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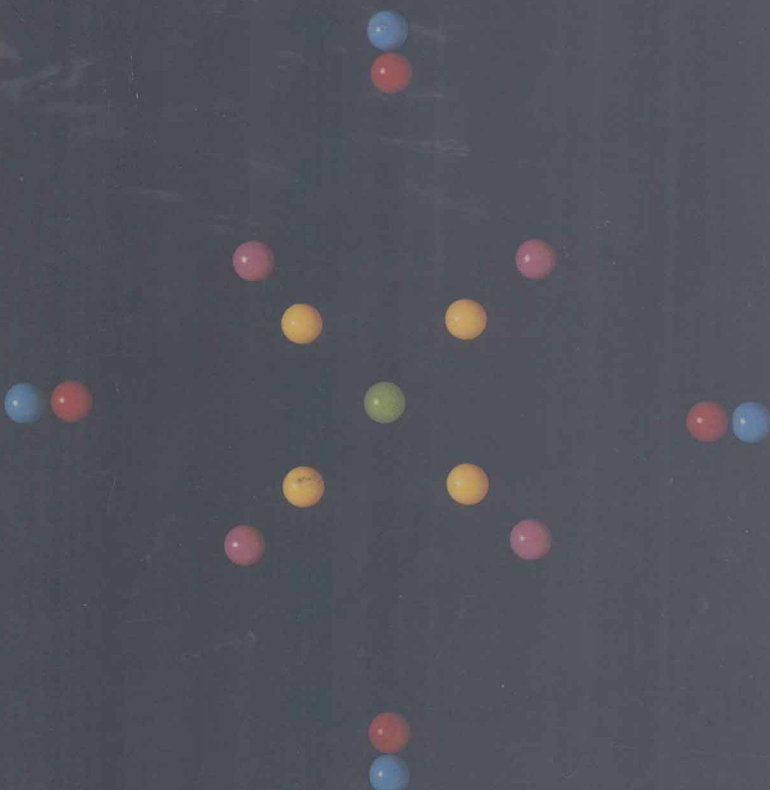
THE PROBLEMS OF CHEMISTRY

W. GRAHAM RICHARDS



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The Problems of Chemistry

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Preface

Chemistry had a beginning. It can be dated fairly precisely as a few hundred thousand years after the 'big bang', which is time zero for the universe as we comprehend it. By then, long before galaxies or solid bodies were in existence, molecules had formed. The formation of molecules and their subsequent reactions to form new molecules, then solids, and ultimately our world, are the stuff of chemistry. Chemistry as an academic discipline is predominantly the study of phenomena at the level of the molecule.

The molecule is the smallest unit of matter which is stable under the conditions prevailing in our world, and therefore the study of phenomena at the molecular level is inevitably wide-ranging. The basic unit of almost everything we see, touch, feel, or indeed are is molecular. Thus chemistry encompasses molecular biology, the nature of materials, and the properties of gases both in the atmosphere and in interstellar space.

That molecules are the building blocks of matter did not become apparent until the nineteenth century, because most substances are complicated mixtures of already complex molecules and were beyond the analytical understanding of early chemists. Once scientists started defining the molecular nature of substances, however, progress was explosive. By the present time, some 20 million separate and distinguishable molecules have been characterized. Theory has advanced to the point where the structures of many molecules can be predicted from a knowledge of their constituent building blocks—atoms. At the same time, the results of mixing molecules to give reactions which create new molecules are still largely deduced from experiment, and even if the products of such reactions can sometimes be predicted, the rate (or speed) of the reactions remains a matter of speculation.

By comparison with its flanking subjects, physics and biology, chemistry often seems unspectacular. As a discipline it does not enjoy the Press or television coverage given to quarks and particle physics, to black holes and astronomy, or to advances in biology and medicine. Despite this, chemistry, of all academic disciplines, has had the most far-reaching impact on social habits and values. The atomic bomb may have been spectacular, but the lives of people have been influenced far more by less dramatic innovations such as detergents, artificial fibres, plastics, synthetic dyes, antibiotics, and the contraceptive pill: all the fruits of chemistry.

