

FEATURE ARTICLE

WHY CHEMISTRY IS WORTH STUDYING

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It has been said that Chemistry is an 'enabling science', that is, it has value not only in itself, but because it makes possible a whole range of other scientific activity. I should like to explore some of the reasons for this claim, to say something about what chemists do and how chemists think, and to show how the subject retains its interest and fascination. My examples will be drawn from my own experience as a professional chemist working in a university, but this experience has not in any way been unusual. Others would choose different examples but I think would make very similar general points.

Chemistry is important in a range of related subjects. This is illustrated in Fig. 1. Anyone working in the fields shown requires at least some knowledge of chemistry, so chemistry must form part of the curriculum for a wide range of professional scientists. Further, it is possible to devise research projects which involve interactions between chemistry and each of these related areas. A few examples will make the point.

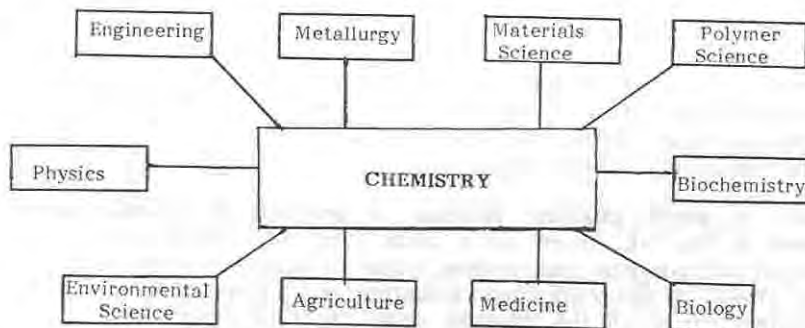


Fig. 1 The central place of chemistry

It was reported in 1987 that a mixed oxide $\text{YBa}_2\text{Cu}_3\text{O}_x$ ($x = 6-7$) was a superconductor at 98 K, some 20 K above the temperature which can be maintained by cheap and readily available liquid nitrogen. Previously, superconductivity, that is the passage of electric current through a material without loss of energy, was observed only at lower temperatures which required the expensive liquid helium as coolant. Now, provided the mixed oxide ceramic can be formed into suitable shapes, a range of engineering and electronic devices and applications can be envisaged. Understanding how the superconductivity arises is essentially a problem for chemistry, manufacturing and processing are problems requiring cooperation between chemists, physicists and engineers. The yttrium barium copper oxide is only one of a series of superconducting ceramic oxides, and discovering how to synthesise further materials is an exciting current chemical challenge (1).

My second example is also from materials science. Components of gas turbines are required to maintain their integrity at very high temperatures under conditions where metals are useless. But substances which are extremely strong or extremely refractory are often difficult to form into intricate shapes. Silicon nitride (Si_3N_4) has high strength, alumina (Al_2O_3) is highly refractory. Replacement of Si-N in silicon nitride by the isoelectronic Al-O gives new materials called Sialons $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$ ($0 < z < 4$) which have both the high strength of Si_3N_4 and the chemical inertness of Al_2O_3 (Note that the Al is 4- rather than 6-coordinate as in Al_2O_3 , so the Al-O bonds are stronger). However, the Sialon solid solutions form liquid with, say, Y_2O_3 at lower temperatures than the pure components so the material can be densified by pressureless sintering making component manufacture much easier. Imaginative application of quite simple chemical ideas makes possible extensive new engineering developments (2).

A much older example of a chemical advance which led to a spectacular engineering development was the discovery by Ziegler and Natta of how to make isotactic polypropylene (3). The addition of a new monomer unit to a growing polypropylene chain produces a new asymmetric centre. In the atactic polymer successive asymmetric centres are randomly left and right handed and the polymer is liquid at room temperature. If the stereochemistry of successive centres is controlled by use of a catalyst consisting of a transition metal chloride and organometallic compound, the polymer strands are regular in shape, and thus pack in extensive crystalline regions. The melting point of isotactic polypropylene is $165-171^\circ\text{C}$: the material can be used for utensils to contain boiling water and the range of applications is vastly extended.

My final example is in the control of the disease schistosomiasis (bilharzia) which afflicts more than 200 million people in at least 80 countries. The life cycle of the parasite involves both human and snail hosts. Chemists can collaborate with doctors, farmers or agricultural advisers to break the cycle at several different points, e.g. by use of drugs (chemotherapy) in the primary host, by attack on the secondary host, or by water treatment and purification. There is important work in Ethiopia on the use of endos as a naturally occurring molluscicide. There are of course many other examples of the use of chemistry in medicine or agriculture: I have not cited them simply because many of the compounds used are organic and I am not an organic chemist, but I certainly do not underrate their importance.

