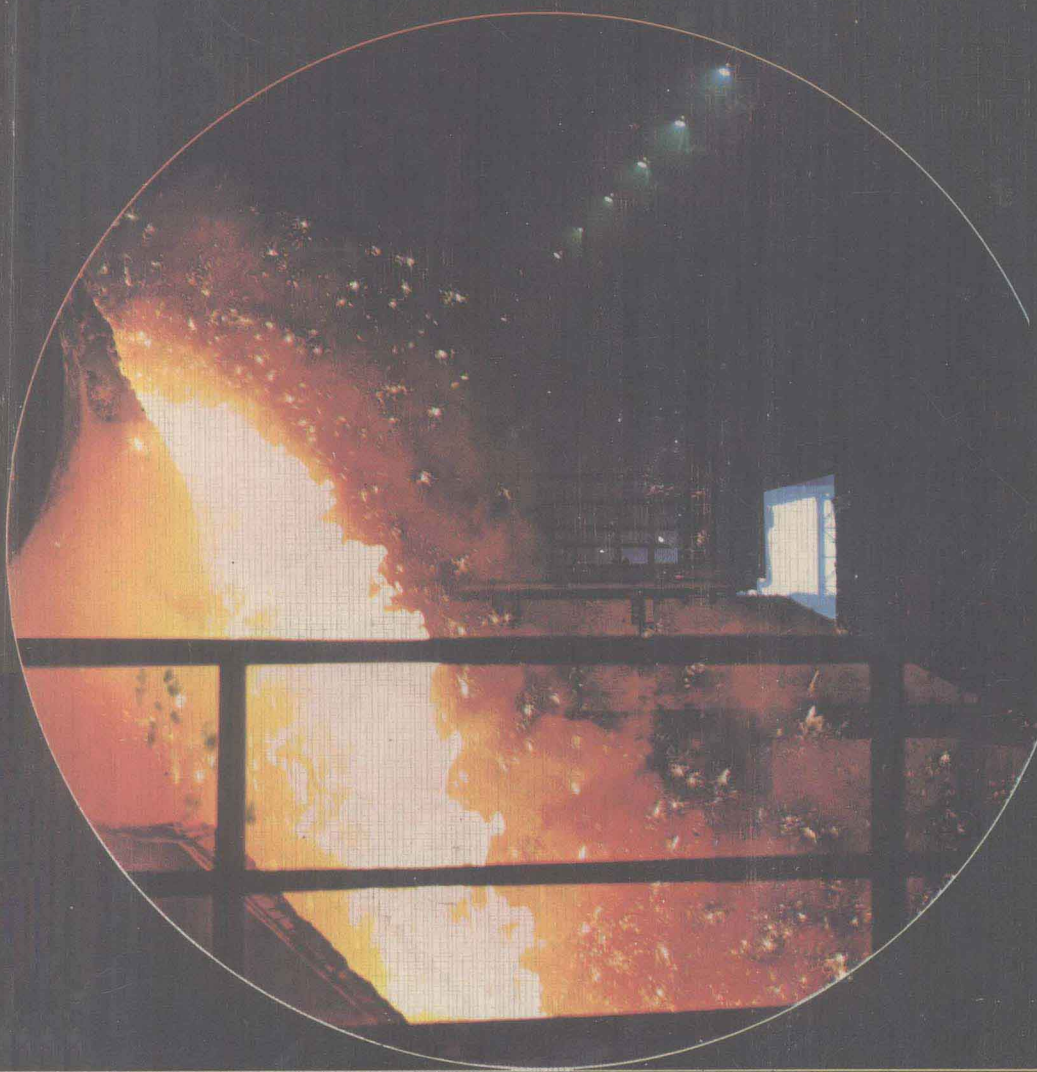# Chemistry

Fifth Edition

D.N. Underwood and D.E. Webster

Chemistry

Fifth Edition of *Chemistry for Colleges and Schools*

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NOTE

1.   Both the words 'inflammable' and 'flammable' mean 'easily set on fire', and their opposite is 'nonflammable'. However, 'flammable' is preferred to 'inflammable' as the latter is often wrongly taken to mean 'nonflammable'.

2.   In order to avoid difficulties arising out of the use of 1 as the symbol for the litre, dm^3 is now increasingly used in place of 1 or litre.

