tion mixture was filtered, and the filtrate evaporated under reduced pressure, the residue taken up in water and evaporated as before. From 5 g. of the acid a yield of 0.6 g. was obtained. Upon treatment of this substance with sodium hydroxide the same reaction, as indicated by the isocyanide odor, was obtained as before. The substance remaining upon the filter paper, after a thorough washing with alcohol, gave no such reaction; it was probably unchanged acid. The presence of the ester in the residue from the soluble portion was thus indicated, but analysis of this residue shows that it contains but a small quantity.

Co obtained	24.43
Co in $H_3Co(CN)_6.H_2O$, calculated	25.00
Co in $C_2H_5H_2Co(CN)_6.H_2O$, calculated	22.35

The product was evidently a mixture of a small quantity of the ester with a larger quantity of the free acid; a result which might have been expected from the course of the reaction.

This shows that the formation of the ester in which the alkyl group is linked with nitrogen is not dependent upon the presence of a silver salt in its preparation.

The attempt was made to prepare a corresponding ester of hydroferricyanic acid, by the action of ethyl iodide upon the silver salt. Such a compound, if formed, is evidently decomposed at once. Contrary to our experience in the preparation of the ester of hydrocobalticyanic acid a perceptible odor of an isocyanide was noted in the reaction flask. Upon evaporation of the filtered solution no homogeneous product was obtained.

Summary.

1. Ethyl dihydrogen cobalticyanide has been prepared by one reaction, and in an impure condition by another.
2. The composition of the substance has been confirmed by the preparation of disilver ethyl cobalticyanide.
3. The decomposition of the ester brought about by the action of sodium hydroxide indicates that at least in some of its molecules the ethyl group is attached to nitrogen, with the strong probability that in others the ethyl group is otherwise linked.
4. The attempt to prepare the corresponding ester of hydroferricyanic acid failed.

DARTMOUTH COLLEGE, HANOVER, N. H.

THE CHEMICAL SIGNIFICANCE OF CRYSTALLIN FORM.

BY THEODORE W. RICHARDS.

Received March 14, 1913.

When in 1669 Nicholas Steno discovered that a given crystallin angle possesses always a constant value for any given substance, an important circumstance concerning the chemical significance of crystallin form was established. The discovery has been abundantly verified in recent years, especially by Tutton. A century and a half after Steno the investigation of Mitscherlich added great weight to this significance; for Mitscherlich showed that substances with analogous composition often possess also analogous or even isomorphous crystallin forms. At that time this discovery assisted in fixing various atomic weights by pointing out the probable molecular magnitudes of a number of previously misinterpreted substances; but to-day other knowledge has rendered this office of isomorphism unnecessary. The discovery of Mitscherlich is now much more useful to us as a means of interpreting the crystal forms themselves, assuming the molecular constitution of the molecules, than as a means of fixing atomic weights.

In the intervening years since that early time the aspect of crystallography has greatly changed. Instead of concerning himself merely with the measurement of external angles and the fixation of external zones, the crystallographer has become interested in the fundamental forms of symmetry which determin the arrangement of associated particles in space; and from the investigations of Hessel (1830) and Frankenheim (1835) to those of Barlow at the present time, the new logical system of crystallography has not so much supplanted as it has developed and supplemented the older crude classification. According to this new system of crystallography the interest lies in the arrangement of space-gratings or points distributed symmetrically in three dimensions. These points we must consider as being the centers of the "crystal units" which build up the solid system, and each of these must be supposed to consist of one or more molecules. In our effort to visualize the nature of a crystal on this basis, we cannot help asking at once two questions: How far does each molecule spread out around the point which marks its center? What forces hold these points in their relative position towards each other, thus maintaining the rigidity of the solid structure?

In 1901 a theory was advanced which seems to provide a plausible and reasonably satisfactory answer to both these questions, namely, the theory of compressible atoms.[1] This theory entirely abandons the old idea of small hard atoms at a distance from one another. It makes no assumption as to just how the "substance" of the atom, whatever that may be, is distributed within the so-called "sphere of influence," but points out the fact that in all the relations in which the volume of the atom is important, the volume of the "sphere of influence" is really the essential thing. The hard particle in the center, formerly imagined to be far from its neighbor, even in a solid, is purely an abstraction and has no correspond-

---

[1] Richards, "The Significance of Changing Atomic Volume," *Proc. Am. Acad.*, **37**, 1 (1901); **37**, 399 (1902); **38**, 293 (1902); **39**, 581 (1904); *Z. physik. Chem.*, **40**, 169, 597 (1902); **42**, 129 (1903); **49**, 15 (1904).

ing basis in observed facts. We have really no right to pretend to know how the material is distributed within the "sphere of influence." The material is somewhere within that space, but the outside of the space which the atom reserves for itself acts as if it were something very real, and cannot be considered but as the boundary really to be reckoned with.