The author is happy to acknowledge the generous editorial help of Hugh Oliver.

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How it all started: molecules in interstellar space

In the beginning, according to the best available theory, there was a huge explosion. The 'big bang', as physicists and cosmologists call it, is generally agreed to have been the unique moment when our universe began. It can be dated to a time some 13,000 million years ago when, with all matter/energy confined in one spot, there was an explosion which sent every particle of matter rushing apart from every other particle. This process continues to our own day as galaxies recede from each other: hence the description 'expanding universe'.

The formation of atoms

Physicists' knowledge of the early universe immediately after the big bang now extends back to less than one-hundredth of a second after the primary event. At this stage, the temperature of the universe was hotter than the centre of the sun and its density more than a billion times denser than water. Since that time, the universe has cooled and its density has diminished, at first rapidly and later more slowly. As the cooling has proceeded, the fundamental constituents of matter have gradually accreted to give more complex, heavier structures—just as, on a simpler scale, steam cools to give first water, then ice.

In the early minutes of the universe, the only matter existing was in the form of the fundamental particles which are the building blocks of atomic nuclei (the cores of atoms). In our time, to study these particles we have to expend massive amounts of energy and do collision experiments to smash up atoms. Such experiments in particle physics are performed with gigantic and expensive accelerators, like those at the CERN (European Centre for Nuclear Research) laboratories in Geneva or the Stanford Linear Accelerator in California.

Some three minutes after the big bang, the inverse of the process we use in atomic bombs or for nuclear power generation occurred: the creation of matter from energy.

In nuclear power-stations, the energy holding together the fundamental particles which make up the nuclei of atoms is released as heat and is used to generate steam to drive turbines: energy is created from matter following Einstein's famous equation, $E = mc^2$—where the energy, E, is related to the mass, m, by the large constant, c^2, the square of the velocity of light. So fast is the speed with which light travels (186,000 miles per second) that only small amounts of matter in the form of uranium or plutonium are needed to create vast quantities of energy. In the early universe, the equation worked in reverse, and energy in vast amounts was used to produce relatively small amounts of matter, some of it in the form of positively charged atomic nuclei and other building blocks of matter like electrons.

The positive electrical charges on these atomic nuclei attracted the very much smaller, negatively charged electrons—just as the north and south poles of magnets attract each other. Working against the attractive forces were the sheer chaos and random motions of the heat-activated particles—like a set of magnets shaken so violently that the attractions are not strong enough to overcome the buffeting as they bang into each other. After a few hundreds of thousands of years, however, the universe cooled sufficiently for the attractive forces to dominate the random chaos. Negatively charged electrons joined with positively charged nuclei to form neutral atoms.

At the same time, different types of atom arose from the fusion of nuclei, resulting in about a hundred distinct chemical elements. (To be precise, there are 92 naturally occurring elements, uranium being the heaviest; and since 1940, about a dozen, heavier, man-made elements have been synthesized.) Each element is distinguishable by the number of positive charges on the nucleus, known as the atomic number. In the electrically neutral atom, the nucleus is surrounded by a corresponding number of negative electrons. Neutral atoms form the basic building units of molecules. If the atom gains or loses an electron it will have a resultant negative or positive charge and is often called an ion.

