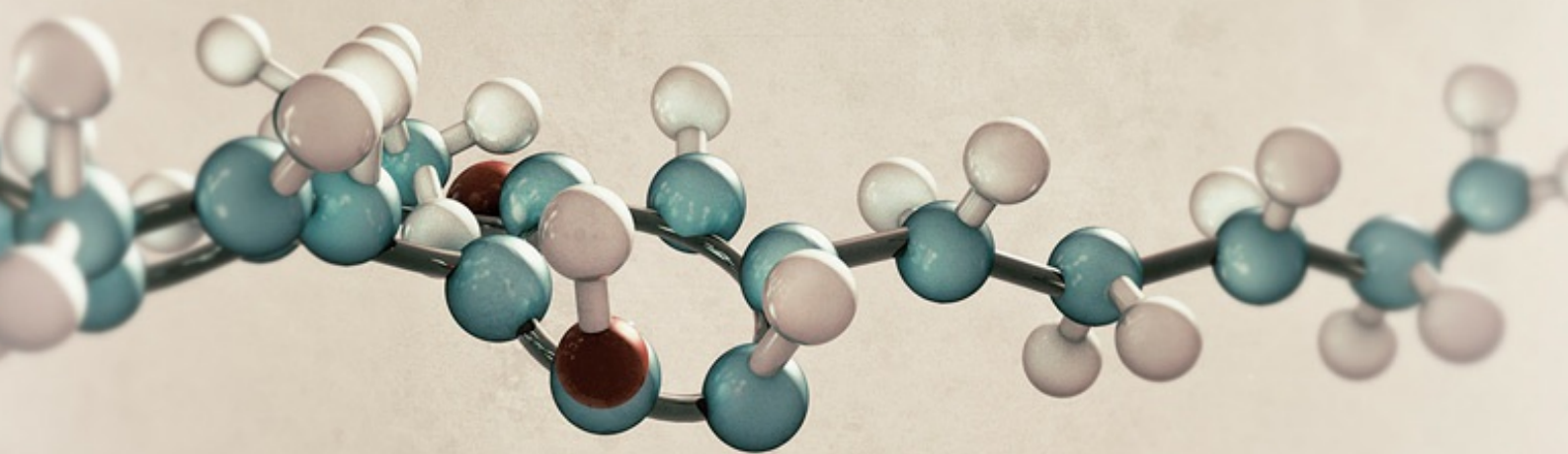# Introduction to Chemistry

A progressive approach

Peter G. Nelson

PETER G NELSON

INTRODUCTION TO CHEMISTRY
A PROGRESSIVE APPROACH

CONTENTS

ACKNOWLEDGEMENTS

I am very grateful to Dr. David Johnson of the Open University UK for reading through drafts of this book and commenting extensively on them.

Illustrations

I have taken most of the illustrations from the internet with my thanks. I have specified the sources in the captions. As far as I know, all are free to copy, but if any are not, I apologize. Two are adapted. The remainder have been kindly supplied by David Johnson.

1 INTRODUCTION

1.1 APPROACH

This book introduces chemistry to beginners. It does this "progressively", that is, the presentation moves logically from experimental observations to theory. No new ideas are introduced without first giving their experimental basis.

This approach means that we follow the historical development of the subject quite closely. The approach is not, however, historical. Chemists had misconceptions sometimes in the development of the subject which we will avoid.

1.2 WHAT CHEMISTRY IS ABOUT

Chemistry is about what things are made of. It is about air, water, salt, brick, cement, plaster, glass, steel, copper, natural gas, petrol, soap, sugar, alcohol, aspirin, and the like. I shall, for the moment, refer to these as "materials".

Some of these materials occur naturally, but most are made from other materials. These are heated, mixed together, or treated in other ways. Many of the changes that take place are remarkable. For example, one way of making copper is by heating together a green mineral (malachite) and a black solid (charcoal), neither of which look anything like copper. Chemistry is about changes like this.

Making a new material in a laboratory
[Kurt Barnett, Wikimedia Commons]

In the next chapter, we meet some important materials and how they are made.

2   SOME IMPORTANT MATERIALS AND HOW THEY ARE MADE

2.1   SOME TECHNIQUES USED IN MAKING MATERIALS

In this section, I describe some of the techniques chemists use to make materials, both in the laboratory and on an industrial scale. Chemistry is as much a craft as a science. Acquiring the ability to use these techniques is an important part of a chemist's training. This requires practice, but is very rewarding.

Heating materials together

This technique is widely used, both in the laboratory and in industry.
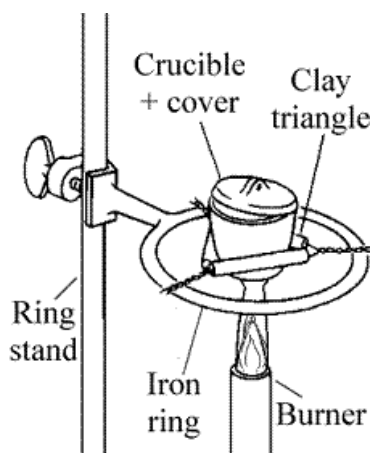
Apparatus for strongly heating a small quantity of solid material in the laboratory
[Kent Schools]

Filtration

Liquids sometimes contain solid particles suspended in them. These can be removed by passing the mixture through a fine sieve or "filter". This process is called "filtration". It is used both to remove solid impurities and to collect solid products.

Filters in the laboratory are usually made of paper or sintered glass. If of paper they are supported in a glass, plastic or porcelain funnel.
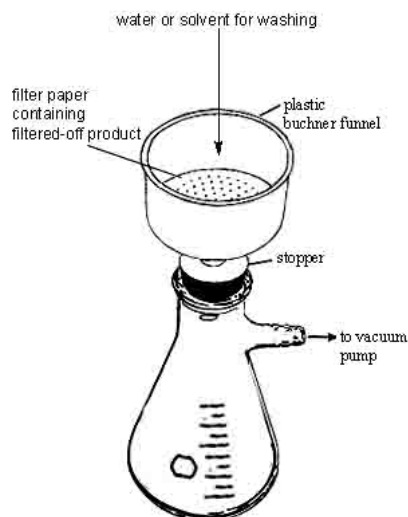
Apparatus for filtering off a solid product in the laboratory.
[UVCHEM]

Distillation

This process is based on the fact that, when a liquid is heated, it boils and gives off a vapour; when the vapour is cooled, it turns back to the liquid (this can be seen when a cold surface is placed above boiling water). Different liquids boil at different temperatures (they have different "boiling points").

Distillation involves heating a liquid in a vessel fitted with a vertical tube up which vapour from the liquid can pass. At the top is a downward bend leading to a tube that is cooled, in which the vapour turns back to liquid. As the temperature is raised, one or more fractions come off and are collected.
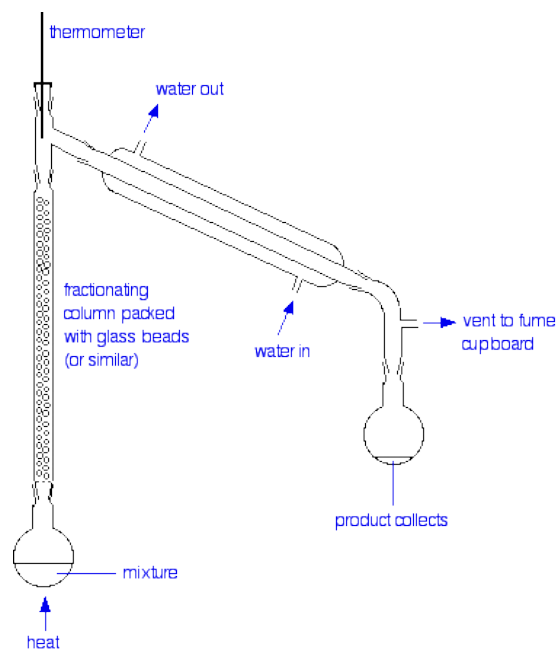
Apparatus for fractional distillation in the laboratory
[chemguide]

Bringing materials together in a solvent

This technique is also widely used. It depends on the fact that some materials are taken up by some liquids. For example, when salt is shaken with warm water, the salt disappears into the water, which develops a salty taste. The salt is said to "dissolve" in the water and form a "solution". Liquids that can do this are called "solvents".

Salt dissolving in warm water
[sweetpics]

Bringing materials together in a solvent facilitates any reaction between them. Heating may still be necessary, but less than without a solvent.
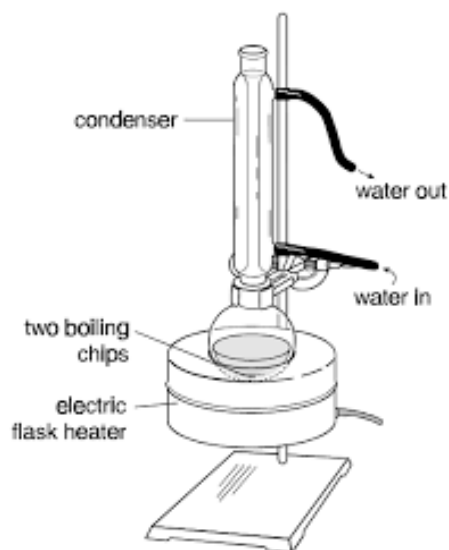
Apparatus for heating materials in a solvent. The solvent vaporizes, condenses in the column, and runs back into the liquid ("refluxes") [Chulalongkorn University]

Download free eBooks at bookboon.com

Solvent-extraction

Solvent-extraction involves agitating a material with a solvent. The resulting mixture is then filtered, and the filtrate distilled to remove the solvent and leave the desired product.

Crystallization

This procedure is used when the desired product is a soluble solid. It depends on the fact that such solids are generally more soluble in hot solvents than cold.

The material containing the desired product is agitated with hot solvent, the solution filtered, and the filtrate left to cool. The desired product crystallizes out of the solution and is filtered off, leaving soluble impurities in the liquid.

Crystals are characterized by having flat faces. Crystals of table salt, for example, are little cubes, as can be seen under a microscope. It is possible to grow large crystals of some materials by allowing a hot solution to cool very slowly.

Crystals of table salt under a microscope
[Pinterest]

Electrolysis

Some liquids conduct electricity (e.g. brine). When they do, changes take place where a direct current enters and leaves the liquid (see box). In the case of brine, for example, where the current enters, a yellow gas is formed, and where it leaves, a caustic liquid (we shall see what these are below). This process is called "electrolysis" (from Greek *lusis*, "loosening").

Box 2.1

Electricity

Electric charges are formed when some solids are rubbed with other solids, e.g. amber (Greek *ēlektron*) with fur. By convention, the charges formed on glass when rubbed with silk are reckoned as positive.

By convention also an electric current is reckoned as a flow of positive charges. In principle, it could equally well be a flow of negative charges in the opposite direction. Which it is we will see later.

Electrolysis is carried out in a container called a "cell". Wires from the electricity supply are attached to conducting rods or plates called "electrodes" which dip into the liquid. The positive electrode is called the "anode" and the negative, the "cathode". When current flows, new materials are produced at the electrodes.
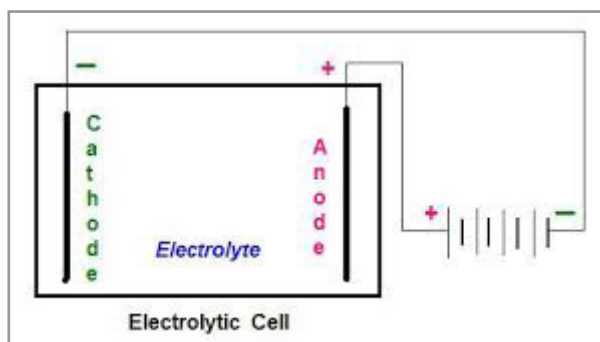
[hho4free]

Electrolytic cells can be used in reverse to generate electricity ("galvanism"). In this mode, instead of electricity being consumed and materials produced, materials are consumed and electricity produced. The polarity remains the same, but the current flows in the reverse direction. I give some examples at the end of this chapter (Sect. 2.4).

Labelling

Good practice requires all materials to be properly labelled. (For clarity, however, materials are pictured in the text without labels.)

2.2   SOME IMPORTANT MATERIALS

The following is a short selection of the many materials that are widely used today.

Air

Air is a mixture of gases. This can be shown by making a small ball of steel wool, moistening it, pushing it to the end of a test-tube, inverting the tube, and standing the open end in water. The steel wool slowly rusts, and water rises up the tube. The process stops when 1/5th of the air has been used up. The remaining gas extinguishes a lighted splint. Chemists call the gas that was used up "oxygen".
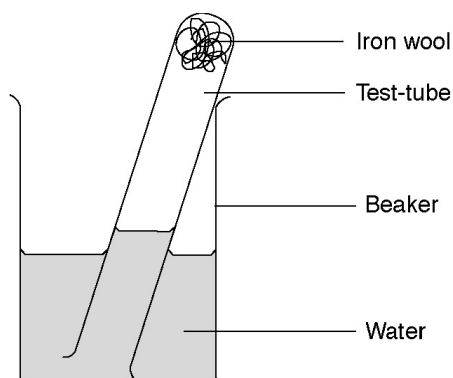
Apparatus for determining the composition of air
[Cambridge University, Education Faculty]

Download free eBooks at bookboon.com

Oxygen is obtained by cooling air to a very low temperature (around -200 ºC). This liquefies the air. The liquid air is then distilled and separated into fractions. One fraction (1/5th) is oxygen. The other main fraction (4/5ths) chemists call "nitrogen".

Materials burn more vigorously in oxygen than they do in air, sometimes explosively. The large amount of heat produced is exploited in welding.
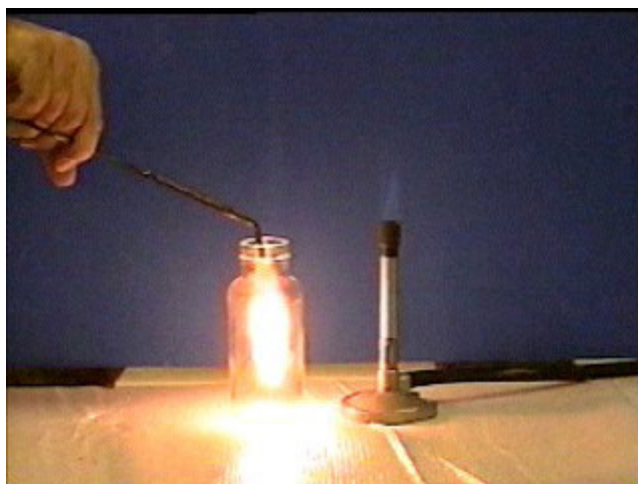
Wood splint burning in oxygen
[Kevin A. Boudreaux, Angelo State University]

Nitrogen does not ordinarily support combustion. It is used when an inactive atmosphere is required.

There are a number of minor components of air (totalling less than 1% by volume) that are even more inactive than nitrogen. I shall provisionally call these the "inactive gases". One is helium, used in balloons. This also occurs in natural gas.

Water

Water is a very good solvent. Most natural waters contain dissolved minerals from rocks. Consequently, most tap water contains such minerals, as can be seen from the white scale that is formed in kettles and boilers, and the white scum that is formed with soap. Water of this kind is called "hard"; water that does not form a scum is called "soft". Pure water can be obtained by distillation.

Salt

Salt occurs naturally as rock salt. It also occurs in brines and in sea water, from which it can be obtained by allowing the water in it to evaporate.

Rock salt
[The Spice Lab]

Chemists call minerals with similar properties to salt "salts" (Sect. 2.3). To distinguish ordinary salt from these, they call this "common salt", or give it its chemical name (Chap. 4).

Building materials

Brick. Bricks are made by heating blocks of clay in an oven. The soft grey clay changes into a hard yellow, orange, or red solid, the colour depending on the clay. Pottery is made in the same way.

Lime. Lime is a white powder, which is used to make mortar and to break down heavy clay soil. It is made in two stages. The first stage is to heat limestone in an oven with a chimney. Limestone is a soft, white mineral, best known in Britain from the white cliffs of Dover; large beds occur throughout the world. The second stage is to add water to the product from the first stage until it crumbles to a powder. The absorption of water takes place very quickly and generates a considerable amount of heat. For this reason, the first product is called "quicklime", and the second "slaked lime". A solution of slaked lime in water is called "lime water".

Lime works
[FreeFoto]

Cement. This is made by heating a mixture of clay and limestone in an oven with a chimney. Concrete is made by mixing sand, cement, and water, and leaving it to set. Mortar is a mixture of sand, lime, cement, and water.

Plaster. This is made by heating gypsum in an oven with a chimney. Gypsum is a colourless or lightly coloured, soft, crystalline mineral. It occurs in large beds in many countries, including Britain. When plaster is mixed with water, it sets hard. The speed at which it sets is determined by the temperature at which it is made. "Plaster of Paris" sets quickly, and is used to immobilize fractured limbs. Builder's plaster sets more slowly.

Glass. Ordinary glass is made by melting together sand, limestone, and "soda-ash" (see below).

Glassblowing
[Uncyclopedia]

Fuels

Wood, natural gas, and coal. These are burnt in air to produce energy. When they burn, they give off water vapour. This can be seen by holding a cold surface over the flames. They also give off a heavy gas that does not support combustion. I shall provisionally call this "flue gas", though you may already know the chemical name for this, "carbon dioxide". When cooled below -78 ºC it forms a white solid ("dry ice") used as a refrigerant. The gas gives a white deposit when bubbled into lime water. This can be shown by using a gas syringe to draw some of the gas away from a flame and then bubbling it into lime water in a test-tube. Chemists call solids deposited out of a solution "precipitates".
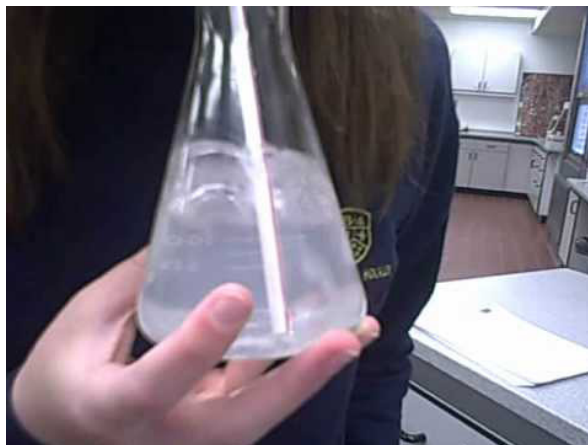
Blowing into limewater, showing that breath contains flue gas
[Wiscolt, YouTube]

Charcoal and coke. Wood charcoal is made by heating wood in an oven with a vent until it stops giving off fumes. Coke is made in a similar way from coal. Both are black solids, and are used as fuels, in metallurgy, and as absorbents. Chemists call the black crystals of which they are mainly composed "graphite". Pure graphite is made by heating coke with sand to a high temperature.

Charcoal
[Rockwood]

When charcoal and coke burn in air or oxygen, they give off flue gas but no water vapour.

Petrol and diesel oil. These are made by "refining" petroleum in a still. As the petroleum is heated, different fractions come off, according to how easily they are vaporized. Many other useful materials are obtained in this way, including fuel oil, lubricating oil, and paraffin wax.

When these materials burn, they give off flue gas and water vapour.

Oil refinery
[Guardian]

Hydrogen. This is a colourless, light, inflammable gas, which is increasingly being used as a fuel. It is made by electrolysis of water. Oxygen is formed where current enters the water (the positive electrode) and hydrogen where it leaves. Water itself is not a good conductor of electricity, but it can be made conducting by dissolving in it a suitable conducting material (e.g. sulfuric acid or caustic soda, see below). Note that energy is required to produce hydrogen, so that the gas is not so much a source of energy but a means of storing it.

When hydrogen burns, it just gives off water vapour. A hydrogen flame is almost invisible.
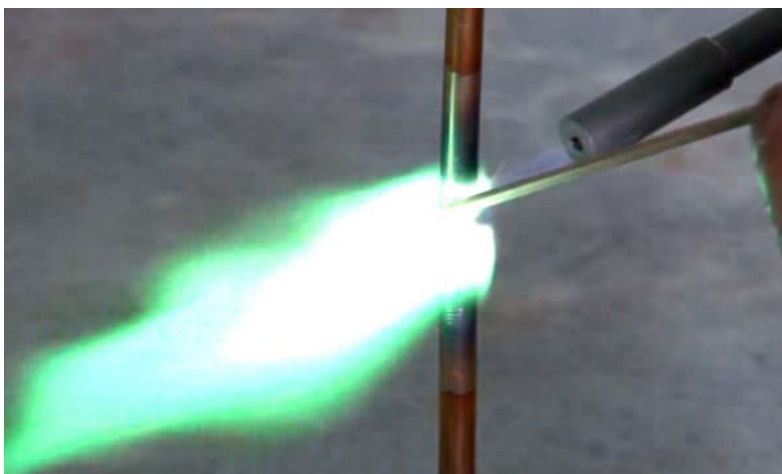
Oxy-hydrogen welding
[New Atlas]

Rocket burning hydrogen with oxygen
[How It Works]

Uranium. This is a heavy grey metal used to generate energy. This is because it is very radioactive (materials are said to be "radioactive" if they emit high-energy radiation). I discuss this further in Chapter 11. The metal is made from its ores in a similar way to aluminium (below).

Metals

There are many different metals. Some will be familiar. They are characterized by being lustrous and good conductors of electricity.

Steel. Steel is made in two stages. The first stage takes place in a tall, brick-lined furnace called a "blast furnace". Iron ore, coke (or coal or charcoal), and limestone are fed in at the top, and hot air is blown in at the bottom. The coke burns and generates heat, and molten "pig iron" is produced. This is run off at intervals, and converted into steel by passing oxygen through it. Several minerals will give pig iron when treated in this way. The one usually used is "haematite", which, as its name suggests, is dark red in colour (Greek *haima*, "blood"). This occurs in large quantities in Australia and Brazil, along with smaller deposits in a number of other countries. The limestone acts as a flux, and is also run off at intervals. It solidifies on cooling to form a slag.