3.   Following the new nomenclature, for the term 'ammonium hydroxide', please read 'aqueous ammonia'.

Introduction to the Fourth Edition

This book is intended for use during the last two or three years of an Ordinary Level Chemistry course and covers the syllabus requirements of the important examining bodies. The theoretical principles are discussed in the earlier chapters followed by a detailed description of the elements and compounds required for the O-Level examination. A final chapter "Chemistry and Society" has been added to give readers a glimpse of the relationship between the chemistry dealt with in the earlier chapters and other areas of human activity. A considerable number of experiments is given throughout, but this book is not intended to provide a systematic practical course.

The first edition of this book was written by one of us (D.N.U.) in 1959, and with modifications was published as a second and a third edition. Continuing changes in the chemistry syllabus have necessitated a further edition, and we decided that the time had come for an almost complete rewriting of the book. Those familiar with the old editions will, therefore, find many changes. These we hope are all improvements.

We have written this book fully aware of the ASE booklet "Chemical Nomenclature, Symbols and Terminology for use in School Science", and related publications by the examining boards. It is evident that although there are many topics therein where there is agreement as to the "best" practice, there are several areas where agreement has not been reached and where no "best" system is to be found. It must also be recognized that the authors of a text-book face a further dilemma. This is that the requirements of a student during the months immediately prior to his or her examination at 16, may be too complex and quite unnecessary when the book is first used some 3 years earlier.

Some of the features of the book are worthy of comment here.

(*a*) We have treated the periodic table more fully than in most O-level text books (and in previous editions of this book). Considerable emphasis is placed on comparative chemistry throughout the text. We hope that readers will find enjoyable the exercises that we have designed to familiarize them with this most important method of chemical classification.

(*b*) The mole is the basis of the quantitative features of this book.

(*c*) For simplicity we have throughout used H^+ for the proton, even in aqueous solution.

(*d*) For the five solid lattices sodium chloride, caesium chloride, ice, diamond and graphite we have used stereoscopic pairs of computer drawn pictures. We hope that readers will find these both interesting and instructional.

(*e*) A large selection of questions is included at the end of each chapter and numerical answers are given at the end of the book.

(f) The final chapter "Chemistry and Society" includes material that is not in most O-level syllabuses. It has not been included to cover the London O-level syllabus of the same name, although readers will find that this book does cover a large part of that syllabus.

(g) We have tried to face up to the problems of nomenclature, symbols and terminology and throughout the reader will find that we have acted as indicated in (1), (2), and (3) below.

1. I.U.P.A.C. (International Union of Pure and Applied Chemistry) nomenclature has been used but other common names for organic compounds are often given in brackets. However, we have (a) not given the oxidation state of inorganic ions where only one such oxidation state exists, e.g. we use sodium and calcium and not sodium(I) and calcium(II), (b) not given the oxidation state of non-metals in common anions and (c) retained the names nitrite and sulphite.

2. We have given the chemical equations in pairs where this is appropriate. This is usually when considering reactions in water. Of these pairs of equations the top one is the simplest form and suitable for use in the early years with the book. The bottom equation is in its ionic form, omits spectator ions (ions that do not participate in the reaction) and includes the state symbols (s), (1), (g) or (aq) for solid, liquid, gas or aqueous solution. These should be useful in later years of the course. It is also educationally valuable to have the two equations together, as the reader can compare them and see whether or not the second conveys more information than the first.

3. In the formulae of ions we never put superscripts for charges immediately above subscripts for the number of atoms. Nor have we, as a general rule, written the formulae of inorganic solids in an ionic form, as these imply, sometimes incorrectly, the nature of the particles (atoms or ions) present in a solid.

We realize that in this area of nomenclature and terminology whatever choice is made will find its critics. But it is our hope that the approach that we have adopted is both rational and *useful* to the 13 to 16 year old pupil and his teacher.

A further noticeable change, in this from previous editions, is the inclusion of a large number of relevant photographs. We wish to express our thanks to the many firms and institutions who have so willingly supplied pictures and given permission for us to reproduce them. Individual acknowledgements occur throughout the book. We are particularly grateful to Aubrey Rendell for taking a number of excellent photographs specially for us including the flame pictures on the back cover. Our thanks are also due to David Binnington for help in testing the experiments; to Tony Dixon for the nitrogen and carbon cycle drawings; to Jenny Berry for typing most of the manuscript and Roger Hateley for reading it all.