The high degree of rigidity, impermeability and permanence possessed by most solids combine to suggest that the substance of the atom is distributed throughout the whole space but not necessarily evenly distributed. It may be on the surface of the "sphere of influence," like the material of a hollow rubber ball, or it may be more concentrated towards the middle, gradually decreasing in concentration on the outside; at present we have no means of deciding.

The attitude of mind with regard to the compressible atom involves not merely a difference in nomenclature. The name "sphere of influence" is vague; on the other hand the limit of approach to the center of an atom is definit, if variable. As used above, "sphere of influence" is used to denote the limit of approach to the atomic center; but the forces residing in an atom doubtless, at least in part, extend further. Hence to call the space occupied by the atom the real effective volume of the atom is to give a definit name to an idea which the phrase "sphere of influence" would describe but vaguely and incorrectly. Faraday's conception of "tubes of force" proved to be a fruitful idea because the conception assisted in visualizing the phenomena concerned; and to even a greater extent the idea of the compressible atom helps in this case, partly because the facts themselves are more tangible.

On this basis the atom must be assumed to be compressible, because its boundary shrinks when mechanical pressure is applied, even, apparently, at the absolute zero of temperature;[1] and the ascription of compressibility to the atom at once clears up a great variety of facts which would otherwise be difficult to understand. Because of its compressibility, the atom must be supposed to be compressed whenever any external force is applied through the action of either chemical affinity, which draws two atoms powerfully together, or cohesive affinity (a similar but less powerful attracting agency) or outside pressure applied mechanically. In a series of papers it has been shown that many facts previously not comprehensible become conceivable and easily correlated with these premises in mind, and the support which the theory thus receives is so great that it may reasonably be used as a working hypothesis in many directions. The wide scope of this idea was recognized immediately by the author. In the second paper concerning it (1902), many of its bearings were briefly catalogued; and in this list the eighth item reads as follows: "It explains

---

[1] Richards, "Faraday Lecture," *J. Chem. Soc.*, **99**, 1207 (1911).

all tri-dimensional relations of material, such as stereochemistry and crystal form, at least as well as any other theory."[1]

The bearing of the idea upon stereochemistry has already been briefly taken up in the Faraday Lecture of 1911;[2] the object of the present paper is to discuss its application to the structure of crystals.

In the intervening time (in 1906) one aspect of the question has been considered by Barlow and Pope[3] in a series of elaborate papers. These distinguished investigators entirely agree with and support the conclusion that the "spheres of influence" (or as I prefer to call them, the atoms themselves) must be closely packed in a crystal in order to account for the maintenance and rigidity of the crystal structure. They reject, however, the idea of the compressibility of the atoms, while admitting deformability, and in spite of the fact that at the same time they assume the possibilities of great arbitrary changes of atomic volume under different circumstances.[4] They make as their 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. This is, of course, entirely inconsistent with Kopp's system of molecular volumes, which, although not by any means flawless, seems less arbitrary than the newer idea.

The assumption concerning the so-called valency-volume seems to me to be a very doubtful tenet, not only because there seems to be no reason *why* each valence in a given compound should have the same volume, but also because it leads at times to extraordinary and improbable conclusions. Although probably each atom present affects every other to some extent, I can see no reason why, for example, all the remaining carbon and hydrogen atoms in benzene should nearly double their volume when four atoms of bromine are substituted for hydrogen, as the Barlow-Pope theory demands.[5] The argument adduced by these investigators as the most striking in support of their remarkable assumption is the set of data found by Le Bas giving the molecular volumes of the liquids of normal paraffins just above their melting points. Entirely apart from the question as to whether or not the arbitrary choice of the temperature of comparison really indicates similarity of physical composition, and also apart from the fact that these figures deal with liquids and not with solids, it

---

[1] "The Significance of Changing Atomic Volume," *Proc. Am. Acad.*, **37**, 410 (1902); *Z. physik. Chem.*, 40, 608 (1902).