Iron ore
[Canadian Business Journal]

Blast furnace
[Pinterest]

Copper. Very small quantities of copper occur naturally. Some is made from ores that give copper when heated with coke, coal, or charcoal. These include "malachite", which is bright green in colour. The metal is in great demand because of its use as an electrical conductor. Most is made from low-grade copper-iron ores by a method that separates copper from iron.

Malachite
[HealingCrystals]

Aluminium. This metal is widely used because of its lightness and resistance to corrosion. It is made from aluminium minerals by electrolysis (for details, see Chap. 4).

Other metals. Some of these occur naturally (e.g. gold, silver, platinum). Others are made by similar methods to those just described. Some can be melted together to form "alloys", e.g. bronze (copper and tin), brass (copper and zinc), and solder (tin and lead). Of interest is mercury, which is a liquid at room temperature, and was used (before chemists realized that its vapour is poisonous) in thermometers. It boils at 357 ºC.

Mercury
[Mining Chemicals Trading Support]

Fertilizers

Conventional farmers use three fertilizers, usually in combination. These are known as "nitrogen", "potassium", and "phosphate" fertilizers. I will explain what these are and how they are made in Chapter 4.

Organics

These are materials obtained, directly or indirectly, from plants or animals. They include materials obtained from natural gas and petroleum, which are from decayed plants or animals. Many medicines come into this category. Here I give some simple examples.

Soap. This is made by heating animal fat or plant oils in caustic soda. Caustic soda is made by electrolysing brine (see below).

Making soap
[Le Petit Éléphant]

Soap is referred to in the Bible (Jeremiah 2:22):

> "'Though you wash yourself with soda and multiply your use of soap, the stain of your iniquity is before me,' declares the Lord God."

Sugar. In Britain, this is made by soaking slices of sugar beet in water. The resulting liquid is run off, filtered through a porous pot, and then boiled. This removes the water as steam and leaves crystals of sugar. Sugar beet is a root crop, in the same family as beetroot. In warmer countries, sugar is made from another plant, sugar cane.

Alcohol. This is made from fruit, grain, and other vegetable materials. These are made into a brew with water, and fermented by adding a little yeast. Yeast is a naturally occurring fungus. The fermented product is then distilled, a process that can only be carried out on a large scale under licence. Alcohol boils at 78 ºC. It can also be made from petroleum.

Acetic acid. Acids are materials that have a sour taste (Latin *acere*, "be sour"). Acetic acid is the acid in vinegar. It is made by allowing alcoholic liquors go sour in the air or from petroleum. Other organic acids include "citric acid" in lemons and "lactic acid" in sour milk.

More inorganics

Inorganics are materials other than organics, i.e. are mineral in origin.

Sulfuric acid. This is an example of a mineral acid. It is used in large quantities to make a wide range of other materials. As its name suggests, it is made from sulfur (old spelling, "sulphur"). Also known as "brimstone", this is a yellow mineral which occurs in the volcanic regions of Sicily and in other parts of the world. This is burnt in air and then in oxygen in the presence of a "catalyst". A catalyst is a material that speeds up a process without itself being consumed in it. The product is a white solid. This is carefully combined with a little water to give "concentrated" sulfuric acid. This is a colourless, very corrosive, oily liquid. Combining this with more water gives "dilute" sulfuric acid. This again has to be done carefully, a great deal of heat being evolved. The correct way is by adding acid to water.

Sulfur
[Mini Me Geology]

Sulfuric acid is a strong acid; it dissolves many metals (e.g. iron) with evolution of hydrogen (see Chap. 4).

Soda-ash. This gets its name from being the ash left after burning seaweed (the ash left after burning land plants is not the same, and is called "potash"). It is made by heating the mineral "trona", large deposits of which occur in the USA and in some other countries. The material is also made from common salt by what is called the "Solvay process".

The characteristic property of soda ash is that it reacts with acids, taking away their sourness and giving off flue gas. This process is referred to in the Bible (Proverbs 25:20):

> "Like someone taking off a garment on a cold day, and like vinegar on soda [which destroys both], is someone singing a song to a troubled heart."

Caustic soda. A more caustic version of soda-ash is made by the electrolysis of brine. Where the current leaves the brine (the negative electrode) a caustic liquid is formed. Evaporation of water from this gives a white solid, "caustic soda". This reacts with acids, but does not give off flue gas.

That soda-ash and caustic soda are related is shown by the fact that they can be interconverted as we shall see in Chapter 4.

Chlorine. This is made at the same time as caustic soda. Where the current enters the brine (the positive electrode) a greenish-yellow gas is formed (Greek *chlōros*, "green"). This condenses to a yellow liquid at -34 ºC and freezes to a yellow solid at -101 ºC. The gas is used to kill bacteria in tap water and swimming pools. It is also bubbled into a solution of caustic soda to make bleach.

Chlorine
[IndiaMART]

2.3   SOME CLASSES OF MATERIAL

Some of the above materials share important properties, and this leads to some useful ways of classifying them.

Organic and inorganic

As we have seen, "organic" materials are those derived, directly or indirectly, from plants and animals. In Chapter 4, I shall give a more precise definition. "Inorganic" materials are those derived from minerals.

Metallic, semi-metallic, and non-metallic

As mentioned earlier, metals are characterized by being lustrous and very good conductors of electricity. Non-metallic materials are the opposite: they are dull and very poor conductors of electricity. Semi-metallic materials have intermediate properties. This class includes semiconductors.

When this classification is used, the conditions need to be specified. Materials can change in character with change of temperature or pressure.

Some non-metallic materials (e.g. common salt) conduct electricity in the molten state and in water with the formation of new materials at the electrodes. Materials that do this may be described as "electrolytic".

Acids, bases, and salts

As we have seen, "acids" have a sour taste. They also have the property of turning litmus (a dye extracted from lichens) red.

"Bases" are materials that "neutralize" acids, i.e. take away their distinctive properties. Bases that are soluble in water are called "alkalis" (Arabic *al-ḳalī*, "the ashes"). Examples are soda-ash, caustic soda, potash, and slaked lime. Solutions of alkalis feel soapy, and turn litmus blue.

What chemists call "salts" are the main products that are formed when an acid is neutralized by a base. Chemists these "salts" because they are similar to common salt, which itself can be made by the neutralization of an acid by a base (Chap. 4). Other products are water and, when the base is soda-ash or potash, flue gas.

Hydrated and anhydrous

Some materials that are soluble in water crystallize from water with water incorporated in them, which can be driven off by heating. The crystals are called "hydrates" (Greek *hudōr*, "water") and the water "water of crystallization". Driving this off leaves the "anhydrous" form. For example, soda-ash, which is anhydrous, crystallizes from water as a hydrate ("washing soda").

2.4   CELLS USED TO GENERATE ELECTRICITY

A simple example of a cell used to generate electricity is the reverse of that used to electrolyse water. Instead of being supplied with electricity, the cell is supplied with hydrogen and oxygen, and electricity taken from it. In this mode it is called a "hydrogen fuel cell".

Another example is a car battery. The cells in this comprise lead electrodes immersed in dilute sulfuric acid. When the battery is charged, a white solid is formed at the negative electrode and a black solid at the positive electrode. When in use, the chemical processes are reversed.
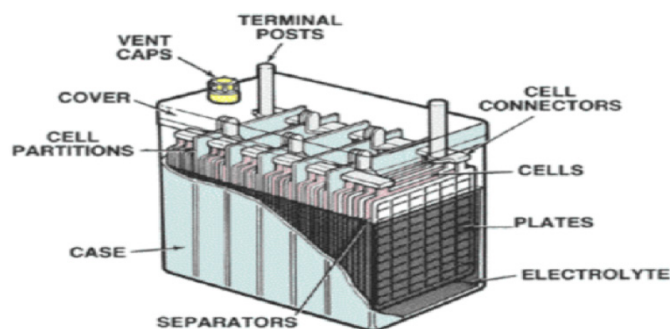
Car battery
[Engineering]

There are many other types of battery, employing different materials.

Exercise

Make a list of other materials you can see around you.

---

3   BASIC IDEAS AND TERMINOLOGY

3.1   INTRODUCTION

Before we proceed any further, it is helpful to introduce some basic chemical ideas and terminology. These include the important concept of *element*. I summarize the definitions of terms in Section 3.5.

3.2   MATTER

Chemists are interested in different kinds of *matter* (air, water, salt, brick, etc.: Chap. 1). Matter occupies space, has mass, and so can be weighed. This distinguishes it from light and similar radiation.

In Chapter 1, I called a particular kind of matter (e.g. air) a *material*. In popular usage this refers to kinds of matter that are intended for some use. I shall use the word in a broader sense and define it as "a particular kind of matter, especially one that is intended for some use". The alternative word, "stuff", chemists rarely use.

There are three main states of matter: *solid*, *liquid*, and *gas*. A solid has its own volume and shape. A liquid has its own volume but takes the shape of the vessel it is in. A gas fills the vessel it is in – it takes up the vessel's volume and shape. (A powder takes the shape of the vessel it is in, but the individual grains have their own shape.)

Solid materials differ from one another in size or shape (e.g. steel plate, steel rod, steel wire, and steel wool), and in what they are made of (e.g. steel wire and copper wire). Materials differing only in size or shape are said to be made of the same *basic* material (e.g. "steel", or more precisely, "mild steel", the ordinary kind of steel).

Steel wire

[Home Depot]

Copper wire

There are two main types of basic material: *homogeneous* and *heterogeneous*. The former appear uniform under an optical microscope, the latter not. The latter are *mixtures* of the former.

Basic materials can be made from other basic materials as we saw in Chapter 2. *Chemistry* may be defined as the study and practice of making basic materials and determining their character. This embraces "pure" chemistry ("the study of…") and "applied" chemistry ("the practice of…"). The ability of basic materials to change into other, often quite different, basic materials is what makes chemistry both interesting and useful.

3.3   SUBSTANCES AND SOLUTIONS

Chemists divide homogeneous basic materials into *substances* and *solutions*. This gives "substance" a technical sense. In popular usage, most homogeneous basic substances are called "substances". To preserve this usage, it is necessary to call substances that are not solutions "single" substances.

A solution is a combination of substances in varying proportions. The principal component is called the *solvent*; minor components are called *solutes*. The principal component is the one that gives the solution its state (solid, liquid, or gas), or, if more than one component does this, the one that is in the larger amount. Ranges of composition always start at 0% of solute; solutions can thus always be diluted by adding more solvent.

A solute (blue vitriol) and its solution in water
[nontoxicprint/Caldwell]

Chemists separate components of solutions by distillation, solvent-extraction, and other methods (Chap. 2). A homogeneous basic material is a substance if, by ordinary chemical methods, it cannot be separated into components that can be recombined in varying proportions as for a solution.

Substances can be distinguished from one another by their state at room temperature and atmospheric pressure (solid, liquid, or gas), colour, density, melting point (mp), boiling point (bp), solubility in different solvents, action on other substances, and other properties.

Substances can exist in different *forms* depending on the temperature and pressure. These are typically: crystalline solid, liquid, and gas (or, for substances that are solid or liquid at room temperature and atmospheric pressure, *vapour*). That the same substance can exist in different forms is suggested by the fact that many coloured substances keep their colour when they change from one form to another (e.g. chlorine keeps its yellow colour when it condenses to a liquid or freezes to a solid; metals retain their colour when they melt).

Gaseous chlorine
[IndiaMART]

Liquid chlorine
[IndiaMART]
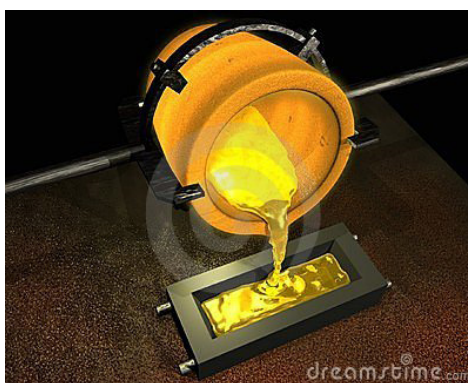
Liquid gold
[dreamstime]

Substances commonly keep their colour when they change form. There are, however, exceptions, especially among changes taking place at high temperatures or pressures (e.g. when mercury boils it gives a colourless vapour). In these cases, the question arises, has the substance changed form, or into another substance? Chemists do not have an agreed answer to this question, but by the colour criterion for differentiating substances, the second answer is surely correct (i.e. mercury vapour is a different substance from liquid mercury).

Boiling mercury showing colourless vapour
[Taofledermaus, YouTube]

Another form of a substance is as a solute in a solution. Coloured substances often keep their colour in solution (e.g. chlorine in water, gold in silver). This implies that they somehow retain their identity in solution. There are, however, many exceptions (e.g. chlorine in caustic soda reacts to give bleach). In such cases, dissolution involves a change of substance. This shows itself (usually) when the resulting solution is re-separated into components: the solute turns out to be a new substance or mixture of substances, formed by action of the solvent on the original solute.

Solution of chlorine in water
[Sciencemadness]

Substances can thus undergo three kinds of change: *physical*, *physicochemical*, and *chemical*. In a physical change (e.g. compression of air) there is no change in substance or form; in a physicochemical change (e.g. melting of a metal, dissolution of chlorine in water) there is a change in form but not of substance; in a chemical change (e.g. rusting of iron, vaporization of mercury, dissolution of chlorine in caustic soda) there is a change of substance. Properties relating to the three kinds of change are likewise called "physical", "physicochemical", and "chemical". The first two categories are usually conflated, but it helps to distinguish them.

Chemists call processes in which two or more substances interact and change into other substances *chemical reactions* (or simply "reactions"). These are represented as in the following example:

hydrogen + oxygen → water
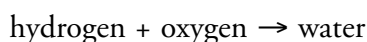
The arrow means "gives".

Substances can also undergo a fourth kind of change: *radiochemical*. In this there is a change of substance and absorption or emission of high-energy radiation.

3.4   ELEMENTS AND COMPOUNDS

Background

That substances can be made from other substances raises the question: are there a certain number of basic substances from which all other substances can be made? This is a question ancient Greek philosophers answered by speculating that all substances are combinations of air, water, earth, and fire. The first chemical list of elements was drawn up by the father of modern chemistry, the French chemist Antoine Lavoisier (1789). Today chemists recognize 120 elements, of which only about 20 are very important. The concept of an element underpins modern chemistry as we shall see.

Antoine Lavoisier
[Ven a mi mundo]
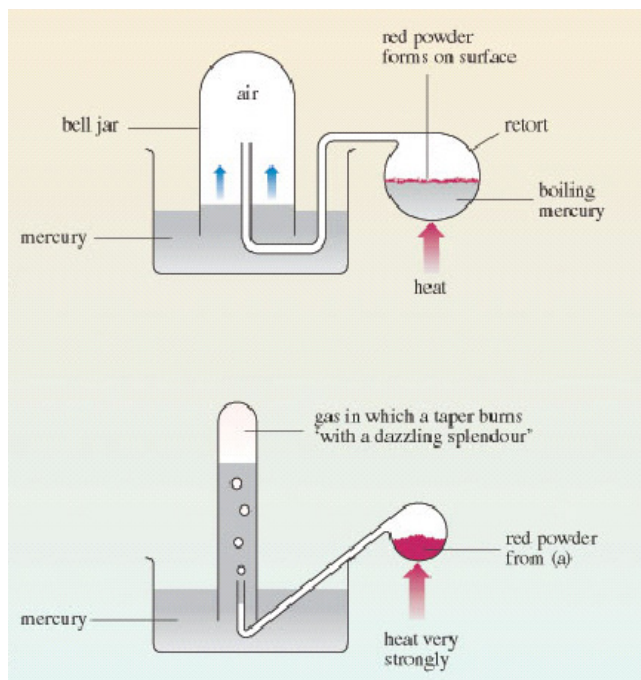
Lavoisier's experiment showing (a) how mercury combines with one component of air (top) and (b) produces this component when the product is heated strongly (bottom) [David Johnson]

Definition

Substances can be divided into *elementary substances* and *compounds* on the basis of the chemical changes they are involved in. Compounds decompose into other substances, elementary substances do not. Likewise, compounds can be made by combination of other substances, elementary substances cannot. Compounds ultimately decompose into, and can be made from, elementary substances.

For example, water can be electrolysed into hydrogen and oxygen (Chap. 2). Further, hydrogen burns in oxygen to form water. Water is therefore a compound. This is supported by burning hydrogen in oxygen and measuring the masses of hydrogen and oxygen used and the mass of water formed. In one such experiment, 3.821 grams of hydrogen were found to combine with 30.343 grams of oxygen (total mass 3.821 + 30.343 = 34.164 grams) to give 34.156 grams of water (Morley 1895). Thus, to within experimental error (about ± 0.010 gram), the mass of water formed is equal to the sum of the masses of hydrogen and oxygen burnt. Since hydrogen and oxygen cannot be split up in the way water can, they are elementary substances. Water is thus a compound of hydrogen and oxygen.

The idea that compounds are formed from elements provides a useful way of naming them, as we shall see in the next chapter. Water, for example, can be called "hydrogen oxide", with the suffix "ide" indicating that the reference is to a compound.

The idea is also a great aid to synthetic chemistry. Knowing what elements a compound contains points to the substances from which to try to make it.

Allotropy

Some elementary substances in the same solid, liquid, or gaseous state can be interconverted without change in mass, and combine with other substances to give the same compounds. For example, graphite and diamond, though apparently very different, can be interconverted at high temperatures and pressures, and both burn in oxygen to give flue gas. Elementary substances of this kind are reckoned to be variants of the same *element* (in the case of graphite and diamond, "carbon", from the Latin *carbo*, "charcoal"). The variants are called *allotropes*, and their occurrence *allotropy* (Greek *allos*, "another", *tropos*, "manner"). Different crystalline forms of an elementary substance are also called allotropes.

Diamond and graphite
[Wikimedia]

Most elements have only one stable allotrope under ordinary conditions (room temperature and atmospheric pressure). In these cases, the element *is* an elementary substance. I shall describe some important elements in the next chapter.

3.5   SUMMARY OF DEFINITIONS

Allotropy: existence of an element as more than one solid, liquid, or gaseous substance, or in more than one crystalline form.

Basic material: what a material is made of as opposed to its size or shape.

Chemical change: one in which there is a change of substance.

Chemical property: one relating to chemical change.

Chemical reaction: process in which two or more substances change into other substances.

Chemistry: the study and practice of making basic materials and determining their character.

Compound: a substance that can be made from or decomposed into elementary substances.

Element: basic type of matter existing as elementary substances that can be interconverted without change in mass.

Elementary substance: a substance that does not undergo chemical decomposition into, and cannot be made by chemical combination of, other substances.

Form of a substance: crystalline solid, liquid, gas, in solution, etc., depending on the substance.

Gas: matter not having its own volume or shape.

Liquid: matter having its own volume but not shape.

Material: a particular kind of matter, especially one that is intended for some use.

Matter: that which occupies space and has mass.

Mixture: a heterogeneous basic material.

Physical change: one in which there is no change in substance or form.

Physical property: one relating to physical change.

Physicochemical change: one in which there is a change in form but not substance.

Physicochemical property: one relating to physicochemical change.

Radiochemical change: one in which there is a change of substance and absorption or emission of high-energy radiation.

Solid: matter having its own volume and shape.

Solute: minor component of a solution.

Solution: a homogeneous basic material that can be separated into components that can be recombined in varying proportions starting with 0% of one.

Solvent: principal component of a solution.

Substance: a homogeneous basic material that cannot be separated (by the methods chemists usually employ) into components that can be recombined in varying proportions as for a solution.

State of matter: solid, liquid, gas, etc.

Vapour: gaseous form of a substance that is a solid or liquid at room temperature and atmospheric pressure.

4   SOME IMPORTANT ELEMENTS

4.1   SCOPE

In this chapter, I shall survey the chemistry of some of the more important elements. I shall do this very briefly, concentrating on some of the main features. I have chosen the order to make the presentation progressive.

4.2   CHEMISTRY OF SOME IMPORTANT ELEMENTS

Oxygen

Oxygen has two allotropes under ordinary conditions, ordinary oxygen and "ozone". Ozone is made by passing an electric discharge through ordinary oxygen. The resulting gas contains up to 10% of ozone, and can be condensed and fractionally distilled to obtain higher concentrations. It is a blue gas with a pungent smell. It is even more reactive than ordinary oxygen and decomposes into it when heated.
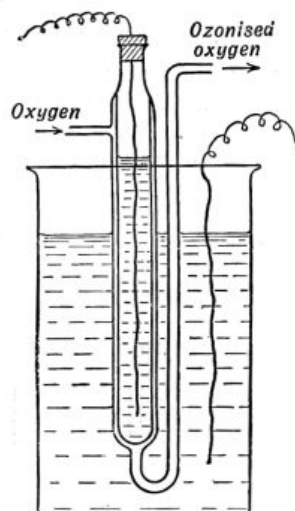
Apparatus for making ozone
[ProteinCrystallography]

Oxygen combines with most other elements. The resulting compounds are called "oxides". Addition of oxygen is called "oxidation" and removal "reduction", though chemists generalize these terms (see my e-book *Introduction to Inorganic Chemistry*).

The name "oxygen" means "acid-former" (Greek *oxus*, "sharp"; *gennaō*, "give birth to"). Lavoisier, the discoverer of oxygen (1774), gave it this name because he thought that all acids were made from oxygen. This is true of many of them, but not all, as we shall see. In fact, all acids contain hydrogen (see below), though not all hydrogen compounds are acids.
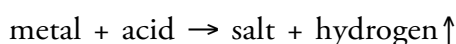
Hydrogen

Hydrogen has one allotrope under ordinary conditions. As we saw in the last chapter, it combines with oxygen to form water. This gives hydrogen its name (Greek *hudōr*, "water"). As we also saw in the last chapter, water may be called "hydrogen oxide", though chemists rarely use this name.