Thanks are due to the following examining boards for permission to reprint questions from past examination papers: Associated Examining Board; University of Cambridge Local Examinations Syndicate; University of Durham Schools Examination Board; University of London; Joint Matriculation Board; Oxford Local Examinations Board; Oxford and Cambridge Schools Examinations Board; Southern Universities Joint Board for School Examinations; Welsh Joint Education Committee. (At the request of the A.E.B. the terminology of their questions has been brought up-to-date.)

Thanks are also due for permission to base diagrams on others published elsewhere to: John Murray (figures 6.25, 6.26 and 6.27 (from "Success in Chemistry" by J. Bandtock and P. Hanson)); Pilkington Brothers Ltd. (figure

Introduction to the Fifth Edition

The fourth edition of this book 6 years ago was almost a complete rewrite of the third. Its content and form have been widely accepted and are retained for this edition. There are two major differences between the fourth edition and this one.

The last chapter "Chemistry and Society." has been completely rewritten, expanded and questions have been added. The format of this chapter has been retained but we have considerably expanded the sections on air pollution, water pollution, mineral resources, energy resources, and food resources and have added a section on the chemical industry. The need for these changes is a reflection of the new O-level syllabuses, the J.M.B. and Hong Kong for example, which place considerable emphasis on the topics in this chapter.

A chapter entitled "The Identification of Common Gases and Ions" has been added. This is a practical chapter. Various tests, that are spread throughout the book, with others added, have been brought together in a form that can be used in the school chemistry laboratory.

Other changes include substantial alterations to the chapter on fuels, changes and simplification to the introduction to organic chemistry and to energy and chemistry, and the addition of sections on oxidation numbers, the diaphragm cell, the fabrication of plastics, physical properties of the elements and Brownian motion. There are also very many minor changes scattered throughout the book.

Although any particular examination board removes some topics from its syllabus when new ones are added, the large number of examination boards, each with a different syllabus, has meant that as we have added topics it has not been possible to remove others; nothing that was in the fourth edition has been removed.

Thanks are due to those who have told us of mistakes, omissions, and obscurities, particularly John Peace and Stuart Warburton. We hope that they will all recognise where their helpful advice has been heeded.

It has been pointed out to us that we have not continually stressed the need to take care when carrying out chemical experiments. This is so. We believe that it is the task of the teacher to develop a sense of experimental responsibility (e.g. the wearing of safety spectacles) in his or her embryo chemists–to be safe and yet not so safe that they never discover, for example, what the common gases smell like. Chemistry is exciting–chemistry at the level for which this book is intended should be very exciting–it is the teacher's task not to make it appear so dangerous (*which it is not*) that the excitement is removed.

D. N. U.
D. E. W.
1981

Contents

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The Nature of Matter

1.1 What is chemistry?

Chemistry is the study of the properties of the matter that makes up the earth and the rest of the universe. The chemist is particularly concerned with the ways in which different substances react together, and with the ways in which some substances are made up from other simpler ones. When beginning a study of chemistry we need to consider the different types of matter.

Matter is anything that occupies space. The amount of matter is its *mass*. Matter is made up of different *substances*. All parts of a substance are chemically the same. Examples of pure substances are diamonds, common salt and water.

1.2 The states of matter

A substance can be either a solid, a liquid or a gas. These are known as *the three states of matter*.

A *solid* has a definite shape with distinct boundaries. Its volume is hardly affected by changes in temperature and pressure.

A *liquid* takes up the shape of any vessel in which it is placed, but like a solid it has a definite volume and is hardly affected by changes in temperature and pressure.

A *gas* has neither a definite shape nor volume. It assumes the shape of any vessel in which it is placed and, moreover, spreads itself evenly throughout any containing vessel. Thus if a gas is put into a large flask the gas will, in a very short time, have spread itself evenly throughout the flask. The volumes of gases are considerably affected by changes in temperature and pressure.

The differing properties of solids, liquids and gases are explained by assuming that all matter is composed of minute particles. In *solids* these particles are in definite positions. They vibrate in these positions but do not move from one part of the solid to another. The state that a substance is in depends on the energy that the substance contains. In the solid state substances have the minimum energy content. As a solid is heated, the energy of the solid is increased and the particles vibrate more vigorously, until at a certain temperature, which is always the same for the same substance, the solid changes to a liquid, i.e., it melts. For the solid this temperature is called the *melting point*. If the source of heat is removed the liquid will cool and at the same temperature as that at which the solid melted, the liquid will solidify. For the liquid this temperature is called the *freezing point*.

