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AN ELECTRON THEORY OF SOLIDS.*

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My object in this paper is not so much to elaborate the details of a theory of solids as to point out that the electronic theory of the constitution of the atom leads quite simply and directly to a theory of solids which, as far as it has been tested, agrees remarkably well with the facts. I wish also to emphasize the point that the most convenient way of testing theories of the structure of the outer parts of the atom is by seeing the consequences they involve as to the properties of the elements when in the solid state. It sounds paradoxical, but it is true, that it may be less laborious to calculate the properties of practically an infinite number of atoms than of a single molecule with only two or three atoms.

The reason for this is very simple. Suppose we are considering a single molecule say of oxygen, as each atom of oxygen has six free electrons, we may regard the twelve electrons as distributed so that four are in the plane *A* bisecting at right angles the line joining the centres of the atoms. Another four are in a parallel plane *B* to the right of the two atoms, and another four in a plane *C* placed symmetrically on the left, with this distribution

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each oxygen atom may be regarded as surrounded by an octet of electrons.

Now the electrons in the plane *A* will be under different forces from those in the planes *B* and *C*. The result will be that the octets will not be cubes but figures like those in Fig. 1 whose geometry is somewhat complicated.

Now let us consider an oxygen atom in a solid crystal of oxygen, each atom will be surrounded by a symmetrical distribution of atoms and electrons and the arrangement of electrons round each atom will be quite symmetrical, so that these electrons

FIG. 1.

will be on a cube instead of on the camera-shaped figure shown in Fig. 1. It is true that in the solid we have in our calculations to take into account the influence of the large number of neighbors which each atom possesses, whereas in a single molecule each atom has but one neighbor, but as a matter of fact when the atoms are, as in a crystal, regularly spaced and arranged, the difficulty of doing this is not great and is far more than counterbalanced by the simplicity gained by having to deal with symmetrical and regular bodies like cubes instead of the distorted figures of the molecule.

The solids which have the simplest constitution are crystals of the various chemical elements since in these all the atoms are of one kind. The valency of the element will have great influence upon the shape and properties of the crystals, for the crystalline shape must be such as to give the right proportion between the number of electrons and the number of atoms, and this proportion depends upon the valency of the element. Thus in a monovalent element like one of the alkali metals there is but one disposable

electron for each atom; in a divalent element there are two; in a trivalent, three, and so on.

In a crystal of a monovalent element the arrangement of atoms and electrons must be such that there is one atom for each electron. Such a proportion is ensured (*a*) if the atoms *A* are placed at the centres of cubes at each corner of which there is an electron *E*, as in Fig. 2; or (*b*) as in Fig. 3, when the atoms *A* and electrons *E* are placed alternately.

In a monovalent element the positive charge on the atom is equal to the negative charge on the electron. Thus in both the arrangements (3) and (4) we have a simple distribution of electrical charges and we can without much difficulty calculate what would be the potential energy due to the forces between them, if these are supposed to vary inversely as the square of the distance. But this is not the only source of potential energy. For by Earnshaw's theorem no system can be in stable equilibrium if the only forces between the bodies are those varying as the inverse square of the distance. There must therefore be between atoms and electrons and atoms and atoms forces in addition to those varying according to this law. I have shown in several papers that if we suppose that these additional forces between atoms and electrons vary inversely as the cube of the distance, we get simple explanations of many chemical phenomena, such, for example, as valency and Mendeleeff's Periodic Law. The result of considering the consequences of the inverse cube law when applied to the theory of solids also furnishes very strong evidence in its support. For supposing that the only forces in addition to those varying inversely as the square of the distance are those forces varying as the inverse cube, we can calculate the potential energy of the crystal. I have made this calculation in a paper published in the April number of the *Philosophical Magazine*, and find that the potential energy for each atom of a monovalent element and its associated electron is when the atoms and electrons are arranged as in Fig. 2, equal to

$$- 1.825 \frac{e^2}{d}$$

where *d* is the distance between two atoms and *e* the charge on

an electron. If M is the mass of an atom, Δ the density of the crystal will be equal to

$$\frac{M}{d^3} \text{ for } \frac{1}{d^3}$$

is the number of atoms per unit volume.

Thus,

$$\frac{1}{d^3} = \frac{\Delta}{M}$$

and as both M and Δ are known, the value of d is determined.

FIG. 2.