Hydrogen forms another compound with oxygen. This contains a higher proportion of oxygen than water and is called "hydrogen peroxide" ("per" meaning "complete" as in "perfect"). It can be made by electrolysing 50% sulfuric acid. While the dilute acid gives oxygen at the positive electrode, more concentrated acid gives a solution with bleaching properties. Distillation of this under reduced pressure gives hydrogen peroxide, a colourless, syrupy liquid. Reducing the pressure brings down the boiling point. At the normal boiling point (150 ºC), the liquid decomposes explosively into water and oxygen. This also happens when it is brought into contact with many solids. It is usually used in solution, where it is more stable.

Hydrogen peroxide solution
[Natural & Thrifty]

As mentioned above, hydrogen forms acids. Accordingly, many metals dissolve in acids with the formation of hydrogen:

$$\text{metal + acid} \rightarrow \text{salt + hydrogen}\uparrow$$

The upward arrow signifies that the hydrogen is given off as a gas. In the laboratory, hydrogen can be prepared in this way by using magnesium or zinc as the metal. If this is carried out in a test-tube, the hydrogen can be ignited and burns with a "pop".

Carbon

There are several allotropes of carbon under ordinary conditions, the most important being graphite and diamond, discussed in the last chapter (Sect. 3.4).

When heated, these combine with a plentiful supply of oxygen to give what I have called "flue gas". In a limited supply of oxygen, another gas is formed. Like flue gas, this is colourless and odourless, but it differs from the former in being inflammable and extremely poisonous. I shall provisionally call the two gases "carbonic oxide" and "carbonous oxide" (this uses an old nomenclature according to which the suffixes "-ic" and "-ous" indicate compounds containing more or less oxygen).
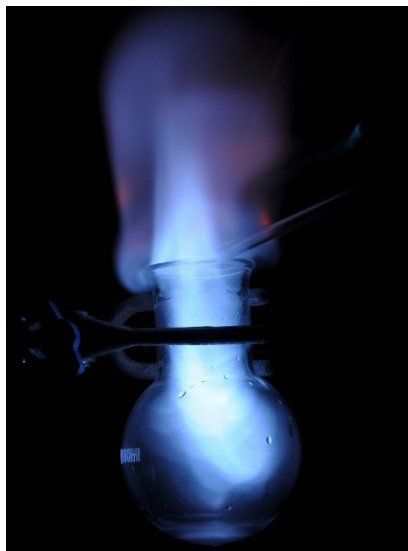
Carbonous oxide burning
[First Alert]

Carbonic oxide is also produced by adding an acid to soda-ash (Sect. 2.2). The gas dissolves in water to give a slightly acidic solution ("soda-water"). Chemists call the acid in this "carbonic acid", and its salts "carbonates". I discuss these further below.

Carbon forms a great many compounds with hydrogen. They are called "hydrocarbons". "Organic chemistry" is the study of these compounds and their derivatives. This is a more precise definition than that given in Section 2.3. The hydrocarbon containing the highest proportion of hydrogen is called "methane" and is the major component (4/5ths) of natural gas.

Many organic compounds contain oxygen as well as carbon and hydrogen. Examples are sugar, alcohol, and acetic acid. Some organic compounds contain other elements as we shall see.

Silicon

The mineral quartz, which occurs in many rocks and as sand, is one crystalline form of the oxide of an element called "silicon" (named after "silica", the general name for the oxide, from Latin *silex*, "flint"). Other minerals in rocks are derivatives of this oxide, formed by reaction with metal oxides while in the molten state. These derivatives are called "silicates" and are studied under "geochemistry".

Silicon itself is made by heating silicon oxide with coke. It is a lustrous grey-black crystalline solid and a semi-conductor (i.e. it conducts electricity, but not as well as a metal). Its electrical properties can be altered by introducing small amounts of other elements. This is exploited in the electronics industry. There is only one allotrope under ordinary conditions.

Silicon
[WebElements]

Sulfur

Sulfur has many allotropes under ordinary conditions. The most stable is the one that occurs naturally ("rhombic sulfur").

As summarized in Chapter 2, when this is heated in air, it gives a colourless gas with a choking smell ("sulphurous oxide"). Heating this gas in pure oxygen in the presence of a catalyst then gives a white solid ("sulfuric oxide"). Careful addition of this to water gives sulfuric acid. This reacts with metals, metal oxides, and alkalis to give "sulfates" (see below).

Sulfuric acid plant
[DSD Chemtech]

When heated in hydrogen in the presence of a catalyst, sulfur gives "hydrogen sulfide". This is a colourless gas with the smell of rotten eggs. It is very poisonous, but its smell usually prevents the inhalation of a lethal amount.

Chlorine

Chlorine has one allotrope under ordinary conditions. It combines with many other elements to form "chlorides".

With hydrogen it forms a colourless gas with an irritating smell. This is called "hydrogen chloride".

Hydrogen chloride fumes in moist air, and dissolves readily in water to form "hydrochloric acid" (an acid not made from oxygen). This reacts with metals, metal oxides and alkalis to give chlorides in a similar way to sulfuric acid.

Hot iron burning in chlorine
[Gooferking Science]

Calcium

Quicklime is the oxide of a metal called "calcium" (Latin *calx*, "lime"). Slaked lime is a combination of this and water. Chemists call it "calcium hydroxide". This combines with carbonic oxide to give a white solid identical to limestone. This is called "calcium carbonate". In this nomenclature, the processes by which quicklime and slaked lime are made (Sect. 2.2) are:

$$\text{calcium carbonate} \xrightarrow{\text{heat}} \text{calcium oxide} + \text{carbonic oxide}\uparrow$$
$$\text{calcium oxide} + \text{water} \rightarrow \text{calcium hydroxide}$$

Calcium, calcium oxide, calcium hydroxide, and calcium carbonate all react with acids to form calcium salts, e.g.

$$\text{calcium} + \text{sulfuric acid} \rightarrow \text{calcium sulfate} + \text{hydrogen}\uparrow$$
$$\text{calcium oxide} + \text{sulfuric acid} \rightarrow \text{calcium sulfate} + \text{water}$$
$$\text{calcium hydroxide} + \text{sulfuric acid} \rightarrow \text{calcium sulfate} + \text{water}$$
$$\text{calcium carbonate} + \text{sulfuric acid} \rightarrow \text{calcium sulfate} + \text{carbonic oxide}\uparrow + \text{water}$$
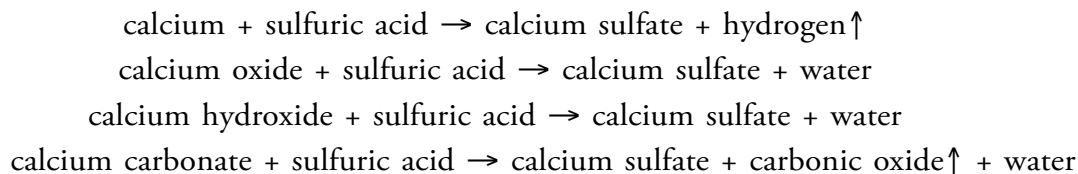
Calcium salts are colourless, but impart a brick-red colour to a flame. Many crystallize with water of crystallization, but this can be driven off by heating. Useful calcium salts are the hydrated sulfate (gypsum), from which plaster is made (Sect. 2.2), and the anhydrous chloride, which readily takes up water and is used as a drying agent.

Calcium flame
[BBC]

Calcium itself can be made by electrolysing molten anhydrous calcium chloride (mp 772 ºC). It is a fairly hard, grey metal. The calcium is formed at the negative electrode, as it is for all metals. Like most elements existing as a metal under ordinary conditions, there is only one allotrope. The metal reacts with water to give calcium hydroxide:

$$\text{calcium} + \text{water} \rightarrow \text{calcium hydroxide} + \text{hydrogen}\uparrow$$
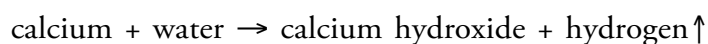
Calcium
[Metabunk]

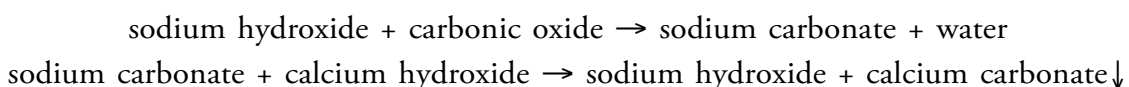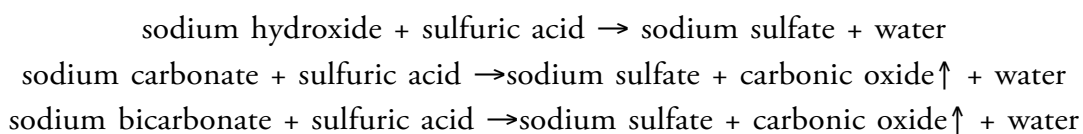### *Sodium*

Common salt is the chloride of a metal called "sodium". Caustic soda is the hydroxide of this metal and soda-ash the carbonate. These can be interconverted by the following reactions in solution in water:

sodium hydroxide + carbonic oxide → sodium carbonate + water
sodium carbonate + calcium hydroxide → sodium hydroxide + calcium carbonate↓

The downward arrow signifies that the calcium carbonate is insoluble and precipitates out.

There is also another carbonate. When carbonic oxide is bubbled into sodium hydroxide solution, sodium carbonate is formed first, and then a compound containing twice as much carbonic oxide. This is called "sodium bicarbonate", and is used under the name "baking soda".

Sodium hydroxide, sodium carbonate, and sodium bicarbonate react with acids to give sodium salts, e.g.

sodium hydroxide + sulfuric acid → sodium sulfate + water
sodium carbonate + sulfuric acid →sodium sulfate + carbonic oxide↑ + water
sodium bicarbonate + sulfuric acid →sodium sulfate + carbonic oxide↑ + water

With hydrochloric acid, the product is common salt.

Sodium itself can be made by electrolysis of molten mixture of sodium chloride and calcium chloride at about 580 ºC, the metal being formed at the negative electrode. It is a soft, white metal which reacts readily with air and has to be kept under paraffin. It also reacts readily with water to give sodium hydroxide:

$$\text{sodium} + \text{water} \rightarrow \text{sodium hydroxide} + \text{hydrogen}\uparrow$$
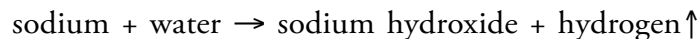
If a small piece of the metal is dropped on to water, it melts as it reacts, and moves rapidly over the surface, sometimes catching fire and burning with a yellow flame. The same yellow colour is produced when a sodium salt is placed in a flame.

Sodium
[Weebly]

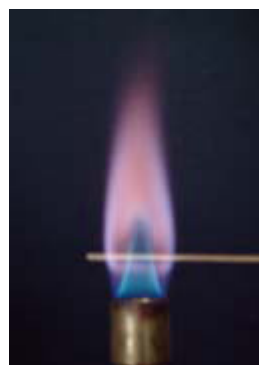Download free eBooks at bookboon.com

Click on the ad to read more

Potassium

This is like sodium except that the colour of its flame is lilac. Potash is potassium carbonate and caustic potash is the hydroxide.

Sodium flame
[NSTA]

Potassium flame
[NSTA]

Potassium is essential for plant growth. Potassium fertilizers are potassium chloride crystals obtained from deposits of this salt. Commercially these are called "potash", but this is a misnomer.

Nitrogen

The name "nitrogen" means "nitre-former". Nitre is a colourless mineral, also called "saltpetre". When this is heated with concentrated sulfuric acid, a colourless liquid distils off. This is concentrated "nitric acid". Addition of water gives dilute nitric acid. This reacts with metals, metal oxides, and alkalis in a similar way to dilute sulfuric acid to form "nitrates". Saltpetre is potassium nitrate. A similar mineral, found in large quantities in Chile ("Chile saltpetre"), is the sodium salt.

Copper dissolving in concentrated nitric acid
[Exploratorium]

Nitric acid can be obtained from nitrogen by passing an electric spark through a mixture of nitrogen and oxygen in a bulb containing a little water. Nitrogen, usually inactive, reacts with oxygen under these conditions to give nitrogen oxides, which react with water to give nitric acid.

Nitrogen forms an important compound with hydrogen called "ammonia". This is made by heating a mixture of nitrogen and hydrogen in the presence of a catalyst (the "Haber process"). Ammonia is a colourless gas with a pungent smell. It dissolves in water to give an alkaline solution. This neutralizes acids with the formation of "ammonium" salts. Ammonium chloride and nitrate are used as a fertilizers, along with other nitrogen compounds.

Many organic compounds contain nitrogen, e.g. proteins.

Phosphorus

This element occurs in combination with calcium and oxygen in "phosphate rock". Heating this with coke and sand gives a white, waxy solid, which has to be kept under water because it slowly combines with oxygen in the air. This is one allotrope of "phosphorus", so-named because the reaction with air makes it glow in the dark (Greek *phōs*, "light"). This allotrope is called "white" phosphorus. There are several others made by the action of heat and pressure. A red form is more stable in the air, and safer to handle. It is the form chemists usually use.

White and red phosphorus
[BBC]

Phosphorus is an essential nutrient for plants. Phosphate fertilizers are made by heating phosphate rock with concentrated sulfuric acid and distilling the resulting mixture. This gives a colourless, syrupy liquid ("syrupy phosphoric acid"), which is diluted with water. This reacts with metals, metal oxides and alkalis to give "phosphates" in a similar way to sulfuric acid. Water-soluble phosphates (e.g. ammonium phosphate) are used as fertilizers. Phosphate rock is calcium phosphate, and is insoluble.

Phosphorus burns in chlorine to form two useful chlorides, which I shall provisionally call "phosphorous chloride" (colourless liquid) and "phosphoric chloride" (yellowish-white crystals).

Some organic compounds contain phosphorus, notably DNA.

Iron

Iron forms two series of salts, "ferrous" and "ferric" (from Latin *ferrum*, "iron"). The metal dissolves in dilute acids to give green solutions of ferrous salts. Addition of sodium hydroxide to these precipitates green ferrous hydroxide. This is rapidly oxidized by air to red-brown ferric hydroxide. The latter dissolves in acids to give violet or yellow solutions of ferric salts, the colour depending on the acid.

Hydrated ferrous sulfate ("green vitriol")
[IndiaMART]

Ferrous oxide is a black solid; ferric oxide is red-brown, the colour of rust. There is an intermediate oxide which is black and magnetic ("lodestone"). Geologists call it "magnetite".

When heated with carbon, iron forms "iron carbide". This is a grey, metallic solid. It is present in pig-iron and steel.

Copper

Copper forms two series of salts, "cuprous" and "cupric" (from Latin *cuprum*, "copper"). The metal dissolves in acids in the presence of oxygen to give blue or green solutions of cupric salts, the colour depending on the acid. Boiling these with copper turnings gives colourless solutions of cuprous salts. Removed from the copper, these readily decompose into cupric salts and copper.

Hydrated cupric sulfate ("blue vitriol")
[nontoxicprint]

Cuprous oxide is red, cupric oxide black.

Aluminium

Aluminium forms one oxide. This is white, and is unusual in that it dissolves in both acids and caustic alkalis with the evolution of hydrogen. With acids, it gives aluminium salts; with alkalis, "aluminates". Both are colourless. The oxide is said to be "amphoteric" (from Greek *amphō*, "both").

This property is exploited in the extraction of aluminium from its ores ("bauxite" and "cryolite"). Dissolving bauxite in caustic soda and filtering removes insoluble iron oxide. Neutralization of the filtrate with acid precipitates the hydroxide, which can be heated to give the oxide. This is dissolved in molten cryolite and electrolysed to give aluminium. The metal is formed, once again, at the negative electrode.

The hydrated double salt, potassium aluminium sulfate ("alum"), has long been used as a mordant.


Alum
[Natural Deodorant Store]

4.3   MORE ON ACIDS, BASES, AND SALTS

Acids vary in their ability to dissolve metals. The strongest dissolve many metals easily. They include sulfuric, hydrochloric, and nitric acids. Organic acids are generally weaker.

In their reactions with acids, metal oxides, hydroxides, and carbonates function as a base (Sect. 2.3):

$$acid + base \rightarrow salt + secondary \ products$$
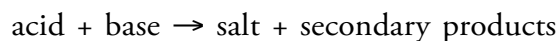
The secondary products are water and, for carbonates, carbonic oxide. Since a metal carbonate is itself a salt, the salt of a weak acid, the reaction in this case can also be thought of as a displacement:

$$salt \ of \ weak \ acid + strong \ acid \rightarrow salt \ of \ strong \ acid + weak \ acid$$
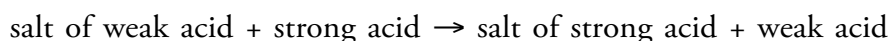
This is followed by decomposition of carbonic acid into carbonic oxide and water.

4.4   TYPES OF ELEMENT

Chemists divide elements into metals, semi-metals, and non-metals (compare Sect. 2.3). This classification is not exact. While *allotropes* can be assigned to one of these classes without any difficulty, some elements cannot be because they form allotropes belonging to more than one class. For example, graphite under ordinary conditions is a semi-metal (its black crystals possess some lustre and conduct electricity, though not as well as metals), while diamond is a non-metal. In these cases, chemists make a judgment as to the predominant characteristic, a judgment that is in some cases disputed.

For the elements we have been looking at, most chemists would accept the following assignments.

Metals: calcium, sodium, potassium, iron, copper, aluminium

Semi-metals: silicon

Non-metals: oxygen, hydrogen, carbon, nitrogen, sulfur, chlorine, phosphorus

Note that, in electrolysis, metals are invariably deposited at the negative electrode, while non-metals are usually formed at the positive. An exception is hydrogen in the electrolysis of water, which is formed at the negative electrode.

5 BASIC LAWS AND PHENOMENA OF CHEMISTRY

5.1 QUANTITATIVE CHEMISTRY

In the history of chemistry, an understanding of chemical reactions came from measuring the quantities of the substances taking part in them, i.e. their masses (m) or, in the case of gases, volumes (V). The volume of a gas varies with temperature (θ) and pressure (p), so these have to be specified. The usual conditions are "standard temperature and pressure" (STP), θ = 0 ºC and p = 1 atmosphere (atm) (= 1.013 bar). Volumes can be converted to STP by invoking the gas laws (see box).

Box 5.1

The gas laws

These may be stated as follows:

Boyle's law (after Boyle 1662): "at low pressures and a constant temperature, the volume of a gas is inversely proportional to its pressure."

Charles law (after Charles 1787 and Gay-Lussac 1802): "at a constant low pressure, the volume of a gas is proportional to (θ + 273.15 ºC)."

Here (θ + 273.15 ºC) is the "absolute" temperature (T). This has its own unit ("kelvin", K) such that the absolute temperature corresponding to θ = x ºC is T = (x + 273.15) K.

From these laws, the volume of a gas under one set of conditions (labelled 1) is related to its volume under another set (2) by the equation:

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

This equation holds for samples of all gases at low pressures, and as an approximation at higher pressures. A so-called "ideal" gas is one for which this equation holds at all pressures.

The mass of a gas can be calculated from its volume if one knows its density (ρ) under the same conditions. This is defined by

$$\rho = \frac{m}{V}$$

from which $m = \rho V$.

In what follows, masses are measured in grams (g), volumes in litres (l), and densities in grams per litre (g/l).

5.2   LAWS AND PHENOMENA OF CHEMISTRY

Studies of the quantities of substances taking part in chemical reactions lead to the following laws and phenomena of chemistry. The phenomena used to be called laws, but the discovery of exceptions means that this status is no longer justified.

Law of conservation of mass

This law was put forward by Lavoisier in 1774. It may be stated as follows:

> **"In any chemical change there is no detectable change in mass."**

"Chemical" here excludes "radiochemical", i.e. changes in which high-energy radiation is involved.

We saw an example of conservation of mass in the last chapter (Sect. 3.4). The American chemist Morley burnt hydrogen in oxygen and found the mass of water formed to be equal, within experimental error, to the sum of the masses of hydrogen and oxygen burnt. A more accurate test can be made on reactions in solution, e.g. between calcium chloride and sodium carbonate to give a white precipitate of calcium carbonate. The two reagents can be placed in a flask, with one of them in a tube standing in the other, and the flask stoppered. The flask is weighed, then agitated to mix the solutions, and weighed again. Very accurate experiments of this kind, with the reagents sealed in the limbs of an inverted U-tube, confirm that the law holds to within one part in 10,000,000 (Landolt 1893−1908).

Apparatus for demonstrating conservation of mass
[Elearnin, YouTube]

Phenomenon of constant composition

> **"Many compounds have the same composition by mass, irrespective of how they are made or what they are made from."**

This was put forward as a law by the French chemist Proust in 1799. I have not called it a law because some compounds have variable composition. Such compounds are called *non-stoicheiometric*, as opposed to *stoicheiometric* compounds which have a fixed composition (from Greek *stoicheion*, "element", *metron*, "measure").

