

May 26, 1898.

The LORD LISTER, F.R.C.S., D.C.L., President, in the Chair.

The following Papers were read :—

- I. "On the Cytological Features of Fertilisation and related Phenomena in *Pinus silvestris*, L." By V. H. BLACKMAN, B.A., F.L.S. Communicated by FRANCIS DARWIN, F.R.S.
- II. "The Skeleton and Classification of Calcareous Sponges." By G. P. BIDDER. Communicated by ADAM SEDGWICK, F.R.S.
- III. "On Surfusion in Metals and Alloys." By W. C. ROBERTS-AUSTEN, C.B., F.R.S.
- IV. "Note on the Complete Scheme of Electrodynamical Equations of a Moving Material Medium, and on Electrostriction." By J. LARMOR, D.Sc., F.R.S.
- V. "Aluminium as an Electrode in Cells for Direct and Alternate Currents." By E. WILSON. Communicated by Professor HOPKINSON, F.R.S.
- VI. "Contributions to the Study of 'Flicker.'" By T. C. PORTER. Communicated by Lord RAYLEIGH, F.R.S.
- VII. "On the Kathode Fall of Potential in Gases." By J. W. CAPSTICK. Communicated by Professor J. J. THOMSON, F.R.S.

The Society adjourned over the Whitsuntide Recess to Thursday, June 9.

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"On the Intimate Structure of Crystals. Part I. Crystals of the Cubic System with Cubic Cleavage." By W. J. SOLLAS, LL.D., D.Sc., F.R.S., Professor of Geology in the University of Oxford. Received January 20,—Read February 3, 1898.

The remarkable advance in our knowledge of the constitution of gases that has marked the latter half of this century has immensely strengthened a belief in the doctrine of atoms. It is to this doctrine, therefore, that we naturally turn to assist us in the study of the intimate structure of solids. The solid, however, stands at the opposite pole to the gas; in the one the particles are unrestrained, free to move about any axis, and along paths of comparatively wide

range, before exerting mutual action on each other; in the solid, on the other hand, they are so closely packed that in many cases the abstraction of heat is accompanied by only a very inconsiderable approach of the atoms to nearer proximity. Thus among metals, that having one of the highest coefficients of expansion is indium; but this only contracts 0.00004 of its bulk for every degree centigrade that it is lowered below the ordinary atmospheric temperature; nor does it continue to contract at this rate, but at a continually diminishing one, as its temperature is progressively reduced. A metal with a very low coefficient of expansion is iridium, which loses only 0.000006 of its volume for every degree that it falls in temperature. Among non-metallic elements we may point to the remarkable case of the diamond, which, with the small coefficient of 0.00000118, actually ceases to contract at all when cooled below 42° C. It may be possible by other means to effect greater reductions in the volume of solids, but so far as the withdrawal of thermal energy is concerned, it evidently accomplishes but very little, at least in the case of solids treated at a temperature considerably below their fusion points.

The assumptions made in the study of gases are of the fewest and simplest kind, but they include one that is of fundamental importance in the investigation of solids, viz., that in some sense an atom is a body occupying space; it is only by making this admission that deviations from important laws like Boyle's find an explanation.

The dominion of an atom over a certain region of space endows that space with form; what that form is we do not know, though we may eventually discover. In the absence of knowledge it is permissible to make some kind of assumption, and then to endeavour to discover how far the consequences of that assumption accord with ascertained facts. I propose to make the simplest assumption possible, and to regard the volume of space appropriated by an atom as having the form of a solid of revolution, and very generally of a sphere. Within this space there exists something, the energy of the atom, or a force of repulsion, or both, which preserves it from invasion by other atoms; outside it there is something, a pressure or force of attraction, which drives the atoms as close together as possible without causing interpenetration. It will probably be found also that these influences, pressures, and thrusts, are directed, or that the atoms are polar.

Dalton's law of multiple proportions seems to meet with its counterpart in crystallography in Haüy's law of "the rationality of the indices," and the conception by which Haüy sought to explain this and other facts relating to the form and structure of crystals presents singular points of resemblance to Dalton's ideas of atoms. Haüy's views on crystalline structure appear to me to contain the

germ of a great truth, which subsequent refinements in the geometrical treatment of the subject have to some extent obscured.

