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Author

Charles S. Sell
Aldington, Ashford, Kent
United Kingdom

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Contents

Preface

Chemistry can be a difficult subject and may seem far removed from the glitter of the fragrance business. However, it is the essential science behind the latter.

Some chapters, especially the first, contain more of the basic principles of chemistry and may seem less relevant than those with regard to fragrance at first sight. But these basic concepts are important because they lay the groundwork on which fragrance chemistry is founded. The reader is advised to bear with them, study them, and refer to them when appropriate while reading the more obviously relevant chapters.

Thoughts and opinions expressed in this book, especially in Chapter 17, are those of the author and hence are not necessarily in agreement with those of the industry, the publisher, or any individual company.

2 January 2019 Aldington, Kent, England

Introduction

To the layman, the world of perfumery conjures up images of glamour, dreams, romance, expensive oils extracted from exotic plants, and so on. The names that spring to mind are those of the great perfumers and fashion houses such as Jean Patou, Francois Coty, Chanel, Christian Dior, and so on. These names and images are part of our fascinating industry, but, in addition, behind all of this allure is a modern industry with a strong scientific basis, and the core science is chemistry. Ernest Beaux, the perfumer who created *Chanel No. 5*, said, 'One has to rely on chemists to find new aroma chemicals creating new, original notes. In perfumery, the future lies primarily in the hands of chemists'. And his words are as true today as in 1921 when he created his famous masterpiece. Many Nobel Prize winners mentioned fragrance chemistry in their prizewinning lectures. It is also significant that the times of strongest growth of a fragrance company are associated, more often than not, with the presence of a first-rate, practicing chemist in a senior position. Thus, to the names of the perfumers, we can add great chemists such as Yves-Rene Naves (Givaudan), Ernst Theimer (IFF), Leopold Ruzička (Firmenich), Ernst Günther (Fritzsche, Dodge, and Olcott), Ernest Polak (Polak's Frutal Works), Paul José Teisseire (Roure Bertrand Dupont), Günther Ohloff (Firmenich), and George Fráter (Givaudan) as key figures in the history of perfumery. Not everyone needs to be a chemist of such a calibre as these, but for all of those individuals working in the fragrance business and in the consumer goods industries that it serves, knowledge of chemistry is invaluable in understanding how fragrance is produced, how it works, and the factors that control its performance in products.

Perfume molecules are compounds of carbon and hence come under the general heading of organic chemistry. Our bodies are also composed of organic chemicals and so are most of the components of consumer goods such as soaps and detergents. This book therefore concentrates on those aspects of organic chemistry, which are of particular importance to the fragrance industry. It is intended for those who have little or no previous training in chemistry and who would like to know enough in order to improve their understanding of perfume and its interactions with the wide variety of products in which it is used.

Chapter 1 covers the nature of matter, the building blocks from which it is made, and how these building blocks are held together.

Chapter 2 describes the basic concepts of how carbon atoms join together to form the backbones of organic chemicals. It also describes the various shorthand methods that chemists use to indicate the composition of materials and the structure of their molecules and so will enable participants to make sense of the 'fried eggs and spiders' that chemists draw. It also gives an insight into the language that chemists use and the names they give chemicals.

Chapter 3 introduces organic materials that contain oxygen, nitrogen, or sulfur as well as carbon and hydrogen. The vast majority of fragrance ingredients fall into this class.

Chapter 4 describes the three states of matter and how one may be converted into another. It also describes how surface-active agents behave at interfaces between immiscible liquids and this behaviour leads on to cover the basis of detergency and the structure of mammalian cell walls.

In order to analyse and manipulate materials, it is important to be able to isolate them from mixtures and obtain them in pure form. The various methods by which purification can be achieved both for analytical and manufacturing purposes are described in **Chapter 5**.

Chapter 6 concerns the methods used to identify and characterise perfume molecules, an activity of vital importance for everything from purchasing of raw materials to studying the fate of fragrance materials after use.

Chapter 7 outlines the factors controlling chemical reactivity and provides a basis for understanding of the chemistry to be described in the subsequent chapters. The chemistry of acids and bases and the relevance of this chemistry to perfume chemistry is the subject of **Chapter 8**, while **Chapter 9** covers oxidation and reduction reactions.

Chapter 10 describes the structure of a fragrance and the effects of this on performance in consumer goods. **Chapter 11** discusses the chemical interactions that occur between perfume ingredients and the other materials present in consumer goods.

Chapter 12 gives a very basic introduction to the chemistry of living organisms, and this paves the way for a discussion of the mechanism of olfaction in **Chapter 13**. **Chapter 14** moves on to describe the variety of chemicals made by plants and animals and, in particular, those that constitute the essential oils and other fragrant extracts.

Chapter 15 follows on by describing how we copy and improve upon the perfume ingredients of nature in order to provide the perfumers with the palette available to them today.

Chapter 16 provides a brief introduction to chemical literature, and it also contains a list of recommended reading. Thus, it serves as a guide for the reader who wishes to pursue the subject in more detail.

The last chapter, **Chapter 17**, surveys the trends that are likely to affect the industry in the future and how we can respond to these to make the industry as sustainable as possible.