Non-stoicheiometric compounds are very much in the minority. The great many organic compounds are nearly all stoicheiometric, as are many inorganic compounds. An example is water. As we saw in Section 3.4, in one experiment, Morley found that 3.821 g of hydrogen combined with 30.343 g of oxygen to form water, that is, one gram combined with 7.941 g. Repeating the experiment gave the same result within experimental error, the average of twelve determinations being one gram to 7.940 g. He also obtained the same value by measuring the combining volumes of the two gases (see below) and their densities.
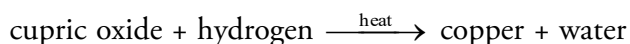
Water can be made in a different way, by passing hydrogen over heated cupric oxide:

$$\text{cupric oxide + hydrogen} \xrightarrow{\text{heat}} \text{copper + water}$$

From the loss of mass of the cupric oxide and the mass of water formed, we can calculate the masses of hydrogen and oxygen in the water. This is an experiment that can be done with simple apparatus. Early experiments of this kind gave, on average, one gram of hydrogen to 7.98 g of oxygen (Dumas 1842). This value is the same as Morley's within experimental error (± 0.05 g).
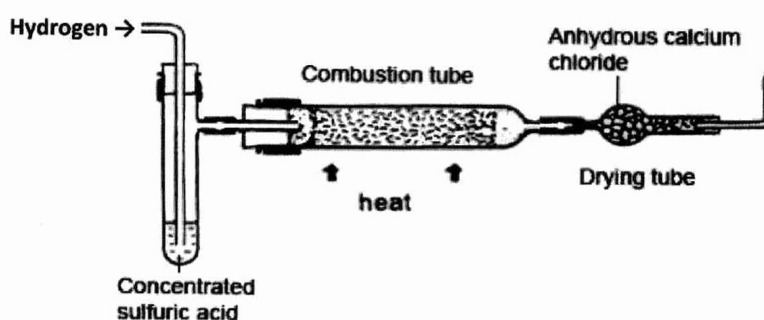
Apparatus for heating cupric oxide in hydrogen and weighing the water formed by absorbing it in anhydrous calcium chloride
[RSC (adapted)]

The composition of water can also be determined by electrolysing it, measuring the volumes of hydrogen and oxygen produced, and converting these to masses. This experiment can also be carried out with simple apparatus. We return to this below.

An example of a non-stoicheiometric compound is ferrous oxide. This contains variable amounts of oxygen, between 0.30 g and 0.34 g per gram of iron.

Phenomenon of multiple proportions

> **"When an element A forms more than one compound with another element B, the masses of B that combine with a fixed mass of A are often in the ratio of small whole numbers."**

This was put forward as a law by the English chemist John Dalton in 1803. It does not hold where there is non-stoicheiometry.

An example is provided by water and hydrogen peroxide. We saw above that water contains about 8 grams of oxygen to one gram of hydrogen. The corresponding quantity for hydrogen peroxide can be obtained by decomposing a weighed sample by heat or contact with a rough solid and measuring the volume of oxygen formed. By this method, Thénard (1818) found that hydrogen peroxide contains nearly 16 g of oxygen to one gram of hydrogen. The ratio of this to the value for water is nearly 2:1.

An accurate test of the phenomenon was made by Stas (1849). He oxidized carbon and carbonous oxide to carbonic oxide, and, by weighing them, found that one gram of carbon is combined with 2.6659 g of oxygen in carbonic oxide and 1.3330 g in carbonous oxide, a ratio of 1.9999:1.
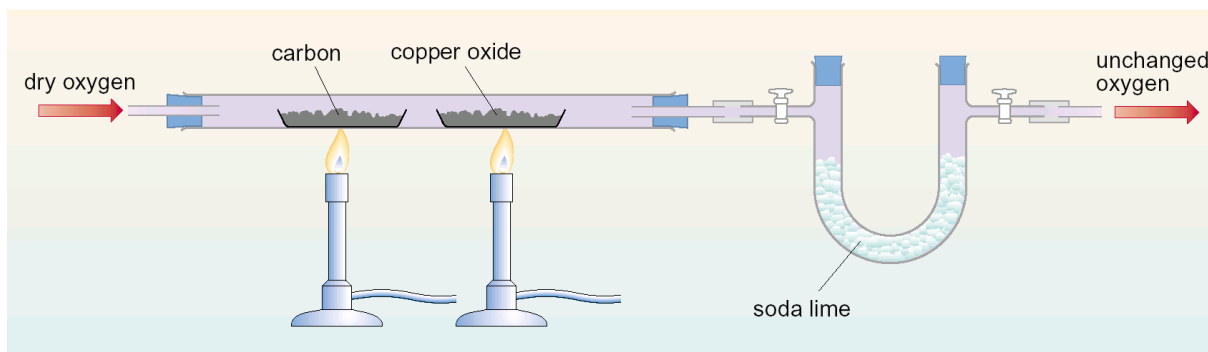
Apparatus for determining the composition of carbonic oxide. The cupric oxide completes the oxidation, and the mixture of sodium hydroxide and lime absorbs the carbonic oxide
[David Johnson]

Phenomenon of proportionate gaseous volumes

> "At low pressures, the volumes of gases taking part in a chemical change, measured at the same temperature and pressure, are usually in the ratio of small whole numbers."

This was put forward as a law by the French chemist Gay-Lussac in 1808. It only fails to hold when there is chemical change within one or other of the gases. Deviations occur at high pressures.

A good example of this phenomenon is the reaction of hydrogen and oxygen to form water. Very careful measurements by Burt and Edgar (1915) gave the ratio of hydrogen to oxygen to be 2.0029:1. This is at STP. Reducing the pressure reduces the deviation from 2:1.

That the ratio is about 2:1 can be demonstrated in the laboratory by using an electrolysis cell with inverted test-tubes containing electrolyte around the electrodes (see figure). As the electrolysis proceeds, the gases that are formed at the electrodes collect at the top of their respective tubes, and their volumes can be compared.
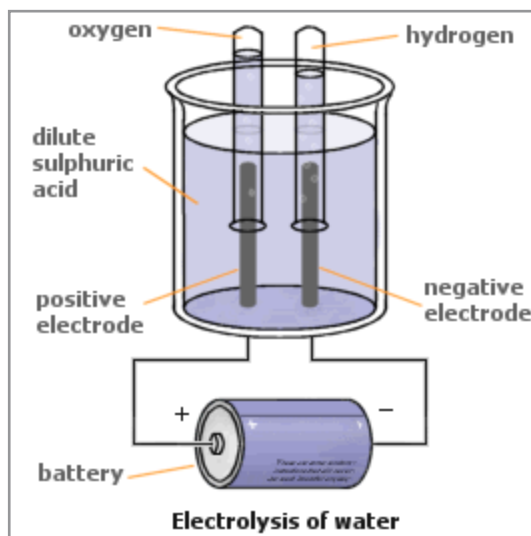
Electrolysis of water showing the different volumes of gas produced
[Science Unleashed]

5.3 PERCENTAGE COMPOSITION OF SUBSTANCES

Up to now, I have expressed the composition of substances in the form: "water contains 7.940 g of oxygen for every gram of hydrogen". This is cumbersome when there are more than two elements. In general, it is better to give the percentage composition. For water, this is 11.2% hydrogen ($\frac{1}{1+7.940}$ ×100), 88.8% oxygen.

Problem

Use Stas's results on the oxidation of carbon and carbonous oxide (above) to calculate the percentage composition by mass of (a) carbonous oxide, (b) carbonic oxide.

---

6   THE CONSTITUTION OF MATTER

6.1   ATOMS AND MOLECULES

Whether matter can be subdivided continuously or is made up of atoms is a question that has intrigued thinkers back to the ancient Greeks if not before. There are several indications that matter may be made up of atoms.

- Many solids are crystalline, with plane faces. This can be explained by the regular packing of small particles. A familiar example of such packing is in snooker, where the red balls are made to form of a triangle.


[Wikimedia Commons]

- Gases are much more compressible than liquids or solids, and when they condense there is a large reduction of volume. These observations can be explained if gases comprise separate particles, which come together in the liquid or solid state.
- When a small quantity of olive oil is poured on to water, the oil only spreads over a limited area of the surface.

Patches of oil on water
[Tony Mangiacapre, St. Mary's Physics]

These considerations, along with the phenomena of Chapter 5, lead to the following theory of matter. This is based on the atomic theory of Dalton (1808) and the hypothesis of Avogadro (1811).
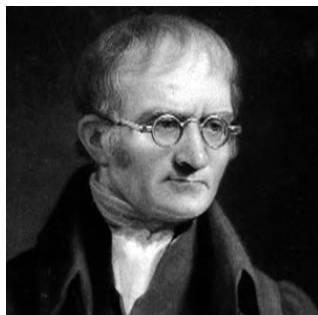

John Dalton

Amedeo Avogadro

1. Matter is made up of atoms.
2. The atoms of an element are chemically all the same, and differ from those of other elements. Atoms are represented by symbols (e.g. O for an oxygen atom and H for a hydrogen atom). We shall see later that atoms of the same element can differ in mass; in terrestrial samples, however, their average mass is almost the same from sample to sample (Chap. 11).
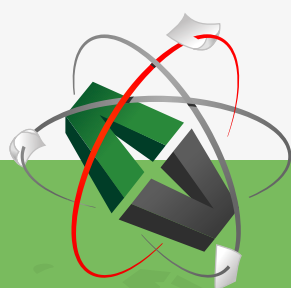
3. Chemical reactions involve changes in the way in which atoms are combined, but not in their numbers.

4. Atoms of different elements often combine in definite ratios.

5. These ratios are often of small whole numbers.

6. At low pressures, equal volumes of gases at the same temperature and pressure contain equal numbers of particles (Avogadro's hypothesis). These particles may be atoms or clusters of atoms joined together ("molecules", meaning "little masses", from Latin *moles*, "mass").

This theory explains the phenomena described in the previous chapter. For example, the phenomenon of constant composition follows from postulate 4, and of proportionate gaseous volumes from postulate 6.

Postulate 6 enables the masses of molecules to be compared. For example, the density of hydrogen at STP is 0.08987 g/l and of oxygen 1.4290 g/l (Morley). So:
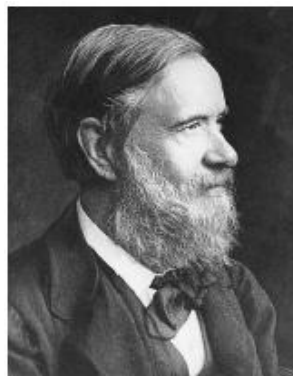
$$\frac{\text{mass of oxygen molecule}}{\text{mass of hydrogen molecule}} \approx \frac{1.4290}{0.08987} = 15.901$$

The result is approximate because of the pressure; the limiting value at low pressures is 15.873. If the mass of a hydrogen molecule (μ) is provisionally made the unit of mass for atoms and molecules, the mass of an oxygen molecule is therefore about 16 μ.

6.2   ATOMIC COMPOSITIONS

To establish the atomic composition of a molecule, a further principle needs to be added to 1–6 (after Cannizzaro 1858). This is:

7. The mass of an atom of an element is the smallest mass of the element found in any molecule containing it.

Stanislao Cannizzaro

This principle is applied in Table 6.1. The masses of some molecules containing hydrogen, obtained from gas densities, are given in column two. The percentage by mass of hydrogen in each of these molecules, as determined by quantitative analysis of the substance concerned, is given in column three. The mass of hydrogen in each molecule (column two × column three ÷ 100) is given in column four. The smallest value of this is 0.5 μ. If the table is extended to other substances containing hydrogen, the smallest value continues to be 0.5 μ. This is almost certainly, therefore, the mass of a hydrogen atom, since no subdivision of this mass occurs in any molecule. A hydrogen molecule (mass = 1.0 μ) thus contains two atoms. Chemists represent this as H_2.

Substance	Mass of molecule	Percentage by mass of hydrogen	Mass of hydrogen in molecule
Hydrogen	1.0 μ	100.0	1.0 μ
Steam	8.9 μ	11.2	1.0 μ
Methane	8.0 μ	25.0	2.0 μ
Alcohol vapour	22.7 μ	13.3	3.0 μ
Ammonia	8.4 μ	17.7	1.5 μ
Hydrogen chloride	18.1 μ	2.76	0.5 μ
Hydrogen sulfide	16.9 μ	6.0	1.0 μ

Table 6.1 Calculating the atomic mass of hydrogen

This procedure can be extended to other elements. Thus, for example, the smallest mass of oxygen occurring in a molecule of any of its compounds is about 8 μ, making this the atomic mass of oxygen. A molecule of oxygen (mass ≈ 2 × 8 μ) is therefore O_2 and of steam (mass ≈ 2 × 0.5 μ of hydrogen + 8 μ of oxygen), H_2O.

A more convenient unit than μ is the mass of a hydrogen atom, or a standard mass of similar magnitude to this. The standard mass now used is called the "unified atomic mass unit" (u). This makes the atomic mass of hydrogen 1.0079 u. Other atomic masses in this unit are given in Table 6.2 (in order of mass). The definition of u will be given later (Section 11.3).

Element	Symbol of atom*	Mass of atom†
Hydrogen	H	1.01 u
Carbon	C	12.0 u
Nitrogen	N	14.0 u
Oxygen	O	16.0 u
Sodium	Na	23.0 u
Aluminium	Al	27.0 u
Silicon	Si	28.1 u
Phosphorus	P	31.0 u
Sulfur	S	32.1 u
Chlorine	Cl	35.5 u
Potassium	K	39.1 u
Calcium	Ca	40.1 u
Iron	Fe	55.8 u
Copper	Cu	63.5 u

Table 6.2 Atoms of important elements
*Symbols are based on the English name except for sodium (Latin *natrium*, "soda"),
potassium (*kalium*, "potash"), iron (*ferrum*), and copper (*cuprum*).
†Average values in terrestrial samples.

From the masses of atoms, the atomic composition of any substance can be determined. For example, pure hydrogen peroxide contains about 6.0 per cent by mass of hydrogen and 94.0 per cent of oxygen. Thus the number of atoms of hydrogen in 100 g is about 6.0 g/1.01u = 5.9 g/u and of oxygen 94.0 g/16.0 u = 5.9 g/u, a ratio of 1:1. A molecule of hydrogen peroxide therefore has a formula that is some multiple (n) of HO, and a mass that is this multiple of the mass of HO (1.0 u + 16.0 u = 17.0 u), i.e. $17.0n$ u. The density of the vapour is about 1.5 g/l at STP. From the formula

$$\frac{\text{mass of molecule}}{\text{mass of hydrogen molecule}} = \frac{\text{mass of molecule}}{2(\text{mass of hydrogen atom})} \approx \frac{\text{density of gas or vapour}}{\text{density of hydrogen}} \qquad (6.1)$$

this corresponds to a molecular mass of about 34 u, whence $n = 34/17 = 2$. Chemists accordingly write the formula H_2O_2. The formula HO is called the *empirical* formula, H_2O_2 the *molecular* formula. The former gives the ratio of the number of atoms, the latter gives the actual number.

The atomic compositions of some other substances are given in Table 6.3. Also given are names based on these compositions using the Greek prefix "mono" for one, "di" for two, "tri" for three, "tetra" for four, and so on. Chemists use these names when a simple name (e.g. carbon oxide) would be ambiguous. This gives us the now-familiar name "carbon dioxide".
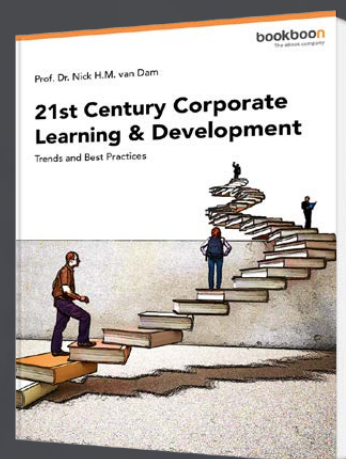
Substance	Empirical formula	Molecular formula	Constitutional name
Hydrogen	H	H_2	
Oxygen	O	O_2	
Water	H_2O	H_2O	
Hydrogen peroxide	HO	H_2O_2	
Carbonous oxide	CO	CO	carbon monoxide
Carbonic oxide	CO_2	CO_2	carbon dioxide
Hydrogen chloride	HCl	HCl	
Sodium chloride vapour	NaCl	mixture of NaCl and Na_2Cl_2	
Sodium chloride crystals	NaCl	see below	

Table 6.3 Atomic composition of some substances

The conclusion that matter is made up of atoms and molecules is supported by the results of the kinetic theory of gases. They show that the properties of a gas can be explained on the assumption that a gas comprises a large number of particles that are continually moving in all directions (Box 6.1).

Box 6.1

Kinetic theory

This theory explains some of the properties of materials. It is based on the idea that materials comprise a large number of small particles in continual motion. In a gas they move throughout the container. In a liquid they move throughout the liquid. In a solid they vibrate but do not move position.

The simplest case is that of a gas. Consider a gas in a cubic container of side L. Suppose that this comprises N particles of mass m. Let us further suppose, for simplicity, that all the particles are moving with the same speed v, and that $N/3$ are moving between the top and bottom face, $N/3$ between the left and right face, and $N/3$ between the front and back. The number of impacts made by a particle on any one face in a period of time δt is $v\delta t/2L$, $2L$ being the distance the particle traverses between each impact with that face. The total number of impacts on the face in this period of time is therefore $(v\delta t/2L) \times (N/3) = Nv\delta t/6L$.

Now on impact, the momentum of a particle changes from $+mv$ to $-mv$, i.e. by $2mv$. The change of momentum of all the particles striking a face in the period δt is therefore $(Nv\delta t/6L) \times 2mv = Nmv^2\delta t/3L$ and the rate of change, $Nmv^2/3L$. According to Newton's second law, this is equal to the force on the wall. The pressure on the wall is therefore given by $(Nmv^2/3L) \div L^2$, L^2 being the area of the wall. Since L^3 is equal to the volume of the gas (V), the result is:

$p = Nmv^2/3V$

This reproduces Boyle's law, $p \propto 1/V$ (Box 5.1).

The result without the simplifying assumptions is:

$$p = Nm\overline{v^2}/3V$$

6.3   MOLECULAR AND NON-MOLECULAR SUBSTANCES

The distinction between molecular and non-molecular substances is an important one in chemistry. I make it here on the basis of simple properties of substances, namely their volatility (ease of vaporization) and solubility. A more precise distinction requires a knowledge of the structures of substances.

Substances can be classified on the basis of volatility and solubility as follows.

Type 1: Volatile substances

These have a low boiling point (≤ 100 °C). If they are coloured, they usually have the same colour as a gas, liquid or solid (e.g. chlorine, Sect. 3.3). Each dissolves in a range of other volatile substances – if coloured, usually without change in colour. These properties suggest that the molecules that are present in the gas are generally also present in the liquid and solid, and in solution. A further implication is that forces between molecules are relatively weak.

Type 2A: Semi-volatile and involatile substances that dissolve in volatile ones

These have similar properties to volatile substances but are less volatile. They dissolve in a range of volatile solvents, and preserve their colours in different phases. Most organic compounds fall into this class. Their properties suggest that substances of this type are also generally molecular in every phase (gas, liquid, solid, and in solution).

Download free eBooks at bookboon.com
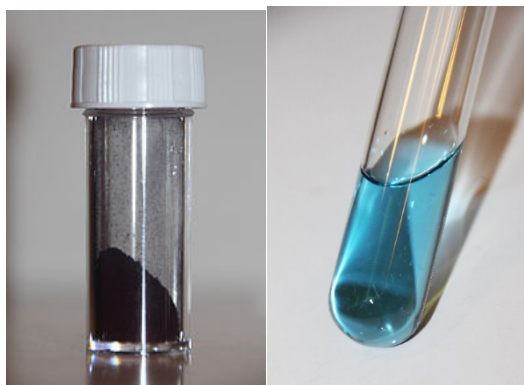
An organic dye (Coomassie brilliant blue G-250) and its
dilute solution in an organic solvent (isopropyl alcohol)
[Wikipedia]

This conclusion is supported by the freezing points of solutions of type 1 and 2A substances. For dilute solutions, the freezing point is lower than that of the solvent, and the depression ($\Delta\theta$) is generally proportional to the fraction of solute molecules (x) in the solution, calculated on the assumption that the solute and solvent molecules in the solution are the same as in the gas phase. This may be written:

$$\Delta\theta = k_f x \tag{6.2}$$

where the value of k_f is characteristic of the solvent. Some solutions do not satisfy equation (6.2), notably those conducting electricity while undergoing electrolysis (e.g. hydrogen chloride in water). These will be considered later (Sect. 10.2).
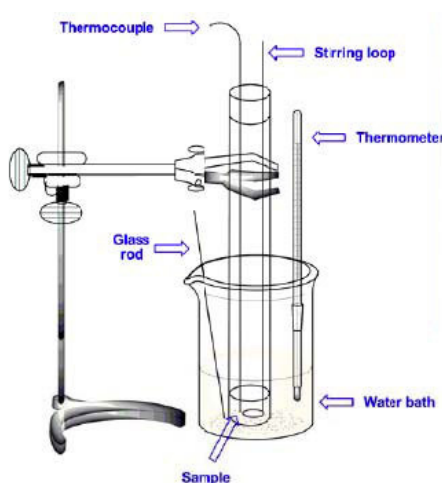

Apparatus for determining freezing points
[Youngstown State University]

The boiling points of substances of types 1 and 2A generally increase with the number of atoms in the molecule, and with the masses of these atoms (though mass itself is not the cause of this). This implies that the forces between molecules of these substances generally increase with the number of atoms and their masses. Type 2A substances can nevertheless dissolve in type 1 substances because, in general, the more atoms a molecule has, the greater the number of solvent molecules it can interact with, and the heavier the atoms are, the stronger these interactions will be.

Type 2B: Semi-volatile and involatile substances that are generally insoluble in volatile ones

These are insoluble in all, or nearly all, volatile substances, other than by chemical reaction. If they are coloured, there is usually a change in colour between the solid or liquid and the gas (e.g. metals). Their boiling points are generally much higher than those of type 1 or 2A substances having similar gaseous molecules (e.g. NaCl, bp 1413 ºC, compared with HCl, bp -85 ºC). This class includes metals, salts, and "adamantine" substances (diamond, quartz, etc.). Salts generally dissolve in water, but their solutions conduct electricity while undergoing electrolysis, and do not obey equation (6.2).

