The Chemistry of Solids.[1]

By Prof. Cecil H. Desch, F.R.S.

It is remarkable how little we know with any certainty about the chemical properties of solids, although the idea of a solid is so fundamental. At the present time we always begin the study of chemistry with the gases on account of the simplicity of their mathematical treatment, but it must be remembered that this simplicity is the result of long study and of many discoveries. To the unscientific mind the solid is simpler, because more tangible. When men have tried to understand gases, they have expressed themselves in terms of solids. The atom, however attenuated it may have become in recent years, was in the first instance essentially a solid sphere, and the elasticity of gases has been explained in terms of the collision of elastic solid particles in motion.

Our conception of liquids has been based in the same way on the idea of moving particles, themselves thought of in terms of the solid state. Yet, of solids themselves, whilst our knowledge of their physical and mechanical properties is very extensive, our chemical information is of the most meagre kind. It was an old doctrine that chemical reactions could only proceed in the gaseous or liquid states, so that chemical action on a solid was always preceded by the tearing off of atoms from the surface under the influence of electrical forces. That view can no longer be maintained. Chemical reactions can occur within or at the surface of a solid, but the experimental difficulties are sometimes such as to make the exact investigation of the subject a difficult matter.

In the modern conception of a solid, the atoms are characterised by a regular arrangement in space, that arrangement being repeated so as to build up a crystalline lattice. Crystals and aggregates of crystals are thus the only true solids, glasses being regarded as under-cooled liquids of high viscosity. The X-ray method developed by Laue and by W. H. and W. L. Bragg has made it possible to determine, not only the class of a crystal, but also the exact lattice possible to crystals belonging to that class. The connexion between the chemical properties and the crystalline structure still remains indeterminate, although it must be very intimate.

There are many reasons why the chemical study of solids should receive greater attention. In metallurgy, although metals and alloys may, and most frequently do, pass through a molten stage in the course of their manufacture, they may undergo many important changes of structure and constitution at temperatures far below that at which the last liquid portions have completely solidified, and these changes may be so far-reaching as to convert an alloy into one seemingly of an entirely different class, although the gross chemical composition has not altered. The petrologist, especially when dealing with igneous and metamorphic rocks, has to consider reactions which proceed in the midst of solids of high rigidity. Several industries, such as that of cement, are based on reactions of the same kind as those with which the petrologist has to deal. Sintering is not always due to the presence of small quantities of molten material between the solid particles, and it is now certain that union of solid masses under pressure may occur without actual melting. This was shown by Spring forty years ago, but for long, although frequently quoted, his results received little consideration.

The most striking application of the principle is seen in the metallurgy of tungsten. This metal was formerly described as very hard and brittle, and it is not possible, by casting it and then annealing, to bring it to a ductile form. The method now adopted is to prepare it in the form of a pure powder, and then to bring it to a compact state by compressing, heating, and hammering while very hot, and finally drawing. As this process is continued, and as an originally thick rod becomes extended into a slender wire, the brittleness progressively disappears, and at last the tungsten is obtained in those beautiful filaments, drawn to extreme fineness, with which we are familiar in our electric light bulbs and wireless valves. A somewhat similar example is that of the adhesion of an electrolytically deposited metal to its support, which is sometimes so perfect as to approach the breaking strength of one of the metals, although interpenetration of crystals is not to be seen under the microscope.

There is another aspect of the chemistry of solids which will make an appeal to some who are not chemists, but amateur students of Nature. The great beauty of natural crystals has attracted the attention of poets and artists as well as men of science. Much of this beauty depends on the varying habit of one and the same crystal species. Even with such a common mineral as quartz, it is possible on entering a mineral collection to point to some of the crystals exposed, and to name their locality, when once the form has become familiar. The same is true of other minerals. Why should there be this variation, when the chemical composition of the distinct varieties may be identical, so far as analysis is able to give information?

