SCIENCE

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## LAWS AND NATURE OF COHESION.

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IN a previous note (*Science*, July 22, 1892, and *Elect. World*, Aug. 8, 1891) a number of reasons were advanced for believing that cohesion is due to an electrostatic force, and it was shown that the results predicted by such a theory agree very closely with the results of experiment.

This theory was, however, only extended to the phenomena of rigidity, elasticity, and tensile strength. It was purposed to follow it with another note on the phenomena of conductivity, surface tension, solution, refraction of light, and compression of gases. Pressure of other work and the necessity of making experiments to determine some doubtful points, will prevent such publication for some time, and it was therefore judged best to give a short preliminary statement of a few of the results so far obtained.

I. Relative closeness of the atoms. It appears to be generally considered that the atoms are at distances from each other which are large in comparison with their diameters, even in the solid state. As an example of the extent of this belief may be mentioned the fact that in a recent article on magnetism, Mr. Steinmitz made the statement that Professor Ewing's theory could not be correct, unless the atoms were close together, but as they were far apart, his theory must be wrong. This conclusion has not been attacked up to the present time But the facts are that all our evidence points the other way, and it is almost absolutely certain that in the solid state the distance between the centres of two neighboring atoms is almost the same as their diameters.

For instance, from Van der Waals' equation we have, at the critical point:—

Volume of gas = 12 times the volume of the atoms themselves, or, the distance between the centres of two atoms is 2.3 times the diameter of a single atom. And this is just at the critical point, so that from the curves of volume, pressure and temperature, the solid elements must have a volume of, at the most, six times that of the atoms themselves, reducing the distance between centres to 1.8 times the atomic diameter.

Again, when a body is at absolute zero it is extremely difficult to conceive why the atoms, having no kinetic energy and the cohesive force still in existence, should not join together so closely as is possible, i.e., till they touch. (We may discard the old "force point" atom as obsolete and without reason for existence, all modern research and theory being in favor of the idea that atoms have most exact and well-defined boundaries.)

If, then, the atoms of silver in the solid state at 0° C., say, were very far apart, then, since we know its change of volume is very slight down to about $-200°$ C., there must be a most remarkable and sudden change at some point in the last 73°. But this is not to be believed, for it is impossible for any such violent change in the space occupied by the atoms to take place without some change in the conductivity of the metals. And we know from the researches of Dewar and others that the curve of resistance is a straight one, and cuts the axis of temperature at absolute zero, if produced.

On the other side, after considerable search, there does not appear to be any reason for believing that the atoms are widely separated in a solid, and the writer would be glad to know of any such reason, other than the fact that certain mathematicians have seen fit to make the supposition because it renders some of the work on surface-tension, etc., a little easier to handle.

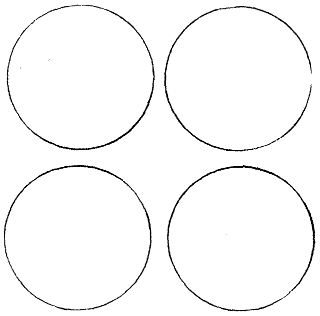
There is, it is true, one fact which is commonly considered as evidence of this nature, but which must rather be looked upon as evidence to the contrary. This is the fact that some elements have a greater volume by themselves than in combination. For instance, 45.5 cubic centimeters of potassium combine with an equivalent of chlorine to form a mass of potassium chloride which occupies only 37.4 cubic centimeters. But a simple geometric consideration will show us that even if the atoms of potassium were actually touching one another in the solid state, the 45.5 cubic centimeters would be able to contract to 31.7 cubic centimeters if the potassium were combined with an element having an atomic volume of less than 18. Similarly, 23.5 cubic centimeters sodium should be capable of combining with an element having an atomic volume of 9.6 to form a compound having an atomic volume of 16.5.