The low volatility of these substances compared with type 1 or 2A substances having similar gaseous molecules implies that their gaseous molecules attract each other much more strongly than those of the latter. The change in colour of coloured substances of this type on condensation further implies that these interactions give rise to a different structure in the liquid or solid, one in which the identity of the molecules is lost. These observations suggest that molecules join together in the liquid or solid state to give a continuous network of atoms, with strong bonds throughout the network. Networks can be envisaged in one, two, or three dimensions.
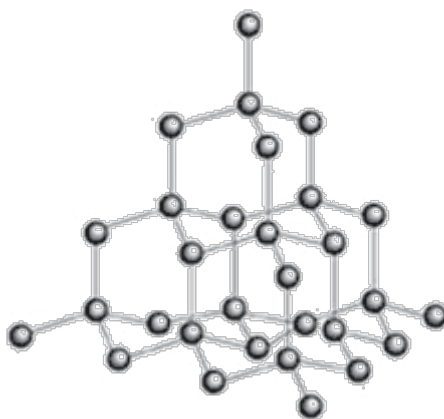
Network structure of diamond; the structure continues in all directions
[Samantha Shanley, University of Bristol]

For these substances to dissolve in a volatile solvent, sufficiently strong bonds have to be formed between units of the network and solvent molecules to overcome the bonding between the units. Since the bonds usually formed by molecules of volatile substances will be too weak for this, type 2B substances are usually insoluble. That salts dissolve in water implies a particularly strong kind of bonding between their units and water molecules. This is discussed further in a later chapter (Chap. 10).

In general, structure determinations confirm the above inferences. There are exceptions, but their number is relatively small.

So, in general, substances of types 1 and 2A can be described as "molecular" and those of type 2B as "non-molecular". Molecular substances made up of very large molecules may be described as "macromolecular". Some authors also describe substances of type 2B as "macromolecular", but this term is best reserved for substances like proteins which, in bulk, still comprise many molecules.

If substances like sodium chloride crystals are non-molecular, how are we formulate them? Chemists write NaCl, but this goes back to a time when they thought the compound was molecular, like hydrogen chloride. The true formula of sodium chloride crystals is $(NaCl)_N$, where N is a large number, with a different value for each crystal. This formula is cumbersome, so I will simplify it to (NaCl). Chemists call NaCl the "formula unit" of sodium chloride, a usage I will follow.

As a general rule, metals and their compounds, under ordinary conditions, are non-molecular. Non-metals and compounds between them are molecular. There are, however, many exceptions (e.g. graphite and diamond are non-molecular).

A final question is, how should we formulate sodium chloride when it is dissolved in water? As already mentioned, we shall discuss the constitution of such solutions later (Chap. 10). What is clear at this point, however, is that the framework structure of sodium chloride must break down in water. We shall provisionally, therefore, write the formula of sodium chloride in water as NaCl(aq), where "aq" is an abbreviation for "aqueous" (from Latin *aqua*, "water").

6.4 AVOGADRO NUMBER

In the calculation on hydrogen peroxide in Section 6.2, I introduced the quantity g/u. This is a number – the ratio between two units of mass. It is called the "Avogadro number" (N_A), not to be confused with the "Avogadro constant" (L) of Section 7.3. It is approximately equal to the number of hydrogen atoms (mass ≈ 1 u) in one gram of hydrogen. It thus relates the atomic scale to the macroscopic. An estimate of its value can be obtained from the area (A) over which a measured volume (V) of oil spreads on water. The thickness of the oil (d) is given by V/A and, if the molecules of oil are cubes, their area is d^2. Their number is therefore A/d^2. From this the value of N_A is about 4×10^{21}. More accurate determinations give 6.022×10^{23}. The error mainly arises because oil molecules are not cubes, but rods which line up at the surface; the length of the rods is equal to d, but their area is much less than d^2.

The Avogadro number is difficult to imagine. It means that, in a speck of iron that is just visible to the naked eye ($\frac{1}{100}$ mm $\times \frac{1}{100}$ mm $\times \frac{1}{100}$ mm), the number of atoms along one edge is about 44,000, the size of a large football crowd.

It is now possible to scan solid surfaces on a very small scale. These show that surfaces on this scale undulate, with peaks where we would expect atoms to be.
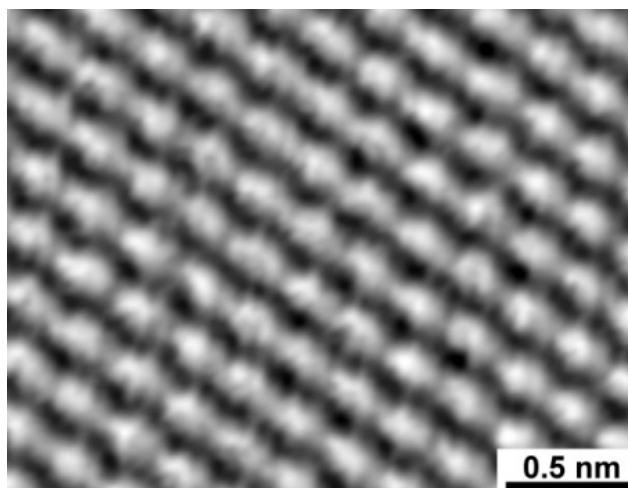
Image of graphite taken with scanning probe microscope showing rows of atoms (nm = 10^{-9} m)
[Hackaday]

Problem

Ethane is a minor component of natural gas, similar to methane. It contains 79.8% by mass of carbon and 20.2% of hydrogen, and has a density of 1.356 g/l at STP. Derive (a) its empirical formula, (b) its molecular formula.

[Remember that equation (6.1) is only approximate at STP. It is more accurate at lower pressures, but higher accuracy is not needed to establish the correct multiple of the empirical formula.]

---

7   CHEMICAL CALCULATIONS

7.1   CHEMICAL EQUATIONS

Knowing the constitution of substances enable us to calculate the masses of the starting materials required for a reaction and of the products expected from it. This involves establishing first an equation for the reaction and then using this to calculate the masses.

First example

So far we have written the reaction between hydrogen and oxygen to give water as follows:

hydrogen + oxygen → water
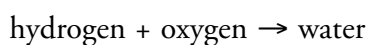
The law of conservation of mass enables us to write the following equation for the reaction:

mass of hydrogen + mass of oxygen = mass of water
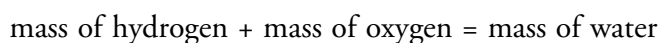
Thus, knowing, for example, the masses of hydrogen and oxygen, we can calculate the mass of water we would expect to be formed.

A more useful equation can be obtained by using the theory of atoms and molecules in the previous chapter. According to this, the law of conservation of mass means that that the number of atoms of each type is conserved in a chemical reaction. This means that, for the reaction between hydrogen and oxygen, both the number of hydrogen atoms and the number of oxygen atoms is conserved.

Now hydrogen comprises H_2 molecules, oxygen O_2 molecules, and water H_2O molecules (Table 6.3). Consider the reaction of one H_2 molecule:
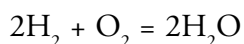
$H_2 + O_2 \rightarrow H_2O$
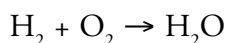
This is not an equation. There are two oxygen atoms on the left-hand side but only one on the right. To make it an equation we have to double the number of water molecules:

$H_2 + O_2 \rightarrow 2H_2O$
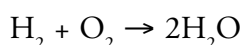
Now, however, the hydrogen atoms do not balance. To balance these, we have to double the number of H_2 molecules:

$$2H_2 + O_2 \rightarrow 2H_2O$$
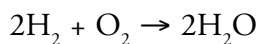
This *is* now an equation, and can also be written:
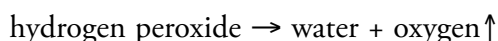
$$2H_2 + O_2 = 2H_2O$$

The procedure we have just gone through is based on the principle of "conservation of atoms" and is called "balancing an equation".

We shall see in the next section how this equation enables the mass of water to be determined knowing only the mass of hydrogen or oxygen.

Second example

Consider the decomposition of hydrogen peroxide:

$$\text{hydrogen peroxide} \rightarrow \text{water} + \text{oxygen}\uparrow$$
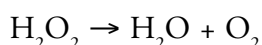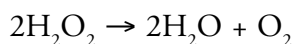
*Hydrogen peroxide solution decomposing
into bubbles of oxygen in the presence of
a black catalyst (manganese dioxide)*
[Chemistry Land CHM130LL]

For the decomposition of one hydrogen peroxide molecule, we can write (from Table 6.3):

$$H_2O_2 \rightarrow H_2O + O_2$$

To balance this, we have to double the number of H_2O_2 molecules and double the number of H_2O molecules:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

7.2   CALCULATING QUANTITIES IN REACTIONS

First example

Suppose we want to calculate the mass of water formed by burning 5.00 g of hydrogen in an excess of oxygen. From Table 6.2, the mass of an H_2 molecule is 2.02 u and of an H_2O molecule 18.0 u. The number of H_2 molecules is therefore

$$\text{no. of } H_2 \text{ molecules} = \frac{\text{mass of hydrogen}}{\text{mass of } H_2 \text{ molecule}} = \frac{5.00 \text{ g}}{2.02 \text{ u}} = 2.475 \text{ g/u} = 2.475 \text{ Av}$$

Here I have used the Avogadro number (g/u, Sect. 6.4) as a counting unit (Avo, abbreviated Av) like a dozen or gross.

Now from the equation for the reaction, the number of H_2O molecules formed is given by:

$$\text{no. of } H_2O \text{ molecules} = \text{no. of } H_2 \text{ molecules} = 2.475 \text{ Av}$$

The mass of water formed is therefore:

mass of water = no. of H_2O molecules × mass of H_2O molecule = 2.475 Av × 18.0 u = 44.6 g

Here I have used Av = g/u.

Second example

Suppose we want to calculate the mass of oxygen formed by the decomposition of 1.00 g of hydrogen peroxide (10.0 g of 10.0% solution). The relevant molecular masses in this case are: H_2O_2, 34.0 u; O_2, 32.0 u. The number of H_2O_2 molecules is

$$\text{no. of } H_2O_2 \text{ molecules} = \frac{\text{mass of hydrogen peroxide}}{\text{mass of } H_2O_2 \text{ molecule}} = \frac{1.00 \text{ g}}{34.0 \text{ u}} = 0.0294 \text{ Av}$$

From the equation for the reaction,

$$\text{no. of } O_2 \text{ molecules} = \frac{1}{2} \times \text{no. of } H_2O_2 \text{ molecules} = 0.0147 \text{ Av}$$
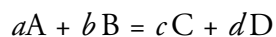
The mass of oxygen is therefore:

mass of oxygen = no. of O_2 molecules × mass of O_2 molecule = 0.0147 Av × 32.0 u = 0.47 g

From the density of oxygen (1.4290 g/l at STP), this corresponds to 330 ml at STP.

General equations

We can generalize the equations used in these calculations as follows. Consider the general reaction

$$a\text{A} + b\text{B} = c\text{C} + d\text{D}$$

where A, B, C, and D represent molecules or formula units. For this

$$\frac{N(\text{A})}{a} = \frac{N(\text{B})}{b} = \frac{N(\text{C})}{c} = \frac{N(\text{D})}{d} \tag{7.1}$$

where $N(A)$, $N(B)$, $N(C)$, and $N(D)$ represent the number of molecules or formula units of each kind consumed or produced in the reaction. This number is given by

$$N = \frac{m(\text{substance})}{m(\text{particle})} \tag{7.2}$$

where m represents mass.

Substances in solution

If a reaction involves a substance in solution, then to use equation (7.1), we need to be able to calculate the number of molecules of the substance from the volume (V) of the solution. This can be done if we know the number concentration (C), defined by

$$C = \frac{N(\text{solute molecules})}{V(\text{solution})} \tag{7.3}$$

From this, $N = CV$.

The number concentration can be calculated from the ordinary mass concentration, defined by

$$\gamma = \frac{m(\text{solute})}{V(\text{solution})}$$

Since

$$N(\text{solute molecules}) = \frac{m(\text{solute})}{m(\text{solute molecule})}$$

C is related to γ by

$$C = \frac{\gamma}{m(\text{solute molecule})}$$

In terms of our counting unit for the number of molecules (Av), the units of C are Av/l.

Gases

The gas laws (Sect. 5.1) can be combined with Avogadro's hypothesis (Sect. 6.1) to give, for an ideal gas (Box 7.1):

$$\frac{pV}{T} = kN \tag{7.4}$$

where k is a constant known as the "Boltzmann constant". From this equation, the number of particles at a particular temperature and pressure is given by

$$N = \frac{V}{V_{\text{mol}}}$$

where V_{mol}, the volume per molecule (V/N), $= kT/p$. This is 22.4 l/Av at STP.

Thus, if we return to the calculation of the volume of oxygen at STP produced by the decomposition of 1.00 g of hydrogen peroxide, we can avoid invoking the density of oxygen by using the above equation:

$$V(O_2) = N(O_2)V_A = 0.0147 \text{ Av} \times 22.4 \text{ l/Av} = 330 \text{ ml}$$

Box 7.1

Derivation of equation (7.4)

Avogadro's hypothesis states that, at low pressures, equal volumes of gases at the same temperature and pressure contain equal numbers of molecules. This means that, at a particular temperature (T) and pressure (p), the volume of gas per molecule

$$V_{\text{mol}} = \frac{V}{N}$$

is the same for all gases.

Now we know from the gas laws that, at low pressures, the volume of a sample of a gas (N constant) is proportional to $\frac{T}{p}$. This means that V_{mol} is proportional to $\frac{T}{p}$. It must therefore be given by

$$V_{\text{mol}} = \frac{kT}{p}$$

where k is a constant having the same value for all gases. Combining these equations gives equation (7.4).

7.3   AMOUNT OF SUBSTANCE AND THE MOLE

For historical reasons, chemists complicate calculations by introducing a quantity called "amount of substance" (n) with the unit "mole" (abbreviated "mol"). This is defined by

$$n = \frac{N}{L} \tag{7.5}$$

where L is a constant called the "Avogadro constant". Substituting this into equations (7.1) and (7.2) gives

$$\frac{n(\text{A})}{a} = \frac{n(\text{B})}{b} = \frac{n(\text{C})}{c} = \frac{n(\text{D})}{d} \tag{7.6}$$

and

$$n = \frac{m(\text{substance})}{Lm(\text{particle})} = \frac{m(\text{substance})}{M(\text{particle})} \tag{7.7}$$

M is called the "molar mass". The mole is chosen to be such that the molar mass of hydrogen atoms is 1.0079 g/mol corresponding to an atomic mass of 1.0079 u (Sect. 6.2). Molar masses of some atoms are listed in Table 7.1.

On this scheme, equation (7.3) becomes

$$\text{amount-of-substance concentration } (c) = \frac{n(\text{solute molecules})}{V(\text{solution})} \qquad (7.8)$$

from which $n = cV$. The units of c are mol/l.

Likewise, equation (7.4) becomes

$$\frac{pV}{T} = kLn = Rn \qquad (7.9)$$

where R is the "gas constant". From this, $n = V/V_m$, where V_m is the "molar volume" (RT/p). This is 22.4 l/mol at STP.

Atom	Molar mass	Atom	Molar mass	Atom	Molar mass
H	1.01 g/mol	Al	27.0 g/mol	K	39.1 g/mol
C	12.0 g/mol	Si	28.1 g/mol	Ca	40.1 g/mol
N	14.0 g/mol	P	31.0 g/mol	Fe	55.8 g/mol
O	16.0 g/mol	S	32.1 g/mol	Cu	63.5 g/mol
Na	23.0 g/mol	Cl	35.5 g/mol		

Table 7.1 Molar masses of some atoms*
*Compare Table 6.2.

Alternative terminologies

The traditional name for c is "molarity" and its unit "molar" (M = mol/l). These names are still widely used, though they break the rule that the name for a physical quantity should not imply a particular choice of unit.

An alternative terminology, advocated by some chemists, is to call n "chemical amount" (c.a.) and c "chemical concentration". I shall use these terms here, along with the unit M.

Example

Let us return to the first example above, calculating the mass of water formed by burning 5.00 g of hydrogen.

From Table 7.1, the molar mass of H_2 is 2.02 g/mol and of H_2O 18.0 g/mol. From equation (7.7), therefore, the chemical amount of H_2 burnt is given by:

$$\text{c.a. of } H_2 = \frac{\text{mass of hydrogen}}{\text{molar mass of } H_2} = \frac{5.00 \text{ g}}{2.02 \text{ g/mol}} = 2.475 \text{ mol}$$

Thus, from equation (7.6) and the equation for the reaction, the chemical amount of H_2O formed is given by:

$$\text{c.a. of } H_2O = \text{c.a. of } H_2 = 2.475 \text{ mol}$$

From equation (7.7), therefore, the mass of water formed is:

$$\text{mass of water} = \text{c.a. of } H_2O \times \text{molar mass of } H_2O = 2.475 \text{ mol} \times 18.0 \text{ g/mol} = 44.6 \text{ g}$$

7.4   QUALITATIVE AND QUANTITATIVE ANALYSIS

Qualitative analysis seeks to answer the question, "What is this unknown material made of? What are its components?" Quantitative analysis seeks to answer the further question, "What are the proportions of these components?"

Chemists use many different methods to tackle these questions. Many of these methods involve making physical measurements with instruments designed for this purpose. These methods are very useful when analyses are required of a large number of similar materials.

For isolated samples, more traditional methods are often used. Traditional methods of qualitative analysis involve carrying out chemical tests in test tubes. Traditional methods of quantitative analysis involve measuring the masses of substances taking part in a reaction ("gravimetric" analysis) or the volumes of solutions of reactants ("volumetric" analysis, Box 7.2).

Box 7.2

Volumetric analysis

This is carried out with the apparatus shown in the Figure. The first step is to measure out a known quantity of one solution. This is done by sucking the solution into a glass bulb (a "pipette") up to a calibration mark near the top and the letting it run out into a flask (picture 1). The second solution is poured into a graduated tube fitted with a tap (a "burette"), and slowly run into the flask, where reaction occurs (picture 2). This is continued until the first reagent has been completely consumed, at which point (the "end point") the volume added is read off the scale of the burette (picture 3). The end point is usually marked by an indicator (a substance that changes colour when there is an excess of the second reagent). The procedure is called "titration".
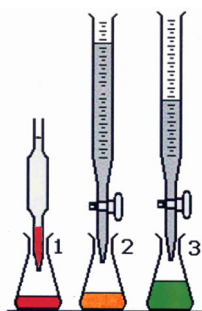
Carrying out a titration
[Doc Brown (adapted)]

Example

Consider a solution thought to contain hydrochloric acid and sodium chloride. The presence of these compounds can be confirmed by carrying out the following tests:

1) Place a drop of the liquid on to blue litmus paper. This turns red with acids.
2) Place a drop of the liquid in a flame. Sodium salts turn a flame yellow.
3) Add a drop of the liquid to silver nitrate solution. This gives a white precipitate of silver chloride with chlorides which slowly darkens in light.

To determine the amount of hydrochloric acid in the solution, we can titrate a measured volume against a solution of sodium hydroxide of known strength. Litmus could be used as an indicator, though there are better ones (e.g. phenolphthalein, which changes from colourless to red).

To determine the amount of sodium chloride, we can determine the total amount of chloride and subtract the amount of hydrochloric acid. To determine the total amount of chloride, we can take a measured volume of the solution, add an excess of silver nitrate solution, filter off the silver chloride precipitate in a pre-weighed sintered glass funnel, dry this and weigh it. Subtraction of the mass of the funnel gives the mass of silver chloride and hence the total amount of chloride. [See further Problem 7 at the end of the next chapter.]

7.5   INCOMPLETE REACTIONS

Some reactions do not proceed to completion. They proceed so far and then stop. An example is in the gas given off when copper dissolves in concentrated nitric acid (Chap. 4). This gas is pale yellow-brown at low temperatures, but as the temperature is raised, it gradually changes to a dark red-brown. The reverse happens when the gas is cooled.

What is happening here is that molecules in the paler gas (N_2O_4) dissociate into molecules in the darker gas (NO_2), and do so increasingly as the temperature is raise. At any given temperature, the dissociation is incomplete (Table 7.2).


Samples of N_2O_4/NO_2 at increasing temperatures
[UCSB Demonstration Library]

Temperature	Average mass of molecule*	Degree of dissociation
21.9 °C (b.p.)	80.2 u	15%
60.2 °C	60.7 u	52%
100.1 °C	49.0 u	88%
140.0 °C	46.3 u	99%

Table 7.2 Degree of dissociation of N_2O_4 at atmospheric pressure and different temperatures
*Calculated from $m/\mu = \rho/\rho_{H2}$ and $\mu = 2 \times 1.0079$ u (Chap. 6).

This phenomenon can be understood on the kinetic theory (Box 6.1). At any given temperature, the molecules in the gas move around the container and collide with each other. Some N_2O_4 molecules acquire more energy than others, enough to dissociate them. At the same time, some NO_2 molecules lose more energy than others, enough to recombine. The two processes reach a point of balance. This is called "equilibrium" and is represented by a double arrow:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$
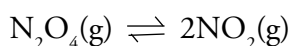
where "g" signifies gas.

The position of equilibrium is governed by what is called the "equilibrium constant" (K). For the general reaction

$$aA(g) + bB(g) = cC(g) + dD(g)$$
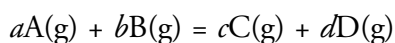
this is given by

$$K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b}$$

where p_X is the partial pressure of X, defined by $p_X = x_X p$, where x_X is the fraction of X molecules in the gas (N_X/N_{total}) and p the total pressure. This equation enables calculations to be carried out on equilibria. Thus for the dissociation of N_2O_4:

$$K_p = \frac{p_{NO_2}^2}{p_{N_2O_4}} = \frac{(x_{NO_2}p)^2}{x_{N_2O_4}p} = \frac{x_{NO_2}^2 p}{x_{N_2O_4}}$$

Since $x_{N_2O_4} + x_{NO_2} = 1$, this can be written

$$K_p = \frac{x_{NO_2}^2 p}{1 - x_{NO_2}}$$

Knowing the value of K_p (0.15 atm at 25 °C), we can use this equation to calculate the value of x_{NO_2} at any pressure p. From the form of the equation, x_{NO_2} will decrease as p increases.

The above equations only hold at low pressures. There are similar equations for reactions in solution, expressed in terms of concentration. These hold for solutions comprising similar molecules, and for solutions at low concentrations.

