanging protons to reform hydronium and hydroxide ions, has very little tendency to take place.

- Neutralization is an exothermic reaction. More energy is released when protons bond with hydroxide ions than is used up pulling them out of hydronium ions.

- At the endpoint of a neutralization reaction, with a strong acid and strong base, neither hydronium ions nor hydroxide ions are in excess.

- Since the heat released and therefore the temperature change in neutralization depends on the number of protons transferred, it can be used to determine the reaction's endpoint.

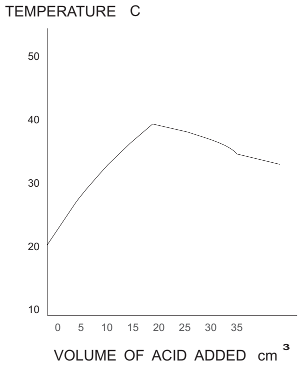
- When precipitation accompanies neutralization, all the ions are removed from the reaction mixture at the endpoint. Since conductivity depends on the presence of mobile ions in a solution, it will drop sharply at the endpoint when these two reactions accompany each other.

- pH values depend on the number of hydronium or hydroxide ions in a solution. Since the number of these ions changes during the course of a neutralization, pH values can also be used to determine the reaction's endpoint.

- The quickest and easiest way to determine a neutralization reaction's endpoint is to use an indicator. Stopping the titration when the indicator just changes from its alkaline to acidic color (or vice versa) determines the reaction's endpoint.

Study Questions
Chapter 10: REACTING ACIDS AND BASES

1



a The above graph shows the temperature changes when 2 cm^3 aliquots (portions) of nitric acid were added to 20 cm^3 of potassium hydroxide. Use the graph to determine the volume of nitric acid needed to react with the 20 cm^3 of potassium hydroxide.

b (i) What ions were present in the reaction mixture when the temperature was rising?

(ii) What ions were present in the reaction mixture when the temperature was at a maximum?

(iii) What ions were present in the reaction mixture when the temperature was falling?

c Write an equation for the reaction which produced the temperature rise.

d Sketch on the graph from part a, the graph lines you would expect if the concentrations of the acid and alkali were
a doubled b halved

e What information would you need to calculate the heat released during the reaction?

2 The quickest and easiest way to determine the volume of acid which reacts with a known volume of alkali is to carry out a titration using an indicator to determine the endpoint.

a Why is it important to continually shake the flask during the titration?

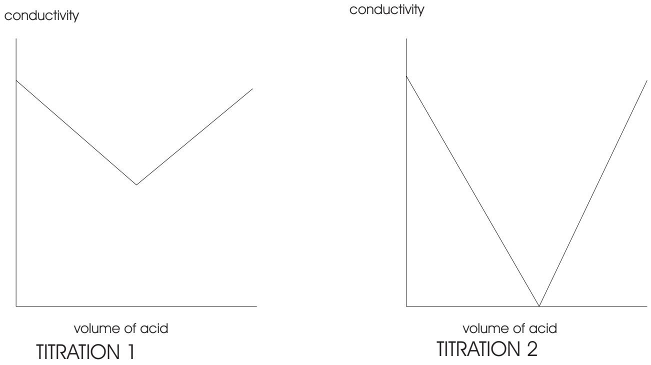
b Why is it useful to carry out a ‘rough’ titration?

c Why it it important to add smaller and smaller volumes of acid the nearer you get to the endpoint?

d Why is it best to carry out at least two ‘accurate’ titrations?

Study Questions continued
Chapter 10: REACTING ACIDS AND BASES

3 The following graphs were drawn using the data collected when electrical conductance measurements were made on two different titration experiments.



Each solution was titrated past the end point. A precipitate was observed in one of the titrations.

a Assign a titration graph to reactants.

b Write reaction equations for each titration.

