Summary.

The theory assigns to the "bond" a physical meaning, the oscillating valence-electron; and this idea is shown to be in harmony with recent theories of the structure of matter. It explains a number of phenomena in a fairly satisfactory way.

Valency is the property or power which an atom possesses of sharing a certain number of electrons with one or more other atoms in such a way that the atoms so united form a relatively stable, electrically neutral system.

The valence-electrons oscillate periodically between the atoms which they unite.

Valency is, therefore, a purely mechanical result of the dynamic relations between molecules and the atoms of which they are composed.

The valency of an atom in a state of combination with other atoms is simply a numerical quantity, neither positive nor negative, but the valency of a radical or an ion may be positive or negative.

Explanations are given of the mechanism of chemical reactions, tautomerism; conduction in metals; association; dissociation and conduction in electrolytes and gases. The following deductions from the theory are made:

Uncharged free atoms can exist only when the element belongs in an even group of the periodic system. Free atoms of elements of odd valency can exist only as ions having charges which are odd multiples of the unit *ionic* charge.

Elements belonging to odd groups of the periodic system will have odd valency, while elements of even groups will have even valency.

Valency varies in steps of two, being always even or always odd for the same element.

The unit electric charge or the charge of an electron is twice the ionic charge or 9.548×10^{-10} E. S. U.

The apparent mass of the electron in cathode rays is $1/850$ of the mass of a hydrogen atom.

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THE CHEMICAL SIGNIFICANCE OF CRYSTALLINE FORM.

BY WILLIAM BARLOW AND WILLIAM JACKSON POPE.

Received January 5, 1914.

In a recent paper,[1] Professor Theodore W. Richards criticizes adversely the work which we have done on the relationships existing between crystal structure and chemical constitution and arrives at the conclusion that many of our arguments are fallacious and that our theoretical deductions must be rejected. We welcome this criticism, not only because of its

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[1] THIS JOURNAL, **35**, 381 (1913).

studied impartiality and its appreciation of the questions at issue, but also because it furnishes us with an insight into the sort of difficulties which the chemical reader is likely to encounter in studying the somewhat complex geometrical and crystallographic problems involved. As we are not in agreement with Richards' presentation of our position (p.383) we may be permitted to state our own case.

We make the following brief statement of the position attained by the study of crystal structure before either party commenced work upon it, previous to discussion whether Professor Richards' criticisms of our mode of treating the subject are legitimate and comparing the fecundity of our mode of treatment with that of his method.

All the properties of crystalline solids harmonize with one simple assumption as to the manner in which the parts of the structure are arranged; this assumption is that the structure is a geometrically "homogeneous" one, namely, a structure the parts of which are uniformly repeated, corresponding points having a similar environment throughout the assemblage.[1] The determination of the number of types of homogeneous structure, including all possible arrangements of points in space, was definitely completed before the publication of the first paper above mentioned. The 230 types recognized, distinguished from one another by the different modes of repetition of their parts, are found on examination to fall under 32 classes of crystal symmetry discriminated by the crystallographer. The limitation of the possibilities of solid crystalline arrangement to 230 types obviously marks but one stage in the determination of crystal structure and throws no direct light on the relationship which exists between crystal structure and chemical constitution; the conception of the closest-packing of the atoms, introduced at a later date, is not a factor in the purely geometrical problem of determining the variety of types of arrangement described.

Regarding the geometrically homogeneous character of crystalline solids as proved, it follows that the units of any particular solid crystalline substance must be regarded as centered at the points of a homogeneous point-system of one of the 230 types. We conclude, further, that all identically similar atoms present in a crystalline assemblage of molecules must be conceived as centered at the points of some such homogeneous point-system, or systems. The structure of a crystalline compound is thus to be regarded as built up of a number of interlaced, congruent point-systems, the points of each component system being the centers of one particular set of the component atoms. The number of component point-systems is thus the same as the number of kinds of atoms, distinguishable materially or by position, contained in the chemical molecules of which the substance is composed.

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[1] Compare Barlow and Pope, *J. Chem. Soc.*, **89**, 1676 (1906).

So far we have dealt with conclusions which have been long accepted or with such simple deductions from those conclusions as will hardly provoke dissent; proceeding from these conclusions as a basis, we now describe our method of attacking the problem involved in the relation between crystal structure and chemical constitution.