In *liquids* the particles move about freely and do not merely vibrate about a fixed position. The particles do, however, attract one another, and these attractive forces give liquids a definite volume. All the particles in a liquid do not

move at the same speed; some move faster than others. Moreover, the particles are continually colliding and exchanging energy and hence their speeds are continually changing. Near the surface of the liquid some particles that happen to be moving rapidly will fly out of the liquid and escape. In this way the liquid *evaporates*. If the temperature of a liquid is increased the particles move more rapidly, and so the rate of evaporation increases. For any substance at a certain temperature, and at a certain pressure, the addition of heat produces no further rise in temperature. At this temperature all of the energy being put into the substance is converting the liquid to a gas, i.e., the liquid is said to vapourize or boil. This temperature, which is markedly affected by pressure, is called the *boiling point* of the liquid. If the heat is removed the gas will cool, and at the same temperature as that at which the liquid boils, the gas will revert to a liquid. For a gas this process is called *condensation*. Gases that are at so low a temperature that they can be condensed by pressure alone are called *vapours*.

In *gases* the particles are much farther apart from one another than in liquids or solids, and consequently the attractive forces between particles are much less important. Each gas particle moves more or less independently of all other gas particles around it. This is why gases have no definite shape or volume, and it also accounts for the remarkable property of *diffusion* of gases. Thus if some hydrogen sulphide is prepared in one part of a laboratory, its smell is very rapidly detected all over the room. The properties of gases are discussed further in chapter 7.

Occasionally when a solid is heated it becomes a gas without passing through the liquid state. This process is called *sublimation*. It occurs when solid carbon dioxide or iodine are heated (see sections 18.3 and 20.3). Carbon dioxide or iodine vapour on cooling condense directly to the solid state. Water vapour goes directly to the solid state when snow flakes (figure 1.1) and hoar frost are formed, in the upper atmosphere and on the earth's surface respectively. The most
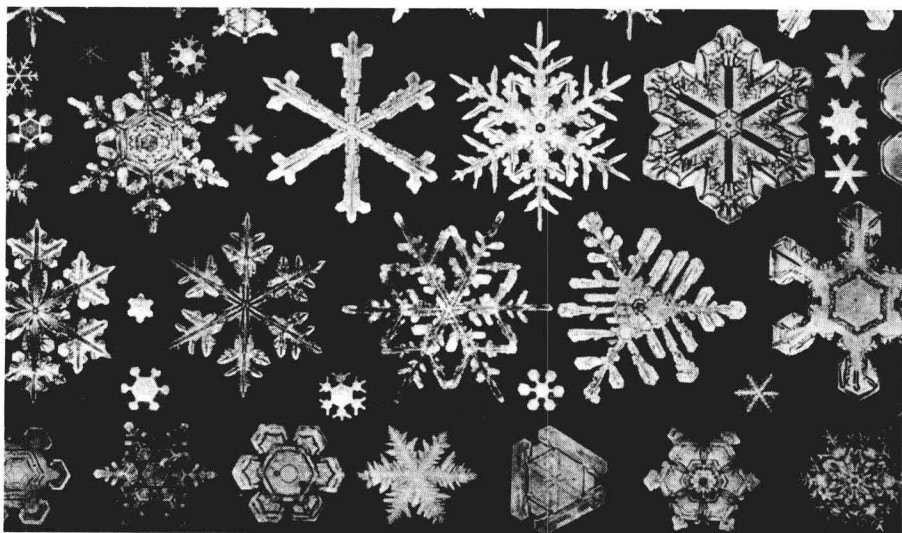

Figure 1.1 Snowflakes. (Photo: Radio Times Hulton Picture Library).

common form of sulphur, a fine yellow powder known as "Flowers of sulphur" is also produced by the condensation of the vapour direct to the solid on a cold surface. The relationships between the states of matter are summarized in figure 1.2.
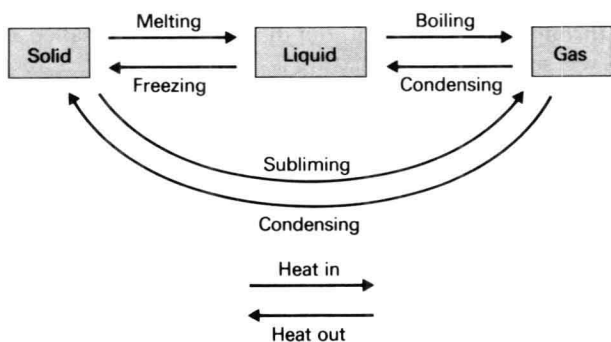

Figure 1.2 The three states of matter.