Problems

1. Write an equation for the combustion of (a) carbon in an excess of oxygen; (b) carbon monoxide in oxygen.
2. Calculate the mass of carbon dioxide produced by the combustion of 5.00 g of carbon in an excess of oxygen.
3. Calculate the mass of carbon dioxide produced by the combustion of 1.50 litres of carbon monoxide at STP in an excess of oxygen.
4. Calculate the chemical concentration of NaCl units in a solution containing 20.0 g of sodium chloride crystals per litre.

For further problems of this type, see end of next chapter.

---

8 FORMULAE OF SUBSTANCES AND VALENCY

8.1 SCOPE

In this chapter, I list the formulae of substances mentioned in Chapter 4. The list is long, but a careful study of it reveals simple patterns among the formulae, which leads to the concept of *valency*. This enables many of the formulae to be worked out, so aiding the memory.

8.2 FORMULAE OF IMPORTANT SUBSTANCES

In this section, I list substances under the names I used in Chapter 4. Compositional names chemists use are in brackets. Formulae of substances in aqueous solution are indicated by (aq). The symbol ~ means that the composition is approximate and that the compound is non-stoicheiometric.

For hydrated salts, I have simplified the formulae for clarity. These are usually written as, for example, $(CaSO_4 \cdot 2H_2O)$. I have simplified this to $(CaSO_4)$ (2). The formulae are for hydrates formed at room temperature. The water molecules in these are usually easily removed by heating to give lower hydrates and the anhydrous salt.

Oxygen

Oxygen: O_2 Ozone: O_3

Hydrogen

Hydrogen: H_2 Water: H_2O
Hydrogen peroxide: H_2O_2

Carbon

Graphite: (C)   Diamond: (C)
Carbonous oxide: CO_2 (carbon monoxide)   Carbonic oxide: CO_2 (carbon dioxide)
Carbonic acid: H_2CO_3 (aq)   Methane: CH_4

Silicon

Silicon: (Si)   Silicon oxide: (SiO_2) (silicon dioxide)

Sulfur

Sulfur vapour: S_8

Sulfurous oxide: SO_2 (sulfur dioxide)

Sulfuric oxide solid: $(SO_3)_3$ (from structure)

Sulfuric acid: H_2SO_4 (aq)

Rhombic sulfur: S_8

Sulfuric oxide vapour: SO_3 (sulfur trioxide)

Concentrated sulfuric acid: H_2SO_4

Hydrogen sulfide: H_2S

Chlorine

Chlorine: Cl_2

Hydrochloric acid: HCl (aq)

Hydrogen chloride: HCl

Calcium

Calcium: (Ca)

Calcium hydroxide: $(Ca(OH)_2)$

Calcium sulfate: $(CaSO_4)$ (2)

Calcium oxide: (CaO)

Calcium carbonate: $(CaCO_3)$

Calcium chloride: $(CaCl_2)$ (6)

Sodium

Sodium: (Na)

Sodium hydroxide: (NaOH)

Sodium bicarbonate: $(NaHCO_3)$

Sodium chloride: (NaCl)

Sodium carbonate: (Na_2CO_3) (10)

Sodium sulfate: (Na_2SO_4) (10)

Potassium

Potassium: (K)

Potassium hydroxide: (KOH)

Potassium chloride: (KCl)

Potassium carbonate: (K_2CO_3)

Nitrogen

Nitrogen: N_2

Sodium nitrate: $(NaNO_3)$

Ammonia: (NH_3)

Ammonium nitrate: (NH_4NO_3)

Nitric acid: HNO_3 (aq)

Potassium nitrate: (KNO_3)

Ammonium chloride: (NH_4Cl)

Phosphorus

Phosphorus vapour: P_4

White phosphorus: P_4

Red phosphorus: (P)

Phosphoric acid: H_3PO_4 (aq)

Ammonium phosphate: $((NH_4)_2HPO_4)$
(diammonium hydrogen phosphate)

Calcium phosphate: $(Ca_3(PO_4)_2)$
(tricalcium phosphate)

Phosphorous chloride: PCl_3
(phosphorus trichloride)

Phosphoric chloride: PCl_5
(phosphorus pentachloride)

Iron

Iron: (Fe)

Ferrous oxide: $(\sim FeO)$

Ferric oxide (Fe_2O_3)

Ferrous hydroxide: $(Fe(OH)_2)$

Ferric hydroxide: $(Fe(OH)_3)$ (variable H_2O)

Ferrous sulfate: $(FeSO_4)$ (7)

Ferric sulfate: $(Fe_2(SO_4)_3)$ (9)

Ferrous chloride $(FeCl_2)$ (4)

Ferric chloride: $(FeCl_3)$ (6)

Magnetite: (Fe_3O_4) (triiron tetroxide)

Iron carbide: (Fe_3C)

Copper

Copper: (Cu)

Cuprous oxide: (Cu_2O)   Cupric oxide: (CuO)

Cuprous sulfate: (Cu_2SO_4)   Cupric sulfate: ($CuSO_4$) (5)

Cuprous chloride: (CuCl)   Cupric chloride: ($CuCl_2$) (2)

Aluminium

Aluminium: (Al)   Aluminium oxide: (Al_2O_3)

Aluminium hydroxide: ($Al(OH)_3$)   Aluminium sulfate: ($Al_2(SO_4)_3$) (18)

(variable H_2O)

Aluminium chloride: ($AlCl_3$) (6)   Sodium aluminate: ($NaAlO_2$)

8.3   GROUPS OF ATOMS

Looking over the formulae in the last section, we see that some groups appear repeatedly in the formulae. One is OH, which appears in ($Ca(OH)_2$), (NaOH), (KOH), ($Fe(OH)_2$), ($Fe(OH)_3$), and ($Al(OH)_3$). It also appears in the formulae of water and hydrogen peroxide if these are written H(OH) and $(OH)_2$. In molecular compounds, a group like this is called a "radical".

A list of important groups is given in Table 8.1.

Formula	Group name	Radical name
OH	hydroxide	hydroxyl
CO_3	carbonate	
SO_4	sulfate	
NO_3	nitrate	
PO_4	phosphate	
NH_4	ammonium	

Table 8.1 Groups of atoms

8.4   VALENCY

Looking further over the formulae in the last section, we see that there are numerical relations among many of the formulae. For example, potassium compounds have the same formulae as sodium compounds:

<div style="text-align:center">

(NaCl)   (KCl)

(NaOH)   (KOH)

(Na_2CO_3) (K_2CO_3)

$(NaNO_3)$ (KNO_3)

</div>

This implies that potassium atoms have the same capacity to combine with other atoms as sodium atoms.

As second example compares chlorides with oxides. In these, oxygen atoms combine with twice the number of other atoms as chlorine atoms do (to extend the comparison, I have included the formula of carbon tetrachloride, a colourless liquid made by burning methane in chlorine):

<div style="text-align:center">

H_2O HCl

(Cu_2O) (CuCl)

(CaO) $(CaCl_2)$

(FeO) $(FeCl_2)$

(CuO) $(CuCl_2)$

(Fe_2O_3) $(FeCl_3)$

(Al_2O_3) $(AlCl_3)$

CO_2 CCl_4

</div>

This comparison implies that oxygen atoms have twice the capacity to combine with other atoms as chlorine atoms.

The capacity of an atom or group of atoms to combine with other atoms or groups of atoms in a family of compounds is called "valency". The qualification "in a family of compounds" allows for the fact that valency can vary from one family of compounds to another (e.g. ferrous and ferric) and can break down altogether (e.g. in many compounds between metals as I discuss below).
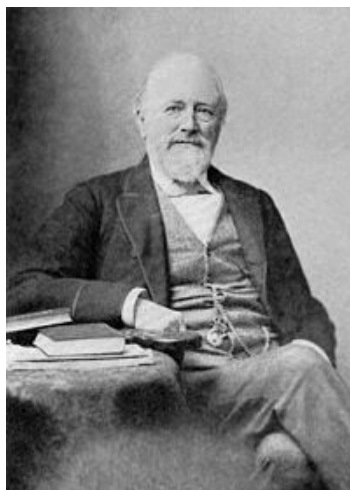
Edward Frankland, who first recognized valency (1852)

There are several kinds of valency, the main one being the "primary" or "classical" valency (v). This applies to most of the compounds listed in Section 8.2. The scale of v is chosen such that $v(\mathrm{H}) = 1$. Values for other atoms (X) can therefore be determined by counting the number of hydrogen atoms that X will combine with to form a molecule $\mathrm{XH}v$, or unit of a non-molecular compound ($\mathrm{XH}v$). Supplementary values can be obtained from the formulae of oxides using $v(\mathrm{O}) = 2$. Values for groups of atoms can be obtained similarly.

The main values for atoms and groups of atoms are given in Table 8.2. Some atoms have more than one valency. To specify a valency, Latin prefixes are used (uni-, bi-, tri-, quadri- etc.), e.g. "bivalent", "bivalency".

Atom	Valency	Atom	Valency	Group	Valency
H	1	Na	1	OH	1
Cl	1	K	1	NO_3	1
O	2	Cu	1, 2	CO_3	2
S	2, 4, 6	Ca	2	SO_4	2
N	3, 5	Fe	2, 3	PO_4	3
P	3, 5	Al	3	NH_4	1
C	4				
Si	4				

Table 8.2 Main valencies of atoms and groups of atoms

From the valencies in Table 8.2, the formulae of a great many compounds can be derived. This involves applying the principle that, in many compounds, the valencies of all the atoms or groups of atoms are satisfied. This is most easily done by representing valencies by small dashes, as in H- and -O-, and lining up dashes:
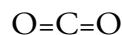
H- -H   H- -O- -H   H- -O- -O- -H
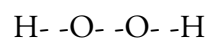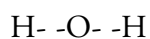
In the case of molecular compounds, we can join up the dashes to form what chemists call "bonds":
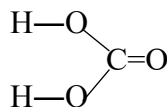
H—H   H—O—H   H—O—O—H
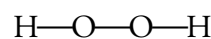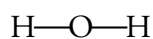
These represent respectively molecules of hydrogen (H_2), water (H_2O), and hydrogen peroxide (H_2O_2).

Bonds can be single, as above, or multiple. For example, the bonds in molecules of oxygen (O_2) and carbon dioxide (CO_2) are double:

$$O=O \qquad\qquad O=C=O$$

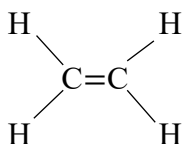Likewise, one of the bonds in molecules of carbonic acid (H_2CO_3):

$$
\begin{array}{c}
H{-}O \\
\qquad\!\!\!\!\searrow \\
\qquad\quad C=O \\
\qquad\!\!\!\!\nearrow \\
H{-}O
\end{array}
$$

Formulae of this kind can also be drawn for some non-molecular compounds. In diamond, for example, structure determinations show that each carbon atom is bound to four others in a continuous framework. Since carbon atoms have a valency of four, this structure can be drawn with single bonds.

For most non-molecular compounds, however, such a structure cannot be drawn. For crystalline sodium chloride, for example, structure determinations show that each sodium atom is bound to six chlorine atoms and each chlorine atom to six sodium atoms. Since sodium and chlorine each have a valency of one, the number of bonds between each pair of atoms (n) is fractional ($n = 1/6$). For compounds of this type, therefore, the little dashes must not be joined up. Instead we must write:

Na- -Cl giving (NaCl)
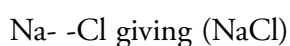
Bond formulae for some small organic molecules are shown in Box 8.1. Chemists' systematic names are in italics. Only "ethanol" is widely used.

Box 8.1
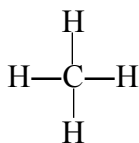
Methane (CH_4)
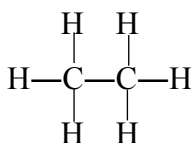
Ethane (C_2H_6)
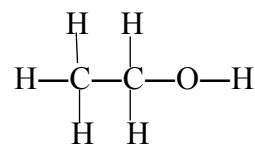
Alcohol (C_2H_5OH)
Ethanol

Ethylene (C_2H_4)
Ethene

Acetylene (C_2H_2)
Ethyne
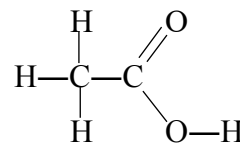
Acetic acid (CH_3CO_2H)
Ethanoic acid

Download free eBooks at bookboon.com

Click on the ad to read more

Intermetallic compounds

As I mentioned earlier, valency does not apply to most intermetallic compounds. This can be seen from the formulae for the compounds formed between the following metals:

sodium and potassium: (KNa_2)

calcium and aluminium: (Al_2Ca)

iron and aluminium: $(\sim Al_3Fe)$, $(\sim Al_5Fe_2)$, $(\sim Al_2Fe)$, $(\sim AlFe)$, and $(\sim AlFe_3)$

Note that the symbols in the formulae are in alphabetical order.

Many pairs of metals do not form compounds. On melting together and cooling, they either form solid solutions with each other over the whole range of concentrations or are more or less completely immiscible.

Problems

Problems 4–7 are further problems on chemical calculations.

1. Zinc (Zn) is a bivalent metal. Derive a formula for (a) its oxide, (b) its chloride, (c) its hydroxide, (d) its carbonate, (e) its sulfate, and (f) its nitrate.
2. Bromine (Br) is a univalent non-metal. Derive a formula for its compound or compounds with (a) hydrogen, (b) chlorine, (c) sodium, (d) potassium, (e) calcium, and (f) iron.
3. Write a bond formula for (a) hydrazine (N_2H_4), (b) nitric acid (HNO_3), and (c) sulfuric acid (H_2SO_4).
4. Write an equation for the reaction between (a) sulfuric acid and sodium hydroxide solution, and (b) calcium carbonate and hydrochloric acid.
5. Calculate the volume of 0.1000 M NaOH solution required to neutralize 25.00 ml of 0.0500 M H_2SO_4 solution.
6. Calculate the volume of carbon dioxide produced at STP when 10.0 g of calcium carbonate are treated with an excess of hydrochloric acid.
7. In the analysis of a solution containing hydrochloric acid and sodium chloride (Sect. 7.4), 25.00 ml was found to be equivalent to 30.00 ml of 0.1000 M sodium hydroxide solution and to give 0.7170 g of silver chloride. What are the concentrations of the two compounds?

   The relevant equations are:

   $$HCl(aq) + NaOH(aq) = NaCl(aq) + H_2O$$

   $$MCl(aq) + AgNO_3(aq) = (AgCl)\downarrow + MNO_3(aq) \ (M = H, Na)$$
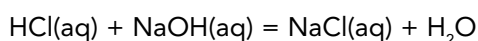
   The symbol Ag comes from the Latin word for silver (*argentum*). The molar mass of Ag atoms is 107.9 g/mol.

---

9   RELATIONS AMONG ELEMENTS

9.1   FAMILIES OF ELEMENTS

Some elements are very similar to each other. We have already seen this in the case of sodium and potassium (Sect. 4.2). This similarity extends to four other elements (lithium, rubidium, caesium, and francium). Together these six elements constitute a family called the "alkali metals".

There are several families of elements. The main ones are as follows (elements in order of atomic mass; those described in earlier chapters in bold):

Alkali metals: lithium, **sodium**, **potassium**, rubidium, caesium, and francium.
Alkaline earth metals: magnesium, **calcium**, strontium, barium, and radium.
Halogens: fluorine, **chlorine**, bromine, iodine, and astatine.
Inactive gases: **helium**, neon, argon, krypton, xenon, and radon.

(In all four families, the last member is highly radioactive.)

The name "halogen" means "salt-former" (Greek *hals*, "salt"). Fluorine is even more reactive than chlorine, bromine and iodine somewhat less so.

Chemists used to call the inactive gases "inert gases", but when they discovered that xenon reacts with fluorine (1962), they changed the name to "noble gases". A better description is "inactive gases". Radon is also better called "emanation" since "radon" was originally the name for one form of it.

9.2 PERIODICITY

A unifying principle of modern chemistry is the Periodic Table. This was developed by a number of chemists in the 19th century, culminating in the work of the Russian chemist, Dimitri Mendeleev (1869).
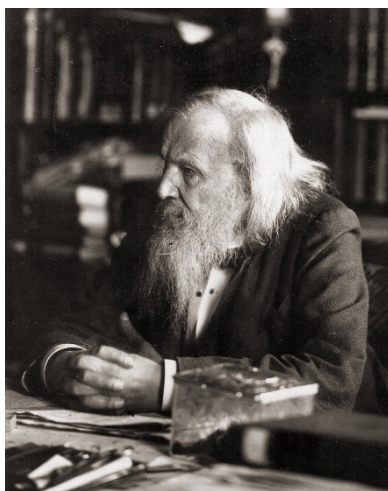
Mendeleev

The basis of the table is the following observation:

> **"If the elements are arranged in order of atomic mass, an approximate repetition of properties is observed, especially of valency."**

Mendeleev called this a law, but the fact that the repetitions are only approximate prevents us from going as far as this.

To see the periodicity, we will, for simplicity, confine our attention to the first 20 elements. Some of these we have met, others we have not. I briefly describe them all below, with atomic masses in brackets. Inactive gases are high-lighted.

Hydrogen, H (1.0 u): non-metal, valency = 1
Helium, He (4.0 u): inactive gas, valency = 0
Lithium, Li (6.9 u): alkali metal, valency = 1
Beryllium, Be (9.0 u): metal similar to aluminium but valency = 2
Boron, B (10.8 u): semi-metal similar to silicon but valency = 3
Carbon, C (12.0 u): non-metal, valency = 4
Nitrogen, N (14.0 u): non-metal, valencies = 3 and 5
Oxygen, O (16.0 u): non-metal, valency = 2
Fluorine, F (19.0 u): halogen, valency = 1
Neon, Ne (20.2 u): inactive gas, valency = 0
Sodium, Na (23.0 u): alkali metal, valency = 1
Magnesium, Mg (24.3 u): alkaline earth metal, valency = 2
Aluminium, Al (27.0 u): metal, valency = 3
Silicon, Si (28.1 u): semi-metal, valency = 4
Phosphorus, P (31.0 u): non-metal, valencies = 3 and 5
Sulfur (32.1 u): non-metal, valencies = 2, 4, and 6
Chlorine, Cl (35.5 u): halogen, main valency = 1; other valencies = 3, 5, and 7
Argon, Ar (39.9 u): inactive gas, valency = 0
Potassium, K (39.1 u): alkali metal, valency = 1
Calcium, Ca (40.1 u): alkaline earth metal, valency = 2

Notice that I have reversed the order of potassium and argon. This is to maintain periodicity. We shall see later that reversal is not necessary if we use another property of atoms instead of their mass. Notice also that chlorine has secondary valencies of 3, 5, and 7. These occur in the aqueous acids HOClO, HOClO$_2$, and HOClO$_3$ and their salts. The highest valency also occurs in the oxide, Cl$_2$O$_7$. This is a colourless, oily liquid, which slowly decomposes at room temperature and rapidly on heating.

Inspection of the above list reveals a considerable degree of periodicity. In the first place, the inactive gases recur with equal intervals between them (eight). The same is true of the alkali metals, alkaline earth metals (linking beryllium with these), and halogens (linking hydrogen with these). Further, members of these four families always occur together in the order halogen, inactive gas, alkali metal, and alkaline earth metal.

Linking beryllium with the alkaline earths and hydrogen with the halogens is justified on the basis of their nature (metallic or non-metallic) and valency. Like the halogens, hydrogen reacts with alkali and alkaline earth metals to form salts, e.g. sodium hydride, (NaH). Moreover, electrolysis of the molten lithium salt (mp 692 ºC) gives hydrogen at the positive electrode, like chlorine in the electrolysis of molten sodium chloride (Chap. 4). (Hydrogen is, of course, formed at the negative electrode in the electrolysis of water.)

The most striking feature of the above chart is the periodicity in valency. Let us redraw the chart with repetitions displayed vertically. The numbers are valencies.

| | | | | | | | H | He |
							1	0
Li	Be	B	C	N	O	F	Ne
1	2	3	4	3, 5	2	1	0
Na	Mg	Al	Si	P	S	Cl	Ar
1	2	3	4	3, 5	2, 4, 6	1, 3, 5, 7	0
K	Ca						
1	2						

Apart from extra valencies for sulfur and chlorine, the valencies are the same in every column.

In this chart, the first period is short (just two elements), but the next two have eight members. These periods display further regularities in valency. Within them, the lowest valency increases in single steps to four and then drops back in single steps to zero. In the third period, the highest valency increases in single steps to seven before dropping back to zero.

This chart forms the basis of the Periodic Table. Extending it to heavier elements introduces complications full discussion of which is beyond the scope of this book. The intervals to the next inactive gas are 18, 18, 32, and 32 elements. This lengthening has to be accommodated in the table. Chemists do this in various ways, leading to different tables. One is reproduced on the next page.

This table shows (in blue) the series of elements that increase the lengths of the periods by ten ("transition elements") and 14 ("inner transition elements"). It also shows two kinds of connection between elements – principal (solid lines) and secondary (broken lines). The former are the main connections between elements in one period and the next as in the chart above. The latter are weaker and include:

- a link between hydrogen and the alkali metals on the basis of their valency of one and formation at the negative electrode in electrolysis as hydrogen is in the electrolysis of water (Chap. 4);
- a link between copper and sodium on the basis of their valency of one (Table 8.2);
- a link between zinc (Zn) and magnesium on the basis of their valency of two;
- a link between chromium (Cr) and sulfur on the basis of their highest valency of six;
- a link between manganese (Mn) and chlorine on the basis of their highest valency of seven.

Chromium and manganese are similar to iron, and form salts in which they have a valency of two or three. They do, however, form some compounds in a higher valency, including salts of the aqueous acids $(HO)_2CrO_2$ (yellow) and $HOMnO_3$ (deep purple), and the oxides (CrO_3) (dark-red crystals) and Mn_2O_7 (dark-red oil).