Figure 1 shows the structures of some of the simpler elements, and Figure 2 part of the periodic table, in which is summarized the structures and many of the properties of the different elements. The periodic table was first devised in 1886 by the Russian chemist Mendeleyev, who was sent to study in France and Germany. Mendeleyev sought to classify the chemical elements according to the weights of their respective atoms (atomic numbers being unknown at that time). At a conference in Karlsruhe in 1860, many of the outstanding questions about atomic weights were settled, providing Mendeleyev with the data

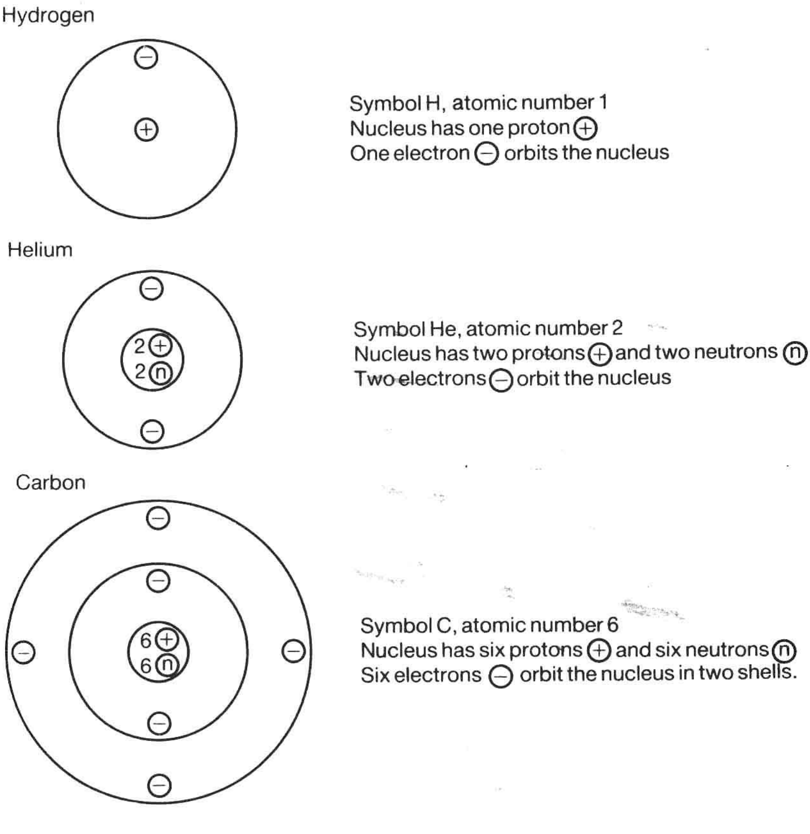

Figure 1. The structures of some simple atoms

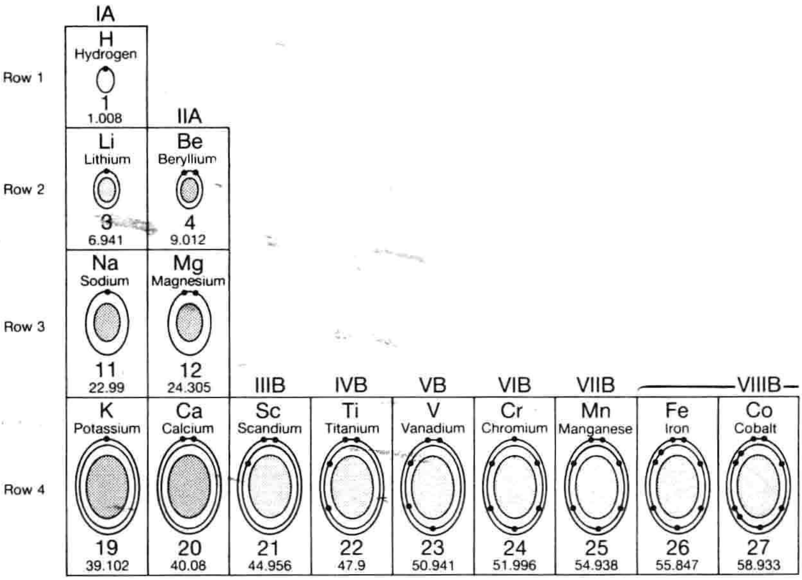
IA
H
Hydrogen
1
1.008
Row 1
IIA
Li
Lithium
3
6.941
Be
Beryllium
4
9.012
Row 2
Na
Sodium
11
22.99
Mg
Magnesium
12
24.305
Row 3
IIIB
IVB
VB
VIB
VIIB
VIIIB
K
Potassium
19
39.102
Ca
Calcium
20
40.08
Sc
Scandium
21
44.956
Ti
Titanium
22
47.9
V
Vanadium
23
50.941
Cr
Chromium
24
51.996
Mn
Manganese
25
54.938
Fe
Iron
26
55.847
Co
Cobalt
27
58.933
Row 4