[2] "Faraday Lecture," *J. Chem. Soc.*, **99**, 1212 (1911); *Smithsonian Report for* **1911**, p. 210; *Revue. Sci.*, 50, 327 (1912); *Naturwissenschaftliche Rundschau*, 26, 494 (1911); *Science*, **34**, 546 (1911).

[3] *J. Chem. Soc.*, **89**, 1675 (1906); **91**, 1150 (1907).

[4] Barlow and Pope, *J. Chem. Soc.*, **89**, 1675 (1906).

[5] The molal volume of benzene is 77.4, of tetrabrombenzene is 130.2. See Barlow and Pope, *J. Chem. Soc.*, **89**, 1679 (1906).

may be readily shown that the figures cannot possess the significance which Le Bas and Barlow and Pope ascribe to them. These investigators calculate atomic volumes on the assumption that a gram-atom of hydrogen occupies 2.97 cubic centimeters and a gram-atom of carbon four times that space, from their assumed premise that the atomic volume depends essentially on the valency. The calculated values for the molecular volumes of the hydrocarbons obtained by adding the corresponding multiples of these figures agree closely with the facts, it is true; but so would values calculated on almost any other assumptions within reason. This is because the higher paraffin hydrocarbons having the formula C_nH_{2n+2} approach closely the composition of the hydrocarbons C_nH_{2n} when n is large; in other words any ratio between carbon and hydrogen which fits one hydrocarbon will fit almost as well another. To illustrate this, it is only necessary to repeat extracts taken at random from the table of Le Bas, giving not only the observed molecular volumes and those calculated on the assumption of Barlow and Pope (H = 2.97 and C = 11.88 cc.) but also another column calculated on an entirely different basis, for example, H = 4.42 and C = 8.84 cc.

Formula of compounds.	Observed molecular volume.	Pope and Barlow calculated vol. C=4 vol. H.	New assumption vol. C=2 vol. H.
$C_{11}H_{24}$	201.4	202.0	203.3
$C_{20}H_{42}$	362.5	362.3	362.3
$C_{27}H_{56}$	487.4	487.1	486.2
$C_{35}H_{72}$	629.5	629.6	627.6

It will be noticed that the new figures, calculated on an entirely different basis, correspond almost as well with the observed figures as those calculated by Pope and Barlow. The greatest difference between fact and theory is less than 1%, and the average difference is less than 0.4%.

When account is taken of the fact that the densities which afford the basis for these molecular volumes depend upon the temperature chosen for the determination, and that the really legitimate temperature for such a comparison is unknown, the agreement shown by the figures in the middle columns seems even less convincing. The average deviation from the facts shown by the figures in the last column corresponds to a difference in temperature of only about 5°, and the true temperature for comparison is certainly not known within that amount. Therefore the last row of figures does not deviate more from the observed quantities than by an amount which may be due simply to the arbitrary temperatures chosen for comparison. In short, as an argument in support of the constancy of the valency-volume in any one substance, the table of molecular volumes of hydrocarbons has no significance.

Some of the other arguments advanced in favor of the approximate equality of the valency-volumes seem to me in the same way to be equally good arguments in favor of almost any other reasonable theory which involves close packing of molecules. On the other hand, the Barlow-Pope theory in its unmodified form fails to account either for the varying angles of some truly isomorphous substances, or for the distortions observable in some of the less symmetrical forms. Moreover, there are other facts shortly to be pointed out which militate gravely against the theory. In brief, I can find no fact brought forward in support of the valency-volume idea which is not equally capable of supporting the theory to be elucidated in the following pages; but on the other hand I can find many facts beyond the reach of the former and explicable with the help of the latter theory.

While greatly regretting the need of thus pointing out the lack of cogency in some of the arguments adduced by these eminent investigators, I take pleasure in expressing my appreciation of their valuable work in collecting and collating a great variety of crystallographic details.