Again, the crystalline system will not account for the differences in the building up of individuals to form aggregates. Rock salt and cuprite crystallise in cubes, and the space lattice has a very similar form in the two minerals; but when the salt forms multiple growths, the cubes arrange themselves in characteristic stepped pyramids, whilst the red oxide of copper may form the most beautiful hair-like threads, a tissue of scarlet silk, as Ruskin calls it. Neither mineral ever assumes a form which is characteristic of the other, the simple cube being once departed from. Why should this be? It is known that the presence of traces of foreign matter may cause differences of habit, the most famous example being that of the crystallisation of common salt in octahedra instead of cubes when a small quantity of urea is added to the solution, but the explanation of these facts is still imperfect.

The work of Johnsen and of Gross has shown that the appearance of a face on a crystal placed in a supersaturated solution is really determined by the velocity of growth in a direction normal to that face,

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[1] From the presidential address delivered at Southampton on August 31 before Section B (Chemistry) of the British Association.

those faces being produced which have a minimum velocity of growth. Some light is thrown on the subject by a study of the growth of a crystal when solvent is completely excluded, the substance used being sublimed in a vacuum. This has been undertaken by Volmer, who finds that cadmium, zinc, and mercury crystals grow in this way in a high vacuum. When small nuclei are present, those grow which have the face with the smallest velocity of growth perpendicular to the stream of impinging molecules. The differences between different faces are large, so that under these conditions either flat tables or long prisms are usually formed, according to the direction of the original nucleus. The crystal grows by the addition of thin laminæ, probably only one molecule thick, which spread over the surface. This is likely to be the process when the crystal is growing in a solution or in a molten mass, as well as in the vapour; and, in fact, when cadmium or tin is being deposited electrolytically at a cathode, or when lead iodide is being formed from a solution of a lead salt and an iodide, the growth of the crystal may be watched under the microscope, when a thin film begins to form at some point on a face, and extends over the face, maintaining a uniform thickness throughout. It is realised that in the presence of a foreign substance, either molecules or ions may attach themselves to such a surface by their residual affinity, and this will necessarily affect the addition of further layers of the original substance. In other words, the velocity of crystallisation in a direction normal to that face will be changed. As the residual affinity of different faces of a crystal must, from the ordinary conception of an atomic space lattice, be different, the habit of the crystal, that is, the relative development of different faces, will be altered by the presence of a foreign substance. It is on these lines that an explanation of differences of habit must be sought.

When a face of a crystal is brought into contact with an etching reagent, such as water for rock salt, hydrofluoric acid for quartz, or cupric ammonium chloride for iron, the surface is not dissolved away evenly, leaving it smooth, but characteristic etching pits are produced, the sides of the pits being evidently crystal faces. This shows that chemical action proceeds more readily along certain planes of a crystal than along others, a fact which we should expect from the general properties of the space lattice. It is not explained, however, why these etching pits should appear at first separate from one another, the intervening portions of the surface being unattacked. Minute particles of some impurity, causing local electrolytic differences, suggest themselves as a possible cause, but it is unlikely that they would be so evenly scattered in, for example, a quartz crystal as to produce the regular distribution which is often observed. Minute inequalities of level, which may be of a periodic character, are more probable, and this suggestion is strengthened by the observation that a polished face of rock salt dissolves evenly in water, whilst a natural cleavage face shows etching pits.

It is now possible, when pursuing the study of solids, to eliminate one of the disturbing factors, the intercrystalline boundary, by making experiments with specimens composed of a single crystal. There are several ways of preparing single metallic crystals of such a size as to allow of the determination of their physical and mechanical properties. Even so brittle a metal as zinc has an extraordinary ductility in single crystals. The mechanism of deformation has been examined in detail by means of X-rays. There is now a large body of evidence as to the directions of slip in a crystal during deformation, and this knowledge is essential to any understanding of the nature of cohesion, with which the chemical properties are no doubt closely connected.