1

The Structure of Matter

The Route to the Atomic Theory

Chemistry is a subject of vital importance to human society. We even measure the progress of civilisation by the chemical technology that our ancestors possessed at various stages in history. Thus, the earliest phase of civilisation is known as the Stone Age, when humans used readily available materials such as stone to form tools. In chemical terms, the stone was used as it was found. The only manipulation was to shape it by physical means into knives, axes, and so on. The discovery of bronze moved civilisation forward significantly and gave birth to the Bronze Age. As an example of this technological advancement, bronze axes could be made with much more acute angles at the cutting edge of the blade than can stone axes, and so fewer strokes were required to cut through a tree trunk. Now chemistry was involved, since ores such as malachite had to undergo a chemical conversion to release the copper metal that they contained. Heating the ore to a high temperature brought about this chemical change. The temperature required to release iron from its ores, such as haematite, is even higher, so it was not until furnace technology had reached the required level that the Iron Age began.

Chemistry is important to all industries to some extent, but to perfumery, it is absolutely central. The odorous substances that produce the sensation of smell, whether of natural or synthetic origin, are chemicals. The receptors in our noses that perceive them are chemicals. Smell begins with the process of chemical recognition of the odorant by the olfactory receptor, and therefore smell is very much a chemical sense. To understand fragrance perception, we must understand chemistry. The products into which perfumes are incorporated are also composed of chemicals and chemical interactions can occur between the perfume and the product. Thus, in order to understand the interaction of perfume with products such as soaps and detergents, we must understand chemistry.

Chemistry is very much a practical science and people were practising it long before theories about the nature of matter and of these chemical processes were developed. Metallurgy, which is one branch of chemistry, started in the Nile Delta in ancient Egypt. Because of the colour of the rich alluvial soil, the Greeks knew this region as 'The Black Country'. Metallurgy was considered to be the art of Egypt, the Black Country, and hence became to be known as the 'Black Art'.

Fundamentals of Fragrance Chemistry, First Edition. Charles S. Sell.

The debate about the nature of matter began in Greece around the fourth century. Democritus (460–370 BCE) and Epicurus (341–270 BCE) argued that matter was made of small indivisible particles that they called atoms. The word atom is derived from the Greek verb *τομεω* (tomeo), which means 'I cut', and *ατομος* (atomos), meaning 'uncuttable' or 'indivisible'. On the other hand, Empedocles (c. 450 BCE) and later Aristotle (384–322 BCE) believed that matter was continuous and composed of four basic ingredients or elements: earth, air, fire, and water. In order to distinguish living from inanimate matter, Aristotle invoked a fifth element or quintessence, which he called spirit. The legacy of his erroneous theory still survives in our language today. Adherents of the Aristotelian philosophy believed that by heating plant material, they were removing the spirit (or quintessence) of the plant and so the oil they obtained was called the quintessential (later shortened to essential) oil. Similarly, we refer to other distillates, such as whisky, gin, or brandy, as spirits. With these two philosophical schools came the first theories of how the sense of smell worked. Epicurus believed that odours were made up of atoms that travelled through the air from the source to the nose. Smooth, rounded atoms gave rise to sweet smells and pointed ones to sharp odours. Aristotle believed that odours radiated from the source to the nose, just as heat radiated from the sun to the earth.

In CE 50, Dioscorides produced a book called *De Materia Medica* in which he listed all the known facts about herbal medicines. The compilation of what was known about the physical universe gained further momentum in CE 866 when Razi began a systematic collection of facts. Around CE 1000 the Arabs invented distillation, which meant that liquids could be produced in a pure state. New solvents for distillation such as alcohol were used in addition to water and therefore allowed for a great increase in the ability to manipulate materials. For instance, the odorous components of plants had previously been capable only of being extracted into fats and oils through the process of enfleurage (see Chapter 4, for details). With distillation, the volatile oils could be extracted directly from the plant material. The availability of alcohol as a solvent meant that the odorous principles could also be extracted from the fatty concretes by dissolving them in ethanol. (Again, more detail will be found in Chapter 4.)

The alchemists of medieval Europe searched for a method to turn base metals into gold. We now know that this is a futile endeavour but, in their work, they built up a fund of experimental evidence about interconversions of substances. In the thirteenth century, Roger Bacon, an English Franciscan friar and scientist, laid the foundations of what we now call 'The Scientific Method'. Scientific method uses five steps in developing theories about the physical universe. These steps are observe, correlate, postulate, test, and revise. Thus, true science begins with the observation of facts. It then seeks to find relationships between them and to devise theories to account for them. The next step is to devise experiments that will test the theories. If the theory passes the test, it remains valid. If not, the theory must be abandoned or revised until a new theory is developed that passes all known practical tests. We must always remember that in science nothing is ever established beyond doubt; every theory, every model is only accepted, while no exceptions are known. The possibility always exists of an inconvenient fact turning up and forcing us to revise our theories again – hence the saying 'The exception proves the rule', the verb prove here being used in the sense of tests.

Armed with Bacon's powerful scientific method, the scientists of the Age of Enlightenment were able to start interpreting the growing body of facts in a more rational way, and, in one sense, the opposing theories of Democritus and Aristotle began to come together to form a more accurate picture of the universe. Democritus had seen each type of matter as being composed of characteristic particles or atoms. Aristotle saw different forms of matter as being composed of combinations of four basic elements. Gradually, a new picture began to emerge in which atoms of a larger number of elements came together in different ways to form other substances.