Let us now develop the somewhat differing line of argument presented by the theory of compressible atoms. This theory maintains that the atoms (or the spheres of influence which represent the atoms in their outward relations) are compressible, and the space occupied by each atom is determined by the varying pressures exerted upon it by other atoms in its neighborhood, as well as by outside pressure. It is clear then, that being pressed upon in different ways on different sides, the atoms must become not only diminished in volume, but also distorted in shape. Clearly, one may conceive that a molecule built up from such distorted shapes would itself be complex in its outer form, and that this complexity might well be the determining factor in deciding the shape of the crystal aggregate when many similar irregular molecules were packed together. Moreover, because not only the atoms, but also the molecules consisting of aggregates of atoms, are to be looked upon as compressible, there is considerable flexibility in this matter of fitting together the imaginary analogous shapes. If we grant the attribute of compressibility, there is nothing at all singular in the fact that although caesium sulphate possesses a larger molal volume than potassium sulphate, its crystal form is not very different. We have only to imagine that in these two substances the arrangement of the atoms is similar, and that the mode of their fitting together is such as to allow the difference in volume wherever it appears to be in part taken up by a readjustment of the internal compressions of different parts of this molecule. The same argument applies to the case of benzene and its tetrabrom substitution product. Moreover, we must remember that the doubling of the bulk of a solid increases its diameter by only about 26%; thus considerable changes might not show greatly in the crystal angle. Similarity in crystallin form in such cases does not necessarily prove, as others have thought, that the theory of valency-volume is the best theory.

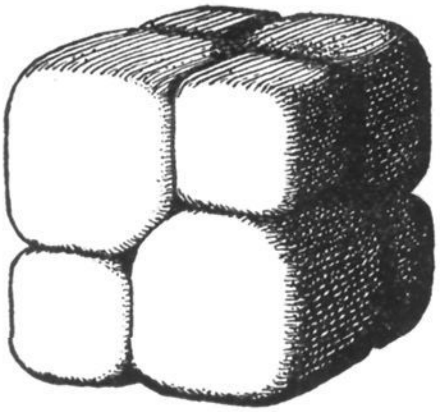
In seeking to apply the theory of compressible atoms to the facts of crystallography, one is struck at once by the obvious difficulty of attacking with any known variety of mathematics a situation so complex; for the theory assumes a system composed of units of varying compressibility, not only as regards one another but also as regards different parts of the same atom, and also the existence therein of many varying internal attractive forces, each tending to produce a different degree of compression. The necessary complication is no argument against this theory, however; nature often presents complicated phenomena which are due to the simultaneous action of simple laws. For example, the apparent path of Halley's comet in the heavens was highly irregular, but it was made of very simple factors. Again, nature does not hesitate to allow three or more bodies to act upon one another by the force of gravitation. Although this action is known to be governed by the simplest and most exact of natural laws, such interaction of three bodies has hitherto defied man's direct mathematical analysis. Hence we must not hesitate to follow out qualitatively the consequences of a reasonable hypothesis, even if mathematical exactness seems far away.

Let us turn first to the simplest case of definit molecular arrangement in solids, namely, the crystallin forms of the elements. It has been known for a long time that about half of the forty elements which have been crystallographically examined crystallize in the regular system, and that about one-third crystallize in the next most symmetrical crystallin form, the hexagonal. The remaining six elements are less symmetrical. Pope and Barlow point out that in some cases, at least, the departure from isometric symmetry is not great, and probably would suggest explaining the distortion by the deformation of their incompressible "spheres." But will this account for all the cases, and is not the idea that the atoms are compressible better able to explain them all? Assuming that the elementary substances are composed of closely packed equal spheres, these investigators do not seem to have attached quite enough weight to the fact that elements are not always necessarily composed of monatomic molecules. In such a solid, the conditions described by Pope and Barlow would be expected to appear, even if the atoms compressed and distorted one another by their equally distributed affinity; for they would do this equally in all directions, and as far as symmetry was concerned would behave just in the same way as accumulated spheres, although they were actually compressed into cubes, dodekahedrons, or hexagonal forms. Even, however, if such elementary substances as solid mercury or metallic copper possess monatomic molecules, we have very good reason for believing that many other elements do not. To be sure those elements possessing diatomic molecules such as chlorine and bromine, could also build up cubical crystals; but this might not be so easy with more complex aggregations. It seems very highly probable that several elements (for example, phosphorus and arsenic) possess at least four atoms to the molecule in the solid state, because we can hardly imagine the solid molecule to be less complex than the vaporized one; and sulphur probably is yet more complicated. The form which determins the crystal must be the form of the molecule or some multiple of it, and evidently one cannot imagine molecules of four atoms to assume easily forms as simple as those taken by monatomic molecules. The existence of a polyatomic molecule must indicate that in the solid the element combines with itself in two different ways; in the first place very firmly to build up molecules from atoms, and in the next place less firmly to cause these molecules to cohere, forming the solid substance. Obviously if atoms are compressible, they will be more compressed by the powerful forces holding the molecule together than they will be by the less powerful cohesive affinity. Hence must arise irregularly shaped atoms and molecules giving opportunity for varied symmetry in external crystal form.