SO$_2$Cl$_2$
[chemistry-chemists.com]

CrO$_2$Cl$_2$
[Wikipedia]
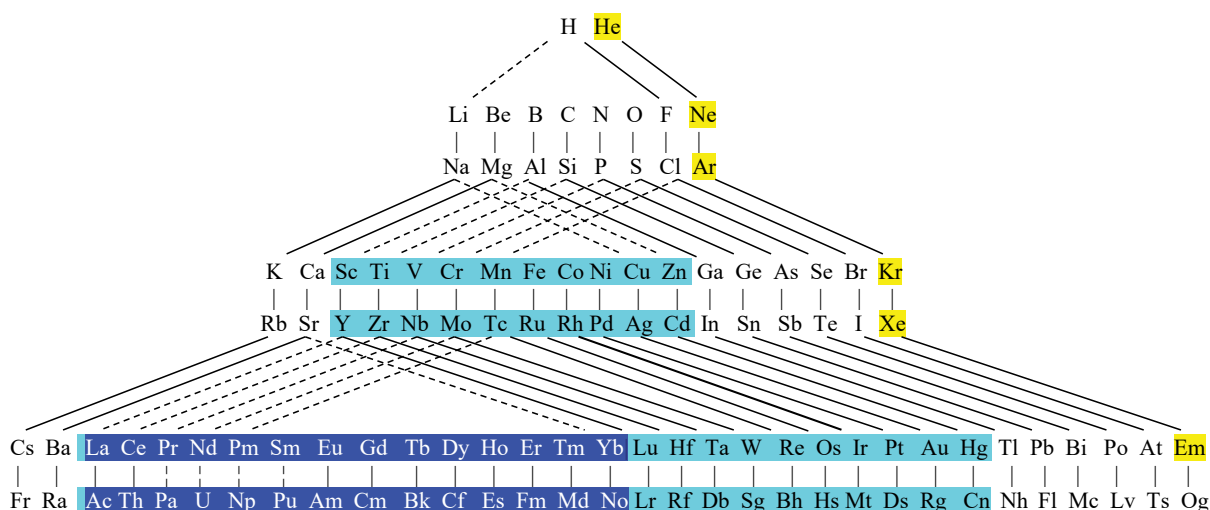
Table 9.1 Pyramidal form of Periodic Table

Solid lines: principal connections
Broken lines: secondary connections
Unshaded and shaded yellow: main-group elements
Yellow shading: inactive gases
*Light blue shading:* transition elements
Dark blue shading: inner transition elements

When Mendeleev drew up his first table, some elements were unknown. He left spaces for these, and predicted their properties from their position in the table. These predictions were remarkably verified when the elements were subsequently discovered (scandium in 1879, gallium in 1875, and germanium in 1886).

For a fuller discussion of the Periodic Table, see my book, *Introduction to Inorganic Chemistry*. This includes later developments following the discovery of the quantum theory. Note, however, that the Periodic Table was established without the quantum theory, as I have shown here.

9.3 ELECTROCHEMICAL SERIES AND ELECTRONEGATIVITY

Electrochemical cells are characterized by the voltage they generate – what physicists call the "electromotive force (emf)". For cells containing aqueous electrolytes, the emf varies with the concentration (c) of the electrolytes, temperature (θ), and, if gases are involved, pressure (p). If conditions are standardized (e.g. to $c = 1.0$ M, $\theta = 25$ °C, and $p = 1$ atm), we can therefore compare cells. Further, if we consider cells with a common electrode (e.g. the hydrogen electrode in acid), we can compare electrodes.
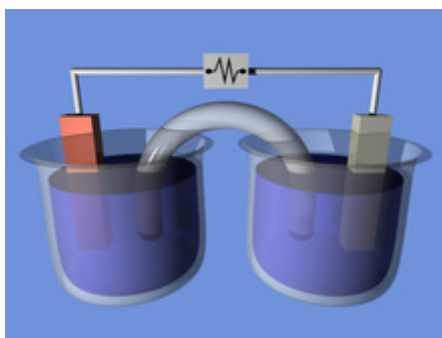
Cell for comparing electrodes. Each electrode dips into its own electrolyte solution, and the solutions are connected by a conducting bridge (a tube containing a jellified salt solution). Gaseous electrodes are jacketed.
[Wikipedia]

When this comparison is carried out, electrodes can be placed in a series according to how positive or negative they are in relation to the chosen standard. The result is called "the electrochemical series". The series for a selection of elements is as follows:

K Na Ca Al Fe H Cu S Cl O F

$\longleftarrow$ more negative   more positive $\longrightarrow$
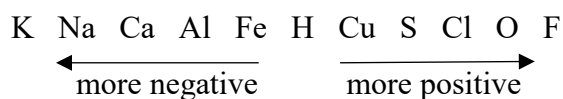
The conditions are those listed above. The order for metals at the beginning of the series is based on the potentials of cells containing molten chlorides. For these metals, aqueous cells are not possible because the metals react with water.

The electrochemical series is useful because many other properties correlate approximately with it (e.g. ease of extraction of metals).

Download free eBooks at bookboon.com

Electronegativity

When an electrode is immersed in an electrolyte solution, the electrode becomes charged and the solution acquires the opposite charge. The solution around a negative electrode thus becomes positive and around a positive electrode, negative. If we focus on the solution, therefore, the electrochemical series is the order of greater *electronegative* character. This is called "electronegativity".

$$\text{K \quad Na \quad Ca \quad \underline{Al \quad Fe \quad H \quad Cu} \quad S \quad Cl \quad O \quad F}$$
$$\xrightarrow{\text{electronegativity}}$$
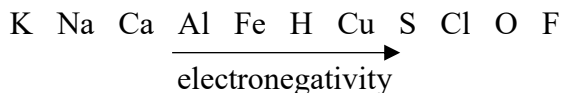
This series is widely used in assessing the polarity of bonds.

For a full discussion, including other measures of electronegativity that have been proposed, see *Introduction to Inorganic Chemistry*.

Problem

Suggest which element scandium (Sc) will be similar to and predict some of its properties. Scandium is in the fourth period.

---

10 MORE ON ELECTROLYTES

10.1 AIM

In previous chapters, we have noted how electrolytes have different properties from other substances. In this chapter, we will elucidate their constitution. This will prepare the way for us to consider the electrical properties of gases and the structures of atoms (Chap. 11).

10.2 ELECTROLYTE SOLUTIONS

In Section 6.3, we saw that molecular substances dissolve in other molecular substances, lowering their freezing point. In many cases, the lowering ($\Delta\theta$) is proportional, at low concentrations, to the fraction of solute molecules (x) in the solution [equation (6.2)]. This holds for solutions of nonelectrolytes in water, which give k_f (water) = 103.1 °C. For solutions of electrolytes, however, the picture is different.

Consider, for example, hydrochloric acid solutions. The freezing points of these at low concentrations are higher than the values given by equation (6.2) with k_f = 103.1 °C. This is if the values of x are calculated on the assumption that the solutions contain HCl molecules (call these values x_{HCl}). Thus if equation (6.2) is used to calculate the number of solute particles in the solution from the observed values of $\Delta\theta$ and k_f = 103.1 °C, the values obtained (call them x_f) are greater than the values of x_{HCl}, as shown in Table 10.1. The limiting value of x_f/x_{HCl} at low concentrations is almost exactly two. This implies that there are actually two particles in the solution for every supposed HCl molecule.

x_{HCl} (†)	$\Delta\theta$	x_f	x_f/x_{HCl}
0.00002	0.00409 °C	0.0000396	1.98
0.00005	0.01016 °C	0.0000985	1.97
0.0001	0.02017 °C	0.0001956	1.96
0.0002	0.03998 °C	0.0003877	1.94

Table 10.1 Fraction of solute molecules in dilute hydrochloric acid solutions*
*Calculated from the data of Randall and Vanselow (1924).
†Values correspond to concentrations of 0.001−0.01 Av/l or M (Chap. 7).

Now what two particles can be derived from an HCl molecule in water? Whatever they are, they must be responsible for the electrical conductivity of hydrochloric acid solutions, as this increases with concentration. The particles must therefore be charged, and the only possibility is that they are charged hydrogen and chlorine atoms, combined in some way with H_2O molecules. Charged atoms are called "ions" (Greek *ion*, "going").

The charges (q) must be equal and opposite ($+|q|$ and $-|q|$) because the solutions are electrically neutral ($|q|$ is the value of q without the sign). Further, since, in a cell containing acid, a hydrogen electrode is negatively charged, the solution around it must be positive. Hydrogen ions must therefore carry a positive charge. We write the formula of these as $H^{+|q|}$ with the charge as a superscript. Hydrochloric acid solutions thus contain $H^{+|q|}$ and $Cl^{-|q|}$ ions, combined with H_2O molecules. Positively charged ions are called "cations" (this is because they move towards the negative electrode or cathode); negatively charged ions are likewise called "anions".

Similar conclusions can be reached for other electrolyte solutions, e.g. sodium and potassium chloride. Some, however, have freezing points implying the presence in the solution of a mixture of undissociated molecules and ions (compare Sect. 7.5). These include weak acids and many salts. For example, Tables 10.2 and 10.3 give the results for acetic acid and cupric sulfate solutions, showing how the degree of dissociation varies with concentration.

Concentration†	Degree of dissociation
0.001 M	10%
0.003 M	8%
0.01 M	5%

Table 10.2 Degree of dissociation of acetic acid molecules in aqueous solution*
*Calculated from the data of Hausrath (1902).
†Total (undissociated molecules plus dissociated).

Concentration†	Degree of dissociation
0.001 M	85%
0.01 M	50%
0.1 M	20%

Table 10.3 Degree of dissociation of $CuSO_4$ molecules in aqueous solution*
*Calculated from the data of Brown and Prue (1955).
†Total.

Note that the interactions between ions and water molecules must considerable. The energy required to dissociate a molecule like HCl into ions has to be more than made up by the energy of these interactions. When we write $H^{+|q|}$ and $Cl^{-|q|}$, we must remember that these are combined with water molecules. They should therefore be written $H^{+|q|}(aq)$ and $Cl^{-|q|}(aq)$ or $[H(OH_2)_x]^{+|q|}$, and $[Cl(H_2O)_y]^{-|q|}$. Structural studies suggest that $x = 4$ and $y = 6$.

10.3 IONIC CHARGES

The charges on ions can be determined from the basic relations of electrolysis and galvanism. These can be stated as follows:

Relation 1: "The mass of any substance produced or consumed at an electrode is generally proportional to the quantity of electricity passed."

Relation 2: "The masses of different substances produced or consumed by the same quantity of electricity are generally proportional to the masses of the atoms or groups of atoms of which they are composed, divided by their valencies."

These relations are based on Faraday's laws (1832, 1833). They cannot be called laws because they do not hold for mixed conductors (conductors that conduct electricity partly like a metal and partly like an electrolyte), e.g. silver sulfide (Ag_2S).

Relations 1 and 2 can be combined to give, for the mass of a substance produced or consumed at an electrode by the passage of a quantity of electricity (Q):

$$m(\text{substance}) = \frac{kQm(\text{particle})}{v} \qquad (10.1)$$

where m(particle) is the mass of the atom or group of atoms comprising the substance, v is its valency, and k is a constant.

Equation (10.1) enables the charge carried by each atom or radical to be calculated. This is given by:

$$|q| = \frac{Q}{N} \qquad (10.2)$$

where N is the number of atoms or groups of atoms produced or consumed at the electrode. Since this number is given by m(substance)/m(particle) [equation (7.2)], equation (10.1) gives:

$$N = \frac{kQ}{v} \qquad (10.3)$$

From this and equation (10.2),

$$|q| = \frac{v}{k} = ve \qquad (10.4)$$

The constant e is called the "elementary charge". The ions in hydrochloric acid solutions are thus H^{+e} and Cl^{-e}. These are written H^+ and Cl^-. Ions carrying a multiple of this charge are written as in Ca^{2+}.

The value of e can be determined from experimental data by using equation (10.1) with $k = 1/e$:

$$e = \frac{Qm(\text{particle})}{vm(\text{substance})} \qquad (10.5)$$

This determination can be done without knowing the absolute value of m(particle), by measuring this in atomic mass units, u (Section 6.2). The value of e is then 96500 C u/g. To obtain the absolute value, we need the value of g/u (the Avogadro number). We saw in Section 6.4 that this is 6.022×10^{23}. This gives $e = 1.602 \times 10^{-19}$ C.

Treatment in terms of chemical amount

In equation (10.3) above, we can substitute $n = N/L$ [equation (7.5)]. This gives:

$$n = \frac{kQ}{Lv} = \frac{Q}{Lev} = \frac{Q}{Fv} \qquad (10.6)$$

Here F (= Le) is called the "Faraday constant", and takes the value 96500 C/mol. This equation can be used to calculate the chemical amount of a substance produced or consumed when a quantity of electricity (Q) passes through a cell.

10.4 SOLID ELECTROLYTES

Like hydrochloric acid solutions, sodium chloride solutions, at low concentrations, are completely dissociated into $Na^+(aq)$ and $Cl^-(aq)$ ions. Does this mean that solid sodium chloride (which is anhydrous) comprises Na^+ and Cl^- ions? Certainly, it has a structure that is consistent with this (each sodium atom is surrounded by six chlorine atoms and each chlorine atom by six sodium atoms). Further, molten sodium chloride conducts electricity electrolytically. But we know that interactions between opposite charges are strong, and so do not know how much these distort the ions in the solid.

Distortions are likely to be greater the higher the charges.

10.5 IMPORTANT IONS

Table 10.4 lists the ions formed by atoms and groups of atoms of the elements described in Chapter 4. The charges on these are determined by their valencies [equation (10.4)]. The latter are from Table 8.2.

| Atom	Ion	Group	Ion
H	H^+	NH_4	$[NH_4]^+$
Na	Na^+	OH	$[OH]^-$
K	K^+	NO_3	$[NO_3]^-$
Ca	Ca^{2+}	CO_3	$[CO_3]^{2-}$
Al	Al^{3+}	SO_4	$[SO_4]^{2-}$
Cu	Cu^+, Cu^{2+}	PO_4	$[PO_4]^{3-}$
Fe	Fe^{2+}, Fe^{3+}		
Cl	Cl^-		
O	(O^{2-})*		
S	S^{2-}		

Table 10.4 Important ions
*Inferred in metal oxides; reacts with water to give $[OH]^-$.

10.6 REACTIONS INVOLVING ELECTROLYTES

A typical reaction involving electrolytes is that between an acid and an alkali to give a salt plus water. Consider, for example, the reaction between hydrochloric acid (solution 1) and aqueous sodium hydroxide (solution 2):

$$HCl(aq_1) + NaOH(aq_2) \rightarrow NaCl(aq_{1+2}) + H_2O \tag{10.7}$$
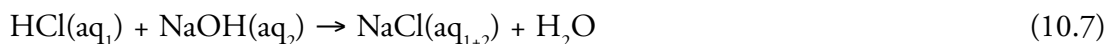
Knowing that HCl, NaOH, and NaCl are completely dissociated in solution, we can write:

$$(H^+ + Cl^-)(aq_1) + (Na^+ + OH^-)(aq_2) \rightarrow (Na^+ + Cl^-)(aq_{1+2}) + H_2O \tag{10.8}$$
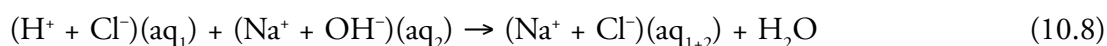
The process thus involves dilution of $Cl^-(aq_1)$ and $Na^+(aq_2)$ and the reaction:

$$H^+(aq_1) + OH^-(aq_2) \rightarrow H_2O \tag{10.9}$$

This same equation applies to any reaction between an acid and an alkali if they are completely dissociated.

The numbers in this equation indicate that the reaction involves the mixing of two solutions. Chemists usually omit these and write:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O \tag{10.10}$$

However, this creates confusion with reactions taking place within a solution, and is best avoided by beginners. Use rather equation (10.9).

Writing equations for reactions involving substances that are incompletely dissociated in solution is more difficult. A general rule is to write equations in terms of whatever predominates, the undissociated molecules or the ions. However, this is not always followed.

Problem

Write an equation for the reaction in aqueous solution between (a) sulfuric acid and sodium hydroxide, (b) acetic acid and sodium hydroxide, and (c) cupric sulfate and sodium hydroxide (these give a blue precipitate of cupric hydroxide).

---

11 STRUCTURES OF ATOMS

11.1 SCOPE

In this chapter, we briefly survey experiments that lead to the structures of atoms, starting with the electrical properties of gases.

11.2 ELECTRICAL PROPERTIES OF GASES AND THE ELECTRON

A suitable apparatus for studying what happens when electricity is passed through a gas is a glass tube with electrodes sealed in at both ends and a side tube through which gas can be pumped out or introduced. When there is a moderately low pressure in the tube, the gas in the tube glows, the colour of which is characteristic of the gas. Discharge through hydrogen, for example, is mauve. If the negative electrode (cathode) is perforated, rays of the same colour emerge through the holes ("canal rays"). At lower pressures, the tube becomes dark, and if there is a hole in the anode (the positive electrode), the glass at the anode end of the tube glows, as if rays are being emitted from the cathode and pass through the hole. These are called "cathode rays".
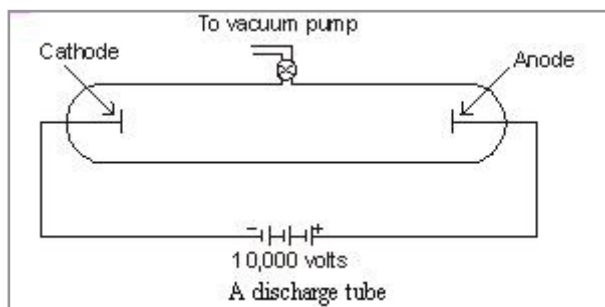
Apparatus for studying the passage of electricity through a gas
[Shiksha Services]
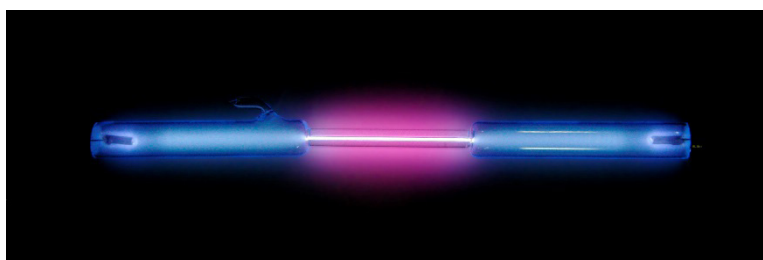
Hydrogen discharge
[Wikimedia Commons]

The nature of the two kinds of ray can be established by passing them through an electric field produced by oppositely charged plates. Canal rays are deflected towards the negative plate and are positively charged; cathode rays are deflected towards the positive plate and are negatively charged.

If the rays comprise charged particles, there are several ways of determining the ratio of the mass (m) to the charge (q) of these particles. A simple one is to pass the rays through a uniform electric field (E), measure the radius (r) of the circular path they take, then use a uniform magnetic field (B) at right angles to the electric field to annul the deflection of the rays. Under the first conditions, the electric force on each particle (Eq) is equal to the particle's rate of change of momentum (mv^2/r); under the second, the electric force is balanced by the magnetic force (Bvq). From these relations

$$\frac{m}{q} = \frac{B^2 r}{E} \qquad\qquad (11.1)$$

Values of m/q for cathode rays are the same for all gases, whereas those for the positive rays depend on the gas. This suggests that the particles in cathode rays are a common component of all substances (Thomson 1897).

Some values of m/q are given in Table 11.1, and compared with the value for hydrogen ions in electrolyte solutions. For the latter, $q = +e = +96500$ C u/g (Sect. 10.3) and $m \approx m(\text{H atom}) = 1.0079$ u (Sect. 6.2), the mass being approximate for reasons that will become apparent.

Ray	m/q	Particle identity	m
Hydrogen ions in electrolysis	$\approx 1.044 \times 10^{-5}$ g/C	$H^+(aq)$	1.007* u
Cathode rays in various gases	-5.69×10^{-9} g/C	e^-	5.49×10^{-4} u
Positive rays in hydrogen	1.044×10^{-5} g/C	H^+	1.007 u
	2.088×10^{-5} g/C	H_2^+	2.015 u

Table 11.1 Values of m/q for some electric rays
*Corrected for mass of electron removed.

In Table 11.1, the value of m/q for cathode rays is only a small fraction (1/1835) of the value for H^+ ions in electrolyte solutions, whereas the value for one of the positive rays from hydrogen is almost exactly the same. This suggests that the latter comprise free H^+ ions, and the former a relatively light particle of charge $-e$, a charge confirmed by other methods. This particle is called the "electron" (designated e^-). The value of m/q for the second positive ray in hydrogen suggests that this comprises H_2^+ ions.

Substitution of $q = +e$ or $-e$ gives the values of m in the table. The value for $H^+(aq)$ has been corrected for the removed electron.

11.3 ISOTOPES

As we noted in Chapter 6, the atoms of many elements vary in mass. This is illustrated in Table 11.2, which lists the values of m/q for positive rays in neon. These show that ordinary neon comprises three kinds of atom with approximate masses of 20, 21, and 22 u. These approximate masses (masses in u rounded to a whole number) are indicated by superscripts to the left of the symbol (^{20}Ne, ^{21}Ne, and ^{22}Ne). They are called "mass numbers" (A), the full significance of which we will see in Section 11.8. There are two sets of rays, a stronger set corresponding to Ne^+ ions and a weaker set to Ne^{2+}. The intensities within each set are respectively 90.5%, 0.3%, and 9.2% of the total, from which the mean atomic mass is 20.18 u. This is the same value as that given by the density of the gas (Chap. 6).
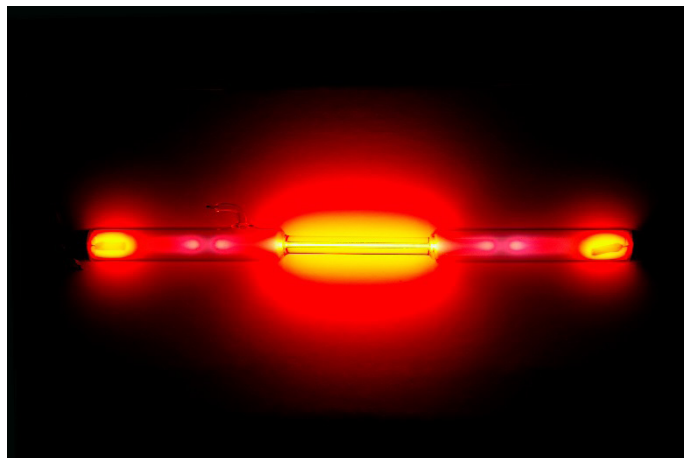
Neon discharge
[Wikipedia]

m/q	Particle identity	Mass of atom*
10.36×10^{-5} g/C	$^{20}Ne^{2+}$	19.99 u
10.88×10^{-5} g/C	$^{21}Ne^{2+}$	20.99 u
11.40×10^{-5} g/C	$^{22}Ne^{2+}$	21.99 u
20.72×10^{-5} g/C	$^{20}Ne^{+}$	19.99 u
21.76×10^{-5} g/C	$^{21}Ne^{+}$	20.99 u
22.79×10^{-5} g/C	$^{22}Ne^{+}$	21.99 u

Table 11.2 Values of m/q for positive rays in neon
*Mass of ion plus mass of electron or electrons removed.