As an illustration, let us look at some chemical relationships between iron and sulfur. These two substances appear in various guises, and so the suspicion arose that they might be elements, basic building blocks of matter. Heating iron ore produces iron, which can be purified by heating to burn off some of the contaminants present and then pouring the molten iron away from the more refractory minerals around it. Sulfur was collected from the rims of volcanoes, hence its former name of brimstone. If iron powder and sulfur are mixed together, they can easily be separated again with a magnet. However, if they are heated together, they form a new substance that turns out to be identical to the mineral known as pyrites or 'fool's gold'. Burning sulfur in air produces an irritant gas that is referenced in Homer's *Odyssey*, when Odysseus burnt sulfur in his house to cleanse it from the traces of those who had occupied it during his famous return journey from Troy. If pyrites is burnt in air, we drive off the same acidic gas and obtain iron. So iron and sulfur can be chemically combined to form a new substance. However, they are not lost, and both can be recovered from the combination. Therefore, we can conclude that they are both elements, as opposed to pyrites, which is a compound of iron and sulfur. Of course, another element, oxygen, is involved in the above conversions. However, oxygen is difficult to characterise and it was not identified as an element until much later.

In this way, a number of elements were identified and then laws about the way they combined began to be discovered. The first was the law of definite proportions that was first defined by J.B. Richter in 1792. This law states, 'The ratios of the weights of elements which are present in a given chemical compound are constant'. So, taking our example of pyrites, the ratio of the weights of iron to sulfur in any given sample will be the same. Then, came the law of equivalent proportions, which states: 'The proportions in which two elements separately combine with the same weight of a third element are also the proportions in which the first two elements combine together'. For example, if we find that 3 g of carbon combined with 1 g of hydrogen to form methane and 3 g of carbon combined with 8 g of oxygen to form carbon dioxide, then we can predict that water, a compound of hydrogen and oxygen, will contain 8 g of oxygen for every 1 g of hydrogen.

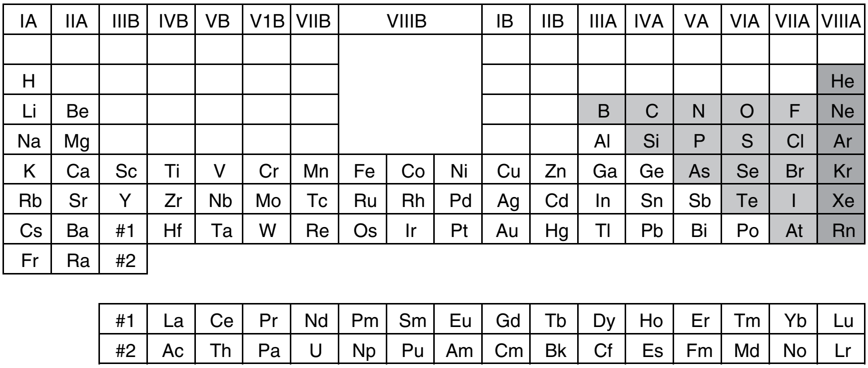
Mixtures are combinations of substances from which the components can be separated by purely physical means. Elements are pure substances that cannot be broken down further into other chemicals. They are made up of atoms, which are the smallest possible pieces of that element that will still retain its chemical properties. Chemical compounds are substances that are composed of atoms of different elements but in which the atoms are held together by a force known as a chemical bond. The smallest unit of a compound that still retains all the chemical properties of that compound is called a molecule.

The Atomic Theory, Atomic Number, and Atomic Weight

Consideration of these and other laws and observations led the English chemist John Dalton to develop his atomic theory in 1806. In this theory, Dalton proposed that the elements were composed of indivisible particles called atoms, each with a characteristic weight, and that chemical compounds were composed of atoms joined together in some way. The ability of atoms to join together is known as valence, and each type of atom has a specific number of valencies or combining power. In 1810, J.J. Berzelius observed that sometimes two elements could combine with each other in different ways. The weight ratios of the elements in these different compounds led him to define the law of multiple proportions that states: 'When two elements combine to form more than one compound, the amounts of them which combine with a fixed amount of the other exhibit a simple multiple relation'. For example, iron can combine in two ways with oxygen to form two different oxides. In one of them 7 g of iron combines with 2 g of oxygen, and in the other 7 g of iron combines with 3 g of oxygen. So the ratio between the weights of oxygen in the two is 2 : 3.

So, elements each seem to have a characteristic weight, known as the atomic weight, and also characteristic valencies. The atomic weights were first expressed in relation to that of hydrogen, the lightest element. Thus, if the weight of a hydrogen atom is defined as one unit, currently called the atomic mass unit or the Dalton, then helium has an atomic weight of 4, lithium 7, and so on. In 1819, the Swedish chemist J.J. Berzelius devised a convenient shorthand system for describing the elements by using the first, or first two, letters of their Latin names. Thus, hydrogen is symbolised by H, carbon by C, iron by Fe (for its Latin name *ferrum*), sodium by Na (for *natrium*), and so on. In 1869, the Russian chemist D.I. Mendeleyev noticed that if the known elements are arranged in order of their atomic weights, a pattern or periodicity about their chemical properties is shown. The periodic interval initially is 8. Thus, for example, the third element, lithium, has similar properties to the 11th, sodium; the fourth, beryllium, to the 12th, magnesium; and so on. The elements were assigned atomic numbers based on their places in this series. Thus, the lightest element, hydrogen, has an atomic number of 1; the next, helium 2; then lithium with 3; and so on. Mendeleyev laid this pattern out in tabular form, thus presenting us with the most complete piece of scientific information, which exists, the periodic table. So powerful is the periodic table that Mendeleyev was able to use it not only to predict the existence of elements unknown at the time but also to describe what their chemical properties would be like.