Recent work by Lord Kelvin, Mr. Tutton, and others, has given great encouragement to those who cherish a hope of ultimately arriving at some sure representation of crystalline structure; but the remarkable observations of Penfield\* on the several species of the mineral chondrodite are of an especially suggestive character. The chondrodites present us with a homologous series of chemical compounds, having the following constitution:—

	No. of atoms of Mg.
(a) $\text{Mg}_3[\text{Mg}(\text{F.OH})]_2(\text{SiO}_4)_2$ .....	5
(b) $\text{Mg}_5[\text{Mg}(\text{F.OH})]_2(\text{SiO}_4)_3$ .....	7
(c) $\text{Mg}_7[\text{Mg}(\text{F.OH})]_2(\text{SiO}_4)_4$ .....	9

As Professor Miers tells us, “the three minerals have almost the same form, but differ only in the length of one crystallographic axis (parameter). The lengths of this . . . in the three minerals are in the ratio of 5 : 7 : 9. Thus the addition of the olivine radicle,  $\text{Mg}_2\text{SiO}_4$ , exerts a so-called ‘morphotropic’ action along one definite axis, and causes a certain constant increase in the length of this axis (parameter).” “It is further a curious fact that the length of this (parameter) varies directly as the number of magnesium atoms in the compound.” The inference that the magnesium atoms are disposed along this axis would seem to follow naturally.

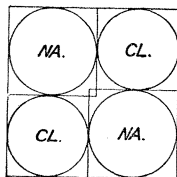
Mr. Barlow has lately completed an investigation into the different ways in which spherical bodies of different volumes may be packed together so as to produce different crystal forms. His method of treatment is general, and many of the arrangements of atoms, which I am myself led to imagine as existing in certain crystals, will, no doubt, be found to fall as special cases under his general laws. But I do not propose in this communication to merely suggest some way in which atoms regarded as spheres may be built up into geometrical forms; my purpose is different, it is to consider certain particular substances, and to endeavour to discover the particular structure which must most rationally be assigned to them. Further, to avoid misconception, it should be added that the “law of closest packing,” which is so admirably developed by Mr. Barlow, does not seem to be obeyed by the greater part of the crystals I have investigated; so far as the cubic system is concerned, there is but one simple substance in which the atoms are as closely packed as possible, that is the diamond.

It is a singular fact that crystals of the cubic system, when composed of salts which are diatomic, such as  $\text{NaCl}$ ,  $\text{KCl}$ , are characterised by a cubic cleavage, while those composed of triatomic salts

\* ‘Amer. Journ. Science,’ vol. 47, p. 188.

such as cuprous oxide ( $\text{Cu}_2\text{O}$ ), or fluorspar ( $\text{CaF}_2$ ), possess an octahedral cleavage. Let us for the moment follow the hint given by Haüy, and regard the cubic crystals with cubic cleavage as reduced by repeated cleavage to a primitive cubelet. How in the case of a diatomic compound composed of atoms of different relative sizes, as, say in common table salt, can the molecules be arranged together so as to produce this cubelet?

FIG. 1.



The only satisfactory way that I can discover is to place one molecule ( $\text{NaCl}$ ) by the side of another ( $\text{ClNa}$ ), as in the diagram (fig. 1), so that tangent planes to the pairs of atoms may form a square prism, and then to rest on the top of this two more molecules, similarly put together, the chlorine of the upper group resting on the sodium of the lower, and the sodium of the upper on the chlorine of the lower; common tangent planes to the exterior of the spheres taken in fours will be found to form a cube.

This is a simple and possible arrangement of the molecules of common salt, but whether it alone and not some other is the actually existent arrangement is a question for argument.

Ever since Kopp formulated his famous laws, the subject of atomic volumes has possessed great interest for the chemist, though the discrepancies which too frequently impair the correspondences discovered by Kopp have evoked a general feeling of mistrust.

Nevertheless I am persuaded that in atomic volumes we possess the touchstone by which our conjectural arrangements may be brought to the test. The study of atomic volumes and crystalline structure cast mutual light upon each other.

Kopp obtained his volumes by dividing the molecular weight ( $m$ ) of a substance by its density ( $d$ ), thus  $m/d = v$ . Evidently if atoms have the form of solids of revolution, this volume is a lump quantity, including not only the volume of the atoms, but of the interstices between them. We shall therefore speak of it as the gross volume ( $V$ ), in contradistinction to the true relative volume ( $v$ ) of the atom.

The shortest way of explaining our method of investigation will be to describe at once the process as applied to the haloid compounds of the alkali metals. Let us commence with common table salt. Its

molecular weight is  $58.513 (\text{Na } 23.06 + \text{Cl } 35.453)$ .<sup>\*</sup> Its density, corresponding to the specific gravity, found as the result of very careful determinations by Retgers, is  $2.167$  at  $17^\circ \text{C}$ . The gross volume is then  $58.513/2.167 = 27.0002$ . If this number be multiplied by 4, it will give the volume of a primitive cubelet, supposed to be built up of 4 molecules, as already described. The cube root of this number ( $108.01$ ) is  $4.7623$ , and represents the length of an edge of the cubelet, or the sum of the diameters of the atoms of sodium and chlorine, by which this edge is determined. The next step is to endeavour to obtain some probable value for the ratio of these diameters, that of the sodium to that of the chlorine atom.