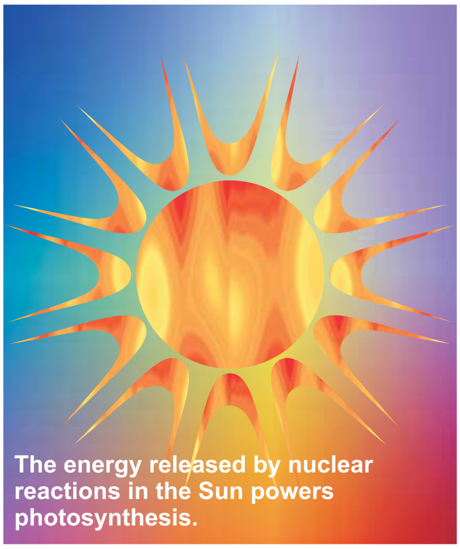
c Account for the shape of each titration plot

d Comment on the different conductances observed at the two endpoints

notes

24 POWERFUL REACTIONS

SOLAR ENERGY

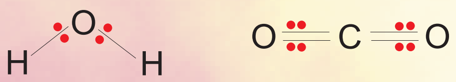

The energy released by nuclear reactions in the Sun powers photosynthesis.

The energy released from nuclear reactions in the Sun powers photosynthesis. This involves a chain of reactions in which work is done transferring electrons up an energy gradient. At the bottom of the gradient, electrons are pulled closely to the electro negative oxygen atoms in carbon dioxide (CO_2) and water (H_2O) molecules; at the end of the reaction series, they are in carbon-carbon (C-C) and carbon-hydrogen (C-H) bonds. When the electrons in these bonds are then pulled back onto electro negative oxygen, in respiration and combustion, energy is released. It is the solar energy used to push electrons up the gradient that is released to do work when the electrons run back down to their lower energy levels in carbon dioxide and water molecules.

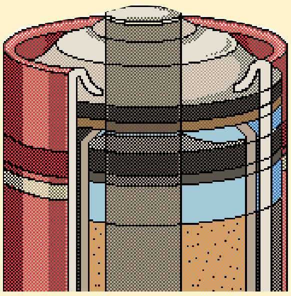
Manufacturing the reactants, which produce the current from a battery or cell, also involves doing work pushing electrons up an energy gradient. The spontaneous tendency for electrons to run back down the gradient can then be used to do work driving a current through a circuit. It is the work done, producing the reactants, that is used to power a torch, wrist watch or any other electrical appliance.

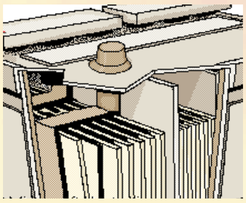
ENERGY STORAGE

Water (H_2O) and carbon dioxide (CO_2) molecules are the reactants for photosynthesis. In both of these molecules the bonding electrons are held closer to the more electro negative oxygen.



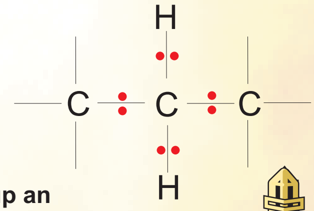
Solar energy is used in photosynthesis to push electrons up an energy gradient. From being close to electro negative oxygen in water (H_2O) and carbon dioxide (CO_2) molecules, to being shared equally in C−C and C−H bonds. When these electrons roll back down this energy gradient, in combustion and respiration, some of the solar energy used to push them up the gradient is released and can be made to do work.

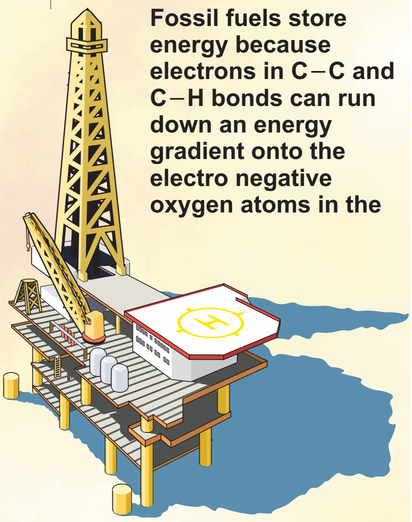




Manufacturing the reactants that produce electricity in a battery or cell consumes energy. It is this energy which is released when a battery or cell produces a current which is made to do work.

