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.

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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.

nature and behavior of the entities which are close-packed. This point will be considered shortly.

Again, as the transatlantic investigators rightly point out, the two interpretations with regard to monatomic elements are geometrically in agreement, although the points of view are so divergent. This is not, however, surprising. The nature of the monatomic element admits only of equidistant atomic spacing, and so far as I am aware no other geometric interpretation of the arrangement of a collection of similar spherical atoms has ever been attempted by anyone. In view of this geometrical similarity, Barlow and Pope express their inability to see wherein my view differs from theirs, saying: "We do not know what theory, as distinct from our own, he has in mind." The difference is nevertheless well marked, even in the case of monatomic elements, for although the geometrical arrangement would here be the same according to each theory, the idea of atomic compressibility introduces a factor in the mechanism involving change of volume, which brings this case into line with the more complicated ones soon to be considered. Each side of each atom would be compressed by contact, but each would be equally compressed. When we come to treat of the more complex allotropic forms of elements having polyatomic molecules, the difference between the two points of view stands out in stronger relief. According to the theory of compressible atoms, the affinity which binds the atoms together to make a polyatomic molecule must have a different compressing effect from the cohesion which knits these molecules into the solid condition. Hence equidistant spacing between the atoms in all directions can no longer exist. The difference between my hypothesis and Pope and Barlow's is here, as indeed in the other cases, entirely concerned with the different interpretations as to the results of the action of the forces binding together the atoms in a molecule, and the molecules with one another. In my interpretation I have endeavored to reconcile the crystalline phenomena with other properties of the substances concerned, such as boiling points, melting points, surface tensions, compressibilities, coefficients of expansion, all of which can furnish some clue as to the forces at work; but Pope and Barlow seem to have made no such effort. Their discussion is essentially a geometrical one, and involves the close-packing of *spheres;* whereas my view imagines the "spheres of influence" as much distorted whenever the molecule is composed of more than one atom.

As a matter of fact, very little emphasis is placed, in the joint thesis of Barlow and Pope, upon the possible magnitudes of the forces holding the atoms together.[1] In reading the paper one feels that the original tenets of Barlow, as set forth in the earlier paper already referred to, are retained. In this paper (which consists of a highly learned and in-

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[1] *J. Chem. Soc.*, 89, 1676 (1906).

genious deductive analysis of the arrangement of Boscovichian atoms in space), the atoms are often alluded to as mutually repellent (*e. g.*, on pages 529, 547, 580, 675, 686), but little is said about their mutual affinities. Some kind of tie or restraint is presupposed where chemical action is concerned, but the binding together of molecules seems to be of the loosest possible sort. In the papers by the joint authors, no attracting force except gravitation (or its like) seems to have been mentioned; but few chemists would be inclined to admit that gravitation is the only force binding the molecules of solids.

The definite statement is made both in Barlow's early work and in the paper of 1906 (by the joint authors) that the spheres of influence are to be considered as incompressible. To be sure, in this latest paper affirmation is made that they are to be looked upon as incompressible only when no change in pressure is put upon them: ". . . . the atomic domains are incompressible because, by definition, no force is operative to compress them;" but according to that definition would not everything be incompressible? Even the most rarefied gas does not change its volume if unacted upon chemically, and if the pressure and temperature remain unchanged. The difference of opinion here seems to be rather one concerning the definition of the word "incompressible," at least as used in the latest paper. The earliest paper by Barlow appears to have used the word in its usual sense.

But entirely apart from any question as to the significance of this term, there is a real and fundamental difference between the two opposing theories. The British investigators enunciated publicly for the first time in 1906 the postulate that the volume which any substance assumes is essentially determined by valency. They contend in their latest paper that this valency volume idea is not an assumption, but a law deduced from the theory of close-packing under the balanced play of centered forces, and that it was obtained as an argued conclusion based upon the interpretation of the facts. Here again one is doubtful as to the definitions which may be given to the terms deduction, hypothesis, theory, and law; but, however these words may be defined, it seems to be perfectly clear that the idea of valency volume is an essential feature in their present quantitative discussion. This is made evident in their definition of equivalence-parameters on page 681 of their paper of 1906. In this paper W signifies the valency volume, and W enters into the value of x; therefore, it also enters into that of y and z, which depend upon x. These values, x, y, and z, are the basis of all their comparisons.

It is this idea of valency volume which I find myself obliged to reject; and the rejection is not by any means based upon minor misunderstandings of the work.

The question at issue seems to be simply as follows: Messrs. Pope and Barlow imagine that their "spheres of influence" of the atoms expand and contract to fit their theory of valency volumes, and this theory has the rigid requirement that in any given compound the volume occupied by an atom is to be assumed as directly proportional to its valency. No plausible reason why this should be so is given.