1.3 Solutions

Some substances, when they are mixed with water, seem to disappear. For example, if a little common salt is mixed with water the most careful microscopic examination of the resulting water-like liquid fails to reveal any trace of the salt. Yet tasting the liquid gives immediate proof of its presence. It is apparent that the salt and water have formed a mixture which is the same throughout, i.e., *homogeneous*, and the mixture will remain homogeneous even if it is left for ever. Such mixtures are called *solutions*, and the salt is said to have dissolved in the water. The dissolved substance, here the salt, is called the *solute*, and the substance that has dissolved it, here the water, is called the *solvent*.

Water is the most common solvent, mainly because it is so widespread on the earth, but there are many others. If you get a stain on your clothes you might try to remove it with a "stain-remover", or if the clothes are very dirty you may take them to be "dry-cleaned". The stain remover and the liquid used by the dry cleaner will be trichloroethene or some similar organic solvent.

There are many other solvents. Polystyrene, used for making toy model kits, is soluble in propanone (acetone). Cellulose ethanoate (acetate), a substance made from wood pulp (see section 26.3.1), is also soluble in propanone or a mixture of propanone and pentyl ethanoate (acetate). The artificial fibre, rayon, is made by squirting a solution of cellulose ethanoate in propanone through a small hole into a warm atmosphere, when the propanone evaporates and leaves a long fibre behind. Nail varnish is a solution of cellulose ethanoate in propanone, as are "balsa cement" and some paints.

Solutions of iodine are often in an alcohol solvent. Perfumes also contain pure alcohol as a solvent. Turpentine, or its substitute, white spirit, is a useful solvent for paint; it is often used for diluting paint, and for removing fresh paint stains.

There are many more solvents—you can probably think of others in addition to those given here.

1.4 Suspensions

Many substances do not dissolve in a particular solvent, and so they are said to be *insoluble* in the solvent. Water, for example, has no effect on glass, sand, wood and many other substances. However, if some fine chalk powder, which is insoluble in water, is shaken with it a milky mixture is formed. Such a mixture, where particles are spread throughout a liquid without dissolving in it, is called a *suspension*. These particles will settle out if the mixture is left long enough. Some medicines are suspensions; hence the instruction to "shake the bottle". Other common examples of suspensions are muddy water and most paints.

1.5 Filtration

If a mixture of water and chalk is poured onto a filter paper, the water passes through the filter paper and the chalk particles are left behind. Filter paper is unglazed paper, similar to blotting paper. It contains many small holes, which, although large enough to allow the water to pass through, retain the much larger particles of chalk. This process is called *filtration*; the liquid that has passed through the paper is called a *filtrate* and the solid left behind on the filter paper a *residue* (figure 1.3).
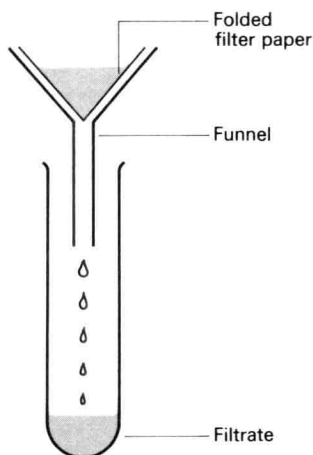

Figure 1.3 Filtration.

Filtration is a much used process, and there are various substitutes for the filter paper depending on the size of the particles to be removed. The most widespread application is in the treatment of our water supplies, where layers of sand and gravel are used to remove suspended particles. In the engine of a car the oil passes through a filter to remove solid particles that if left in the oil would cause damage, and for the same reason dirt particles in the air and petrol are removed by filters before they pass into the engine (figure 1.4).