It is quite certain if the sodium and chlorine atoms do not both occupy the same space, that the volume of sodium, and the other alkali metals, is very different in the free state and in combination. This is a conclusion to which Kopp was led, who found that by assuming a reduction of the volume in the free state to one-half when the element entered into combination, he obtained fairly constant differences on subtracting the half volumes of the metals from the volumes of the chlorine salts. Our investigations support this opinion of Kopp. In the following table data for investigation are given for such haloid compounds as are open to study.

Metals.	<i>m</i> .	<i>d</i> .	V.	T.	F.
Lithium .....	7.03	0.578	12.162	—	186.0°
„ .....	—	0.589	11.936	—	—
Sodium .....	23.06	0.984	23.46	0°/4°	95.6
Potassium .....	39.14	0.865	45.25	15°	62.0
„ .....	—	0.875	44.732	13°	—

*m*, atomic weight; *d*, density; V, gross volume; T, temperature at which sp. gr. was determined; F, fusion point.

Salt.	<i>m</i> .	<i>d</i> .	V.	T.
Lithium chloride....	42.483	2.074	20.484	3.9
Sodium chloride ....	58.513	2.167	27.0002	17.0
Potassium chloride..	74.593	1.989	37.7503	16.0
Lithium bromide....	86.993	3.102	28.004	17.0
Sodium bromide ....	103.023	3.079	33.404	17.0
„ .....	—	3.198	32.217	17.3
Potassium bromide ..	119.103	2.7	44.12	—
Lithium iodide.....	133.89	3.485	33.218	23.0
Sodium iodide .....	149.92	3.654	41.029	18.2
Potassium iodide....	166.0	3.959	54.266	—
„ .....	—	3.079	53.914	—

<sup>\*</sup> In this and all subsequent cases the atomic weights are those given by Ostwald to oxygen, 16, as a base.

With the exception of the densities of sodium and potassium chlorides, which have been very exactly determined by Retgers, the densities given above cannot be regarded as more than approximations, not to be trusted in the second place of decimals, not always in the first. If one-half of the volumes of the metals given in the first table be subtracted from the volumes of the salts given in the second, we obtain the following results:—

Salt.	V.	$\frac{1}{2}$ V. Metal.	V. Haloid elements.
Lithium chloride ....	20·484	5·968	14·516
"      ....	—	6·08	14·404
Sodium chloride .....	27·002	11·73	15·272
Potassium chloride ..	37·7503	22·625	15·1253
Lithium bromide ....	28·004	5·968	22·032
"      ....	—	6·08	21·92
Sodium bromide .....	32·217	11·735	20·487
Potassium bromide ..	44·112	22·625	21·487
Lithium iodide .....	138·318	6·07	32·23
Sodium iodide .....	41·029	11·73	29·299
Potassium iodide ....	53·914	22·625	31·289
"      ....	54·266	—	31·641

It will be observed that the difference between the gross volume of the salts containing the same haloid element and the gross volume of the metal they contain is approximately equal in all cases; thus, the common difference in the case of the chlorides varies from 14·4 to 15·27; in the case of the bromides, from 20·487 to 20·032; in that of the iodides, from 32·23 to 29·299. It was assumed by Kopp that these differences corresponded to the volume of the haloid element. We make the same assumption, and by treating the subject from another point of view obtain a more consistent agreement between the differences which represent the volumes of the haloids.

The system in which lithium bromide crystallises is not known; the same is true of lithium iodide, and these salts are in consequence necessarily excluded from our inquiry. Neglecting them, it will be seen by inspection that the greater the difference between the gross volume of metal and the haloid with which it is combined, the smaller is the value found for the volume of the haloid; thus, in the case of the chlorides, the smallest value found for chlorine is 14·4, and the disparity between the volumes of lithium and chlorine is the greatest in the series. In the same way the bromine in sodium bromide has a less volume than that in the corresponding potassium salt, and the volumes of sodium and bromine are farther removed from equality than those of potassium and bromine. This is a necessary consequence of such an arrangement of spheres as

we have imagined to exist in the case of common salt, already described, for it can readily be shown, and will presently appear, that the ratio of the volumes of the eight spheres forming a primitive cubelet to the volume of the interstices continuously diminishes as the spheres approach equality, or, more precisely, the total volume of the cubelet, including interstices, is to the volume of the contained spheres as 1·9099 : 1 when the spheres are all equal, and diminishes from this down to a limit, of which we shall have more to say presently, of 1·7125 when the two kinds of spheres have attained the greatest possible degree of inequality consistent with the arrangement assigned to them.