Atoms differing in mass are called "isotopes" (Greek *isos* "equal", *topos* "place" [in Periodic Table]). They differ slightly in physical properties. The differences are most pronounced for the isotopes of hydrogen.

Isotopes of hydrogen

Hydrogen has three isotopes, with mass numbers of one (^{1}H), two (^{2}H), and (^{3}H). They are called respectively "protium", "deuterium" (D), and "tritium" (T) after the Greek for "first", "second", and "third". Ordinary hydrogen comprises 99.985% of protium and 0.015% of deuterium, too little to affect our discussion of Table 11.1 (tritium is radioactive and only occurs in traces). Deuterium can be separated from protium by repeated electrolysis of water, the heavier isotope accumulating in the residue. Ordinary water freezes at 0.0 ºC and boils at 100.0 ºC; "heavy" water (D_2O) freezes at 3.8 ºC and boils at 101.4 ºC. The ions $^{1}H^{+}$, D^{+}, and T^{+} are called a "proton" (p), "deuteron" (d), and "triton" (t) respectively.

Unit of mass

The modern definition of the unit of atomic mass can now be given (cf. Sect. 6.2). It is:

$$u = \frac{m(^{12}C)}{12}$$

Carbon-12 is 98.9% of natural carbon. Defining u in terms of one isotope allows accurate atomic masses to be determined.

11.4 THE NUCLEUS AND ATOMIC STRUCTURE

We have established that electrons are a component of all substances. This means that atoms contain electrons. For electrical neutrality, they must also contain positive charges. How these charges are distributed can be deciphered from the scattering of electric rays by metal targets (Rutherford 1911).

Suitable rays are those from radioactive substances ("α-rays" or "β-rays"). Values of m/q for these rays enable the particles in them to be identified as $^4He^{2+}$ ions and electrons respectively (Table 11.3). When these particles strike a metal target, while most pass through with little scattering, some are scattered back towards the source. This suggests that the positive charges in atoms are concentrated in a relatively small volume. This is called the "nucleus". An atom may accordingly be pictured as a positively charged nucleus with negatively charged electrons surrounding it.
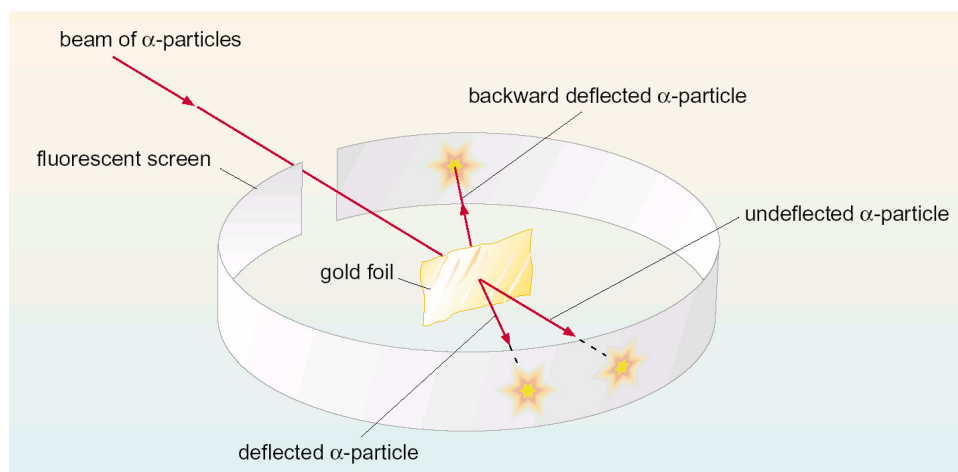
Rutherford's experiment
[David Johnson]

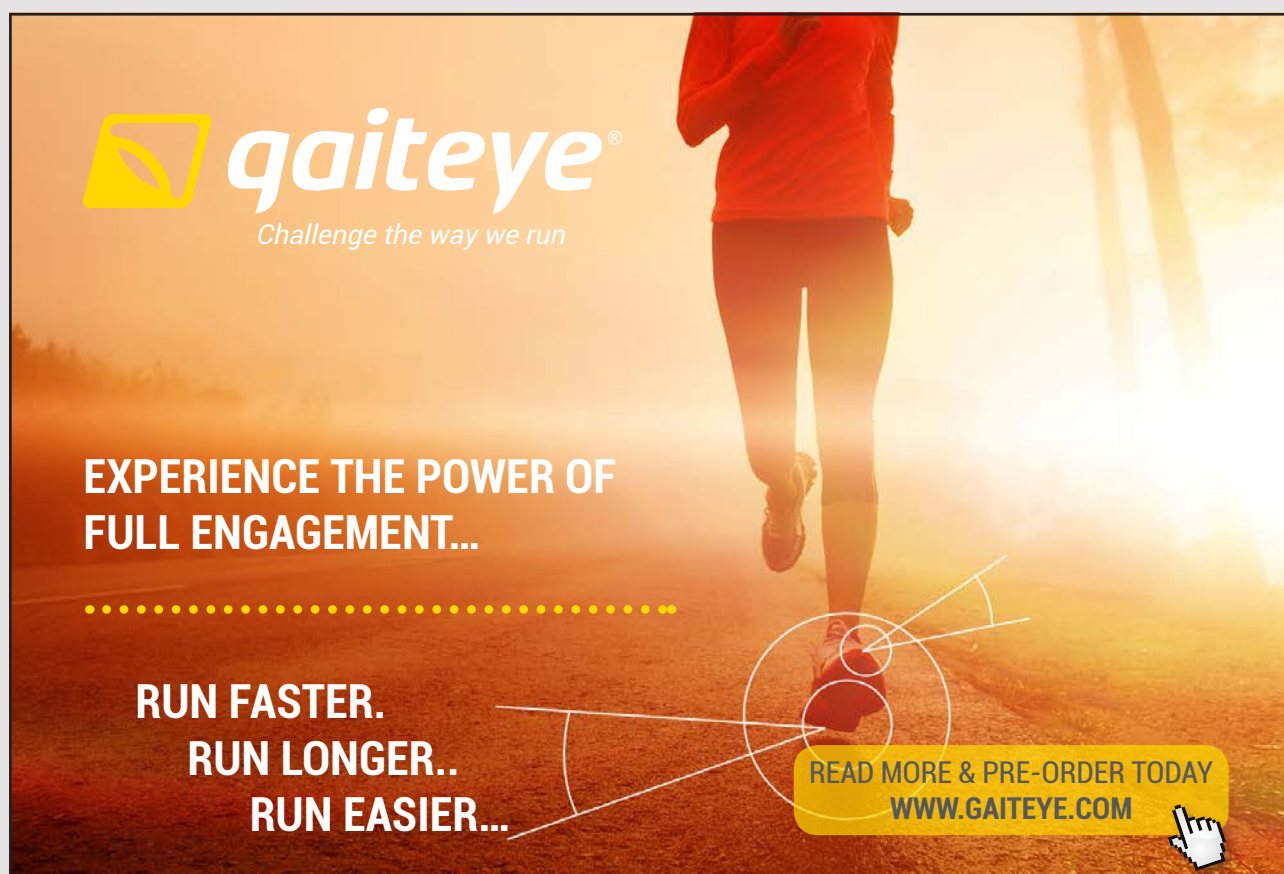| Ray	m/q	Particle identity	m
Positive rays in helium	2.074×10^{-5} g/C	$^4He^{2+}$	4.002 u
	4.148×10^{-5} g/C	$^4He^+$	4.002 u
α-rays	2.074×10^{-5} g/C	$^4He^{2+}$ (inferred)	4.002 u
β-rays	-5.7×10^{-9} g/C	e^-	5.5×10^{-4} u

Table 11.3 Values of m/q for α- and β-rays compared with those for positive rays in helium*
*This comparison because α-rays generate helium from impacts with their surroundings.
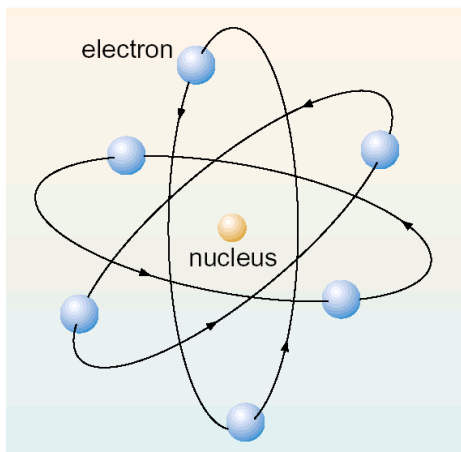
Rutherford's model of atom
[David Johnson]

From the fraction of α- or β-particles scattered through known angles by metal foils, nuclear charges (q_n) can be calculated. Values obtained in this way (Table 11.4) support the proposition that q_n/e is equal to atomic number (Z), the ordinal number of an element in a chemically derived Periodic Table and a number correlating with the frequencies of lines in the X-ray spectra of atoms (Moseley 1913−14). An atom thus has Z electrons.

Element	q_n/e	Atomic number
Copper	29.3 ± 0.5	29
Silver	46.3 ± 1.0	47
Platinum	77.4 ± 1.0	78

Table 11.4 Nuclear charges determined by scattering of α-particles compared with atomic number*
*Chadwick (1920)

11.5 CONFIGURATIONS OF ELECTRONS IN ATOMS

How are the electrons in an atom distributed round the nucleus?

A big clue is provided by the periodicity in valency (Sect. 9.2). This suggests the following simple model for main-group atoms (after Lewis 1916).
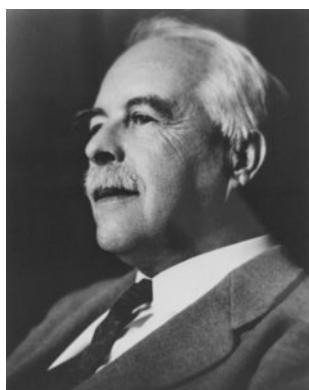
Gilbert N. Lewis

1. Electrons in an atom are in shells, with the outer electrons responsible for valency. Inner electrons and the nucleus constitute a "core".
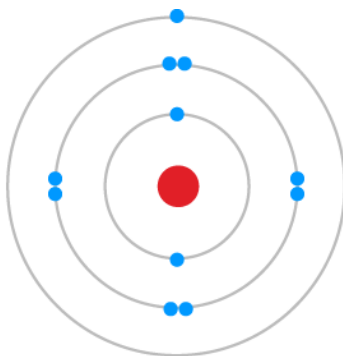
Shell structure of sodium atom pictured in two dimensions; there is one outer electron
[BBC]

2. For hydrogen and helium, the capacity of the valence shell is two. For other main-group elements, it is eight (Table 11.5).

Atoms	Capacity of valence shell	Number of valence electrons
Hydrogen	2	1
Helium	2	2
Lithium group	8	1
Beryllium group	8	2
Boron group	8	3
Carbon group	8	4
Nitrogen group	8	5
Oxygen group	8	6
Fluorine group	8	7
Neon group	8	8

Table 11.5 Valence shells of main-group atoms

3. Atoms of the inactive gases have full shells.
4. Atoms seek to acquire a full shell of electrons in combination with other atoms.
5. Atoms with a small number of valence electrons (metal atoms) lose these electrons to form cations. For example, sodium atoms with one valence electron lose this electron to form Na^+ ions; these have the same configuration as neon. This can be represented as

$$\textbf{Na·} \rightarrow \textbf{Na}^+$$
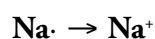
where the dot represents the valence electron and the bold symbols the core. In practice, ordinary symbols are usually used, giving these a double meaning:

$$Na· \rightarrow Na^+$$
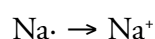
6. Atoms needing a small number of electrons to complete their valence shell (non-metal atoms) acquire these electrons to form anions. For example, chlorine atoms with one electron short of a full shell gain one electron to form Cl^- ions; these have the same configuration as argon. This can be represented as

$$:\overset{..}{\underset{..}{Cl}}\cdot \rightarrow \left[:\overset{..}{\underset{..}{Cl}}:\right]^-$$
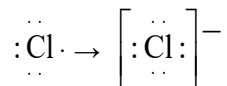
7. Atoms also share electrons to acquire a full shell. For example, a hydrogen atom, one electron short of a full shell, combines with another hydrogen atom by sharing their electrons so that they both achieve a full shell. This is represented by

H : H

Comparison with the bond formula for H_2 (H—H, Sect. 8.4) shows that the shared pair of electrons forms a single bond.

Similarly, a chlorine atom combines with another chlorine atom by sharing one electron and likewise with a hydrogen atom:

$$: \overset{..}{\underset{..}{Cl}} : \overset{..}{\underset{..}{Cl}} : \qquad\qquad\qquad\qquad H \; : \overset{..}{\underset{..}{Cl}} :$$
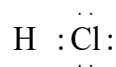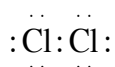
In the second formula, the bonding pair is drawn nearer to the atom that attracts it more strongly (Cl) as reflected in the electrochemical series (Sect. 9.3).

This model can be extended to include transition and inner-transition elements, and is widely used in chemistry. For further details, see *Introduction to Inorganic Chemistry*.

Metals

Metals may be pictured as cations (postulate 5) bound together by electrons moving freely among them. This explains why valency does not apply to intermetallic compounds (Sect. 8.4). It also answers the question of whether the charge carriers in metal wires are positive or negative (Box 2.1).

11.6 QUANTUM THEORY

There is an obvious problem with Lewis's model. According to classical physics, opposite charges attract each other with a force that increases as the distance between them gets smaller (Coulomb's law). The electrons in an atom would therefore be expected to collapse on to the nucleus. Lewis suggested that Coulomb's law breaks down on an atomic scale, but the modern view is that it is the laws of motion that break down. Motion on this scale is now described by the quantum theory, a theory developed by physicists in the early decades of the 20th century. According to this theory, electrons in an atom can be in motion without collapsing on to the nucleus, but their motion is limited to certain energies, and can only be described in terms of the probability of finding electrons at different points in space. The calculated distributions of probability, however, largely support Lewis's model. For details, see textbooks on the quantum theory.

11.7 RADIOCHEMISTRY

As we saw in Chapter 2, uranium is radioactive. It comprises two main isotopes, ^{235}U (0.7%) and ^{238}U (99.3%). These are both radioactive, but ^{235}U much more so. This is separated from ^{238}U and used to generate energy.

Both isotopes emit α-radiation. When they do they change into radioactive isotopes of the element thorium (Th). This can be shown by adding a reagent to a solution of a uranium salt that precipitates thorium but not uranium. A slight radioactive precipitate is formed. When this is filtered off, more precipitate is slowly formed.

Uranium
[Wikipedia]

Thorium
[Ru Wikipedia]

You will find both elements near the beginning of the last row of the Periodic Table in Chapter 9. Thorium is two places to the left of uranium. Their atomic numbers are 90 (Th) and 92 (U). The isotopes produced are respectively ^{231}Th and ^{234}Th. What is happening is that the nuclei of the uranium atoms are losing two units of positive charge and four units of mass. These are coming off as α particles (^{4}He^{2+}).

Isotopes of other elements that emit α-rays behave in the same way. They change into the element with two fewer units of nuclear charge and the isotope with four fewer units of mass number:

$$^{A}_{Z}X \rightarrow \ ^{A-4}_{Z-2}Y + \ ^{4}_{2}He$$
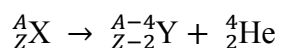
Here the symbols X, Y, and He represent nuclei; the nuclear charges (subscripts) and mass numbers (superscripts) both balance. Isotopes of elements that emit β-rays, on the other hand, change into the element with one more unit of nuclear charge (the next element in the Periodic Table) and the isotope with the same mass number:

$$^A_Z X \rightarrow \ ^A_{Z+1} Z + \ ^0_{-1} e$$
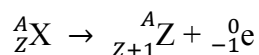
In both cases, the rays evidently come from the nucleus; β-rays do not come from the outer electrons.

Study of these phenomena forms a separate branch of chemistry called "radiochemistry".

11.8 STRUCTURE OF THE NUCLEUS

The composition of the nucleus of an atom can be inferred on the basis of the following considerations.

First, the nuclear charge of all the elements is a multiple Z of the charge on a proton. This suggests that the nucleus of an atom contains Z protons.
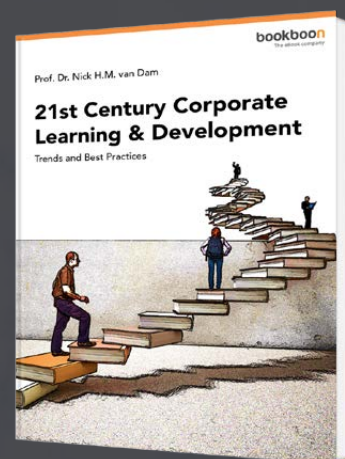
Second, the mass number of all the isotopes of the elements are multiples A of the mass number of a proton. This suggests that the nucleus of an isotope contains $(A - Z)$ neutral particles with a similar mass to the proton.

The second suggestion is supported by the discovery of the "neutron" (n) by Chadwick in 1932. It raises the question of how nuclei, composed of protons and neutrons, can emit β-particles (electrons). The answer is by a neutron changing into a proton and an electron, a process that has been confirmed by experiments.

We are now in a position to give a more precise definition of mass number (Sect. 11.3). It is the total number of particles (protons plus neutrons) in the nucleus of an atom.

The study of nuclei, including how the particles in them are held together, is a branch of physics ("nuclear physics").

Problems

1. Write a structure of the kind suggested by Lewis for (a) H_2O, (b) CO_2, (c) C_2H_2, and (d) N_2.
2. What are the compositions of the nuclei of (a) isotopes of hydrogen, (b) isotopes of neon?

12 FURTHER STUDY

This book is an introduction to chemistry. From this point, the subject branches out in several directions. The traditional divisions are into inorganic, organic, analytical, and physical chemistry. To these can be added biochemistry, geochemistry, radiochemistry, theoretical chemistry and solid-state chemistry. Some chemists add applied chemistry, but this properly comes under the other branches.

There are introductions to these various branches of chemistry available on the internet and in bookshops. These include my own e-book, *Introduction to Inorganic Chemistry*. Many colleges and universities provide advanced courses in chemistry that include practical work and the development of laboratory skills.

In the laboratory
[Science & Belief]

ANSWERS TO PROBLEMS

Chapter 5

    a) 42.86% carbon, 57.14% oxygen
    b) 27.28% carbon, 72.72% oxygen

Chapter 6

a) CH_3

b) C_2H_6 [Equation (6.1) gives ≈30.4 u. This is approximately equal to twice the mass of CH_3 (30.1 u).]

Chapter 7

1. (a) (C) + O_2 = CO_2

   (b) 2CO + O_2 = $2CO_2$

2. 18.3 g

3. 2.95 g

4. 0.34 M
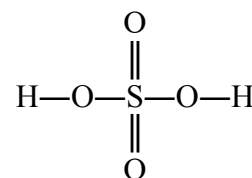
Chapter 8

1. (a) (ZnO), (b) $(ZnCl_2)$*, (c) $(Zn(OH)_2)$, (d) $(ZnCO_3)$, (e) $(ZnSO_4)$*, (f) $(Zn(NO_3)_2)$*. [*Anhydrous form; crystallizes from water as a hydrate.]

2. (a) H—Br, (b) Br—Cl, (c) (NaBr), (d) (KBr), (e) $(CaBr_2)$*, (f) $(FeBr_2)$* and $(FeBr_3)$*. [*As under 1.]

3.
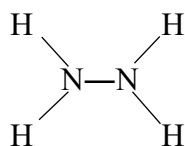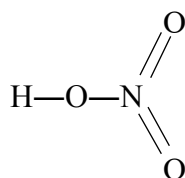
(a)   (b)   (c)

4. (a) $H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O$
   (b) $CaCO_3 + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2\uparrow + H_2O$

5. 25.0 ml

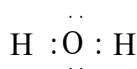6. 2.24 l

7. HCl(aq), 0.120 M; NaCl(aq), 0.080 M

Chapter 9

Aluminium. Mendeleev successfully predicted the existence and properties of scandium before it was discovered by Nilson in 1879.
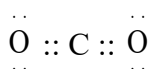
Chapter 10

a) $H^+(aq_1) + OH^-(aq_2) \rightarrow H_2O$
b) $CH_3CO_2H(aq_1) + OH^-(aq_2) \rightarrow CH_3CO_2^-(aq_{1+2}) + H_2O$
c) $Cu^{2+}(aq_1) + 2OH^-(aq_2) \rightarrow (Cu(OH)_2)\downarrow$

Chapter 11

1.
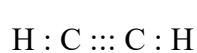
(a)   (b)   (c)   (d)

2. (a) $^1H = p$, $^2H = p + n$, $^3H = p + 2n$;
   (b) $^{20}Ne = 10p + 10n$, $^{21}Ne = 10p + 11n$, $^{22}Ne = 10p + 12n$.