Dust particles are filtered from the waste gases of power stations and other industrial plants to stop this dirt being expelled into the air where it would be a major source of atmospheric pollution. For these industrial uses, where the volume of air to be filtered is very large, a filter paper method would be much too slow. A special type of filter is used called an electrostatic precipitator (figure 1.5).
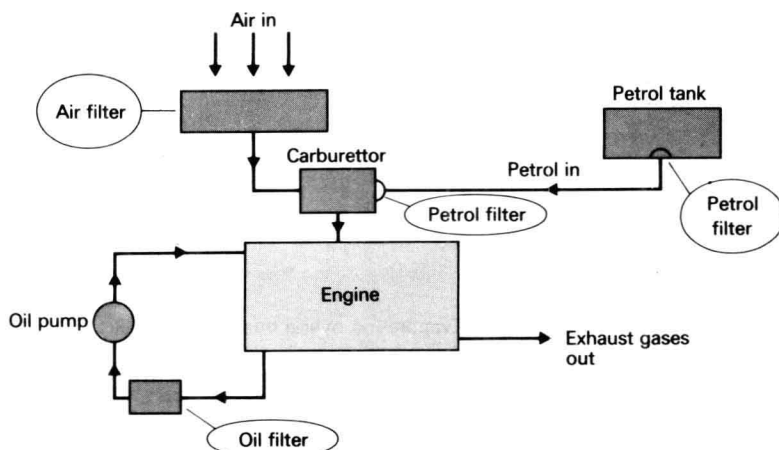
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Figure 1.4 Schematic diagram of a car engine showing the air, oil and petrol filters.
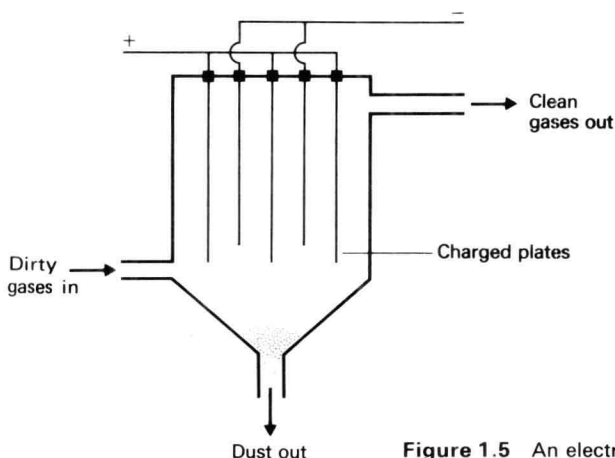

Figure 1.5 An electrostatic precipitator.

In this the dust particles are electrically charged and they then become attached to metal plates of opposite charge. After a time the electric current through the plates is switched off, and the dust then falls to the bottom of the precipitator when it can be removed.

1.6 Evaporation

In section 1.3 we saw that salt dissolves in water to give a solution. The salt cannot be separated from the water by filtration; they both pass straight through the filter paper. To obtain the salt the solution must be heated, when the water escapes as steam leaving the involatile salt. A porcelain dish called an evaporating dish is often used (figure 1.6). If the solution is heated until all the water has been vapourized the process is called *evaporation to dryness*. When doing this care must be taken towards the end; the solution becomes very
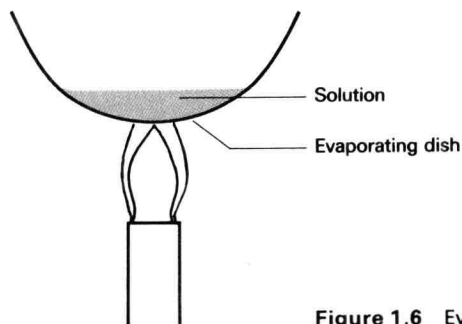
Figure 1.6 Evaporation over a bunsen burner.

concentrated and will spit out of the dish as steam is formed beneath semi-solid parts of the mixture. To minimize spitting gentle heating must be used.

As the process of evaporation removes the water, it concentrates the salt. If a solution that has been concentrated is allowed to cool, crystals of the salt may form. This process is called *crystallization* and is discussed further in section 1.14.

When an inflammable solvent, such as ether or alcohol, is being evaporated, the solution must not be heated with a naked flame, but instead a hot water-bath or a steam-bath is used (figure 1.7).

A beaker containing water at a high enough temperature to cause evaporation can be used as the steam-bath. Even with a steam-bath great care must be taken when evaporating liquids whose vapours are inflammable and heavier than air, such as ether or carbon disulphide, as these vapours can fall around the water-bath and become ignited. For such liquids the only safe procedure is to completely remove the flame before putting the solution on the water-bath.
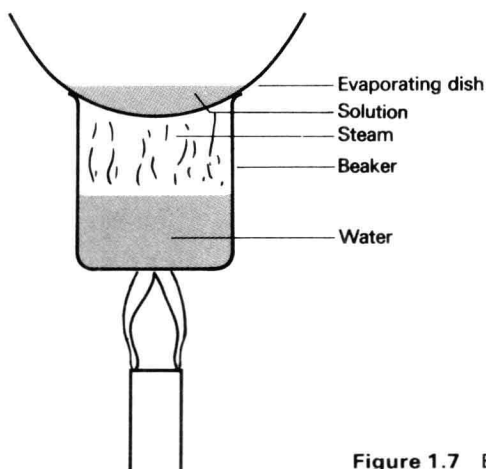

Figure 1.7 Evaporation on a steam bath.