Chemistry is worth studying because it provides a valuable educational experience.

In the UK, there are a little over 2000 chemistry graduates per year. About half continue their studies, mainly in academic research and teacher training. These are the professional scientists from whom many of the advances in the subject come. Of the thousand or so who seek employment immediately on graduation (after three years in Britain) about a third obtain jobs in scientific research, design and development. These too are professional scientists using their degree subject more or less directly in their employment. The remaining two thirds (500-600 graduates per year) enter a wide range of professions, in administration and management, scientific support services, marketing, management services, financial and legal work, personnel, social and medical services. Chemistry is of course not unique among university subjects in providing for a variety of professions but the astonishing range of occupations which chemists take up and make a success of suggests that the education which the subject provides is useful and enabling over many fields.

I think there may be at least two reasons for this. First, a chemist has to be both numerate and literate. Parts of the subject are like physics where problems are usually extremely well-defined and the challenge is to find as precise an account of them as possible, often in carefully formulated mathematical language. Parts of chemistry are however more like biology

where the sheer complexity of the problems tackled makes precise quantitative description inherently impossible. Statistical formulations or accurate accounts in words of results and arguments are required. Secondly, a chemist's thinking has to shift between two distinct frames of reference: on the one hand the observations and measurement which are made at the bench, and on the other the models or theories which are used to interpret them. These areas are of course related but it is vital for the professional chemist to be clear in which category - observations (fact) or theory - a particular statement is to be placed.

I should like to illustrate some problems of chemical thinking by reference to two questions which we sometimes ask 18-year old students applying for admission to the University of Sussex to study chemistry. The first is: "**Why do you believe in atoms?**" This usually produces quite a long silence: most students find the question difficult to answer and it is clear that they have not thought about the question before. Most eventually reply that they believe in atoms because that is what they have been taught. There is nothing wrong with this: most beliefs start this way but the response shows how insecure even university students, who have already taken chemistry for several years at school, are in their grasp of their subject. A belief cannot of course be proved: it is something we know and hold because it enables us to make sense of and respond to a whole a range of varied experience. Each time we test our belief in a new situation we strengthen and confirm it. Beliefs taken on trust from someone else without personal reaffirmation often prove to be inadequate in new situations.

Experience with graduate students over a number of years has convinced me that it sometimes takes a long time before a belief in atoms provides a sound framework for research. Suppose a chemist gets a low yield in a synthesis. There is no point in repeating the experimental procedure in exactly the same way, yet that is that what many graduate students do. A chemist who believes in atoms (conserved during a reaction) will ask several questions about the low yield.

Has all the starting material been consumed?

If yes, where have key elements or group of atoms gone?

Can side reactions be avoided by change in temperature or solvent?

Is product being lost in the work up procedure?

Failure to ask questions such as these (and to act accordingly) shows that belief in atoms is insufficiently established to provide a safe framework for chemical thinking. A good research chemist thinks about every move he makes, passing easily from measurements and observations to postulates and theory - and back again.

The second question which I often put to 18-year old students is: "**How do you know that methane is tetrahedral?**" In this case, the answer is usually given without hesitation: 'Because carbon is sp^3 hybridised'. This answer is revealing in several ways. First the answer is like that to the earlier question, second-hand. Eighteen year old students cannot be expected to know much about spectroscopic methods, electron diffraction, or quantum mechanics. They know methane is tetrahedral because that is what they have been told. Secondly, the answer confuses observation and theory. We introduce the concept of hybridisation to describe electrons in a tetrahedral molecule. Hybridisation does not itself determine the shape. Most of us 'know' (or should we say 'believe?') methane is tetrahedral because such a postulate makes possible the correlation of a mass of physical measurements. The assumption that the coordination at saturated carbon is tetrahedral makes sense of an even greater body of observations on organic compounds and, historically, this second mass of evidence led to the postulate of tetrahedral methane before the advent of physical methods. Hybridisation is a useful concept in organic chemistry: if we wish to describe the electrons in methane when they are disturbed, e.g. by UV absorption, or

when one is removed, hybridisation is not a useful concept. Further, there are some carbon compounds where the coordination is not tetrahedral: the writers of a recent textbook (4) have pointed out that carbon may have coordination numbers from 1 to 8 (Fig. 2). Only when carbon makes four bonds is sp^3 hybridisation useful: for other coordination numbers the concept is unhelpful. This leads to my next point.