If the atoms and electrons are arranged as in Fig. 3, the energy per atom with electron is equal to

$$-.885 \frac{e^2}{d'}$$

where d' is the distance between an atom and an electron and is given by

$$\frac{1}{d'^3} = \frac{2\Delta}{M}$$

Now if we compress the solid we shall alter d , and with d the energy of the crystal. From the preceding expressions we can find the energy required to produce any specified compressions, and from this we can deduce the coefficient of compressibility of the solid. In this way I find that the bulk modulus K (which is the reciprocal of the compressibility) is given by the relation

$$K = \frac{3.65}{9} e^2 \left(\frac{\Delta}{M} \right)^{\frac{4}{3}}$$

for the arrangement in Fig. 2 and by

$$K = \frac{2.2}{9} e^2 \left(\frac{\Delta}{M} \right)^{\frac{4}{3}}$$

for that in Fig. 3. As e and $\frac{\Delta}{M}$ are known for the different elements, we can find the value of K . The following tables contain

the values of K calculated by the first of these formula and also the value found by Richards in his invaluable researches on the compressibility of the elements.

	K calculated	K found by Richards
Lithium.....	$.14 \times 10^{12}$	$.114 \times 10^{12}$
Sodium.....	$.068 \times 10^{12}$	$.065 \times 10^{12}$
Potassium.....	$.03 \times 10^{12}$	$.032 \times 10^{12}$
Rubidium.....	$.022 \times 10^{12}$	$.025 \times 10^{12}$
Cæsium.....	$.016 \times 10^{12}$	$.016 \times 10^{12}$

Thus we see that not only the relative values of the compressibility, but also the absolute ones, are given accurately by the expression which corresponds to the arrangement represented by

FIG. 3.

Fig. 2. The values corresponding to the arrangement in Fig. 3 are little more than half these, and are ruled out of court by Richards' experiments. We conclude then that Fig. 2 represents the arrangements of atom and electrons in the alkali metals.

A further test of theory is got by considering the elements with higher valencies. Let us take first the divalent elements where there must be two disposable electrons for each atom. This necessitates an arrangement of electrons quite different from that for the alkali metals. One arrangement which gives two electrons for each atom is to place the electrons at the corners of hexagonal prisms and the atoms at the centres of the prisms. As each corner is the meeting place of six prisms the twelve electrons will only count as two, and there will be two electrons for each atom. This would give hexagonal symmetry and would involve crystallization in the hexagonal system. As a matter of fact most divalent elements do crystallize in that system. The calculation of the energy corresponding to this distribution of electrons is more complicated than that for the alkali metals, because two lengths are required to fix the hexagonal prism; *viz.*, the height and the radius of the base. This makes the numerical calculations

somewhat lengthy, and I have not yet completed them. I have, however, calculated the energy for another distribution of electrons which would also give two electrons per atom, which would correspond to crystals with uniaxial symmetry, and for which the geometry is simpler. In this arrangement the atoms are at the centres of cubes, and the electrons at the corners of the cubes and at the middle points of *one* pair of parallel faces.

For this distribution I find that the potential energy per atom with two electrons is

$$-10.27 \frac{e^2}{d}$$

where e is the charge on an electron and d the size of the cube. If Δ is the density of the crystal and M the mass of the atom

$$\frac{1}{d} = \left(\frac{\Delta}{M}\right)^{\frac{1}{3}}$$

so that the potential energy is

$$-5.13 e^2 \left(\frac{\Delta}{M}\right)^{\frac{1}{3}}.$$

FIG. 4

It follows from this that K , the bulk modulus, is given by the equation

$$K = \frac{10.26}{9} e^2 \left(\frac{\Delta}{M}\right)^{\frac{1}{3}}.$$

The values of K , calculated from this expression, and the values found by Professor Richards, for the divalent element, are given in the following table

	K calculated	K observed
Magnesium.....	$.408 \times 10^{12}$	$.378 \times 10^{12}$
Calcium.....	$.185 \times 10^{12}$	$.182 \times 10^{12}$
Zinc.....	$.72 \times 10^{12}$	$.67 \times 10^{12}$
Cadmium.....	$.45 \times 10^{12}$	$.53 \times 10^{12}$

Let us now consider the trivalent elements; for these there are three electrons per atom. There are several ways in which the electrons might be arranged which would correspond to different systems of crystallization. The arrangement corresponding to the cubical form is when the atoms are placed at the centres of regular dodecahedra with the electrons at the corners. Space can be packed with these dodecahedra, and when this is done each of the six four-edged corners of a dodecahedra is the meeting place of six dodecahedra, while each of the eight three-sided corners is the meeting place of four; thus the six four-edged corners count as one and the eight three-edged as two, and, therefore, the fourteen corners of the dodecahedra as three.

We can show that when dodecahedra are packed in this way the centres are arranged like a system of face-centred cubes; the electrons are at the middle points of the sides of these cubes and also at the centres of the eight smaller cubes into which a cube is divided by planes bisecting its sides at right angles.