A simple representation of the periodic table is shown in Figure 1.1. The elements are arranged left to right in order of their atomic numbers. The first row



IA	IIA	IIIB	IVB	VB	V1B	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	#1	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	#2															

#1	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
#2	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Figure 1.1 The periodic table of the elements.

(or period) contains only two elements. The next two rows have eight elements each, and are followed by two rows of 18. The last two rows contain 32 elements each but are usually drawn as in the figure with two blocks of 15 elements shown separately in order to prevent the table becoming so wide as to be unwieldy. The column of elements in darker shaded boxes are the inert or noble gases, so called because of their very low chemical reactivity. The vertical columns are normally referred to as groups and the group numbers are shown in the bar across the top of the figure. The inert gases thus belong to group VIIIA. One of the things Mendeleyev had noticed was the similarity in chemical properties in each group. The elements of group VIIA, for instance are known as the halogens, or salt-forming elements. Group IA are known as the alkali metals and are the most reactive metals. The next group is known as the alkaline earths. The alkali metals all form salts with the halogens in the ratio of one metal atom to one halogen atom, giving formulae of the type MX, where M represents the metal and X the halogen. Examples would include common salt or sodium chloride, NaCl. The alkali earths, on the other hand, form halide (or halogen) salts in which there are two halogen atoms for each metal, for instance magnesium bromide is $MgBr_2$. The elements in lighter grey shaded boxes are non-metals, those in clear boxes are metals.

The metals in group VIIIB are very interesting. The first row contains iron, cobalt, and nickel. These elements are all important in forming catalysts including natural catalysts such as cytochrome P450 and vitamin B_{12}, which contain iron and cobalt, respectively. The other six metals in this group are known as the platinum metals (including platinum), and these are of considerable importance as catalysts in the manufacture of fragrance ingredients. The heaviest naturally occurring element is uranium, number 92. The transuranic elements, those with a higher atomic number than 92, are only formed in nuclear reactors and are unstable, breaking down quickly into lighter elements.

A list of the elements is shown in Table 1.1. The table includes their names, symbols, atomic numbers, and atomic weights. For sake of completeness, all of the elements are shown in both Figure 1.1 and Table 1.1. This list is not intended to discourage the reader, as this book will concentrate on only a small number of

Table 1.1 The elements.

Atomic no.	Name	Symbol	Atomic weight	Atomic no.	Name	Symbol	Atomic weight
1	Hydrogen	H	1.0079	53	Iodine	I	126.9045
2	Helium	He	4.0026	54	Xenon	Xe	131.29
3	Lithium	Li	6.941	55	Cesium	Cs	132.9054
4	Beryllium	Be	9.01218	56	Barium	Ba	137.33
5	Boron	Be	10.81	57	Lanthanum	La	138.9055
6	Carbon	C	12.011	58	Cerium	Ce	140.12
7	Nitrogen	N	14.0067	59	Praseodymium	Pr	140.9077
8	Oxygen	O	15.9994	60	Neodymium	Nd	144.2
9	Fluorine	F	18.9984	61	Promethium	Pm	145a)
10	Neon	Ne	20.179	62	Samarium	Sm	150.36
11	Sodium	Na	22.98977	63	Europium	Eu	151.96
12	Magnesium	Mg	24.305	64	Gadolinium	Gd	157.25
13	Aluminium	Al	26.98154	65	Terbium	Tb	158.9254
14	Silicon	Si	28.0855	66	Dysprosium	Dy	1262.5
15	Phosphorus	P	30.97376	67	Holmium	Ho	164.9304
16	sulfur	S	32.06	68	Erbium	Er	167.26
17	Chlorine	Cl	35.453	69	Thulium	Tm	168.9342
18	Argon	Ar	39.948	70	Ytterbium	Yb	173.04
19	Potassium	K	39.0983	71	Lutetium	Lu	174.967
20	Calcium	Ca	40.08	72	Hafnium	Hf	178.49
21	Scandium	Sc	44.9559	73	Tantalum	Ta	180.9479
22	Titanium	Ti	47.88	74	Tungsten	W	183.85
23	Vanadium	V	50.9415	75	Rhenium	Re	186.207
24	44 Chromium	Cr	51.996	76	Osmium	Os	190.2
25	Manganese	Mn	54.938	77	Iridium	Ir	192.22
26	Iron	Fe	55.847	78	Platinum	Pt	195.08
27	Cobalt	Co	58.9332	79	Gold	Au	196.9665
28	Nickel	Ni	58.69	80	Mercury	Hg	200.59
29	Copper	Cu	63.546	81	Thallium	Tl	204.383
30	Zinc	Zn	65.38	82	Lead	Pb	207.2
31	Gallium	Ga	69.72	83	Bismuth	Bi	208.9804
32	Germanium	Ge	72.59	84	Polonium	Po	209a)
33	Arsenic	As	74.9216	85	Astatine	At	210a)
34	Selenium	Se	78.96	86	Radon	Rn	222a)
35	Bromine	Br	79.904	87	Francium	Fr	223a)

Table 1.1 (Continued)