1.7 Distillation

Evaporation gives only the involatile salt from the salt solution; the water has boiled away into the atmosphere. To obtain the water, it is necessary to condense the steam by cooling. A Liebig condenser, fitted to a distillation flask is normally

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used, and the apparatus is assembled as shown in figure 1.8. A small piece of broken pottery in the flask enables the solution to boil smoothly.

This process is called *distillation*, and the water obtained in this way is *distilled water*. Distilled water is very pure water and is usually obtained by the distillation of tap water. It is used when dissolved solids in the water are undesirable, such as in experiments in the chemistry laboratory and in car batteries.
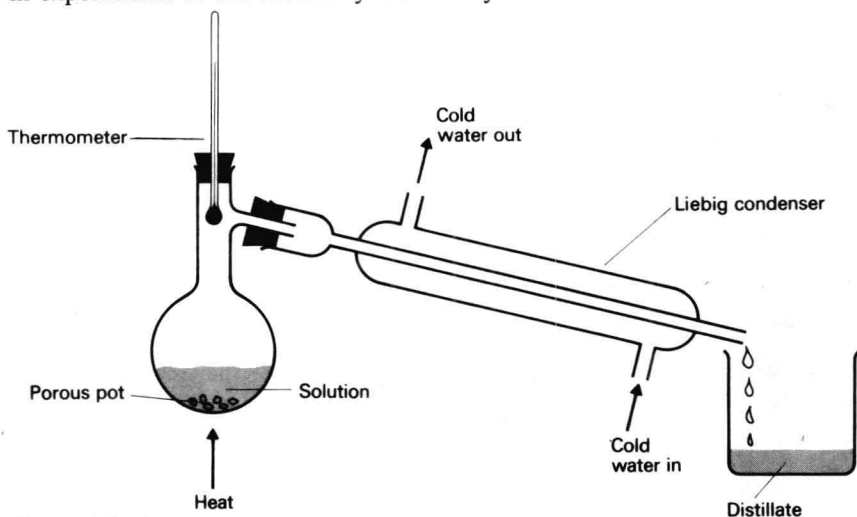

Figure 1.8 Distillation.

The process of distillation has been used for several thousands of years, mainly to concentrate the alcohol in wine by making spirits (see section 1.8). Also, over the past centuries distillation was an important process for the chemists' predecessors—the alchemists. The alchemist, in his search for methods of turning other metals into gold (a process that, we hope, the readers of this book will appreciate is rather difficult—see section 6.3.4) developed the very simple, all-glass piece of distillation apparatus called the retort (figure 1.9). The retort has become one of the symbols of the alchemist. Paintings of alchemists, such as that
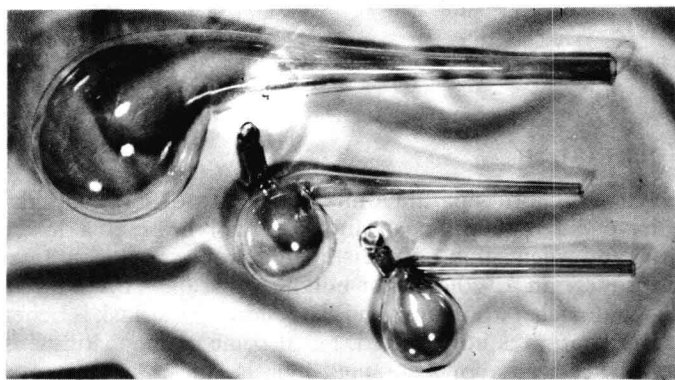

Figure 1.9 Retorts. The large one was made in Germany during the 19th century. The smaller ones, with ground glass stoppers, are modern. (Photo: A. Rendell).

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by J. Stradanus in the Palazzo Vecchio in Florence (figure 1.10), abound with retorts and distillation equipment.

Retorts are not used much nowadays, but they are useful when distilling a liquid that attacks metal, rubber and other materials. For example, retorts are sometimes used in the school laboratory for preparing nitric acid and bromine, both of which are highly corrosive liquids. Modern all-glass apparatus with ground joints is, however, just as good and much more convenient to assemble and to dismantle and clean (see sections 16.6.2 and 20.2.3).