To take another example, sodium chloride should have an atomic volume of about $\{(23.5 \times .92) + 17\} \times \sqrt{\tfrac{1}{2}} = 27.02$. The actual atomic volume of $Na\,Cl$ is 27.1. $Na\,OH$ should have an atomic volume of 17. Its actual volume is 18.

$K\,O\,H$ should have atomic volume of 25.5. Actual volume is 27.

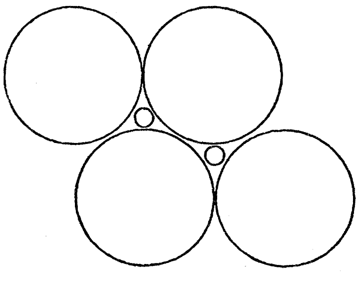
Similarly with the salts of cæsium, rubidium and the other metals which have large atomic volumes. For, of course, it is only with these elements which have great atomic volumes that this contraction on combination will be very noticeable.

The geometric explanation referred to is that in a monoplex element (element having under the conditions taken only one atom to the molecule), owing to the forces at work, the atoms will take the positions that a lot of balloons would that were fastened together by very short strings, thus,



four atoms occupying four times the space of one.

While if a new element is introduced, they will take this position



(shown in two dimensions only) where the atoms occupy a space $\sqrt{\tfrac{1}{2}} = .70$ of what they did originally. The fact that the calculated values are always a little smaller than the observed, and never larger, is one of the strongest proofs that the atoms are really fairly close together in the solid state. While this is to be regretted from a mathematical point of view, it is very satisfactory from a physical and crystallographic standpoint.

[NOTE.— In passing it is curious to note that the number of "space nets" into which an infinite number of points (each point similarly situated to every other point) may be arranged is sixty-six, or just the number of the well-defined elements. So that imagination may picture Spencer's homogeneous cloud of atoms splitting up into these different "space net" arrangements, each kind of net being a different element.]

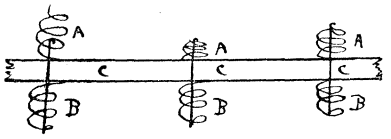
2. Solution. The chief opponent of the disassociation theory of solution is Professor Pickering; and his chief argument against it (for, of course, the disassociation theory allows the formation of hydrates as well as Professor Pickering's own hydrate theory does) is the fact that while disassociation almost always takes place with absorption of heat, solution generally emits it. This anomaly can be explained very satisfactorily by the electrostatic theory of cohesion. For whether a substance is a solid (or fluid) or a gas depends on whether the fraction

$$\text{I.}\qquad \frac{\text{cohesive force of atoms.}}{\text{repulsive force due to kinetic energy of atoms + attraction of atoms for other atoms}}$$

is greater or less than unity. We can thus turn a substance into a gas by either decreasing the numerator or increasing the denominator. The numerator we cannot change. The first term of the denominator we can increase by heating the substance, the second term by placing the substance in contact with a solvent.

In the last case the atoms of the solid part company with each other. But their cohesive force is not lost; it is simply added to that of the solvent, as shown by the increase of surface tension and of boiling point of a solution over that of the solvent. Since the solvent takes up the stress there is no necessary evolution or absorption of heat. A mechanical simile will make my meaning clear: Suppose a spiral spring, *A*, fixed on a board, *C*, which when compressed gives out heat from some reversible cause, so that it will absorb the same amount of heat in expanding. This is similar to the behavior of a gas — when compressed it gives out heat, when it expands again it absorbs heat.

But now suppose a second spring, *B*, placed beneath the board, *C*, similar in every respect to the first spring, and its axis a prolongation of that of *A*. Suppose an iron rod fastened to the bottom of *C*, extending up the centre of both springs, the rod being somewhat longer than one of the extended springs, and having a hook on the end of it.



In Fig. 1 both springs are extended. In Fig. 2, the spring *A* is compressed, heat being given out.