Of the different possible modes of packing in the cubic system, the one we have adopted is the only one that gives this result, within the limits of difference in size which we are considering; every other kind of simple packing leads to an increase in the gross volume when the two sets of constituent spheres depart from equality in dimensions. There is but one exception to this statement, and this does not affect our argument, as it is true of one particular ratio only, and is not applicable to the haloid salts of the alkalis.

Returning now to the imagined cubelet of common salt, we are able to give a value to the diameter of the sodium atom it contains; thus, the gross volume of the sodium is 11·73, one-half of the gross volume of sodium in the free state; suppose eight atoms of sodium built up into a cube in the same way that the four molecules of sodium chloride were imagined to be built up, one sphere to each corner of the cube, then the edge of the cube will be equal in length to the sum of the diameters of two sodium atoms. Thus, the gross volume of sodium  $11\cdot73 \times 8 = 93\cdot84$ , the gross volume of eight atoms, and  $\sqrt[3]{93\cdot84} = 4\cdot5443$ , the length of the edge of the cube; this divided by 2 gives the diameter of a sodium atom as 2·2721.\* But the length of the edge of a cubelet of sodium chloride was found to be 4·7623; deducting the diameter of a sodium atom from this, we have  $4\cdot7623 - 2\cdot2721 = 2\cdot4902$ , the diameter of an atom of chlorine.

Using the value found for the diameter of an atom of sodium as a basis, we may proceed to treat all the haloid salts available for examination in the same way as follows:—

	Diameters of atoms.		Diameters of atoms.
LiCl.....	4·3433	KCl.....	5·3216
—Cl.....	2·4902	—Cl.....	2·4902
	<hr/>		<hr/>
Li =	1·8531	K =	2·8314

\* This could of course be directly obtained from the gross volume, which might be regarded as the cube circumscribing the sodium sphere; but I am anxious to preserve a parallelism in treating the salts and the elements.

Diameters of atoms.		Diameters of atoms.	
NaBr .....	5·051	KBr .....	5·6089
—Na .....	2·2721	—K .....	2·8314
Br = 2·7789		Br = 2·7775	
NaI .....	5·4750	KI .....	6·0099
—Na .....	2·2721	—K .....	2·8314
I = 3·2029		I = 3·1785	

These results, however, are merely approximate,\* for, as Professor Miers has pointed out to me, the diameter of the second sphere in a cube cannot be obtained by simply subtracting the diameter of the other from the edge. Professor Miers shows that the relation between the length of the edge of the cube ( $A$ ) and of the radius of the larger spheres ( $R$ ) and of the smaller ( $r$ ) may be expressed by the equation—

$$(R+r)^2 = [A-(R+r)]^2 + [\sqrt{2}(R-r)]^2,$$

from which he obtains—

$$R = \frac{1}{2} \{2r + A \pm \sqrt{(8Ar - A^2)}\},$$

or

$$r = \frac{1}{2} \{2R + A - \sqrt{(8Ar - A^2)}\}.$$

Employing this formula, the diameters of the atoms are found to be as follows:—

Lithium chloride .....	Li	1·8848	Cl	2·4954
Sodium chloride .....	Na	2·2721	Cl	2·4954
Potassium chloride .....	K	2·8372	Cl	2·4954
Sodium bromide .....	Na	2·2721	Br	2·807
Potassium bromide .....	K	2·8372	Br	2·772
Potassium iodide .....	K	2·8372	I	3·1957
Sodium iodide .....	Na	2·335	I	3·1957

There does not appear to be any sound reason why the volume of an element should remain absolutely constant and independent of the element with which it is associated, even in a homologous series, and I am inclined to think that the differences which appear in our investigation are not wholly due to defects in our knowledge of the specific

\* It has since occurred to me that a slight modification in our conception of the manner in which the atoms are arranged will render our determinations exact; this will be the case if we consider the atoms to be situated with their centres on the nodes of a cubic lattice; we shall recur to this in a subsequent part of this communication.



gravity of the different salts, but that they are real and of significance. The difference in the coefficients of expansion for the different haloids suggest a certain want of constancy in volume. Thus, Fizeau obtained for the linear coefficient of expansion of

		$\Delta\alpha/\Delta\theta$ .
NaCl .....	0·00004039	4·49
KCl .....	0·00003803	5·15
KBr .....	0·00004201	9·78
KI .....	0·00004265	16·76

and since it is improbable that the component atoms of these salts all possess the same coefficient of expansion, it would seem that an absolute constancy of relative volume is in a high degree improbable. It is sufficient, however, for our purposes if it can be shown that the deviation from constancy is confined to narrow limits, as indeed, from the results so far obtained, appears to be the case.

The importance of these results for our inquiry is, however, this, that they cannot be obtained by any other method of packing; other methods, instead of minimising the differences between the gross volumes, would, on the contrary, exaggerate them.