We may now turn to the subject of chemical reactions which take place in the interior of a solid, either originating at the surface or from nuclei which make a spontaneous appearance in the course of cooling below the melting point. A chemical change which has begun at some point in or at the surface of a homogeneous crystalline mass cannot advance unless the atoms are able in some way to change their places. Gross movements, represented in gases and liquids by convection currents, are out of the question, but the slower process of diffusion, by which atoms or molecules can make their way through the solid, must be possible. Experiment shows that diffusion in solids, whilst naturally a slow process in comparison with diffusion in liquids, proceeds at quite measurable rates.

The classical example of such measurements, and for many years the only one, is the study of the diffusion of gold in solid lead, undertaken by Roberts-Austen in 1896. A much simpler example is that of silver and gold, two metals which resemble one another closely in chemical character and in atomic volume, so that diffusion causes less change of properties than in any pair of less closely similar metals. The experimental results prove, as might have been anticipated, that diffusion is a much slower process when there is so little difference in chemical character. When the two kinds of atoms are closely alike, the tendency to diffuse must be small, but it is certainly not zero. By making use of an ingenious device, Hevesy has been able to determine the coefficient of self-diffusion of liquid and solid lead. Two isotopes should not differ appreciably in their rates of diffusion, so that when the radioactive isotope thorium B is allowed to diffuse in ordinary lead, the experiment is equivalent to selecting a certain number of lead atoms and attaching labels to them by which they may be identified in the course of their journey. In this way he found that the diffusion in liquid lead near to the melting point was of the order of that of salt in water, but that in the solid state it was very small. Further experiments, using a thin foil, proved that at 2° below the melting point the rate was 1/10,000 of that in molten lead.

When a liquid mixture of two substances which are miscible in the solid as well as in the molten condition, such as an alloy of copper and nickel or a fused mass of albite and anorthite, begins to solidify, the composition of the crystals has to adjust itself continuously in order to maintain equilibrium with the changing liquid phase, as was shown by Roozeboom in his classical work on solid solutions. Such an adjustment is only possible by means of diffusion, and when cooling is sufficiently slow, the adjustment does in fact keep pace with the change in the liquid, but with more rapid cooling the interior of each crystal differs in composition from its outer layers, there being a concentration gradient from the centre to the boundary. This condition produces the "cored" crystals which are familiar to every metallurgist, and the "zoned" crystals of the mineralogist. In most alloys this want of homogeneity disappears after a sufficiently long period of heating at some temperature below that at which the first drops of liquid are formed, but alloys of bismuth and antimony fail to become uniform even after weeks of annealing, whilst the felspars and similar minerals have never been persuaded to lose their zoned structure by any methods known in the laboratory.

Bruni has shown and Vegard has confirmed the observation by the X-ray method, that true interdiffusion occurs between potassium and sodium chlorides when mixed and heated in the solid state. Electrolytic transport is observed in the solid halides of silver and in mixtures of silver and copper sulphides; but the modern view of the structure of such substances represents them as built up of ions rather than of neutral atoms, and this must be taken into account in any interpretation of the facts. The apparent absence of diffusion in minerals which have once solidified, even when given geological periods of time, is a serious difficulty in the way of any general theory of diffusion. Such examples of the passage of alkali metals through quartz and other silicious minerals under the influence of a difference of electric potential are probably not examples of true diffusion at all, but merely of the passage of traces of impurities through a mass which is not completely impervious.

A new field of investigation has been opened up by Tammann in his attempts to determine the arrangement of the atoms in solid solutions by purely chemical means, by studying the action of chemical reagents on the solid. It is a familiar fact that the "parting" of silver and gold in assaying, which consists in dissolving out the silver from the alloy by means of nitric or sulphuric acid, is only possible when the silver forms more than 60 per cent. of the alloy. When gold is present in excess of this proportion, only a little silver is removed from the surface, and the action then comes to a standstill, the acid being unable to penetrate to the interior. Assuming the alloy to be completely crystalline, the atoms of silver and gold will occupy the points of the space lattice, and as the two metals have face-centred lattices of only slightly differing dimensions, the amount of distortion will be small. There are, however, different ways of arranging the two kinds of atoms. They may be distributed at random, or they may be so regularly arranged as to form two interpenetrating cubic lattices.