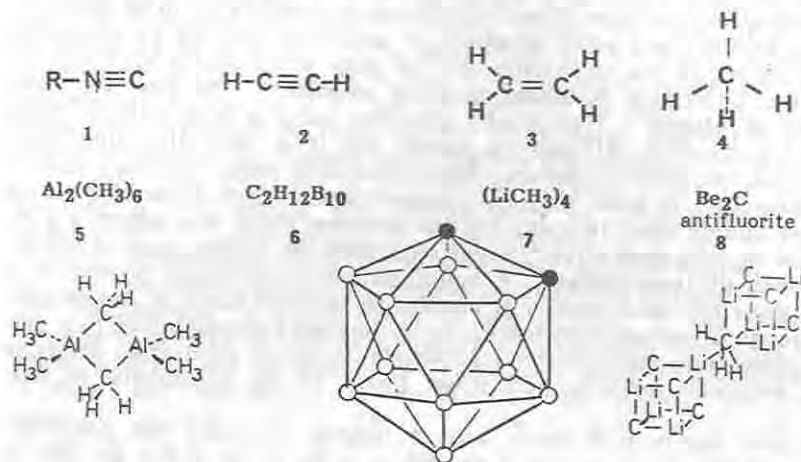
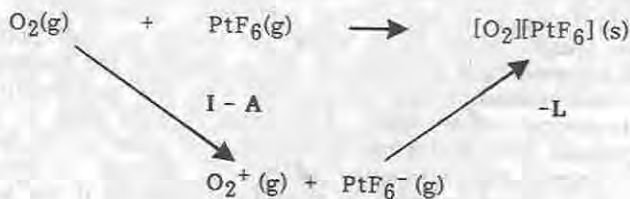


Fig. 2 Coordination of carbon. The structures of $Al_2(CH_3)_6$, $C_2H_{12}B_{10}$ (open circles BH, filled circles CH) and $(LiCH_3)_4$ are shown. The $(LiCH_3)_4$ tetramers are linked by weak $Li \cdots C$ bonds making C 7-coordinate and resulting in low solubility in organic solvents.

Chemistry is worth studying because there are surprises in store. Scientists need always to be prepared to modify their theories to accommodate new facts. What seems to be well established in one generation is changed in the next. This assertion can be illustrated by reference to some examples where what I was taught as an undergraduate is no longer accepted. This does not mean that I was taught a lot of errors, merely that all generalisations are conditional. They apply only to facts already established, not necessarily for ever.

(a) I was taught that the noble gases were inert because they had complete valence octets and so could not form compounds. This was shown to be incorrect by Bartlett in 1962 (5,6). The reaction between dioxygen and platinum (VI) fluoride gave a compound identified as $[O_2][PtF_6]$ with an ionic structure like that of $[NO][PtF_6]$. A simple thermodynamic cycle shows that the energy required to ionise the O_2 (I) must be provided by the electron affinity of PtF_6 (A) and the lattice energy of the product (L). But the ionisation potential of Xe (1170 kJ mol^{-1}) is very similar to that of O_2 (1180 kJ mol^{-1}). This encouraged Bartlett



to try to oxidise xenon with PtF_6 and the belief that the noble gases could not form chemical compounds had to be modified. A number of compounds e.g. XeF_2 , XeF_4 , XeF_6 , XeOF_4 , XeO_2F_2 , XeO_3 are now known. The interesting point about the way the earlier belief was changed is that it required reasoning taught to all first year undergraduates. The crucial extra requirements were imagination and the ability to see the implication of a new piece of information (the oxidation of dioxygen) in the light of information already established (the ionisation potentials of dioxygen and xenon).

(b) I was taught the transition metals could not form stable organometallic compounds because M-C bonds were weak. This idea appeared in a number of papers and textbooks in the 1950's. Now, of course, many such compounds are known, and I shall mention only one example from our own work at Sussex. The reaction between the organolithium compound $\{(\text{CH}_3)_3\text{Si}\}_3\text{CLi}$ and halides MX_2 (M = Mg, Zn, Cd, Hg, or Mn) gives dialkyls MR_2 (7,8)



The manganese compound melts without decomposition at 290°C ; there is no evidence that the Mn-C bond is particularly weak.

(c) It used to be said that elements in the first row of the Periodic Table differed from those in the second row in that the former could form double bonds whereas the latter could not. This generalisation was supported by numerous examples: CO_2 is gaseous at room temperature and has a molecular structure but SiO_2 is a refractory solid with an extended three dimensional array held by strong Si-O bonds. Alkenes were well known, silenes were not, Dinitrogen and dioxygen are gases, phosphorus and sulfur are liquid or solid with oligomeric or polymeric structures. The 'double bond rule' which said that only first row elements could form double bonds can no longer be defended. Some of the compounds which have recently been described are shown in Fig. 3(9-16). Double bonds involving second row elements are somewhat weaker than those between first row elements but not very much weaker. They are, however, considerably more reactive so that alternative products are often formed more easily than with the first row elements. It is significant that new types of molecule are obtained when large substituents block some of the decomposition paths observed with compounds with smaller substituents. The same principle applies in (b) above.