If it is now allowed to expand, the same amount of heat will be absorbed. This latter represents the turning of a solid into a gas by heating it.

But suppose, being compressed, the iron rod is hooked over the top of it. Then when it is let go it will expand and assume the position of Fig. 3. But no heat will be generated in the system, for it is evident that *B* will give out just as much as *A* absorbs. If the amount of heat given off by unit contraction of *A* were greater than that given off by *B*, the resultant effect would be a cooling of the system. If it were less, the resultant would be a heating. So we see, that while the expansion of *A* by itself would always absorb heat; when it is joined to *B*, the resultant effect depends on *B*.

Now, this is a very fair simile of what goes on when a solid is dissolved in a solvent. The solid loses its stress, which is taken up by the solvent, the result being an increase of cohesion between the molecules of the solvent, producing as a natural consequence increase of surface tension, lowering of the freezing point, and raising of the boiling point.

If the added electrostatic strain produces a greater amount of heat in the solvent than the loss of strain in the solid would absorb heat, the resultant would be a heating of the whole solution. Since, when a dissolved substance is plated out by electrolysis, the result resembles the cutting of the iron rod, *D*, in Fig. 3, there is an absorption of energy or cooling, so that work must be done to plate the dissolved substance out, and the electromotive force necessary to do this, since the ampères are constant for all equivalents, must depend on the rate at which the surface tension varies per withdrawal of unit weight of the electrolysed substance, allowing also for any heating or cooling during the electroplating.

3. Compression of gases. The ordinary formula for the compression of gases is that of Van der Waals, i.e.: —

$$\text{I.}\qquad \left(p+\frac{a}{v^2}\right)\ \left(v-b\right)=RT.$$

If the electrostatic theory of cohesion is correct, the equation should read

$$\text{II.}\qquad \left(p+\frac{a}{v^{\frac{4}{3}}}\right)\ \left(v-b\right)=RT.$$

for reasons evident to those who have read the previous note (*Science*, Aug. 22, 1892).

This is no longer a cubic, and it is pretty certain that the equation for the compression of gases should be one on account of the shape of the pressure-volume curves of carbonic acid gas. But we can transform the above equation, II., into a cubic by putting $a$, no longer as a constant but equal to a constant multiplied by $v^{\frac{2}{3}}$. The equation then reads: —

$$\text{III.}\qquad p+\ \frac{c\times v^{\frac{2}{3}}}{v^2}\Bigg)\ \left(v-b\right)=RT.$$

in which $c$ is the same for all gases. The experimental data agree with this modified equation, as shown by table I.

*Table I.*

| Substance. | $a \times 10{,}000$. | $v$ (*ab*). |
|---|---|---|
| Dyethylamine | 355 | 58 |
| Ethyl. Acet. | 348 | 55 |
| Ether | 324 | 57 |
| Benzine | (438) | 51 |
| Ethyl. Form. | 304 | 48 |
| Chloroform | 287 | 44 |
| Acetone | 273 | 44 |
| Methyl. Acet. | 248 | 39 |
| Alcohol | 236 | 37 |
| Ethyl. Chlor. | 227 | 40 |
| $CS_2$ | 219 | 33 |
| $SO_2$ | 123 | 24 |
| $NO_2$ | (74) | 19 |

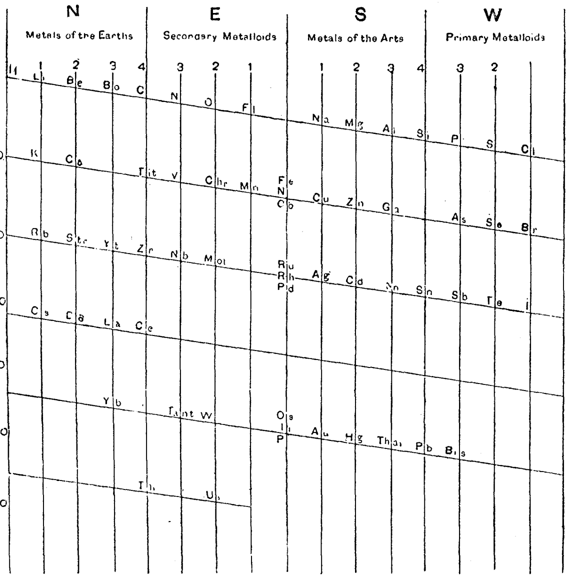
as closely as can be expected.