The two forms of distribution may be distinguished by means of the X-rays, but Tammann has also drawn conclusions on the point from the action of various reagents on the alloys. He finds that each reagent which attacks silver ceases to act on the alloys when the proportion of gold atoms in solution exceeds a certain limit, which is not the same for different reagents, but he states that it is always capable of being expressed as 1/8, 2/8, 3/8, and so on, of the total number of atoms. The limits so found are not consistent with the distribution according to the laws of probability, but they may be accounted for by a regular distribution on the assumption that a certain number of inactive atoms is necessary to protect each atom of silver.

On the basis of these results, an ingenious theory of the action of reagents on solid solutions has been constructed, and although the accuracy of the experimentally determined limits is not high, and there are several exceptions to the rules, an interesting case has been made out.

If our knowledge of the chemical properties of the interior of a crystal be very incomplete, what are we to say of its surface? Of this we know still less. Even in a crystal of a pure metal there must be some difference in the structure at the immediate surface, on account of the unsymmetrical forces between the atoms in the outermost layer and its neighbours. For so far as the radius of sensible atomic forces extends, therefore, there must be a condition different from that which prevails at a depth below the surface. One consequence is that the surface has residual affinity, which shows itself in the ease with which foreign atoms or ions will attach themselves to it. That the forces acting are chemical is shown by the great effect on the extent of adsorption of the chemical character of the solid and of the adsorbed substance. Films, often one atom thick, attach themselves to the solid, and are only removed with the greatest difficulty. Their presence makes the investigation of the properties of a surface difficult, as the surface actually examined may be in reality quite different from that which is assumed to be present. In photochemical experiments with mercury it is usual to prepare a completely fresh surface of the liquid metal by causing it to flow continuously in a fountain, but this device cannot be applied to solids. Only rarely can experiments be made with perfectly defined solid surfaces. Films of metal prepared by sublimation or sputtering in a vacuum are probably the most under control, but other surfaces are commonly covered by invisible films.

Schumacher has recently shown that mercury wets glass and silica more and more readily as care is taken to remove films from them, and the property of not being wetted by mercury is probably not one of glass and silica, but of those substances coated with a film of gas. Metals most readily take up atoms of oxygen or other elements, forming persistent films, which play an important part in the phenomena of resistance to corrosion.

There is one way of preparing a fresh surface of a crystalline solid for examination, and that is by cleavage. A freshly cleaved plate of a mineral may be supposed to be clean at the moment of its formation, although it will rapidly take up foreign atoms from the surrounding gas. Tammann has made the interesting observation that a fresh surface of mica is more soluble in water than an older one. Washing with water immediately after cleaving extracts a quantity of alkali salts which is much above the normal solubility of mica, and later washings extract only the normal quantity. It is suggested that the separation of the flakes of mica exposes the alkaline part of the molecules, which would be more readily attacked by water than the silicious part. It will be interesting to see whether the X-ray examination of mica confirms this arrangement. Again, however, a word of warning as to the effect of possible impurities must be uttered. Natural minerals are not pure, and any uncombined alkaline salts present might well segregate along cleavage planes in the process of crystallisation, and so give rise to the effect noticed above, but the figures recorded by Tammann are striking and suggestive.

In this hurried review of a large field it may seem that I have presented rather our ignorance than our knowledge, my intention having been to show how much remains to be done before we can understand the chemical relations of solids as we do those of liquids and gases. One department of research is, however, more advanced than might have been supposed from my brief references to it. That is the study of the internal changes in metallic alloys as revealed by the microscope and by thermal and electrical methods. Metallography has made wonderful progress since the days of Sorby, and it would repay students of physical chemistry to give some attention to its main results, even though they may not intend to make a special study of the subject. Nowhere are the benefits of the doctrine of phases of Willard Gibbs to be more clearly traced, whilst the recognition of every change of phase by microscopical examination, making use of a technique which has been brought to a high state of perfection, gives concrete reality to the study by direct verification of its conclusions.