The relative dimensions of the atoms already considered may be tabulated as follows :—

Element.	Diameter.	Volume.	Element.	Diameter.	Volume.
Li .....	1·8848	3·5059	Cl .....	2·4954	8·1274
Na .....	2·2721	6·1408	Br (in KBr)	2·772	11·1526
„ (in NaI)	2·325	6·6659	„ (in NaBr)	2·807	11·5804
K .....	2·8372	11·960	I .....	3·1957	17·1276

In the next table the sum of the volumes of the atoms in a molecule is compared with the gross volume of the salt, and exhibited in the form of a ratio.

Salt.	I.	II.	III.
LiCl .....	11·6333	20·484	1 : 1·7608
NaCl .....	14·2682	27·0002	1 : 1·8923
KCl .....	20·0874	37·7503	1 : 1·8793
NaBr .....	17·7212	32·217	1 : 1·818
KBr .....	23·1126	44·112	1 : 1·9085
NaI .....	23·7935	41·029	1 : 1·7244
KI .....	29·0876	54·265	1 : 1·8656

- I. Sum of the volumes of the atoms.
- II. Gross volumes of the salts.
- III. Ratio of I to II.

It will be observed that in every case the ratio is smaller the greater the difference between the size of the component atoms.

It may next be pointed out that there exists a very important limitation to our power of arranging pairs of atoms or diatomic molecules in the manner we have suggested; the two atoms of the molecule may be equal in size, or they may be unequal, so long as the inequality does not exceed the value of  $1 : 0.7286$ .\*

I owe to the kindness of Professor Miers the following method of finding the value of this limit. Let the centres of the spheres be referred to three edges of the cube, meeting at one corner, as the axes  $x$ ,  $y$ , and  $z$ . The coordinates for the centre ( $C_1$ ) of the larger sphere are  $A-R$ ,  $R$ ,  $R$ , and for the centre  $C_2$  of the smaller sphere  $r$ ,  $r$ ,  $r$ . Then

$$(C_1C_2)^2 = (A-R-r)^2 + 2(R-r)^2.$$

In the limiting case, when the two larger spheres are in contact,

$$A = R(2 + \sqrt{2}),$$

$$\therefore (C_1C_2)^2 = R^2(5 + 2\sqrt{2}) - 2Rr(3 + \sqrt{2}) + 3r^2.$$

Also

$$(C_1C_2)^2 = (R+r)^2,$$

$$\therefore R^2(4 + 2\sqrt{2}) - 2Rr(4 + \sqrt{2}) + 2r^2 = 0.$$

$$\left(\frac{R}{r}\right)^2 = 2 \frac{R}{r} \cdot \frac{5.4142}{6.8284} + \frac{1}{3.4142} = 0.$$

$$\therefore R/r = 0.7929 \pm \sqrt{0.3358} = 1.3724 = 1 \div 0.72865.$$

When the smaller spheres fall below the limiting value  $0.729$  the tangent planes to the spheres no longer define a cube, but a figure which is a hemimorphic form of the rhombohedral or hexagonal system; and in all cases that I have yet examined of diatomic salts, belonging to a homologous series crystallising in the cubic system with cubic cleavage, I find that directly one of the atomic volumes falls below this limit the salt passes out of the cubic system and presents itself under hemimorphic hexagonal forms. This is the case with silver iodide, which is fully discussed in the second part of this communication. That the substances to which we have at present restricted our attention consist of pairs of atoms which lie within the prescribed limit is shown by the following table, in which the ratios of the diameters are

\* If the centres of the spheres be situated on the nodes of a cubic lattice, the value of this limit will be changed.

$\frac{\text{Li}}{\text{Cl}} = \frac{1.8848}{2.4954} = 0.7556.$	$\frac{\text{Na}}{\text{Cl}} = \frac{2.2721}{2.4954} = 0.9108.$	$\frac{\text{Cl}}{\text{K}} = \frac{2.4954}{2.8372} = 0.8792.$
$\frac{\text{Na}}{\text{Br}} = \frac{2.2721}{2.807} = 0.8094.$	$\frac{\text{Br}}{\text{K}} = \frac{2.772}{2.8372} = 0.977.$	$\frac{\text{Na}}{\text{I}} = \frac{2.2721}{3.1957} = 0.7307.$
$\frac{\text{K}}{\text{I}} = \frac{2.8372}{3.1957} = 0.8878.$	Maximum limiting ratio, 1 : 0.72865.	