Thus such elements as copper and silver, possessing probably very simple molecules, would be expected to crystallize in the isometric system, whereas elements such as arsenic and sulphur with more complex molecules would be expected to assume less symmetrical shapes. This is exactly what really happens. Thus it appears that the theory of compressible atoms explains the crystallin form of the cubic and hexagonal elements as well as Barlow and Pope's theory, and also that it reveals much more clearly than that theory the probable cause of less symmetrical crystal forms in the cases of polyatomic molecules.

From the elements we may turn to the binary compounds. Barlow and Pope assume that each element in a binary compound possesses the same atomic volume,—that the formation of caesium chloride, for example, from caesium with an atomic volume of 71, and chlorine with an atomic volume of 25.7 would cause both chlorine and the caesium to occupy the same atomic volume, 21.4 (the molecular volume of caesium chloride being 42.4). They seem to regard the cubic form of such compounds as affording evidence that the two atoms assume the same size when combined; but in reality it is quite as easy to conceive of the formation of a cube from molecules composed of two unequal atoms as from those composed of two equal atoms. A diagram is appended to illustrate this fact. This diagram refutes much of Barlow and Pope's reasoning without further discussion. On the other hand, among binary compounds composed of atoms of unequal size, we should expect to find a decided diminution in the occurrence of hexagonal symmetry, because the unequal binary compound would not so well lend itself to this form of symmetry. This is indeed exactly what the facts quoted by Barlow and Pope indicate. Among 67 binary compounds studied, 68.5% (instead of 50% as in the case of the elements) crystallize in the isometric system and only 19.5% (instead of 35% as in the case of the elements) crystallize in the hexagonal system. Hence the assumption of inequality in the sizes of the atoms in binary compounds is consistent with the facts.

To return to a specific case, probably both the caesium and the chlorine contract in the act of combination; but as chlorine is somewhat more compressible than caesium, the former may be supposed to contract somewhat more in proportion to its bulk than the latter. If one were to venture to prophesy, one would be inclined to say that chlorine in caesium chloride may have a molecular volume not over 12, and the caesium perhaps about 30. These figures are given only to show the possible order of magnitude of the two, and do not pretend to be a precise prediction as to their values. If the atoms were compressed into almost cubic forms by their mutual compressions, their edges would then bear to one another the ratio of about 2.3 to 3.1, approximately that indicated in the diagram given above. Cubes formed of such molecules, although strictly isometric, would be expected to exhibit hemihedral tendencies; and this expectation is often fulfilled. The diagram gives an interesting idea of the "crystal unit" as distinguished from the molecule. Such crystal units may be supposed to be the entities necessary to relieve metastable supersaturation.



Diagrammatic sketch showing in perspective how compressible spheres of two very different sizes may build up a cube when pressed together. (This may be supposed to represent the imaginary "crystal unit" of caesium chloride.)

In this connection it should be pointed out that the theory of compressible atoms explains why exact identity in molecular volume or in facial angle is not necessary for isomorphism; slight differences could be adjusted by the elasticity of the component molecules. On the other hand, one would expect to find a limit to the power of compression or adjustment of an atom or molecule to fit into the place occupied by another. Such a limit seems to have been overstepped, for example, by potassium in relation to sodium, for although the chlorides of both crystallize in the isometric system, these salts are not isomorphous, *i. e.*, they will not crystallize together.[1] Sodium chloride crystallizes usually in unmodified cubes, whereas potassium chloride, although also isometric, shows much more tendency to develop plagihedral or gyroidal faces. Now the atomic volume of sodium is not far from that of chlorine in the elementary state, and they may be supposed to be about alike in the compound. On the other hand, potassium chloride resembles much more that of caesium; its

---

[1] Krickmeyer, *Z. phys. Chem.*, **21**, 82 (1896).

molecules, although still capable of building cubes, may be supposed to form cubes with the hemihedral structure shown in the diagram, because the potassium probably occupies more space than the chlorine. In short, on the basis of the compressible atom theory, one would expect potassium chloride, although still isometric, to have a decided hemihedral tendency, and sodium chloride to have much less hemihedral tendency, as the facts really show.

These heteromorphous relations of common salt and potassium chloride do not seem to be adequately accounted for by the theory of Barlow and Pope, according to which there seems to be no reason why either should show any gyroidal tendency, or why they should not crystallize together; for would not the theory allow sodium to expand to fill the space occupied by potassium? Such an explanation would be no more arbitrary than that chosen in other cases.