We make the fundamental assumption that the crystal structure affected by a substance is an equilibrium arrangement of the atoms composing the material, each atom being regarded as a center of opposing and attractive forces of the nature of kinetic repulsion and gravity attraction; the particular set of intercalated point-systems representing a specific crystalline solid is thus an equilibrium arrangement of the forces resident in the component atoms, one atom being centered at each knot of the set in point-systems. The condition thus conceived may be easily visualized in connection with the crystalline form of a monoatomic element, in which, presumably, all the component atoms are identically similar and are similarly placed with respect to the crystal structure. The crystalline condition of such an element is to be regarded as one of equilibrium between forces of attraction and repulsion emanating from, or referable to, a single flock of points homogeneously arranged in space, namely, of points of a single homogeneous point-system; the consideration of this simple case reveals the need of a method for determining what is the equilibrium arrangement of the flock of Boscovichian points exercising identical mutual influence. Our method of solving the problem thus presented introduces the conception of closely packed spheres of influence above referred to; it assumes that the forces present obey some inverse distance law operating similarly and uniformly in every direction from each similar center and treats the influence exerted by other centers immediately surrounding any selected center as so much greater than the influence exerted by centers further removed that their influence may be regarded as negligible.

The equilibrium arrangement of the set of points thus similarly endowed with kinetic energy and attracting each other with a force of the gravity kind, will, according to the conception referred to, be that homogeneous arrangement which, with a given density of distribution of the points, gives a maximum distance between nearest points.

Since the points are equidistant, equal spheres can be described with centers at these points of such a magnitude as to be in contact; it can be shown that, with a given density of distribution of the points, a maximum distance between nearest points and consequently a maximum volume for the spheres, or, in other words, closest-packing of the spheres, will be presented when each sphere of the assemblage, regarded as indefinitely extended, is in contact with twelve others. Two different kinds of arrangement of twelve spheres about a single sphere are, however, equally available for this; the prescribed homogeneity of arrangement can be achieved with either of these kinds present alone or with a symmetrical intermixture of them.

Of the two closest-packed homogeneous assemblages in which one or other of these two kinds of arrangement is alone present, one has cubic symmetry, and is represented in (Fig. 1) while the other (Fig. 2) possesses hexagonal symmetry.

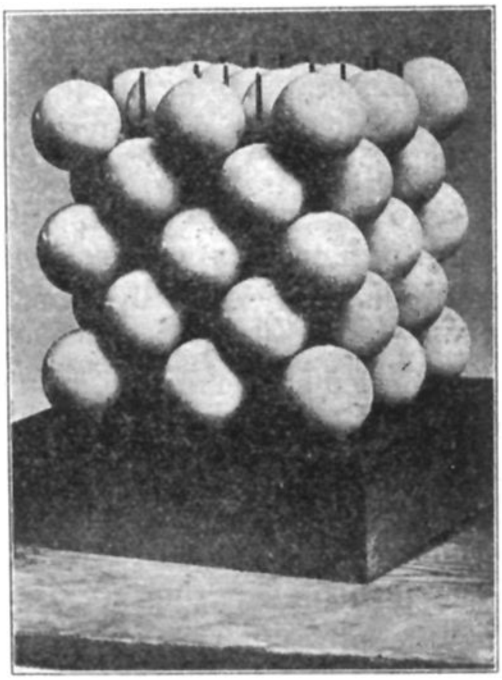

Fig. 1.

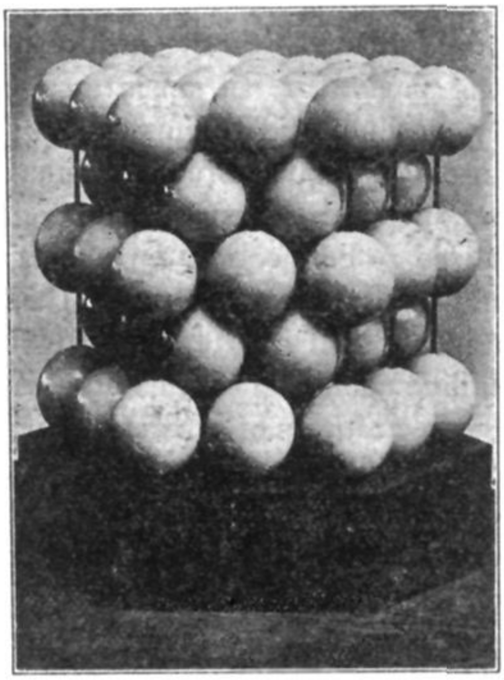

Fig. 2.