If the arrangement of the atoms in the crystals under consideration be, as I conceive, the actually existing arrangement, it is certainly not the one to which views on close packing would have led us. Nature does not appear to have been at all parsimonious of space, and that atoms should be disposed in such comparatively open order and yet produce structures of great rigidity, almost inevitably suggests the existence of poles or directed forces. The importance of the question renders it necessary to probe the matter deeper, and we may naturally seek for further confirmation of our hypothesis. Since the arrangement at which we have arrived is the most open probable, we may expect if any other arrangements exist to find evidence of closer packing. We turn, therefore, to the evidence afforded by solutions. In a solution the molecules are not, as a rule, constrained to oscillate about fixed positions, they are not built up into a solid architecture, but are free to glide over one another, and to migrate from place to place. In their case open packing is not to be expected; in the absence of arrangement, the closest packing will prevail. Closest packing among equal-sized spheres exists when one is surrounded by twelve others in contact. It is the arrangement met with in triangular piles of round shot. In a stack of this kind the ratio of the volume of the balls to the volume of the pyramid they form, including interstices, is as 1 : 1.35.

On introducing a crystal of common salt into water the crystalline edifice is destroyed, and the separated molecules become surrounded by those of the solvent in closest packing. As the solution is made very dilute the molecules of the salt are resolved into their ions, which wander about in the solution, still under the influence of internal pressures, adapting themselves to the law of closest packing.

Under these circumstances what change of volume is naturally to be expected when common salt passes into brine? Clearly a contraction, and that to a considerable amount, such, indeed, as is always actually observed whenever the haloid salts of the alkalies are dissolved in water. This general observation affords strong confirmation of the truth of our hypothetical arrangement, which will be still further strengthened if we pursue the subject into quantitative comparison. The ideas involved in the expression atomic volume are less simple in the case of a liquid than in that of a solid. In any case the atomic volume must be regarded as an

average effect, but in a liquid there are more factors to be integrated. The results of the following investigation are necessarily, therefore, only first approximations.

From the numbers which we have already assigned to the relative volumes of the atoms the relative density follows from the relation  $m/v = d$ , and by dividing  $d$  by the factor 1·35 we obtain the density of the substance, which would be produced by the atoms, when most closely packed together. Data are given in the following table:—

Element.	Atomic weight.	Volume of atom.	Density.	$D \div 1 \cdot 35$ .
Li.....	7·03	3·5059	2·0009	1·4853
Na.....	23·06	6·1408	3·7552	2·7816
„ in NaI...	..	6·6659	3·4594	2·5625
K.....	39·14	11·960	3·2727	2·4243
Cl .....	35·453	8·1274	4·3622	3·2312
Br .....	79·963	11·1526	7·17	5·311
„ in KBr ..	..	11·5804	6·905	5·1148
I .....	126·86	17·1276	7·4238	5·4991

The researches of chemists have given us exact determinations of the specific gravity of solutions of the haloid salts of the alkalis, and from these we may calculate the density of the ions. From the equation  $A/d_1$ ,  $B/d_2 = 100/D$ , where A and B represent the percentage of salt and water respectively,  $d_1$  and  $d_2$  the density of each, and D the density of the solution. The specific gravity of the solutions examined will be found given in Watts' 'Dictionary of Chemistry,' or Whetham's 'Solution and Electrolysis,' and need not be repeated here; they are derived from Gerlach's tables, published in 1869, in the 'Zeitschrift für Analytische Chemie,' vol. 8, p. 245. Wherever possible, I have selected for examination a solution containing a gram-molecule of the salt to a litre of water. Making  $d_1$  in the equation above =  $x$ , its value, as found for the different haloid salts, is given in the table below:—

Salt.	Density of molecule.	Density of molecule $\div 1 \cdot 35$ .	Density found from solution.	Number of gram-molecules in 1 litre of solution.
LiCl.....	3·6518	2·7051	2·5585	1·0
NaCl.....	4·0741	3·0178	3·4605	1·0
KCl.....	3·7134	2·7507	2·6731	1·0
NaBr .....	5·8404	4·3262	3·938	0·9687
KBr.....	5·1532	3·8172	3·4916	0·4198
NaI.....	6·3009	4·6673	4·1118	0·721
KI .....	5·7069	4·2273	3·5976	1·0

As close a correspondence appears as could be expected from the conditions of the case, and it would seem that the crystalline structure attributed to the haloid salts, while inconsistent with no known group of facts, is in quantitative accordance with all that we have investigated, and throws unexpected light on hitherto recondite phenomena. The subject of solution must not, however, be left without giving the densities found for more dilute solutions: they are shown in the following table:—

Salt.	Gram-molecules per litre.	Specific gravity of solution.	Calculated density of molecule.
LiCl.....	0·1	1·0021	3·6093
NaCl .....	0·1	1·0038	5·557
KCl .....	0·1	1·0046	3·9989
NaBr .....	0·4854	1·04	4·7223
KBr .....	0·072	1·063	3·488
NaI.....	0·346	1·0374	3·993
KI.....	0·1	1·0112	4·2709