On the other hand, the point of view which I am defending maintains that when two atoms are drawn together by a stronger chemical affinity, the volumes of their spheres of influence[1] must be diminished at the surfaces of contact, and that when the molecules are bound together by strong cohesive affinity, their volumes are again diminished by the cohesive pressure exerted upon the contiguous surfaces. This theory maintains that both affinity and cohesion not only hold the atoms together, but that they *pull* the atoms together. Hence the volume occupied by a solid or liquid is dependent upon the variable forces which come into play. The forces are shown to be not arbitrarily determined, but to be inherent in the atoms; and every change in affinity must produce its corresponding change in volume.

These two points of view are perfectly definite and entirely antagonistic. Messrs. Pope and Barlow think that they have obtained support for theirs in some of the facts of crystallography. In my last paper I endeavored to show, as they state, that all the facts adduced by them are inconclusive, being capable of explanation in other ways. On the other hand, in support of the opposing theory (which maintains volume to be determined not by an arbitrary choice of valence on the part of the crystallographer, but rather by the actual affinities which play upon the atom), very many facts have been brought forward in my papers upon the significance of changing atomic volume[2] seeming to leave no doubt that solid and liquid volumes are really determined in this way.

Countless facts quoted from these papers might be reviewed to show the reasonableness of ascribing to chemical affinity and cohesion an important share in determining the volume of solids and liquids; for instance, the fact that the less cohesive elements have large molecular volumes and large compressibilities, the fact that, in general, among isomers the more volatile are also the more compressible, less dense, possess less surface tensions and greater coefficients of expansion, the fact that, in general, the exhibition of greater chemical affinity seems to involve greater diminution in volume,

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[1] Because these "spheres of influence" always accompany the atoms and seem always to represent them in their volume relations, I call the "spheres" the atoms themselves. The term "spheres of influence" seems to be unfortunate, because in all compounds these spaces occupied by the atoms can scarcely be spherical; and, moreover, some influences of the atoms unquestionably extend beyond them.

[2] A bibliography of these papers is in THIS JOURNAL, 36, 624 (1914).

all point in one direction.[1] On the other hand, the theory of Messrs. Barlow and Pope seems to take account of none of these things.

Because of this effect of the powerful forces coming into play, the complete solution of the problem of crystalline form demands many more far-reaching arguments than ones concerning mere matters of crystallographic detail. The knowledge necessary for the satisfactory mathematical treatment of the subject involves an understanding of the enormous internal pressures which bind solids together, quite beyond the reach of any mortal today. A deductive method is convincing only when all the factors determining a given phenomenon are taken into account; and it seems to me that some of the chief factors have been left altogether out of consideration in the mathematical theory under discussion. One is at a loss, for example, as to how the theory of Barlow and Pope can account for the enormous shrinkage in volume (to much less than half of the original bulk of the reacting elements) which occurs when caesium combines with liquid chlorine. The interstices in the most loosely close-packed system in the original substances (the elements) could not account for this, because geometrically the cube is less than twice the volume of the inscribed sphere. This change of volume is not accidental, and the fact that the heat evolved and the free energy change exhibited by such changes show a traceable connection with the work involved in the compression shows that such volume changes are deeply significant and fundamental. Atoms cannot be expected to contract and swell up to conform to the exigencies of a deductive geometric theory; their volume-changes must be expected to be far more logically caused.

Again, no notice is taken in the immediately preceding paper of a typical case emphasized in mine, namely, the relation between benzene and tetrabromobenzene. This is not an isolated case, but is typical of a very plentiful class of phenomena, and yet the authors have not attempted to throw light upon it. Benzene has a molecular volume of 77.4, tetrabromobenzene 130.2. They both have the same number of valencies within them, namely, 30, if carbon is considered as a tetrad. It is evident then that the theory of Barlow and Pope demands that the carbon should be the same fraction of the total volume in each case, and the same doctrine holds true with regard to the two residual atoms of hydrogen. This involves the assumption that these atoms (or their "spheres of influence") nearly double their bulk when the other associated atoms are exchanged on a purely univalent basis. No reason whatever for this extraordinary increase in volume has been assigned, and I cannot help thinking that any chemist who has seriously considered the subject of molecular volume will agree with me in thinking that the Pope-Barlow assumption is irreconcilable with the

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[1] "The Faraday Lecture of 1911," *J. Chem. Soc.*, 99, 1201 (1911); *Science N. S.*, 34, 537 (1911).

phenomena. The more reasonable explanation is that the atomic volume of bromine in combination is much larger than that of hydrogen, as all of the well-known considerations of Kopp indicate. Let me emphasize once more the fact that this is a typical case, and that it was advanced in my previous paper as a direct challenge. The fact that it was ignored seems to imply that it could not be answered.