*Table II.*

| Substance. | $\pi$ | $a$ | $b^2$ | $27\ b^2$ | $\frac{a}{27\ b^2}$ |
|---|---|---|---|---|---|
| Ether | 36.9 | 324 | 3249 | 87.723 | 36.9 |
| $CS_2$ | 74.7 | 219 | 1089 | 29.403 | 74 |
| $SO_2$ | 78.9 | 123 | 576 | 15.552 | 79 |
| Alcohol | 62.1 | 236 | 1369 | 36.963 | 63.8 |
| Eth. Chl. | 52.6 | 227 | 1600 | 43.200 | 52.5 |
| Benzine | 49.5 | 438 | 2601 | 70.227 | 62.3 |
| Acetone | 52.2 | 273 | 1936 | 52.272 | 52.2 |
| Eth. Acet. | 42.6 | 348 | 3025 | 81.675 | 42.6 |
| Chloroform | 54.9 | 287 | 1936 | 52.272 | 54.9 |
| Eth. Form. | 48.7 | 304 | 2304 | 62.208 | 48.8 |
| Meth. Acet. | 57.6 | 248 | 1521 | 41.067 | 60.3 |
| Diethylam | 38.7 | 355 | 3364 | 90.828 | 39 |
| Nitrous oxide | 37.1 | 74.2 | 376.4 | 10.116 | 73 |

This table shows that $a$ varies as (volume) $^{\frac{2}{3}}$. Two substances do not agree with this theory — benzine and $NO_2$. This is owing to the fact that the data are given wrongly in the table from which this is copied (i.e., that in Ostwald's "Outlines of General Chemistry"). This is seen by the following facts. From the cubic equation we find that at the critical point, $\pi$, the critical pressure $= \frac{a}{27 b^2}$. Table II. gives the results of this calculation, and it will be seen that the values for benzine and $NO_2$ do not coincide with the values for $\pi$. As the values of $a$ and $b$ were originally calculated from $\pi$, it is evident that some misprint has crept into the tables, and there is little doubt but that if the correct values for $a$ and $b$ were substituted, they would fall into line and that in all cases the quantity $a$, in Van der Waals' equation, must be taken as equal to a quantity $c$, which is constant for all gases, multiplied by the atomic volume to the $\frac{2}{3}$ power.

4. Electrical conductivity. As before mentioned linked atoms cannot conduct. If we examine the enclosed cube of the elements, we see that the non-conducting elements are found on sides *E* and *W* of the cube, and these are the elements whose atoms are linked or plexed. We can tell this in the following ways:—



CUBE OF THE ELEMENTS.

1st, By their low specific heats. Those who are acquainted with chemical physics will recognize this fact and the necessary deduction. Briefly, if the kinetic energies of all molecules are the same at the same temperature, then if the sulphur molecule in solid sulphur is triatomic, or has its mass three times that of one atom; then since all the $\frac{1}{2} m v^2$ s are equal, solid sulphur will only have $\frac{1}{3}$ the specific heat it would have if the molecule were monatomic (provided that no work is spent in disassociating the molecule.)

The standard atomic heat is 6.4. The following substances have low specific heats, and are all insulators or poor conductors: Sulphur, 5.4; phosphorus, 5.4; fluorine, 5; silicon, 3.8; carbon, 1.8.