Electrons are shared equally in the carbon carbon (C−C) and carbon hydrogen (C−H) bonds produced in photosynthesis.





Fossil fuels store energy because electrons in C−C and C−H bonds can run down an energy gradient onto the electro negative oxygen atoms in the carbon dioxide and water molecules formed in combustion.

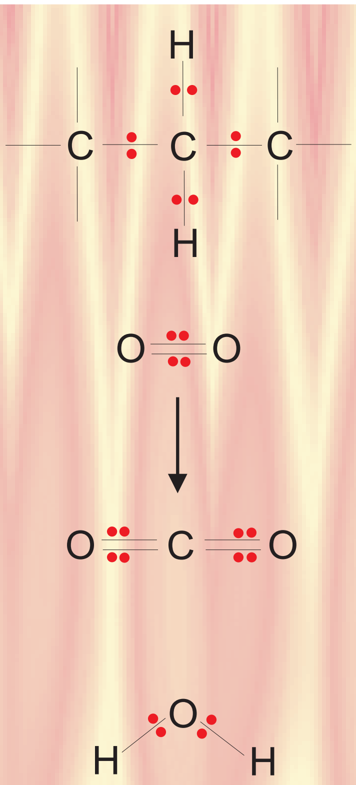
REARRANGING TO RELEASE ENERGY

Rearranging atoms or ions in chemical reactions involves changing electron arrangements. The energy changes involved are a consequence of the electrostatic force of attraction between charged particles; positively charged protons and negatively charged electrons. Energy is released when electrons are attracted to protons and bonds are made. Energy is absorbed when electrons are pulled away from protons and bonds are broken. Reactions are exothermic when more energy is released making bonds than is absorbed breaking bonds.

The energy changes in chemical reactions are due to changing arrangements of electrons; nuclei remain unchanged. However this is not the case in all reactions. In some circumstances, a long way energetically from a chemistry laboratory where temperatures reached by the Bunsen burner are the norm, nuclei can change. In stars like the Sun, or in the core of a **nuclear** reactor, **reactions** take place that **involve protons** and **neutrons** (collectively known as nucleons). In terms of energy changes these reactions are in another league; they release energy in quantities which dwarf the energies associated with changes in electron arrangements.

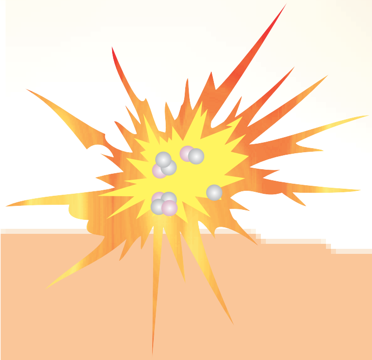
The immense energies associated with nuclear reactions are a consequence of the nuclear force. This force extends over a very limited distance (10^{-13} cm) but it is much stronger than the electrostatic force between charged particles. At distances greater than 10^{-13} cm positively charged protons repel each other; only when they are pushed together, with a force which is greater than the electrostatic force, can they be made to approach each other. The closer they get, the greater the electrostatic force of repulsion, and, therefore, the greater the force needed to push them together. Until, that is, they cross the frontier where the nuclear force takes over. When protons are closer than 10^{-13} cm, the electrostatic force becomes insignificant, the much stronger nuclear force takes over and bonds the protons together.

REARRANGING ELECTRONS



In combustion electrons are pulled out of C−C and C−H bonds onto the oxygen atoms in carbon dioxide (CO_2) and water molecules (H_2O). This rearrangement of electrons releases energy.

REARRANGING NUCLEONS



Deuteron (1 proton, 1 neutron) and tritium (1 proton, 2 neutrons) are isotopes of hydrogen. When the nuclei of these hydrogen isotopes collide with sufficient energy (this happens at temperatures between 50.000 to100,000 °C when the hydrogen atoms exist as a plasma, stripped of electrons) they can get close enough for the nuclear force to overcome electrostatic repulsion, between the positively charged protons, and make the nuclei fuse.

$${}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n}$$

$$\frac{\text{mass number } A}{\text{atomic number } Z}\ \text{symbol}$$

Every time a mol of deuteron and tritium nuclei fuse, 106 MeV of energy are released (equivalent to ≈ 10^6 joules). With so much energy released during the reaction, more deuteron and tritium molecules are likely to collide with the energy needed to initiate further reactions. If the gas is dense enough there will be enough energetic collisions to initiate a chain reaction. This is the chain nuclear reaction which takes place when a 'hydrogen' bomb explodes.