Since some of the other objections raised in my previous paper seem to have been misunderstood, the more important differences of opinion about them may be briefly reviewed. For example, with regard to the results of Le Bas, the eminent controversialists seem to have overlooked the fact that while I explicitly referred to the obviously closer agreement of their calculated figures as compared with those corresponding to my assumption, I pointed out that even the most divergent results fit the facts quite as closely as anyone has a right to expect, because of the arbitrary assumption as to the temperature of comparison. Barlow and Pope chose the ratio: volume H = $^1/_4$ volume carbon (exactly); and in order to show that the deviations produced even by a great departure from this proportion were unimportant, I chose the entirely different ratio: volume of hydrogen = $^1/_2$ volume of carbon. It is easy for anyone to calculate, however, that if such a ratio as 1 : 3.5 or 1 : 4.5 or even 1 : 5 is chosen, results of the same order of accuracy as those obtained from Barlow and Pope's exact ratio 1 : 4 are obtained; for example, if hydrogen is taken as 2.553 cc. and carbon is taken as 12.765 cc. (five times the hydrogen) the theoretical values calculated for the first fifteen hydrocarbons in the table of Le Bas agree on the average at least twice as well with the observed facts as those computed according to Barlow and Pope's assumption of the ratio 1 : 4.[1]

TABLE GIVING TYPICAL COMPARISONS OF HYDROCARBONS WITH LESS THAN 30 ATOMS OF CARBON.

	Mol. vol. at melting point. Found.	Barlow and Pope's assumption. Vol. C = 4 Vol. H.	Error.	New assumption. Vol. C = 5 Vol. H.	Error
$C_{11}H_{24}$..........	201.4	202.0	0.6	201.7	0.3
$C_{13}H_{28}$..........	237.3	237.6	0.3	237.4	0.1
$C_{15}H_{32}$..........	273.2	273.2	0	273.2	0
$C_{18}H_{37}$..........	326.9	326.7	0.2	326.8	0.1
$C_{22}H_{46}$..........	398.3	398.0	0.3	398.3	0
$C_{27}H_{56}$..........	487.4	481.1	0.3	487.6	0.2

How, therefore, they can claim that these figures afford any significant support for any exact ratio, I do not understand. To me it seems that their argument amounts to a process which might be called mathematical hair-splitting, especially when the quality of the data in question is taken

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[1] The last three with over thirty atoms of carbon to the molecule are not quite so conformant, but, even as a whole, the series of calculated results is about as good as Pope and Barlow's.

into consideration. Moreover, the paraffin hydrocarbons were liquids, not crystals, at the temperatures measured; and in any case, they are unique in their properties, hence it is not safe to transfer conclusions drawn from them to other compounds.[1] The principles used by Le Bas and Barlow and Pope, if applied to aromatic hydrocarbons, completely collapse. In the light of these remarks, a careful perusal of my earlier statements upon page 385 will furnish evidence which needs no further elucidation. I beg leave to dissent entirely from their statement with regard to this matter on page 1681 of their paper.

The immediately foregoing paper contains several examples brought forward in order to show that the theory of Barlow and Pope is capable of showing resemblances between morphotropic organic and inorganic substances. It seems to me that these examples add little to the general argument; they are really of the same class as the partial symmetries of organic substances discussed in my earlier paper. The bringing forward of these examples seems rather to indicate a misunderstanding as to the general criticism of the method. I have from the first admitted cordially that the mathematical method of equivalence-parameters involving valency volume is capable of showing resemblances; the difficulty with it is rather that it seems to be capable of showing resemblances where none exist, and, therefore, its results must be received with great caution.

In a number of minor points also there seems to be misconception or misunderstanding. For example, Mr. Barlow and Professor Pope must adopt some other structural formula for ammonium chloride than that which corresponds with my notion. They often arbitrarily choose, in assigning their valency volume, the lowest valency which an element exhibits, regardless of the actual valency in the particular case. For example the radical of ammonium is supposed to have seven valencies in all; $NH_2 + H_2$ seems to be considered as a univalent complex. But is not this (like a number of their other methods) rather an arbitrary proceeding? To me NH_4Cl seems to have ten valencies, five on the nitrogen, one on each hydrogen, and one on the chlorine. Therefore, if each valency had an equal volume, nine volumes would belong to ammonium and one to chlorine. Again, the intimate structure of the cube of caesium chloride, as illustrated in my previous paper, must certainly be considered as hemihedral, because both the chlorine atoms and the caesium atoms are arranged in tetrahedral symmetry.[2] The fact that externally the form is cubic, makes the structure holohedral only from a superficial geometric point of view. The question here is, of course, entirely as to the significance attached to the words hemihedral and holohedral, which in this case would differ according as the surface of the crystal or its ultimate structure is

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[1] L. J. Henderson, "The Fitness of the Environment," p. 215 (Macmillan), (1913).