If, in each of these two assemblages, tangent planes are drawn at all the points of contact of the spheres, each sphere becomes enclosed in a circumscribing 12-faced polyhedron. As a result of the operation of the inverse distance law the surfaces of the polyhedra thus derived mark the boundaries of the domains of predominant influence of the individual atoms, each point in space experiencing under this law predominant influence from the atomic center nearest to it. Points on the boundary planes of the polyhedral cells are equidistant from two or more centers.

Of the elements which have been crystallographically examined, 50% are cubic and 35% are hexagonal; we have suggested that the crystal structures of these 85% of the elements are represented by the two closest-packed assemblages just described, or by some very simple combination of them. We have also shown that the remaining elements, which crystallize in systems of lower symmetry, present crystallographic peculiarities which lead to the conclusion that their crystal structures are represented by slight distortions either from cubic or from hexagonal symmetry; we have also indicated that this distortion may be the geometrical consequence of the aggregation of atoms to form polyatomic molecules and, in the case of carbon, have shown that a slight distortion of the hexagonal assemblage, which might be caused by atomic aggregation, would account for the crystalline form of graphite and for the oxidation of this allotrope of carbon to mellitic acid. We have also pointed out that the crystalline form of an element which departs from the simple cubic or hexagonal type of symmetry is always colored while those modifications which conform to the two simpler types of symmetry are in general colorless; thus, the colorless diamond and ordinary phosphorus are cubic, while the black graphite and red phosphorus are respectively monosymmetric and orthorhombic.[1]

A perusal of our published papers will show that the correspondence between the assemblages which have been constructed and the crystalline forms of the elements is of a highly quantitative character. But probably Richards will agree with us in this part of our work, since he, like ourselves, is prepared to refer the departure from the symmetry of the two simple forms of assemblage above described, which are presented by about 15% of the elements, to a modifying effect traceable to the formation of groups or atomic aggregates; in view, however, of the detail in which we have discussed the subject, his suggestion that we "do not seem to have attached quite enough weight to the fact that elements are not always necessarily composed of monatomic molecules" (p. 387), appears of obscure applicability. In any case the validity of our valency volume law does not come into question with a crystalline element and when Richards says "it appears that the theory of compressible atoms explains the crystalline form of the cubic and hexagonal elements as well as Barlow's and Pope's theory" (p. 388) we do not know what theory, as distinct from our own, he can have in mind.

It will have been seen that we allot to each atom present in crystalline structure, a point, which may be taken as representing the center of gravity of the atom, and a plane-faced polyhedral domain, termed the sphere of atomic influence, which on our conception of equilibrium represents the region over which its centered atom exerts predominant influence by reason of its attractive and repulsive forces. Prof. Richards has well indicated our relative positions by the following statement:[2] "the so-called 'sphere of influence' of the atom is the actual boundary by which we know the atom and measure its behavior. Why not call this the actual bulk of the atom?" In accordance with this idea, Prof. Richards translates our term "sphere of atomic influence" by "volume of the atom" or by "compressible atom." These several terms are, for his and our purposes,

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[1] *Proc. Roy. Soc. (Dublin)*, **8**, 535 (1897); *J. Chem. Soc.*, **91**, 1159 (1907); *Ibid.*, **89**, 1741 (1906); *Reports Chem. Soc.*, **5**, 270 (1908).

[2] Richards, "The Faraday Lecture of 1911;" *J. Chem. Soc.*, **99**, 1206 (1911).

quite freely interchangeable. Richards suggests, however, because his atomic domains are compressible while the spheres representing atoms which we have used are said by us to be incompressible, that the respective views as to the nature of matter are antagonistic.