Atomic no.	Name	Symbol	Atomic weight	Atomic no.	Name	Symbol	Atomic weight
36	Krypton	Kr	83.8	88	Radium	Ra	226.0254^b)
37	Rubidium	Rb	85.4678	89	Actinium	Ac	227.0278^b)
38	Strontium	Sr	87.62	90	Thorium	Th	232.0381^b)
39	Yttrium	Y	88.9059	91	Protactinium	Pa	231.0359^b)
40	Zirconium	Zr	91.22	92	Uranium	U	238.0289
41	Niobium	Nb	92.9064	93	Neptunium	Np	237.0482^b)
42	Molybdenum	Mo	95.94	94	Plutonium	Pu	244^a)
43	Technetium	Tc	98^a)	95	Americium	Am	243^a)
44	Ruthenium	Ru	101.07	96	Curium	Cm	247^a)
45	Rhodium	Rh	102.9055	97	Berkelium	Bk	247^a)
46	Palladium	Pd	106.42	98	Californium	Cf	251^a)
47	Silver	Ag	107.868	99	Einsteinium	Es	252^a)
48	Cadmium	Cd	112.41	100	Fermium	Fm	257^a)
49	Indium	In	114.82	101	Mendelevium	Md	258^a)
50	Tin	Sn	118.69	102	Nobelium	No	259^a)
51	Antimony	Sb	121.75	103	Lawrencium	Lr	260^a)
52	Tellurium	Te	127.6				

a) Mass number of longest-lived isotope.
b) Atomic weight of most commonly available long-lived isotope.

these elements. One thing to note about the elements listed in Table 1.1 is that, for the majority of them, their atomic weights are close to whole numbers. This quality provides an important clue about the structure of the atom.

Atomic Structure

The structure of atoms was elucidated in the early part of the twentieth century. For the purposes of this book, we can assume that atoms are composed of three more fundamental particles, namely, protons, neutrons, and electrons. Protons and neutrons each have an atomic mass of 1 Da. Protons carry a positive electrical charge, and neutrons, as their name suggests, are neutral. Electrons carry one unit of negative electrical charge each and have no mass. Atoms have a structure rather like that of a planetary system. At the centre is a nucleus composed of neutrons and protons, and the electrons orbit around the nucleus similar to the way planets orbit around their stars. In order to maintain electrical neutrality, the number of electrons orbiting the nucleus equals the number of protons in the nucleus. The factor controlling the chemistry of an element is the number of protons in its nucleus. The simplest atom therefore, the hydrogen atom, has a nucleus containing one proton only. This proton is balanced by one electron. Since the electron has no mass and the proton has a mass of 1 Da, the hydrogen atom has an atomic mass, or atomic weight, of 1 Da. This fact is the case for most hydrogen atoms. However, some hydrogen atoms have one neutron also in their nucleus. The charge in the nucleus is still one positive charge, and so there is still one electron in orbit and the chemical properties are still those of hydrogen. However, the atomic weight is now 2 Da. When atoms exist with the same atomic number (i.e. the same number of protons) but with different atomic weights (i.e. different numbers of neutrons), we call them isotopes.

Isotopes

The word isotope comes from Greek and means 'same place'. The atoms have the same place in chemistry as each other. The hydrogen isotope having a mass of 2 Da is known as deuterium, and the symbol D is often used to denote it. More properly, it should be identified by the symbol ^{2}H, while ^{1}H would then specify the more common isotope of hydrogen. Both isotopes will have the same chemical properties. It is also possible to have two neutrons in a hydrogen nucleus, and this isotope is called tritium, ^{3}H. However, in this case, the nucleus is unstable and breaks down, or decays, into smaller fragments, emitting radiation in the process. Such unstable isotopes are called radioactive isotopes or radioisotopes because of the radiation they emit. In Table 1.1, some of the elements do not have an atomic weight like the others but are shown with the weight of the most stable or longest-lived isotope, because such elements, like radium, are intrinsically unstable and undergo radioactive decay into lighter elements.

Normal hydrogen contains a mixture of its three isotopes. In a natural sample, there are far fewer deuterium atoms than protium (as ^{1}H is also known) and even fewer atoms of tritium. If we calculate the atomic weight based on a proton or neutron weighing 1.0000 Da, the result will be the average of some atoms with a weight of 2, some with a weight of 3, and most of them with a weight of 1. This average is why the atomic weight of hydrogen is shown as being 1.0079 in Table 1.1.

Carbon is the element that concerns us most in perfumery. It has three isotopes, and all of these are important to us in different ways. The atomic number of carbon is 6, and so each atom of carbon has six electrons and six protons. The most common isotope, and hence the most important, has six neutrons in the nucleus. The atomic weight of carbon is therefore close to 12, 12.011 to be precise. Some carbon atoms have seven neutrons and therefore an atomic weight of 13. This is therefore known as ^{13}C or carbon-13 and is important in spectroscopy, as we will see in Chapter 5. If there are eight neutrons in a carbon nucleus, then it is designated ^{14}C or carbon-14. This isotope is unstable and therefore radioactive. This isotope and its radioactive decay are the basis of so-called carbon dating of archaeological specimens and, in our industry, give us one tool in determining the 'natural' status of fragrance and flavour ingredients as will be seen in Chapter 6.