2d, By their vapor densities. If a substance has a biatomic vapor it is not likely that it will be a monatomic solid. The following substances have two or more atoms to the molecule when in the state of vapor: sulphur, iodine, bromine, chlorine, selenium, tellurium, phosphorus, arsenic. And these are all insulators or poor conductors, while mercury, cadmium, zinc, and sodium have monatomic vapors and are good conductors.

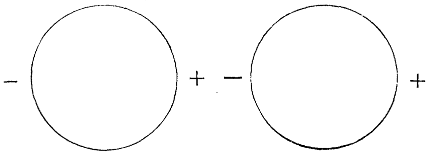
As regards metals in the allotropic state. Allotropic is a word which has been used to cover a multitude of sins. Every time an erring element goes wrong and misbehaves itself by emphasizing some of its previous peculiarities, or developes some new ones, it is stigmatized as "allotropic." For instance, we see it stated that when iron amalgam is strongly heated the iron left behind is allotropic because it takes fire in the air. But such an action does not show that any new property has been developed, it merely emphasizes a fact already well known, i.e., that iron oxidizes when exposed to air. A fine cambric needle will catch fire when held in the flame of a Bunsen burner for a second, and will continue to burn like a match after it is withdrawn. When the iron is in a finely divided state, the surface exposed is greater, and, the oxidation per unit of mass being much greater, the temperature of the iron is raised much more, thus favoring oxidation still more.

If, then, we are to use the word allotropic in this sense, we should logically speak of kindling-wood as an allotropic form of timber, for, as fire underwriters know, heavy timber is one of the most fireproof of substances. We might also speak of that form of conscience which large corporations are supposed to possess, as an allotropic conscience.

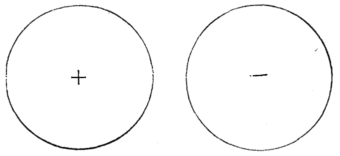
If, however, we do apply the word allotropic to such forms as Joule's iron, Cary-Lea's silver, etc., then we need another word to express the changes in the physical behavior of metals which are not due merely to the accenting of known properties but to the development of new properties, due to the joining of two or more atoms of a metal into one molecule. Polymerism might do, but it does not lend itself easily to use, and for myself I prefer to use the word plex, and to speak of diplexed iodine, triplexed sulphur, and of an element in a plexed form; though I have no doubt that if Clifford were still with us he would say that two-linked and three-linked are good enough for any honest Anglo-Saxon.

As regards the conductivity of "allotropic" elements, there is no reason to suppose that the conductivity of Joule's iron is different from that of ordinary iron. But when the elements are plexed, as we have seen above, the resistance will be much increased and the temperature sufficiently lowered, because heating increases disassociation nearly as fast as it lessens rigidity, or even in the case of those alloys or elements with negative temperature coefficients, faster.

[NOTE.—With regard to the previous paper, it may be noted that the explanation of the difference between cohesion and chemical combination, that in cohesion the atoms are charged similarly in every way except as regards position, thus —



while if any third substance short circuits the atoms they are left chemically combined, thus —



is also an explanation of a law which will probably be found true in the near future, i.e., no two substances can combine with each other without the presence of a third, thus making all chemical action the result of catalysis, plexed forms of the substances being capable of acting third substances. As regards the shortening of stretched rubber by heating, it is of course not to be supposed that the two parts of India rubber are literally contained one inside a sphere of the other, but that rubber rather resembles a tangled reel of silk embedded in jelly. If we consider any element of the jelly, and we see that it is bounded on all sides by threads of silk, and that these will act as the cell-wall of the previous paper, only "more so." The heating of rubber when stretched may be explained conversely by the compression of the jelly-substance by the cell-wall substance. R. A. F.]

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## THE GROOVE IN THE PETIOLE OF LEAVES.

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IN the spring of 1892, I had the pleasure of making some observations and brief studies, in conjunction with Mr. H. L. Jones, upon the origin and more particularly the function of the groove found in the petiole of many leaves, especially of Endogens.