Some of these numbers are less concordant with the density deduced from the crystalline structure than those obtained with stronger solutions, as presented in the preceding table, but it is to be remarked that whatever errors exist in the observations are all thrown on to the values we have obtained; the numbers given in the third column bear all the burden of error arising when dealing with very minute quantities. To show how greatly our results are influenced by slight variations in specific gravity, as given in the second column of numbers above, I have calculated backwards from the density of the atoms to find what specific gravity should give us identical values for the density, as calculated from the crystalline structure and from solution. It is not necessary to give the results for more than two salts; in the case of potassium chloride the specific gravity of the solution, to accord with theory, should be 1·0038 instead of 1·0046 observed, to reduce the density 3·9989 to 2·7668, its value on the assumptions we have made; in the case of sodium chloride the specific gravity should be 1·0019 to give a density of 3·0467, instead of the 1·0038 found. Although different observers do not always give the same specific gravity for the same solutions of salts, it is certain that the discrepancies between theory and observation before us are not to be explained away by blaming the observations; we have before us an interesting residual phenomenon, susceptible of more explanations than one.

It will be observed that those salts the density of which is in excess of that predicted, are those whose volumes are relatively

small. It is only when the ions possess a volume identical with that of the molecules of water that exact agreement between theory and observation can result. The molecular volume of water at 15° is  $0.9987/18.006 = 18.083$ , and if its molecules are closely packed, the true molecular volume will be obtained by dividing this number by 1.35; this gives 13.395; the diameter of the molecular volume is 2.9465. Comparing the diameter of the ions with this, taken as unity, we have:—

Water*.....	1.0
Li .....	0.6289
Na.....	0.7711
K .....	0.9609
Cl .....	0.8259
Br .....	0.9472
I.....	1.0828

It will be seen that the ions of potassium bromide and iodide make the nearest approach to equality with the atomic volume of water, and should consequently give the most accordant results with theory; this will be found to be the case on reference to the tables, the differences which appear are well within the limits of experimental error. The chlorides are all characterised by giving to theory a density which is in excess.

Alternative explanations may be offered; on the one hand, the molecular volume of water has been taken as spherical, because its molecules are most probably in rotation, but it is quite within the bounds of possibility that the ions in their migrations may roll upon the constituent atoms of the water molecules, and thus to some extent invade the boundary of the molecular volume.

In the case of the smaller ions with relatively small volume this would lead to a considerable increase in the calculated density, while in the case of the larger ions it would be scarcely affected. It is also possible when the commingled spheres of the ions and water molecules are of a diameter bearing a certain ratio to each other that closer packing may be brought about, so that the volume of interstices we have allotted to the smaller ions would be reduced; this is a question for geometers.

The crystallographic study of these salts remains for consideration. There are two ways in which the primitive cubelets may be arranged in the construction of crystals: they are shown in plan in figs. 2 and 3; both give homogeneous assemblages in the cubic system, but that shown in fig. 3 is holohedral, that in fig. 2 is hemihedral.

\* *March 4.*—But, as Ramsay and Shields have shown, the molecule of liquid water includes four molecules of the formula  $H_2O$ ; the difference between its dimensions and those of the ions is therefore greater than is given here.

FIG. 2.

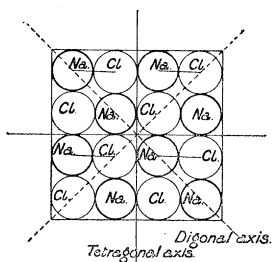
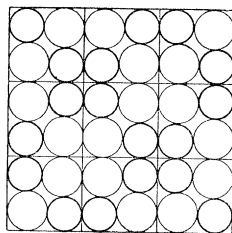


FIG. 3.



When, as until recently, sodium chloride was assigned a holohedral symmetry, it would have been natural to suppose that the arrangement of its molecules was that of fig. 3; but lately it has been placed among hemihedral crystals with which potassium chloride has long been associated. The structure of these salts, and judging by analogy of most of the alkaline haloids, is thus that represented by fig. 2.

It is of interest to observe that in the holohedral arrangement similar atoms are brought into contact; this is not the case with hemihedral symmetry. Perhaps in this is to be found an explanation of the fact that diatomic compounds of monads do not possess holohedral symmetry.

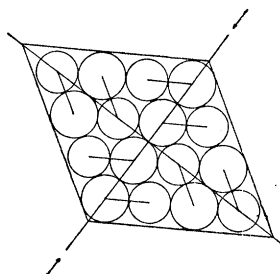
A plagiohedral asymmetry is revealed in the structure both of common salt and potassium chloride by the action of solvents, which produce etch-figures bounded by faces of a hexakis-octahedron. The factors which determine the forms produced by solution are unknown, but probably include the disposition of the chemical bonds of the atoms in the molecule, and the relation of the water molecules to the disposition of the atoms in the crystal. It is evident, however, both from models and figure that there is a skew in the distribution of the chemical bonds of our molecules, and this may be connected with the skew faces produced by solution.