[2] See Barlow, *Loc. cit.*, p. 550.

taken into consideration. That Barlow, in 1897, proposed and rejected something analogous to the arrangement which I pictured was overlooked by me, because his diagram is so very different in appearance (*loc. cit.*, p. 550), but the fact does not change my opinion that the aforesaid picture is the most reasonable explanation of the facts. If the atom is acknowledged to be compressible, this arrangement is as closely-packed as any other, and it would be firmly tied together by the strongly attractive affinity of the two components, thus forming a thoroughly stable system. The substitution of potassium for some of the caesium would not be difficult in a compressible system. Incidentally, the introduction of this question gives me the opportunity of acknowledging that Professor Sollas in a very interesting paper published in the Proceedings of the Royal Society in 1898,[1] proposed a structure of sodium chloride essentially similar to that advocated by me for caesium chloride, without, however, the addition of the idea of atomic compressibility. Sollas's theory with regard to this substance seems to me far more reasonable than that of his antagonists, but his concepts are less satisfactory when they depart from the idea of close-packing.

It would be wearisome to consider here every detail of the misunderstanding involved in the paper of Mr. Barlow and Professor Pope; indeed, this is not necessary, for a careful perusal of the papers in question will give the intelligent reader abundant opportunity to decide between the alternatives according to his appreciation of the cogency of the respective arguments. It is important to note that no evidence in any way contrary to the theory of compressible atoms has been adduced by the eminent transatlantic investigators.

Nevertheless one further point introduced by their paper seems worthy of further discussion, especially since it concerns the general principles of research. The authors feel that a qualitative argument must necessarily give way before a highly developed quantitative one; and because this feeling seems to be general with regard to many physicochemical phenomena, I am glad to take this opportunity to express my attitude. No one could believe more completely than I in the importance of quantitative mathematical discussion; I have given most of my life to the attempt to secure more accurate quantitative data of many kinds. A scientific argument which is wholly lacking in quantitative support cannot be satisfactory; but on the other hand a highly developed mathematical treatment which rests upon unsound premises is usually much worse than none. Such a treatment is likely to carry with it a false feeling of security, and to be less valuable than a merely qualitative discussion based upon sound premises. To cite an extreme example, the qualitative discussion of the nature of oxygen by Rey, Hooke, and Mayow in the seven-

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[1] W. J. Sollas, *Proc. Roy. Soc.*, 63, 273 (1898).

teenth century was much more nearly correct than the later quantitative explanation of the ultra-phlogistonists, which ascribed negative gravity to phlogiston in order to explain many of the same facts. The latter explanation appeared to be at least consistent from a quantitative point of view, but was very ill-founded as regards its fundamental premises. Not only in this matter of crystalline form, but in many other physico-chemical problems, it seems to me highly desirable that the fundamental premises or original assumptions should be reasonable, and in accordance with as wide a variety of facts as possible, even if the resulting system appears to us now to be too complex to receive complete mathematical treatment.

Besides, the fact should be emphasized that my views concerning the significance of changing atomic volume by no means rest upon a mere qualitative basis; they are supported by many observations of a highly quantitative nature.

To sum up the situation, it seems to me that the immediately preceding paper under discussion has not attempted to answer some of the most important objections to the deductive theory; that the authors have misunderstood others; that they adopt a mathematical treatment which tends often to make disagreeing results more harmonious, and then find crystallographic confirmations of their deductive tenets which do not seem to me to be cogent; that here as before they seem to have essentially overlooked the very large internal pressures which must exist in solids, and have not heeded the arguments from which the existence and effects of these pressures are inferred; that the paper gives evidence of an illusory security sometimes felt by those who put their trust in a complex mathematical superstructure rather than in a firm foundation of sound assumptions, and that no argument has been advanced to show that my fundamental assumptions are not sounder than those of the joint authors. On the other hand, the various papers on the significance of atomic volume have brought forward so many evidences in favor of atomic compressibility as to put the burden of proof on any contrary hypothesis.

In conclusion it gives me much pleasure to express once more my appreciation of the real service which Mr. Barlow and Professor Pope have done by collating a great quantity of crystallographic data; and to this expression I must add my regret that I have found their fundamental doctrine of valency volume irreconcilable with a broader view of the nature of solids and liquids and the mechanism of chemical change.

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Additional Note by William Barlow and William Jackson Pope.

The perusal of the two foregoing communications will probably convince the reader that little of public utility will result from the further