Figure 1.10 "The Alchemist" by J. Stradanus (from the Palazzo Vecchio, Florence) Photo: Mansell Collection.

1.8 Fractional distillation

By distillation it is also possible to separate a mixture of two or more liquids, provided that they have different boiling points. Ethanol boils at a lower temperature than water and when a mixture is distilled the vapour will contain a comparatively high proportion of the lower-boiling ethanol. This vapour condenses to give a distillate richer in ethanol, and the residue in the flask is richer in water. A complete separation is not effected, but if some of the distillate is redistilled a liquid still richer in ethanol is obtained. This is exactly what is done during the making of malt whisky.

The ethanol solution produced by the fermentation process is distilled twice,

the final liquid distillate being whisky. The distillation flasks used are much larger than those used in the laboratory, are made of copper and are called stills. Figure 1.11 is a picture of two whisky stills. These stills each hold over 20 000 litres of solution. Instead of a Liebig condenser, a copper spiral inside a container of cold water, shown on the right hand side of figure 1.11, is used to condense the vapour.
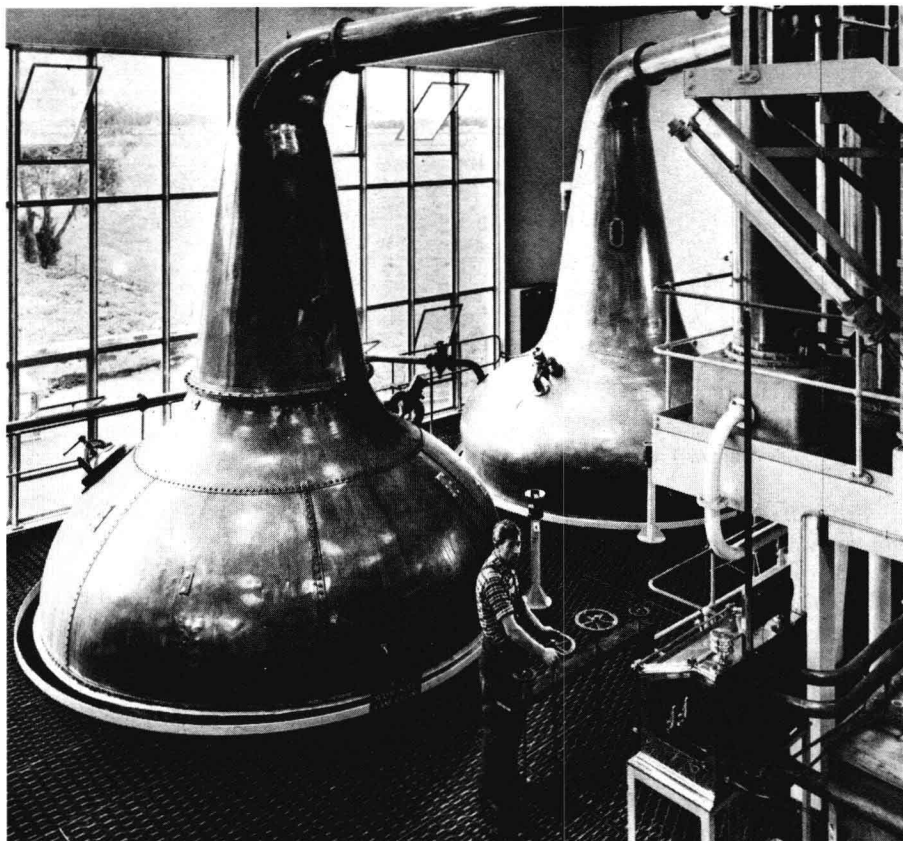

Figure 1.11 Malt whisky stills at the Royal Brackla Distillery at Nairn in Scotland. (Photo: The Distillers' Co. Ltd.).

Often, however, it is necessary to obtain each of the liquids that make up the mixture in as pure a form as possible. To achieve this a *fractionating column* is used. There are many different types; one of the simplest consists of a long tube packed with small glass beads. This tube is fitted to the neck of the flask containing the liquid to be distilled (figure 1.12). When a mixture of vapours passes up the column those of the less volatile liquid condense on the glass beads more readily than those of the more volatile liquid. Liquid that has condensed on the column is evaporated by the hot vapours, and the more volatile liquid evaporates most readily. As a result of the many evaporations and condensations the vapour moving up the column becomes progressively richer in the more volatile liquid. At the top of the column the vapour will be mainly the more volatile liquid, and this is then collected in the receiver.