Turning now to more complex compounds, the problem of course becomes enormously increased in difficulty. The best method of procedure is that adopted by Barlow and Pope in comparing the crystallin forms of isomorphous or similarly constituted bodies. Pope and Barlow cite the striking and well-known series measured by Gossner of the orthorhombic chloro- and bromoethanes. The table of data is repeated here, arranged in the order of the molecular volumes of these substances.[1]

	M. V.	$a : b : c$.
C_2Br_6	131.8	0.5639 : 1 : 0.3142
$C(BrCl_2)_2$	120.2	0.5646 : 1 : 0.3192
$C_2(Br_2Cl)Cl_3$	116.7	0.5612 : 1 : 0.3171
C_2Cl_6	113.3	0.5677 : 1 : 0.3160

It will be noted that the introduction of chlorine causes a diminution in the molecular volume, and that this diminution is partly dependent upon the place in which the substitution occurs. It is noteworthy also that the symmetrical introduction of chlorine causes a lengthening in the axis a in relation to b, and that the unsymmetrical substitution shortens the axis a. The axis c is least in the pure bromine compound.

These are real differences both as to molecular volume and crystal form. The molecular volume varies more than the crystallin form, probably for the reason already stated, namely, that a change in volume produces only the cube root of its proportional effect when applied in any one axial direction.

With these compounds Barlow and Pope compare the *monoclinic* pentabromoethane, having a molecular volume of 126.5 and axial ratios $a : b : c$, 0.5650 : 1 : 15590 ($\beta = 91.19°$). The introduction of the hydrogen instead of bromine causes not only a very great lengthening in the axis c but also a decrease in molecular volume and a decided departure

---

[1] Barlow and Pope, *J. Chem. Soc.*, **89**, 1682 (1906).

from the orthorhombic symmetry. For the sake of bringing this form into harmony with the other four, the commentators have arbitrarily divided c by 5. To the figures thus corrected they have then applied their method of calculating "equivalence parameters." This is a mathematical device, based upon the hypothesis of constant valency-volume, which has the effect of reducing rather widely deviating data to much nearer agreement—partly because the last operation suffered by the function is the extraction of its cube root. Under the circumstances, therefore, it is not surprising that the "equivalence parameters" of these five substances show a closer agreement than the original axial ratios. In another connection it will be shown that this method is capable of bringing such very widely different substances into apparent harmony that one cannot but suspect the method to be somewhat too efficient in its harmonizing tendency. The study of the actual measurements of the crystals incline one to believe that the substitution of one hydrogen for a single halogen causes more upheaval in the crystallizing tendency than is clearly shown by the table of "equivalence parameters."

According to the theory of compressible atoms, however, the facts all seem to be reasonable and need no preliminary mathematical treatment. There are many reasons for believing that chlorine really occupies less space than bromine. One argument is found in the atomic volumes of the elements. Bromine, although far less volatil than chlorine, has even at the same temperature a perceptibly greater atomic volume. If for comparing these elements we choose corresponding temperatures (*i. e.*, like fractions of their absolute boiling points, for example, 20° C. for bromine and —65° for chlorine) we find that chlorine has an atomic volume of only 21.8[1] whereas bromine has an atomic volume of 25.5. Doubtless when these elements combine with others, their atomic volumes change, but under similar conditions we should expect chlorine to occupy less space than bromine, and this is what we find in the case of the five compounds cited in the preceding discussion. It is perhaps more than a coincidence that six times the difference between these two atomic volumes, namely, 22.2, is not very far from the actual shrinkage (18.5) in the molecular volume of the substituted ethane when six atoms of chlorine take the place of six atoms of bromine, although such an idea is entirely incompatible with constant valency-volume. We should expect also to find about such changes in the axial ratios as really exist.

Turning now once more to the compound containing 1 atom of hydrogen, we see here great difference in crystal form. This is also just what we should expect in a compressible system, provided that the newly introduced member of the system possessed not only a different molecular volume, but also a different chemical nature. Under such circumstances a marked

---

[1] Knietsch, *Ann.*, **259**, 100 (1890).

change in the habit and a twisting distortion of the symmetry might very well be supposed to occur.