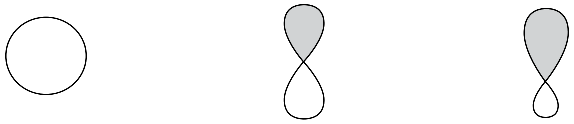
The Electronic Structure of Atoms

The electrons orbiting a nucleus are not distributed randomly but are confined to volumes of space around the nucleus that we call orbitals. It is the pattern of these orbitals and their occupancy by electrons that determine the chemical properties of atoms. In order to understand the nature of an electron, we can picture it as either a wave or a particle. In reality, it is neither, but sometimes it is easier to make sense of its properties if we picture it as a one or the other. If we picture the electron as a particle, the orbital therefore becomes a probability distribution in space of where the particle might be. If we picture the electron as a wave, then the orbital becomes a standing wave of negative electricity around the nucleus. In either case, an electron in an orbital can be viewed as something possessing a definite distribution in space, a negative charge, and as something that can be distorted by electrical charges around it. In other words, the surface of an atom or molecule is not hard like a miniature billiard ball, but is more like a balloon or a cloud, which is affected by other charges around it. It is attracted by opposite charges and repelled by similar charges.

The orbitals are considered in order of the energy required to keep an electron in them. The first or lowest orbital energy orbital has a capacity for only two electrons and is spherical in shape with the nucleus at its centre. It is called the 1s orbital. The names of the orbitals are derived from the number of the shell and the quality of the lines associated with them in their atomic spectra. Thus, *s* stands for sharp, *p* for principal, *d* for diffuse, and *f* for fundamental. The hydrogen atom therefore has one electron in its 1s orbital. Similarly, the helium atom has two electrons in its 1s orbital, and the orbital is full. Electrons have a property called spin. We can picture this as the way the electron, as a particle, will spin about its axis. There are two directions of spin and as a simple picture; we can see this as left-handed and right-handed spin. Each electron likes to pair up with another with the opposite spin. So, in the helium atom, the electrons are happy in that they are paired up and the orbital is full. Chemistry involves electrons moving from one atom to another. The electrons in helium have no desire to do this and so the helium atom is very unreactive chemically. The hydrogen atom, on the other hand, has only one electron in an orbital designed for two, and the single electron has no spin partner. Hydrogen therefore wants to do something with its electron to rectify the situation and consequently is chemically reactive.

The 1s orbital completes what is called the first valence shell, and the electrons of the next eight elements populate the second valence shell. We now see the physical basis behind Mendeleyev's arrangement of the periodic table, with two elements on the first row and eight on the second.

The second valence shell contains four orbitals, each capable of holding two electrons. One of these is another s-type orbital, the 2s orbital. The other three are known as p orbitals and have a shape reminiscent of a dumbbell. The three p orbitals are arranged at right angles to each other in space, all with their centres on the atomic nucleus. The shapes of s and p orbitals are shown in Figure 1.2. As the orbitals are filled, each additional electron fits into the next empty orbital. When all four of the two orbitals are occupied, the next electron pairs up with the one already in the 2s orbital, thus filling it. This then continues across the 2p orbitals.



An s orbital A p orbital An sp^3 orbital

Figure 1.2 Shapes of orbitals.

For example, the first element of the second row of the periodic table, lithium, has three protons in its nucleus and therefore has two electrons in the 1s shell (as do all subsequent elements) and one electron in its second shell. This latter electron occupies the 2s orbital. The next element is beryllium and has one of its electrons in the 2s orbital and the other in one of the 2p orbitals. Boron has one electron in the 2s orbital and one in each of two of the 2p orbitals. Carbon has one electron in each of its four 2 orbitals. As we move on to nitrogen, we now see the second shell electrons doubling up. Two of nitrogen's electrons are in the 2s orbital, and the remaining three are distributed across the three 2p orbitals. Oxygen has four of its second valence shell electrons paired up and two single electrons. Fluorine has only one unpaired electron and neon has none. This process of building up the valence shell by adding each new electron to the available orbitals in order of increasing energy is known as the 'Aufbau principle'. (Aufbau is German for building up.) Figure 1.3 shows this schematically with the electrons being represented by arrows with an upward pointing arrow indicating one spin direction and a downward pointing arrow representing an electron with the opposite spin. The three 2p orbitals are designated *x*, *y*, and *z* to represent the three orthogonal axes.

As stated above, unpaired electrons are unhappy and need to do something to find a partner; this process is called chemical bonding. On inspecting Figure 1.3, it is clear that lithium has one unpaired electron, beryllium two, boron three, carbon four, nitrogen three, oxygen two, and fluorine one and neon – like helium – has no unpaired electrons. These numbers are the same as the common valencies of

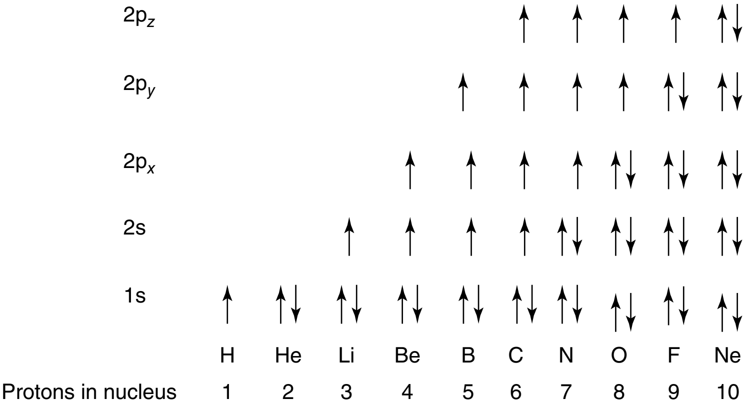


Figure 1.3 The electronic configurations of the first 10 elements.

the elements, and now we have the explanation for the periodicity that Mendeleyev noticed. Lithium has one unpaired electron and a valence of one just like sodium, the first element in the next row. Fluorine has a valence of 1, and so one lithium atom will bind to one fluorine atom to give lithium fluoride, LiF. On the other hand, beryllium with its valence of 2 requires two fluorine atoms to form beryllium fluoride, BeF_2. Compounds with oxygen are referred to as oxides, and we can now predict from Figure 1.3 that lithium oxide will have the formula Li_2O, whereas beryllium oxide will be BeO. Formulae of the type LiF, BeF_2, Li_2O, and BeO are known as an empirical formula and the subscript numbers tell us the proportions of the various atoms in the basic unit of the chemical compound.