We must point out that this suggestion is based upon an entirely false conception of the views of the two parties. Richards, in common with us, adopts the hypothesis that in a crystalline solid the spheres of atomic influence fill the available space without gaps or interstices; each atomic domain, polyhedral in shape, represents to him an atom and since a substance changes its value on subjection to pressure he necessarily regards the atoms as compressible. We, dealing with a different branch of the subject and using a different terminology, find it convenient to construct models representing the comparatively static conditions prevailing in a crystalline solid under a given fixed set of external conditions; to indicate the mode of constructing the model we have suggested the use of "deformable, incompressible" spheres because, on application of adequate pressure, a mass of such spheres would undergo deformation, without changing in actual volume, and would become converted into polyhedra filling the available space without appreciable interstices. Under the conditions which prevail in our static systems the atoms or atomic domains are incompressible because, by definition, no force is operative to compress them, namely, to diminish their volume. With a change in the conditions external to the atom—change in temperature, passage of the atom from one compound to another, or by the application of external pressure—a dynamic condition is established under which the polyhedral atomic domains will necessarily alter in volume; we have considered at some length, exactly on the lines which Richards appears to approve, the change in volume of the spheres of atomic influence with change of temperature and during passage from one compound to another.[1]

Turning next to what we have called the "valency volume law," it should be remarked that we have not, as Richards suggests, made as our "guiding principle the assumption that each valency in a given compound has essentially the same volume and, hence, that the atomic volumes of combined elements are directly proportional to their valencies" (p. 384); our guiding principle is that in every crystalline solid the system of arrangement of parts is an equilibrium one reached by the operation of centered forces. We do not put the law of valency volumes forward as a mere plausible working hypothesis but have deduced it as an argued conclusion based on the interpretation of the facts. Having deduced the law, we have in our various papers subjected its validity to a series of simple quantitative tests and have thereby obtained abundant confirmatory evidence indicating that the law is quite generally obeyed among crystalline

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[1] *J. Chem. Soc.*, 89, 1679 (1906).

solids. Further, LeBas showed that the molecular volumes of a series of paraffins, determined in the liquid state at the melting points, indicate that the atomic volume of carbon in these substances is four times that of hydrogen, and hence suggested that the valency volume law applies even in liquids.[1] To this Richards retorts (p. 385) that "values calculated on almost any assumption within reason" would also do so. But is this correct? Richards quotes the values for four hydrocarbons stated in LeBas' table, and calculates the molecular volumes on our view (C = 4 times H) and on the one he selects to illustrate his point (C = 2H).

	Observed mol. Volume.	Barlow & Pope. C = 4H.	New assumption. C = 2H.
$C_{11}H_{24}$	201.4	202.0	203.3
$C_{20}H_{42}$	362.5	363.3	362.3
$C_{27}H_{56}$	487.4	487.1	486.2
$C_{35}H_{72}$	629.5	629.6	627.6

A short calculation will show that the mean differences between corresponding figures in Columns 2 and 3 is 0.3, while that between Columns 2 and 4 is 1.3; the calculations made according to the results of our conclusions concerning valency volume thus agree four times better with the observed values than do those made on the arbitrary assumption that the atomic volume of carbon is twice that of hydrogen. This result, which becomes far more striking when the values for the whole set of hydrocarbons discussed by LeBas are considered, hardly leads logically to the conclusion that "as an argument in support of the constancy of the valency-volume in any one instance, the table of molecular volumes of hydrocarbons has no significance" (p. 385). The testimony in confirmation of the conclusion that the atomic volume of carbon is about four times that of hydrogen in any given compound becomes overwhelming when the further work of LeBas is considered, namely, that in which he deals with the mass of data collected by Young on the relation between the density of substances at corresponding temperatures.

Large numbers of cases are known in which an obvious relationship exists between the crystalline form of two or more substances, which are chemically related. When the chemical relationship is very intimate, as, say between K_2SO_4 and Rb_2SO_4, close crystallographic similarity in general also exists; the two substances are said to be isomorphous and the axial ratios, representing the comparative dimensions of the crystal structure along three-dimensional coördinates, are nearly the same for the two substances. But in addition to cases of isomorphism, numerous instances are known in which both the chemical and crystallographic similarity are less marked, although still perfectly distinct; substances of this kind are described as morphotropically related and, previous to our work, no clue was available by means of which the morphotropy could be eluci-

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[1] *J. Chem. Soc.*, **91**, 112 (1907); *Phil. Mag.*, **14**, 324 (1907); **16**, 60 (1908).

dated. Thus, *d*-camphoric anhydride, $C_{10}H_{14}O_3$, is morphotropically related to the compound which *d*-camphoric acid forms with acetone, $C_{10}H_{16}O_4.{}^1/_2(CH_3)_2CO$; both substances are orthorhombic and the axial ratio, c/b, is nearly the same in both. If the valency volume law is valid it might be expected to furnish a clue to this mysterious morphotropic relationship in the following manner.