Figure 2

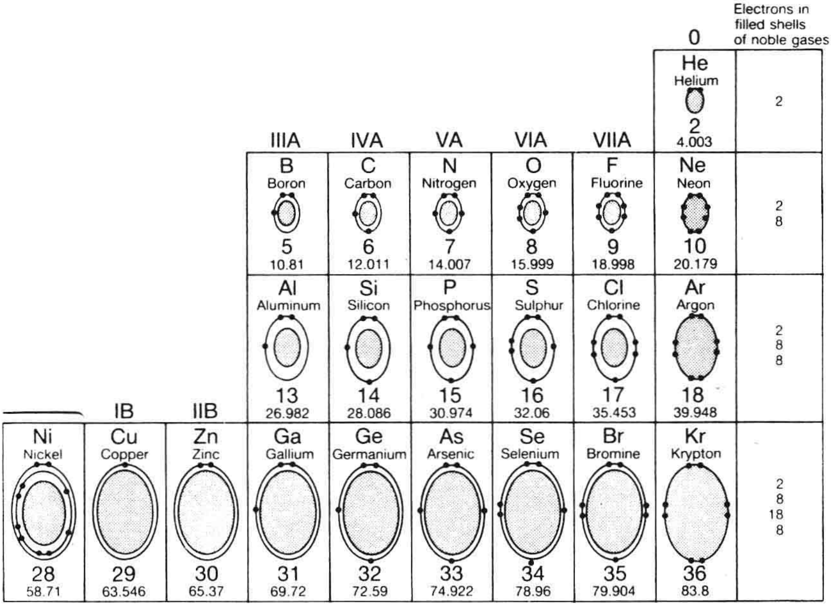

Figure 2. Part of the periodic table of elements

The progressive buildup of atoms is shown by the filling of shells with electrons (dots). The first-row shell is filled with 2 electrons; the second-row shell with 8 electrons; and the third-row shell also with 8 electrons. The fourth row adds 18 electrons in two subgroups which accept up to 10 and 8 electrons respectively. The atomic weights of the elements are the small numbers under the atomic numbers. They are all based on an assignment of exactly 12 as the atomic weight of the carbon-12 isotope.

upon which to make his classification. Arranged in order of increasing atomic number, the chemical elements exhibit some properties in common down the table and, to a lesser extent, across the table. For example, the properties of magnesium are quite similar to those of beryllium and calcium above it and below it in the group known as the alkaline earth metals, and magnesium also shares some properties with sodium and aluminium on either side of it in the horizontal period.

Modern knowledge has revealed that the order inherent in the periodic table depends on the arrangement of the electrons around the atomic nucleus or, in other words, on the way in which the atomic number is made up. The electrons occupy what are called 'shells', and each shell has a specific number of electrons that it can contain before it becomes 'full'. The number of electrons outside the filled shells is primarily responsible for the chemical properties of an element, including the types of molecule it will form.

The formation of molecules

For the most part, atoms are joined to other atoms. Although they are electrically neutral, atoms have a strong tendency to combine so that their electrons can form certain stable groupings. A situation with two electrons orbiting an atomic nucleus is stable in a way in which a single electron orbiting a nucleus is not. Thus hydrogen, with its single negative electron orbiting the nuclear charge of one positive unit, is not stable as a single atom. By combining, two hydrogen atoms form the more stable hydrogen molecule, in which the two electrons orbit both of the two nuclei.