Electronic Structure of Transition Metals

The third valence shell contains three types of orbitals. In addition to the s and p orbitals that we found in the first two shells, it contains a new type, the d orbitals. The five d orbitals of the third shell can hold a total of 10 electrons. However, they are slightly higher in energy than the 4s orbitals and so do not start filling until after the latter. This accounts for the broadening of the periodic table in the fourth row. Having filled the 3s and 3p orbitals at the inert gas argon, the next electron goes into the 4s orbital to give potassium, and the next electron completes the 4s orbital giving calcium. Instead of going into the 4p orbital, the next electron goes into the first 3d orbital to give scandium, and it is not until the 3d orbitals are full (at zinc) that we start feeding into the 4d orbitals at gallium. The fourth shell also contains f orbitals – which are slightly higher in energy than the 5p orbitals – and so we see another broadening of the periodic table after element 57, lanthanum. There are seven f orbitals in each shell, and so there are places for 14 elements in these series. These elements are called lanthanides and actinides after the elements that immediately precede them.

The fact that the orbitals of the higher valence shells overlap each other in energy means that electrons can be moved relatively easily from one to another and thus the elements in these central blocks exhibit variable valency, depending on how the electrons are arranged. The importance of this property will be seen in Chapter 8.

Hybridisation of Orbitals

As stated above, the carbon atom has two electrons in its first valence shell and four in the second. These latter are distributed with one in each of the 2s, $2p_x$, $2p_y$, and $2p_z$ orbitals. However, carbon can combine these orbitals though a process known as hybridisation. Hybridisation of one s orbital with one p gives two sp orbitals, one s with two p orbitals gives three sp^2 orbitals, and one s with three p orbitals gives four sp^3 orbitals. This phenomenon is a very important feature of carbon chemistry, and since fragrance ingredients are all compounds of carbon, it is imperative to understand for all that follows in this book. The shape of an sp^3 orbital is shown in Figure 1.2; it is essentially a dumbbell in which one side is much larger than the other.

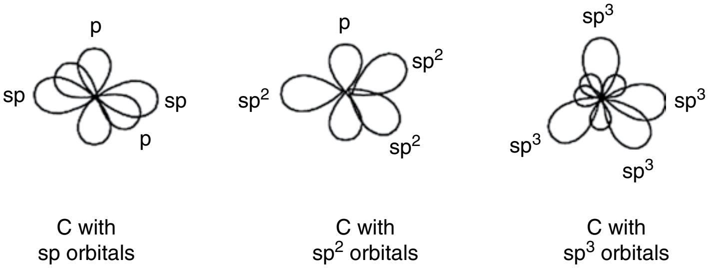


Figure 1.4 Carbon atoms with hybridised orbitals.

The spatial distribution of these hybridised orbitals is also very important and is shown in Figure 1.4. A carbon atom with sp hybridisation has two sp orbitals arranged in a straight line on opposite sides of the nucleus and two p orbitals mutually at right angles to each other and to the line of the sp orbitals. Thus, in Figure 1.4, the vertical p orbital and the two sp orbitals should be viewed as lying in the plane of the page, and the other p orbital has one lobe projecting directly upwards from the page and the other downwards behind it. In the sp^2 hybridised carbon atom, the p orbital and the left-hand sp^2 orbital are both in the plane of the paper, while one of the other two sp^2 orbitals projects forward from the page and other lies behind it. If this atom is viewed from directly above the p orbital, there is an angle of 120° between each of the three sp^2 orbitals. In the case of the sp^3 hybridised atom, the four sp^3 orbitals point towards the corners of a regular tetrahedron with an angle of approximately 119° between any two of them. Thus, in Figure 1.4, the upper and left-hand orbitals lie in the plane of the paper, and one of the right-hand orbitals projects forward, while the other recedes behind the page.

Chemical Bonding, Ions, Cations, Anions, and Molecules

We have already seen that only the inert gases have atoms that are happy as they are; all other atoms contain unpaired electrons that seek to form a pair with another electron. This pairing can be achieved by forming a chemical bond. There are two main types of bonding: ionic bonds and covalent bonds.

If we look at the two ends of the third row of the periodic table, we will find the alkali metal sodium at the left and the halogen chlorine at the right, just before the inert gas argon. Sodium and chlorine atoms both have two full shells of electrons, the first shell with two electrons and the second with eight. In the third shell, sodium has one electron and chlorine has seven. So, each has one unpaired electron, and each would really like to achieve the configuration of the nearest inert gas. For sodium, this would be most easily achieved by losing its one unpaired electron to give the same electronic structure as neon. On the other hand, chlorine would like to gain an electron, thus pairing up its single odd one and gaining the electronic structure of argon. So, if a sodium atom comes across a chlorine atom, it can donate its unpaired electron to the chlorine atom, and both can achieve inert gas-like electron shells. However, the sodium atom now has only 10 electrons, but it still has 11 protons in its nucleus. So overall, it has a surplus positive charge equivalent to that of one proton. Such charged species are called ions, and those with positive charges are called cations. Similarly, the chlorine atom now has 18 electrons but only 17 protons and therefore has a net negative charge of one unit. Negative ions are called anions.