To understand more thoroughly the mechanism of these changes in alloys and to extend its application to salts, minerals, and rocks, we need a fuller knowledge of the relation between crystal structure and chemical behaviour. Research on the mechanical side is discovering the direction of planes of slip in the atomic space lattice under stress, and it remains to determine the corresponding planes of greatest and least chemical activity towards a given reagent. Next follows the still unsolved query as to the nature of the intercrystalline boundary, and the solution of these two problems will make it possible to define exactly the chemical character of a given aggregate of crystals. The results will be of extreme interest for the study of metallurgy, of mineralogy, and of petrology, besides filling a serious gap in chemistry, serious because of the extent to which solids compose the world around us, and of the part which they play in our daily life.

The Meaning of Wages.[1]

By Miss LYNDA GRIER.

IT is as little within my intention as it is within my power to put forward a theory of wages. My business is one of analysis, not of construction, of restatement, not of creation. My purpose is twofold: first, to discuss certain aspects of wages, and then to review from those aspects certain payments made to or on behalf of employees.

Let us then consider three aspects of wages, each important in its way. First, there is the distributive or competitive aspect, from which wages are regarded as a factor determining where labour shall go, who shall command it, in what manner labour of certain types and given efficiency shall be employed. Competition between employers seeking the best workers is expressed in the wage they offer, and competition between workers seeking the best employer is expressed in the wage they accept. This competition tends to bring the wages of workers of equal efficiency to equality and to ensure that the wages of workers of unequal efficiency shall be unequal.

Taken alone, this idea of wages treats of the supply of labour as being fixed independently of the wage, and of the wage as powerful only in directing the available supply. It is therefore a short-period consideration, dealing with market price rather than normal value; as in all short-period considerations, stress is laid on the quantitative side, on the notion of value falling with an increase in the supply of labour and rising with a limitation of supply.

Secondly, there is the idea of wage payment which treats of work and wages as completely interdependent, since the product of each worker constitutes his payment. The product of each worker, represented by his wage, makes an effective demand for the produce of other workers. His addition to wealth is his claim upon it. Numbers are important only if with alteration in numbers there are consequent alterations in productive power per head, or if the proportions between the different types of labour required be ill-adjusted.

Finally, we may take the aspect of wage payments which is concerned with their effect on work and on the supply of workers, the wage being regarded as something that maintains the worker.

These three aspects of wages are not antagonistic. It is clear from the outset that there is no contradiction between the first two, between that from which they are regarded as a distributive force and that from which they are regarded as the actual product of the wage-earner. The idea that the worker produces so much wealth and that his work is paid in proportion to the wealth he produces is, indeed, associated with the idea that the demand for and supply of such labour as he has to offer determines its value. Wages so determined are known as "fair" or "normal": fair in that they are equal to those of other workers of similar capacity, normal in that they are the wages that tend to be paid under conditions of free competition.

Each worker on this reckoning tends to get what his work is worth. It may be worth little. This admission does not apply only to bad workers. It certainly does apply to them, whether the badness of their work be due to bad character, bad health, or bad mental equipment. But the question is one not only of efficiency but also of the type of ability and of the number of other workers possessed of that particular type. Work which is not entirely unskilled may be ill-paid if the numbers competent to do it are great. This is, perhaps, especially the case with women's work.

For the most part, earnings are low in occupations that offer no special attractions and are filled by workers who, thanks to heredity, or sex, or environment, have little chance of entering others. The able man or woman has not only the fun of being clever, but also the advantage of high earnings through belonging to a grade in which the numbers are relatively small.

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[1] From the presidential address delivered at Southampton on August 28 before Section F (Economic Science and Statistics) of the British Association.