The law indicates that in each of these substances the atomic volumes of carbon, oxygen and hydrogen are in the ratios of 4 : 2 : 1; we, therefore, represent the unit of each compound by a rectangular block of volume equal to the sums of the respective component valencies (the so-called valency volume = W) and calculate the rectangular dimensions of these blocks, taking them as in the ratio expressed by the axial ratios. The three rectangular dimensions, x, y, and z, we term the "equivalence parameters," and they, with the axial ratios, $a : b : c$, are stated in the following table:

	W.	$a : b : c$	$x : y : z$
d-$C_{10}H_{14}O_3$..............	60	1.0011 : 1 : 1.7270	3.2654 : 3.2618 : 5.6331
d-$C_{10}H_{16}O_4.{}^1/_2(CH_3)_2CO$..	74	1.2386 : 1 : 1.7172	4.0435 : 3.2646 : 5.6060

It will be seen at once that the approximation between the axial ratios c/b is translated in the equivalence parameters by an approximation between the respective values for y and z; a little consideration will show that if the units of volume selected in the two cases differed markedly from the relative proportion of the values for W, the valency volume, this correspondence could not occur. We conclude that, unless the morphotropic relationship is wholly fortuitous, it is the result of the operation of the valency volume law.

A remarkable morphotropic relationship has long been recognized between the minerals of the so-called humite group.[1] The monosymmetric mineral chondrodite, $Mg_3(SiO_4)_2.2Mg(F,OH)$, the orthorhombic humite, $Mg_5(SiO_4)_3.2Mg(F,OH)$, and the monosymmetric clinohumite, $Mg_7(SiO_4)_4.2Mg(F,OH)$, in each of which the interaxial angle $\beta = 90°$, are related in such a way that, while the axial ratio, a/b, is practically the same in all, the ratio, c/b is approximately in the proportion of 5 : 7 : 9 for the three substances respectively. Assigning to Mg, Si and O, valency volumes of 2, and to F and H, volumes equal to unity, and assuming for the sake of simplicity, that the isomorphously replaceable fluorine and hydroxyl are present in equivalent quantities, the valency volumes corresponding to the above compositions become 34, 48 and 62, respectively; these values are roughly in the proportion 5 : 7 : 9 shown by the axial ratios, c/b.

The nature of the morphotropic relationship is exhibited more accurately in the equivalence parameters stated at the beginning of the accompanying table; while the values for x and y are practically constant for the three

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[1] Penfield and Howe, *Z. Kryst. Min.*, **23**, 78 (1894).

minerals, the whole effect of the change in valency volume falls on the axis *c*. This is also shown by the constancy of the values *z*/W, which indicates that the length of the axis *c* is very closely proportional to the valency volume.

Mineral.	W.	*a* : *b* : *c*	*x* :	*y* :	*z*	*z*/W.
Chondrodite.....	34	1.08630 : 1 : 3.14472	2.3367	2.1510	6.7644	0.19895
Humite.........	48	1.08021 : 1 : 4.40334	2.3343	2.1610	9.5155	0.19824
Clinohumite.....	62	1.08028 : 1 : 5.65883	2.3384	2.1646	12.2491	0.19756
Prolectite:	20					
Observed........		1.0803 : 1 : 1.8862	2.3130	2.1411	4.0385	0.19977
Calculated.......		1.0818 : 1 : 1.8618	2.3365	2.1589	4.0211	0.19968
Forsterite:	14					
Observed........		0.9296 : 1 : 1.1714	2.3426	2.1778	2.7442	0.19601
Calculated.......		0.9240 : 1 : 1.1741	2.3365	2.1589	2.7433	0.19595

The minerals chondrodite, humite and clinohumite have been very accurately determined and, as will be seen, form a kind of homologous series in which the homologous increment has the composition Mg_2SiO_4; subtracting this increment from the composition of chondrodite, the residue $MgSiO_4.2Mg(F,OH)$ is left. This is the composition attributed to prolectite[1] which may thus be regarded as the first member of the humite series. Further, the mineral forsterite, Mg_2SiO_4, has the composition of the homologous increment of the series.