The arrangements of electrons which have the greatest stability are revealed by looking at one particular group of elements in the periodic table—the rare or inert gases, helium, neon, argon, krypton, xenon, and radon. The atoms of these gases do not normally combine with other atoms. Hence the arrangement of electrons in their shells must have special stability. The stable totals for the electron shells, as revealed by the electron arrangements in these rare gases, are 2, 8, 8, 18, 18, and 32. The precise significance of these specially stable groupings is now readily understandable from quantum mechanics, which can predict how many electrons confer special stability on particular shells.

In elements other than the rare gases, similar shell structures of electrons are found, but the outermost shell is incomplete and can achieve the special stability only by gaining or losing electrons (which will leave the atom negatively or positively charged) or by sharing electrons (as in the hydrogen molecule). The tendency of atoms to combine so as to produce stable electronic arrangements leads to the formation of molecules. Among the different chemical elements, there are millions of possible combinations. Simple examples of molecules are water (H_2O), ammonia (NH_3), and alcohol (C_2H_5OH). These formulae indicate which atoms of a particular type are present in molecules of a pure substance and how many there are of each type.

Molecules, as mentioned at the beginning, are the building blocks of all the substances we see and experience in everyday life.

Molecular models

The molecule is the building block which helps to explain the widest range of phenomena in medicine and biology as well as in chemistry. The simplest and most convenient way of representing the molecular idea is through models. Atoms can be thought of as spheres whose sizes, known from experiment, depend on the number of orbiting electrons (equal to the positive nuclear charge) they contain and the shell structure of these electrons. Indeed, atoms are conventionally represented by coloured spheres of appropriate relative sizes. Each sphere is a scaled-up representation of an atom, the size increased by approximately one hundred million times (Figure 3 gives some simple examples).

The models may also show how the atoms combine to form the stable electron pairings of the rare gases. For example, hydrogen needs one more electron whereas carbon needs four more electrons for a stable grouping to be obtained. And it is here worth noting that chemical elements in the same vertical group in the periodic table have similar electronic arrangements (especially in terms of the number of electrons needed to fill their outer shells), which explains why their chemical properties are similar.

Where electrons are shared between atoms, chemists speak of 'bonds' being formed. These electron-shared bonds (covalent bonds as they are sometimes called) are strong, and at normal

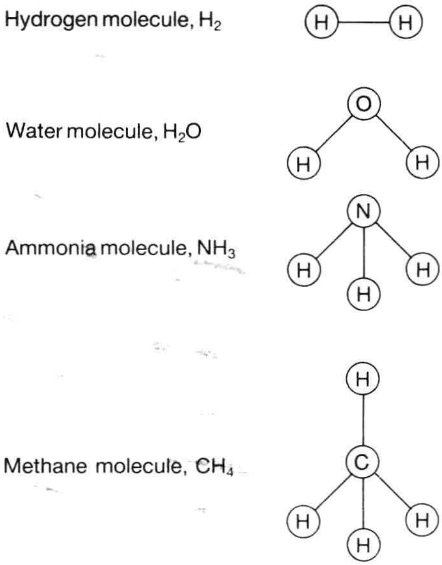

Figure 3. Molecular models

temperatures the molecules formed by this bonding of atoms are quite stable. Thus, although in heating water we may separate the molecules from the weak forces which hold them together as a liquid, we do not disintegrate the individual water molecules (H_2O) into hydrogen and oxygen unless we use very large amounts of energy.

Interstellar molecules

Some molecules were formed in the early years of the universe by atoms combining to give systems of shared electrons which became more stable as the temperature fell. As the fireball expanded and cooled, gravity caused some of the atomic and molecular matter to aggregate and to form clusters of galaxies and individual galaxies. Within each galaxy, clouds of atomic and molecular particles condensed to form dust particles, leading to further aggregation, and, ultimately, to the formation of stars like our own sun. In the hot interior of stars, nuclear reactions give rise to the hundred or so different sorts of atom (i.e. chemical elements), which, as we have seen, combine to give millions of different types of molecule.