The new substance produced is called sodium chloride, also known as common salt, the stuff we use to season food. The bond between sodium and chlorine in common salt is called an ionic bond. The process is depicted in Figure 1.5 where the shaded circle represents the electronic core equivalent to that of neon, the outer circle represents the third valence shell, and the dots represent the electrons of that shell. Similarly, when magnesium reacts with chlorine to give magnesium chloride, the magnesium atom donates one of each of its two unpaired electrons to one of each of two chlorine atoms to give a magnesium cation carrying a double positive charge and two chlorine atoms, each with a single negative charge. Thus, magnesium chloride contains one magnesium cation, Mg^{2+}, and two chloride anions, Cl^-.

Because ions carry electrical charges, ionic compounds (substances made up of ions, for example, common salt) tend to be solids (for reasons that will be clear later) and are usually more soluble in polar solvents. Polar solvents are those whose component molecules contain some areas that are positive and some that are negative and/or in which the charge distribution in the molecule is easily distorted.

In the latter case, the molecule is said to be readily polarisable. It is easy to see how the charged ions of a salt are more easily taken up and supported in a polarised or polarisable solvent. Water, H_2O, is a polar solvent as the hydrogen atoms in each water molecule carry partial positive charges and the oxygen atoms carry negative charges. Thus, when salt, NaCl, dissolves in water, each sodium cation will be surrounded by negative oxygen atoms from the water molecules, and conversely, the chloride anions will be held by the positively polarised hydrogen atoms of the water. In the solid state, the cations and anions will be held in a fixed array. Opposite charges attract, and so each cation will be surrounded by anions and vice versa. The exact way in which the ions are arranged relative to each other will determine the shape of the crystals that the salt will form. A small part of the crystal structure of sodium chloride is shown in Figure 1.6. Each sodium cation is surrounded by six chloride anions arranged at right angles to each other, at the corners of a regular octahedron. Similarly, each chloride anion is surrounded by six sodium cations. This lattice extends indefinitely in all directions. The basic unit of the structure, called the unit cell, is a cube, and so the overall shape of the entire assembly is a cube. If you grow salt crystals from a brine solu-

Figure 1.5 Formation of an ionic bond between sodium and chlorine.

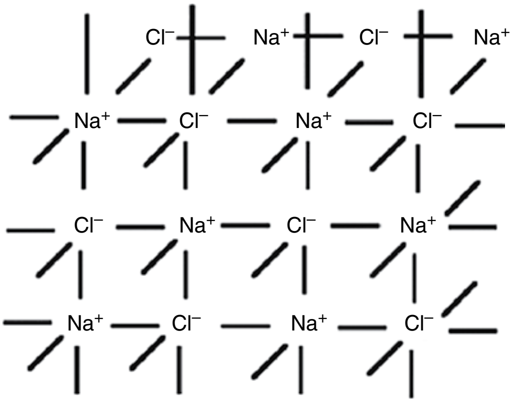


Figure 1.6 A fragment of the sodium chloride crystal lattice.

tion, you will indeed observe that the crystals are cubic in shape. This is an example of how the bulk properties of matter are dependent on their atomic and molecular properties.

The other form of bonding involves sharing electrons to form covalent bonds. For example, two hydrogen atoms can share their unpaired electrons as shown in Figure 1.7. The electrons become paired and inhabit what is called a molecular orbital. This orbital covers the space around both nuclei and therefore holds them together. There are two protons, one in each nucleus, and two electrons, so the electrical charges are balanced, and the hydrogen molecule is electrically neutral.

Similarly, one carbon atom can form covalent bonds with four hydrogen atoms to form CH_4, a gas known as methane. This occurrence is shown in Figure 1.8 where the solid circles around the hydrogen nuclei now represent a complete first electronic shell, as in the helium atom. The outer circle around the carbon nucleus represents its complete second valence shell.

The carbon orbitals used in forming methane are sp^3 orbitals, and so the methane molecule will have a hydrogen atom at each corner of a regular tetrahedron. There are various ways of depicting this as shown in Figure 1.9. The most common method used in written figures is to depict the bonds as lines between the symbols representing the nuclei. In Figure 1.9, the bonds are shaded to show perspective. Regular lines are used for bonds in the plane of the paper, solid shading for bonds coming forward out of the plane of the paper and hatched shading for bonds that recede behind the plane of the paper. The formula CH_4 is known as the empirical formula of methane. The first drawing shown in Figure 1.9a,

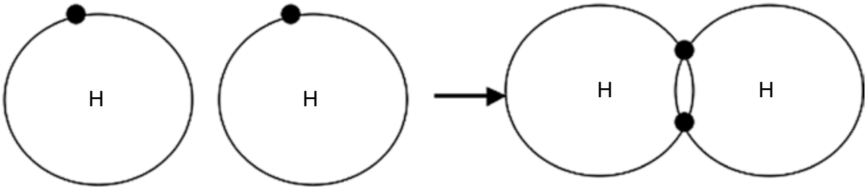


Figure 1.7 Formation of a covalent bond between two hydrogen atoms.