Prolectite and forsterite have been less well determined than the preceding three minerals but, on the basis of the valency volume law, we can calculate the axial ratios and equivalence parameters of the two substances in question from the more accurate data available for the first three. The table gives this calculated data together with the observed axial ratios and the equivalence parameters calculated therefrom. The correspondence between the observed and calculated values is very close; it is seen that the directions *a* and *b* in forsterite correspond to the equivalence parameters *y* and *x*, respectively. For the purpose of these calculations the only modifications which have been made in the published axial ratios of the five minerals is that, in the case of forsterite, unit length along the axis *b* has been divided by two.

We have given, above, two out of a great number of available instances of the service rendered by the equivalence parameters in illustrating the valency volume law and in giving a quantitative significance to morphotropy. In addition to the cases which we have ourselves exposed, Armstrong and Rodd[2] and Jerusalem[3], Colgate and Rodd,[4] and Armstrong,[5]

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[1] Sjogren, *Z. Kryst. Min.*, **26**, 103 (1896).

[2] *Proc. Roy. Soc.*, **87A**, 204 (1912); **90A**, 111 (1914).

[3] *J. Chem. Soc.*, **95**, 1275 (1909); **97**, 2190 (1910); **101**, 1268 (1912).

[4] *Ibid.*, **97**, 1585 (1910).

[5] *Ibid.*, **97**, 1578 (1910).

Glover and Lowry[1] have, with the aid of the equivalence parameters greatly increased our knowledge of the chemical significance of morphotropic relationships.

Professor Richards rejects the equivalence parameters as being a "mathematical device" and because "the facts all seem to be so reasonable and need no preliminary mathematical treatment" (p. 391), but crystallography is an exact science which can only be correlated with chemistry by quantitative methods. His attack on the calculation of equivalence parameters from axial ratios which have been subjected to division of multiplication consists mainly in a restatement of our own preliminary warning concerning their legitimate and illegitimate use and the extent to which importance could be attached to them;[2] although from the nature of axial ratios, their fractionation is often necessary and legitimate operation, we have, in no crucial instance from which we draw a conclusion of importance, made use of axial ratios which have been subjected to modification.

We submit that the method of quantitative treatment which we have devised for the elucidation of the relationship between crystalline form and chemical constitution, the first comprehensive method introduced, has proved so fertile in coördinating the two subjects of chemistry and crystallography that it cannot be affected by adverse criticism of the kind employed by Professor Richards. The subject has been carried too far on a highly quantitative basis to be touched by vague qualitative criticism involving suggestions as to what is "reasonable" or as to what "we should expect." To be successful, the critic must put forward a comprehensive quantitative scheme obviously superior to the one which we have applied to the camphoric acid derivatives and the humite minerals dealt with in the above table, as well as to numbers of other problems involved in our detailed papers.

Several more points still merit mention. The arrangement suggested by Richards for crystalline caesium chloride (p. 389) was described sixteen years ago[3] and was rejected as representative of the halogen compounds of the alkali metals for a number of reasons. Thus, the arrangement in question is a holohedral cubic one and so does not fit the facts; further, in such an arrangement the equilibrium conditions expressed by close-packing will be so delicately balanced that a slight change in their relations, such as would be involved in the passage from caesium chloride to potassium chloride, or rubidium chloride, bromide or iodide, must be expected to involve a change of crystalline form. For these and other reasons we

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[1] *J. Chem. Soc.*, 101, 1902 (1912).

[2] *Ibid.*, 89, 1683 (1906).

[3] Barlow, *Proc. Roy. Soc.* (*Dublin*), 8, 549 (1897).

gave the preference to the type of arrangement which we ultimately described.[1]

The difficulty suggested by the isomorphous replacement of potassium by ammonium in the sulfate, in which our theory demands the replacement of a potassium atom of volume one, by an ammonium group of volume seven (not nine as stated) elicits the comment (p. 394) that "it is hard to see how any sort of analogous symmetry could be constructed in the two cases under these circumstances." We have given an example[2] which indicates how a closely analogous difficulty may be met by our theory in connection with the isomorphism of potassium and ammonium chlorides. We foresee no special difficulty in constructing assemblages, in accordance with our method, which will present geometrical relationships compatible with the isomorphism of potassium and ammonium salts; at the same time we must ask to be judged by what we have already done and not by what still remains for us to do. Moreover, the difficulty which occurs in dealing with the isomorphism of potassium and ammonium does not arise from acceptation of the law of valency volumes and is certainly not surmounted by the view that the potassium atom and the ammonium group occupy approximately the same volume in crystalline potassium and ammonium chloride. The following substances are all alums crystallizing in the cubic system.