NUCLEAR BINDING ENERGY

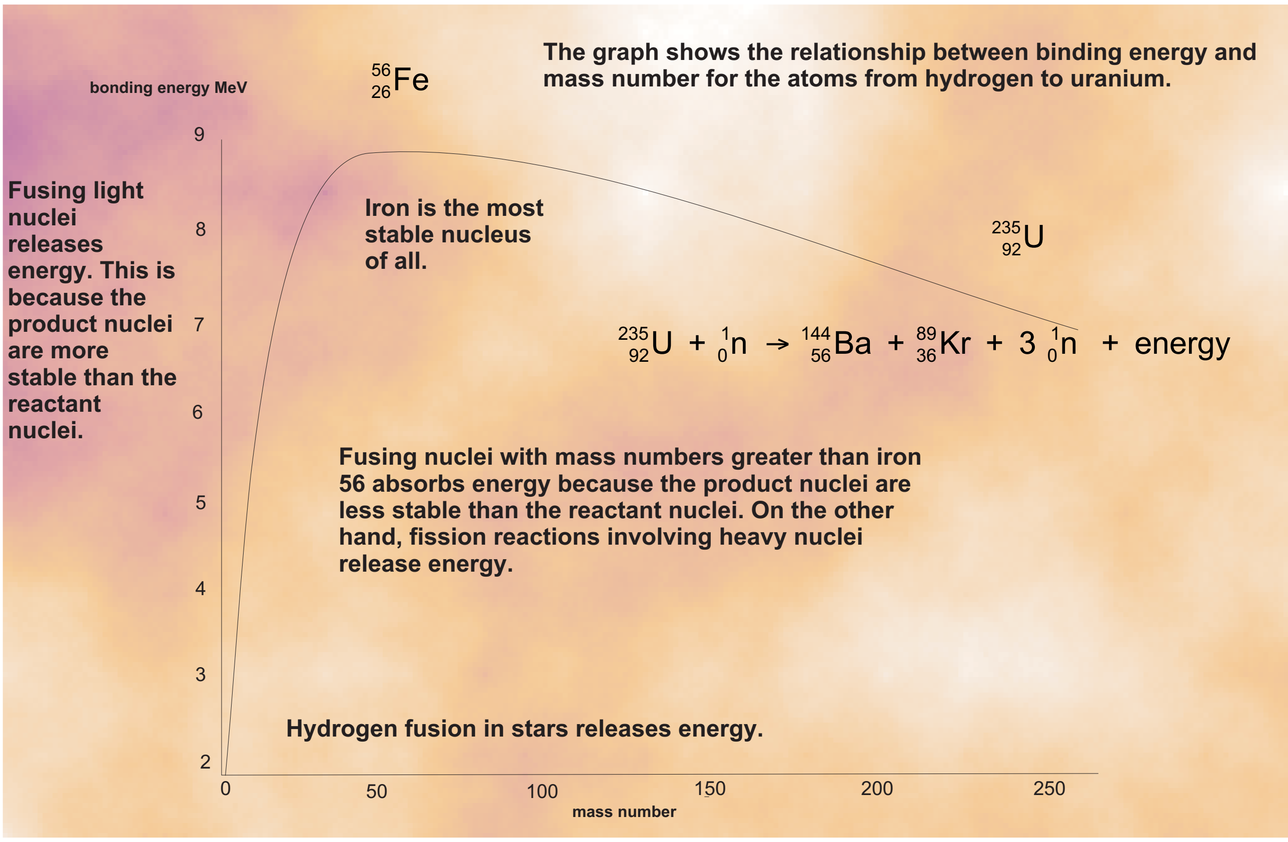
Strange as it may seem, protons and neutrons have a smaller mass together, in nuclei, than they do when they are separate from each other. A helium nucleus with two protons and two neutrons has a mass of 4.0015 amu, the individual protons and neutrons have a mass of 4.0320 amu. Thus combining two individual protons, with two individual neutrons, into a helium nucleus results in a loss of mass (0.035 amu). This mass defect is a consequence of relativity theory in which mass and energy are viewed as different forms of the same thing and are related by a constant in **Einstein's equation**: **$E = mc^2$**, in which **E** is **energy**, **m** is **mass** and **c** is the **velocity of light**. Since the speed of light is a huge number, small reductions in mass changes are related to huge changes in energy. For example, the mass defect when two moles of neutrons and two moles of protons react to form a mole of helium nuclei produces energy in the order of 10^9 kilojoules (in contrast, burning a mole of methane molecules releases $\approx 10^2$ kilojoules).