Planes can be drawn through the assemblage of fig. 2 parallel to the faces of the cubelets without crossing any of the molecules; these may be regarded as planes of cleavage.

When a cube of rock salt is truncated at two opposite edges, parallel to planes of a rhombic dodecahedron, and pressure is exerted on the crystal in a direction normal to these faces, a persistent compression results in the direction of the diagonal, and accompanying this a doubly refracting stripe appears. With increased pressure a clean fracture is produced, parallel to one of the rhombic dodecahedral faces to which pressure is applied.

All this is in complete consistence with the structure hypothetically assigned to the crystal. The effect of pressure, as I imagine it,

FIG. 4.



is shown in the diagram (fig. 4), the molecules are forced to slide over each other; those lying on the diagonal along which pressure is exerted make a nearer approach to each other; those at right angles are driven further apart. Up to the critical point, compression and accompanying anisotropy are produced; beyond it the gliding plane becomes a plane of fracture.

The question of elasticity must be left to elasticians; but I would venture to point out the facts elicited by Voigt and Koch; Voigt found for the elasticity modulus of rock salt a coefficient of 4170 kilograms per square millimetre parallel to the tetragonal axes or edges of the cube, 3400 kilograms parallel to the digonal axes or normal to the rhombic dodecahedral faces (110), and 3180 kilograms parallel to the trigonal axes or normal to the octahedral faces (111). Koch found for potassium chloride, 4009 kilograms parallel to the tetragonal axes, and 2088 kilograms along the digonal axes. Voigt obtained very similar quantities. Looking at the plane of assemblage given in the figure (fig. 2), one would suggest that these results are of a kind to be expected; the force exerted along the tetragonal axis is chiefly effective in producing compression of the atoms, along the diagonal axis in distorting the structure. An exact correspondence is obtained by Lord Kelvin between the theoretical elasticities of a hypothetical cube and the results obtained by direct measurement of potassium chloride, but the correspondence does not extend to the results of observation for rock salt, and the structure we have assigned to our crystals is not that considered by Lord Kelvin in his investigation.\*

The hardness of rock salt in different directions has been investigated by Exner, who finds that its value is at a maximum parallel to the edge, and at a minimum parallel to the diagonals, of the face of a cube. This result was obtained by determining the weight, with which it was necessary to load a finely pointed needle, to cause it to

\* "On the Elasticity of a Crystal according to Boscovich," 'Roy. Soc. Proc.,' vol. 54, p. 69.



scratch the face of the crystal. It was found that if it required a load of one to produce scratching parallel to the edge of a face of the cube, a load of 1·3 was necessary parallel to a diagonal. Looked at broadly, it will be seen by reference to the figure that the effect of a force acting parallel to a diagonal should be to that acting parallel to a side, as  $1 : \sqrt{2}$ , *i.e.*, as 1 : 1·414. Considering how complicated the problem actually is, this correspondence is quite as close as could possibly be expected.

By several distinct lines of argument, resting on the study of molecular volumes, of the density of solutions, of the symmetry and physical characters of crystals, we have been led to the same result; given the atomic volumes in the ratios we have assigned to them, no other was possible; and we may now with greater confidence proceed to the investigation of other diatomic compounds, which will be found to throw a surprising light on the molecular tactics of crystals.

“On the Intimate Structure of Crystals. Part II. Crystals of the Cubic System with Cubic Cleavage. Haloid Compounds of Silver.” By W. J. SOLLAS, LL.D., D.Sc., F.R.S., Professor of Geology in the University of Oxford. Received January 27,—Read February 3, 1898.

The haloid compounds of silver offer more points of interest in the study of crystal tactics than those of the alkalis, especially as they include that remarkably anomalous substance—iodide of silver.

Silver itself crystallises in the cubic system, and possesses the same kind of structure as all other metals which possess cubic symmetry, *i.e.*, its atoms are arranged on the plan of most open packing: unlike the alkali metals it undergoes no change of volume on entering into combination. Its atomic weight is 107·93; its density has been differently determined by different observers, for silver heated *in vacuo* Dumas found 10·512, and Roberts-Austen 10·57; we take the mean of these numbers 10·541. The atomic weight, 107·938, divided by 10·541, gives 10·233, the gross atomic volume. From this the diameter of the atomic sphere is found to be 2·17152, and its volume 5·3616.

Both the chloride and bromide crystallise in the cubic system, and are regarded from analogy as possessing the same crystalline structure and symmetry as the corresponding salts of potassium and sodium.

The specific gravity of silver chloride is obtained from the solid after fusion. The latest determinations give for silver chloride a