K, with $Al(SO_4)_2.12H_2O$	Potash alum.
NH_4, with $Al(SO_4)_2.12H_2O$	Ammonia alum.
$NH_3.CH_3$, with $Al(SO_4)_2.12H_2O$	Methylamine alum.
$NH_3.C_2H_5$, with $Al(SO_4)_2.12H_2O$	Ethylamine alum.
$NH(CH_3)_3$, with $Al(SO_4)_2.12H_2O$	Trimethylamine alum.
$NH_3.C_5H_{11}$, with $Al(SO_4)_2.12H_2O$	Amylamine alum.
$NH_3.C_8H_{15}$, with $Al(SO_4)_2.12H_2O$	Coniine alum.
$NH(C_7H_7)_3$, with $Al(SO_4)_2.12H_2O$	Tribenzylamine alum.

The facts thus tell us that the 44 atoms of the tribenzylamineammonium group can replace the potassium atom in potassium aluminium sulfate without the occurrence of a change in crystalline system; Professor Richards' mode of regarding crystallographic problems makes him confess the difficulty of seeing how any sort of analogous symmetry could survive the replacement of one unit of volume, the potassium atom, by seven units of volume, the ammonium group, in a salt. It can surely not be maintained that cubic symmetry survives the replacement of one potassium atom by 44 other atoms because the 44 occupy the volume originally occupied by the one potassium atom.

The clue to the whole problem here concerned lies, we suggest, in the possibility of homogeneous arrangement of groups or atomic domains of different relative sizes in the same class of crystal symmetry, while, at

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[1] *J. Chem. Soc.*, 91, 1179 (1907).

[2] *Ibid.*, 91, 1204 (1907).

the same time, close dimensional correspondence subsists which is traceable to the operation of the valency volume law.

We may here terminate our present contribution to this discussion, leaving untouched many points which have been raised against us by Professor Richards because they seem to us mainly based on minor misunderstandings of our work. The only one of the conclusions which Professor Richards states in his summary with which we agree is that numbered (3)—"Some facts seem to be quite beyond the reach of their hypothesis."

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

FURTHER REMARKS CONCERNING THE CHEMICAL SIGNIFICANCE OF CRYSTALLINE FORM.

BY THEODORE W. RICHARDS.

Received February 21, 1914.

The preceding paper on "The Chemical Significance of Crystalline Form,"[1] by Mr. William Barlow and Professor William Jackson Pope, replying to one of mine[2] with the same title, has been submitted to me through the courtesy of the editor of THIS JOURNAL and of the authors of the paper. For this courtesy I am much obliged, and hope that their kind act may be the means of clearing up quickly several misunderstandings which seem to have arisen with regard to the matter in question. Polemics are rarely if ever expedient; but good-natured discussion, either in print or *viva voce*, may serve a useful purpose.

As Messrs. Pope and Barlow infer, I find no fault in the idea of the close-packing of the atoms in crystals. This idea has been, indeed, more or less tacitly assumed in most discussions of the chemical significance of crystalline form. Barlow in his interesting deductive analysis of the geometrical properties of crystalline forms in 1897 begins his final summary with the following sentence: "The main ideas which form the basis of the foregoing inquiry, *viz.*, closest-packing, mutual repulsion of particles, ties, or restraints on this mutual repulsion, are all old conceptions—they have been used by earlier writers and are still adopted by living scientists."[3] Thus we all agree about close-packing. The only difference is as to the

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[1] THIS JOURNAL, 36, 1675 (1914).

[2] *Ibid.*, 35, 382 (1913).

[3] "A Mechanical Cause of Homogeneity of Structure and Symmetry Geometrically Investigated" (read June 16, received for publication June 18, and published December 20, 1897, appearing as paper lxii in the 8th volume, N. S. of the Scientific Proceedings of the Royal Dublin Society, November, 1898).

Comp. "Molecular Constitution of Matter," by Sir William Thomson, in *Proc. Roy. Soc. of Edinburgh*, 16, 693–715 (1890), quoted by Barlow.