The axial ratios in the camphor series presented by Barlow and Pope a few pages afterward show somewhat the same sort of treatment. The first point that strikes one upon comparing the figures is that hexagonal camphor and its orthorhombic substitution products are very different from one another in their actual crystal forms and that the dibromcamphors differ much among themselves. Barlow and Pope have been interested in devising a mathematical method which should reconcile these figures; but if the method had been less arbitrary, it would have been more convincing. In order, for instance, that the orthorhombic dibromcamphors may be reconciled at all with hexagonal camphor, arbitrary multiples of the axes must be chosen, one of them being as complicated as 5/3. One cannot but wonder if any similarity in crystallin form would have been detected between these substances if one had not happened to know beforehand that they had a similar structure. Grave doubts may well arise as to the legitimacy of turning away thus from the indication of the actual external crystallin forms.

It will be clear from the foregoing statements that the interest of these investigators has been primarily to show *analogies* of crystal form. While this is very suggestive, to me the *differences* seem to be even more interesting than the analogies; for the differences give us a clue whereby further insight into the internal nature of crystals may be obtained.

There are many other cases of approximate similarity of form, where it is hard to see how Barlow and Pope's theory may be made to apply, for example, the interesting series of nitro-dihalogen-benzenes recently studied by Repossi.[1] A table giving the axial ratios of four of these compounds follows:

1-Nitro-2,5-dibromo benzene	1.3854 : 1 : 0.7876
1-Nitro-2-chloro-5-bromobenzene	1.3823 : 1 : 0.8196
1-Nitro-2-bromo-5-chlorobenzene	1.4159 : 1 : 0.8157
1-Nitro-2,5-dichloro-benzene	1.4385 : 1 : 0.8223

It will be noted that there is a very distinct difference in the fundamental axial ratios of these four highly analogous substances, amounting to several per cent. Clearly the introduction of chlorine causes a relative shortening of the axis *b* even more evident than that shown in the substituted ethanes. How this decided distortion could be accounted for on the hypothesis proposed by Barlow and Pope, it is difficult to see. On the other hand, the flexibility of interpretation allowed by the theory of compressible atoms is amply sufficient to account for just this sort of thing.

Similar small but significant differences in isomorphous crystal shapes

---

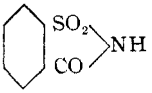
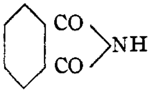
[1] E. Repossi, *Z. kryst. Min.*, 46, 202; through *Chem. Zentralb.*, **11**, 273 (1909).

are pointed out in a recent interesting paper by Gossner.[1] Here again the evidence that in isomorphous mixed crystals the two components mutually influence each other in such a way that their properties are no longer those of the pure state is an outcome which might have been definitly predicted from the point of view of the theory of compressible atoms.

The data presented by Groth's "Chemische Krystallographie"[2] concerning not only inorganic but also a great variety of organic substances will enable anyone interested to test for himself these statements. In general, it will be seen, as has been pointed out above, that the rigid application of the theory of definit valency-volume is impossible and that according to it many facts such as those given in Repossi's table above are inexplicable.

The cases cited by F. M. Jaeger[3] in favor of the Barlow-Pope theory may be used (insofar as they show significant parallelism) equally well to support the theory of compressible atoms. The two theories are similar, as had already been pointed out, in the ideas of close-packing and definit marshalling. Hence in these and in other cases the arguments with regard to these two matters apply about equally to each; but when Jaeger calls the crystals of phthalimide and saccharin closely similar in form, one cannot help thinking that the argument is somewhat far-fetched.

Here follow the actual crystallographic data:

		$a : b : c.$	$\beta.$
Saccharin	 SO$_2$ CO NH	1.356 : 1 : 0.430;	(94° 3′)
Phthalimide	 CO CO NH	1.491 : 1 : 0.497;	(91° 18′)

These marked differences in axial ratios, amounting to 10% in the case of a, must correspond with real differences in internal conditions; the extra oxygen in saccharin and the substitution of sulfur for carbon are by no means unimportant matters. The method of "equivalence parameters" reduces these data to much closer agreement; thus x, corresponding to the axis of a, is found to be 2.518 in one case and 2.462 in another. The difference is only about 2% instead of 10. Such a circumstance cannot convince me that the crystals are to be considered as alike; I am more inclined to believe that the outcome gives evidence of the efficiency of the mathematical method in hiding real differences in crystal forms.

Jaeger's earlier statement that the Barlow-Pope theory is not to be regarded as affording an explanation of valency, nor as a substitute for the theory of structure of organic chemistry, nor as furnishing an indica-

---

[1] B. Gossner, *Krystallographie*, 44, 417.

[2] Groth, P., *Chemische Krystallographie*, Leipzig, Engelmann.