The nuclear force, which binds protons and neutrons together, depends on the total number of nucleons (protons and neutrons) in an atom's nucleus. The binding energy per nucleon, the energy required to remove a proton or neutron from a nucleus, depends on an atom's mass number. Graphing this relationship shows that **binding energy** reaches a **maximum** in the **iron nucleus**, **mass number 56**. Thus fusion reactions, in which light nuclei fuse to produce a nuclei with a mass number below this peak, release energy. Similarly fission reactions, in which heavy nuclei split to produce nuclei with mass numbers greater than this peak, will also produce energy. In both cases more energy will be released forming nuclei than will be used up splitting nuclei.

MASS TO ENERGY

$${}^{1}_{1}p + {}^{1}_{1}p + {}^{1}_{0}n + {}^{1}_{0}n \rightarrow {}^{4}_{2}He$$

Fusing two protons and two neutrons to make a helium atom involves a loss in mass of 0.0305 amu. It is this mass defect which produces the energy released in the reaction.
Since mass and energy are related in an equation, with the speed of light squared as a constant ($E = mc^2$), small changes in mass produce large amounts of energy.



The graph shows the relationship between binding energy and mass number for the atoms from hydrogen to uranium.

Fusing light nuclei releases energy. This is because the product nuclei are more stable than the reactant nuclei.

Iron is the most stable nucleus of all.

$${}^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{144}_{56}Ba + {}^{89}_{36}Kr + 3\,{}^{1}_{0}n + \text{energy}$$

Fusing nuclei with mass numbers greater than iron 56 absorbs energy because the product nuclei are less stable than the reactant nuclei. On the other hand, fission reactions involving heavy nuclei release energy.

Hydrogen fusion in stars releases energy.

SUMMARY

- The electrostatic force of attraction between negatively charged electrons and positively charged protons produces the energy flow into and out of rearranging atoms or ions; the nuclear force produces the energy flow when nuclei fuse or break apart.

- Fusion nuclear reactions in stars are the ultimate source of all energy. Relativity theory views mass and energy as different forms of the same thing related in Einstein's equation $E = mc^2$. Since the constant in the equation is a huge number (the speed of light squared) small changes in mass are reflected in huge changes in energy.

- Iron $_{56}$ is the most stable nucleus. Fusing light atoms to produce nuclei with masses lighter than Fe $_{56}$ releases energy; fusing heavier nuclei absorbs energy. Fission reactions, involving atoms which produce nuclei which are more stable, are exothermic.

- In fission chain reactions more neutrons are produced than are used up.

- Nuclei with proton neutron ratios outside the band of stability spontaneously decay into nuclei closer to or in the band of stability.

- Nuclear power plants use the energy released in fission nuclear reactions to make the steam to drive a generator. Fast breeder reactors produce more fissionable material than they consume by using neutrons to make their own fissionable uranium or plutonium.

- The tendency of reactants to lose and gain electrons in redox reactions is used in cells and batteries to generate electricity.

- Different metals have different tendencies to ionize in solutions of their ions. Connecting two metal electrodes with a metallic conductor and an electrolytic conductor makes a cell.