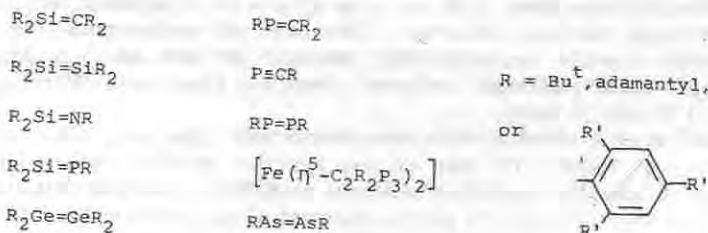


Fig. 3 Compounds with multiple bonds to second row elements.

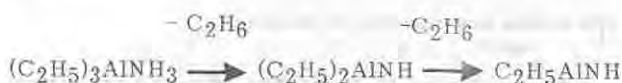
Many more examples could be chosen to make the same point. There will be as many surprises in the next thirty years as in the last thirty. Scientists will climb new mountains and discover whole new areas for exploration on the other side.

However, resources are limited. Not all worthwhile research can be done and not all mountains can be climbed simply because they are there. How are we to decide which problems to tackle and which mountains to climb? There

are two main models for the allocation of funds. The most popular one is used by governments and grant awarding bodies throughout the world, which attempt to identify proposals showing the greatest "timeliness and promise". They decide which are the most important problems and then invite chemists to solve them. This approach is illustrated by the current funding for work on superconductors; or by the drive to find therapy for diseases such as AIDS, cancer, or bilharzia. Most industrial research is of this kind and there is no doubt that a good deal is achieved. However, the approach is not without difficulties. Governments, research managers and grant awarding bodies tend to formulate problems in simplistic terms and do not always ask quite the right questions or formulate the right tasks. Applicants have to be optimistic in writing proposals in order to be funded, and when short term results are not achieved fashions can change very quickly. Almost all industrial research workers are familiar with the frustration which results from frequent changes in research objectives and almost all university research workers are familiar with the problems of modifying proposals to make them seem relevant to the latest centrally directed initiatives.

The second approach is to allow research (at least in universities and in some parts of industry) to be curiosity-driven. Researchers are allowed to tackle problems which they think are worthwhile or interesting and allowed to climb mountains simply because they are there. This approach may produce solutions before problems are formulated. What is necessary then is that research scientists should be aware of what problems need solutions and that those who identify problems are aware of possible solutions which have already been found. It is one of the main functions of the learned societies, both national bodies such as the Chemical Society of Ethiopia or organisations such as the International Union of Pure and Applied Chemistry to bring together academics, industrialists, civil servants, and teachers and through meetings and publications facilitate the free exchange of ideas. There are many examples of curiosity-driven research which have eventually found application. One that is frequently quoted is the rapid development of liquid crystal displays, made possible by the availability of long thin organic molecules synthesised in university laboratories without awareness of any possible application. One of the students at Sussex has been working recently on the interaction between alkali metal ions and clay minerals, an important subject in connection with clay dispersion and land erosion (17). He had studied Na^+ and K^+ and his supervisor said "You may as well test your results further by looking at the effects of Rb^+ and Cs^+ even though the interaction of these ions with clays has no practical application". A week later the Chernobyl accident occurred. Removal of radioactive ^{137}Cs from the environment became an extremely pressing problem and no doubt literature on the interaction between Cs^+ and clays has been very thoroughly examined in the last couple of years.

My last example comes from my own work. The very first research paper I published at Sussex (18) was on the reaction between triethylaluminium and ammonia. I and two research students described how the initial product lost ammonia on heating to give a glassy material of composition EtAlNH



At the time no one was very interested: the work was published and, I thought, forgotten. In the last few years, however, it has been realised that aluminium nitride has considerable potential as a material for high power microelectronic circuits. Compared with similar materials it has high thermal but low electrical conductivity and its thermal expansion is very similar to that of silica. The synthesis of high purity aluminium nitride has thus become an important research

objective in several laboratories throughout the world. Our work of twenty years ago has been read and considerably extended and the results have been described in a recent patent (19).

Chemistry is however worth studying only if a clear distinction is made between what we know for sure (measurements or experimental facts) and what we know only provisionally (theories, models, hypotheses). This is important for all who teach and have the responsibility of ensuring that the subject is kept open-ended, interesting, and exciting. It is also important for those who allocate resources for research and who have to strike the right balance between funding short term projects with clearly defined objectives and long term work designed to gain insight into the subject and develop fundamental understanding.

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