I have calculated the potential energy per atom and their electrons for this arrangement and find that it is equal to

$$-14.4 \frac{e^2}{4^{\frac{1}{3}}} \left(\frac{\Delta}{M} \right)^{\frac{1}{3}}$$

and the bulk modulus is

$$\frac{28.8}{9} \frac{e^2}{4^{\frac{1}{3}}} \left(\frac{\Delta}{M} \right)^{\frac{1}{3}}$$

where Δ is the density of the crystal and M the mass of the atom. Aluminium is a trivalent element crystallizing in the regular sys-

tem, for which $\frac{\Delta}{M}$ is

$$\frac{2.65}{27} \times \frac{1}{6.4 \times 10^{-24}}.$$

Substituting this value we find the bulk modulus to be $.98 \times 10^{12}$, the value found by experiments is $.78 \times 10^{12}$.

For quadrivalent elements there must be four electrons for each atom. The arrangement which would give this proportion and produce crystals belonging to the regular system is when the atoms are at the centres of cubes and the electrons at the corners and middle points of all the faces of the cube.

I have shown¹ that the potential energy per atom with four electrons is equal to

$$-16.67 \ e^2 \left(\frac{\Delta}{M} \right)^{\frac{1}{3}}$$

and that the bulk modulus is equal to

$$\frac{33.35}{9} \ e^2 \left(\frac{\Delta}{M} \right)^{\frac{4}{3}}.$$

The diamond crystallizes in the regular system, for it $\Delta = 3.52$. This would make the bulk modulus for the diamond 8.1×10^{12} ; this is very much higher than the value 2×10^{12} obtained by Richards. This difference suggests that the unit in the case of the diamond is a group of three or four atoms and not a single atom. We see from the preceding investigation that whatever be the valency of the element the expression for the bulk modulus contains the factor $\left(\frac{\Delta}{M} \right)^{\frac{4}{3}}$; the other factor depends only on the valency and increases as that increases.

The expressions for the potential energy of an atom with its associated electrons given above are for atoms in the body of the crystal; for atoms at the surface the potential energy will be greater. Suppose that βE is the excess of an atom at the surface over the energy E possessed by an atom in the interior. If d be the distance between the atoms, the number of atoms per unit area of surface is $\frac{1}{d^2}$, so that the excess of energy possessed by unit area of surface is $\frac{\beta E}{d^2}$, and this must equal to T the surface tension; hence since, as we have seen, E varies as $\frac{1}{d}$

$$T = \frac{\beta'}{d^3}$$

where β' is a constant proportional to β and depending upon the valency. But K , the bulk modulus $= \frac{\gamma}{d^4}$, where γ is quantity, depends on the valency, thus

$$T = \beta' \frac{K^{\frac{3}{4}}}{\gamma}.$$

For substances of similar constitutions both β' and γ will have the same values; hence for such substances T will be proportioned to $K^{\frac{3}{4}}$. This relation was discovered by Richards.

¹ *Philosophical Magazine*, April, 1922.

Hitherto we have confined our attention to elementary substances; similar principles will also apply to compounds, though for these the calculation of the potential energy is much more complicated. The reason for this is that when the atoms are different the distribution of electrons round one kind of atom need not be the same as that round the other kind. Thus, take NaCl as an example; there are eight electrons for each molecule of the salt. If the atoms of Na and Cl are arranged alternately as in Fig. 4, one way of disposing of the electrons would be to place them at the corners of cubes whose centres are at the chlorine atoms and whose sides are parallel to the lines of the space lattice formed by the sodium and chlorine atoms. With this arrangement the crystals would belong to the regular system. The measure of its physical properties would depend upon the dimensions of the cube of electrons round the chlorine atoms. If the side of this cube is small compared with the distance between the atoms of sodium and chlorine, we can prove without difficulty that the expression for the bulk modulus would be the same as given for the arrangement Fig. 3 for a monovalent element, the bulk modulus calculated on this assumption would be much less than the value found by Richards for NaCl. If we go to the other extreme and suppose that the cube round the Cl atom extends half-way to the Na atom, the electrons will be arranged as face-centred cubes and the expression for the energy and bulk modulus will be that given for a quadrivalent element. The bulk modulus calculated in this way is much greater than that found by Richards; thus for some dimensions of the cube intermediate between these values the calculated value of the bulk modulus will agree with that found by Richards. If we know the intensities of the forces varying inversely as the cube of the distance, we can calculate the dimension of the cube of electrons, the calculation is, however, somewhat lengthy, and I must leave it for another occasion. I may remark, however, that Richards' result for the halides of the alkali metals show that these are in very fair agreement with the general result that for similar bodies the bulk modulus is proportional to $\left(\frac{\Delta}{M}\right)^{\frac{4}{3}}$.

An Alcohol Problem.—At the last meeting of the Association of Official Agricultural Chemists, a discussion was held in regard to the respective advantages of the tables published by the Association and those recognized by the United States Pharmacopeia. The A.O.A.C.