- The metal electrode with the greater tendency to ionize develops the greater electron pressure.

- The electrode which develops the greater electron pressure pushes electrons onto the electrode which develops the smaller electron pressure.

- From the point of view of the reactions taking place, the electrode which develops the greater electron pressure becomes the anode, the electrode with the smaller electron pressure becomes the cathode.

- Electrode potentials are measured against a standard hydrogen electrode. Since ion concentration (pressure if a gas is involved) and temperature affect electrode potentials these conditions must be specified. Standard ion concentration is taken to be 1 mol dm^3, standard pressure is 1 atmosphere and standard temperature, 298 K.

- Standard electrodes which push electrons onto a standard hydrogen electrode are given negative potentials. If a standard hydrogen electrode pushes electrons onto a standard electrode, the latter is given a positive electrode potential.

- To write an overall equation for the reaction taking place in a cell, the half reaction with the lowest electrode reduction potential is reversed and written as an oxidation. The electrons lost and gained are balanced and the electrode potentials are added to give the overall cell potential.

Study Questions
Chapter 24: THERMODYNAMICS

1 Photosynthesis is an endothermic reaction; both respiration and combustion are exothermic reactions. Relate the energy changes in these reactions to the position of bonding electrons in reactants and products.

2 Nuclear reactions involve energy changes on a different scale to those associated with chemical reactions. Use Einstein's equation $E = mc^2$ to explain why nuclear reactions are so much more energetic than chemical reactions.

3 a Explain the difference between nuclear fission and nuclear fusion reactions. Give an example, with an equation, for each reaction.
  b Explain why fusion reactions involving nuclei lighter than $_{56}$Fe are exothermic.
  c Explain why fission reactions involving nuclei heavier than $_{56}$Fe are exothermic.

4 Stable nuclei have proton neutron ratios that fall in a 'band of stability'. Nuclei with ratios outside this 'band of stability' spontaneously decay.

  a Describe with examples how nuclei with excess neutrons decay.
  b Describe with examples how nuclei with excess protons decay.
  c Describe with examples how 'heavy' nuclei with too many protons and neutrons decay.

5 a Describe with an equation, a fission chain reaction involving ^{235}uranium.
  b What is meant by the term 'a reactant's critical mass'?
  c Describe how the above reaction can be exploited to generate electricity.

6 How does a 'breeder' reactor differ from a reactor which uses ^{235}uranium to generate electricity? Identify some of the technical problems which make breeder reactors more difficult to manage than conventional nuclear power plants.

7 Compare the potential problems and risks associated with generating electricity using power plants that exploit nuclear reactions with those that burn fossil fuels.

8 Explain in general terms how batteries exploit redox reactions to generate electricity.

9 Compare the extent of ionization when the following metals are added to water: sodium, magnesium, zinc and copper.

10 Zinc atoms react with copper ions in a redox reaction. Explain how this reaction can be exploited to produce a flow of electrons through a circuit.

Study Questions
Chapter 24:THERMODYNAMICS

11 Electrode potentials are measured quantitatively by comparison with a standard hydrogen electrode. Why is it necessary to specify temperature (298K), pressure (1atmosphere if a gas is involved) and ion concentration (1 mol dm^{-3}) when comparing standard electrode potentials?

12 a Draw diagrams of the following cells:

(i) magnesium hydrogen cell
(ii) silver hydrogen
(iii) magnesium silver.

b Label the anode and cathode in each of the cells.
c Indicate the direction of electron flow through the external circuit in each of the cells.
d Label the ‘salt bridge’ and indicate the direction the ions flow through the salt bridge in each of the cells.
e Write an overall reaction for each cell.
f What potentials would be developed if standard half cells were connected?
g What effect would reducing the ion concentration in the metal half cell have on the standard potential in the magnesium hydrogen and silver hydrogen cells?
h What effect would increasing the ion concentration in the metal half cell have on the magnesium hydrogen and silver hydrogen cells?
i What would be the effects of changing ion concentrations on the potential of the magnesium silver cell?

13 Explain the difference between primary and secondary cells. Give an example of each.

notes