[3] Jaeger, F. M., *J. Chem. Soc.*, 93, 517 (1908).

tion of the occurrence or non-occurrence of miscibility among solid phases, seems to have more justification. The single advantage cited by Jaeger, that the Barlow-Pope hypothesis enables one to predict similarities in crystallin form, would apply equally well to any reasonable theory involving definit close-packing of the spheres of influence, if some elasticity in these spheres is allowed—and the facts seem to demand the admission of the existence of this latter property.

Many other cases are considered by Barlow and Pope, some of them with great ingenuity, and all with profound knowledge of crystallography. Some of the arrangements are very plausible, but most of them would hold quite as well if not better according to several other hypotheses as to the relative volumes of the several atoms, especially if we take into account atomic compressibility. The explanation for the similarity in crystallin form of sodium nitrate and calcium carbonate is especially interesting and ingenious because, according to their theory, the former has a different total valency volume from the latter. This similarity also can be explained in other ways than on their basis. The well-known older explanation, supposing the similarity of form to be due to the fact that the two molal volumes are almost identical and the number of atoms in each the same, is quite as convincing as Barlow and Pope's more elaborate theory.[1] Indeed this older explanation fits in very well with the idea defended by the present paper; for the attribute of atomic compressibility is all that is needed to explain the indisputable fact that two somewhat differently combined but otherwise analogous groups of atoms of approximately but not exactly equal bulks can be pressed into very similar forms.

There are other cases of isomorphism which seem to be wholly beyond the reach of the valency-volume theory of Barlow and Pope—for instance, the familiar isomorphism of ammonium and potassium salts. Here the idea of valency-volume gives ammonium nine volumes, but potassium only one; and it is hard to see how any sort of analogous symmetry could be constructed in the two cases under these circumstances. On the other hand the theory of compressible atoms plausibly suggests that the five atoms making up the radical ammonium (which seem together to possess about the same volume as potassium[2]) must be compressed by their mutual affinities until a shape not unlike that occupied by the compressed and distorted potassium is obtained.

It is very questionable if at present there is any use in attempting to make models of the molecules of very complex substances, in view of the many variables which seem to exist within their structure. Because of

---

[1] Barlow and Pope, *J. Chem. Soc.*, **93**, 1528 (1908).

[2] The molal volumes of potassium and ammonium chlorides are respectively 37.8 and 35.0 cubic centimeters.

the fact that sometimes exceedingly complicated structures, such as crystallized ammonium alum, assume very simple crystallographic forms, one is inclined to proceed cautiously with them in his attempt to represent pictorially the actual arrangement of the atoms in a crystallin structure.

Nevertheless it seems clear, at least to the writer, that the tenets of the theory of compressible atoms give the most reasonable point of attack in a research of this kind. For the theory not only postulates causes which do not seem to be at variance with common sense, but it also gives just that sort of flexibility in atomic volumes and in the mutual adjustment of the effects of the several affinities which seems to be indicated by the slightly differing angles and the varying relations of isomorphous but not exactly identical crystallin forms.

Summary.

In this brief paper the following points are emphasized:

1. The assumption of valency-volume made by Barlow and Pope in 1906, in spite of its great ingenuity, is shown to be not the most reasonable explanation for the actual molecular volumes of solids.

2. The cases presented by them as arguments may be explained quite as well (or often better) in other ways and, therefore, afford no arguments in favor of their assumption as against others.

3. Some facts seem to be quite beyond the reach of their hypothesis.

4. In 1902 the theory of compressible atoms indicated a more reasonable method of explaining the tridimensional relations of material, including the symmetry of crystals.

5. This theory assumes like Barlow and Pope's later hypothesis the close packing of the atoms in solids, whereby the form is maintained and the rigidity caused. It proposes, however, that the atoms are compressible and that their volumes are not arbitrary, but depend upon the pressure to which they are subjected.

6. The theory of compressible atoms explains the usual forms of elements and binary compounds better than Barlow and Pope's.

7. The theory shows why elements forming isomorphous compounds need not have exactly the same atomic volume.

8. The theory affords a conceivable picture as to how potassium and ammonium can replace one another isomorphously, a problem apparently beyond the reach of the hypothesis of constant valency-volume.

9. In general, none of the facts cited by Barlow and Pope, and no other crystallographic facts known to the author, conflict with the postulate of atomic compressibility.

10. Complex compounds possess too many variables for satisfactory

treatment at present; but insofar as interpretation is possible, the theory of compressible atoms seems to apply.

WOLCOTT GIBBS MEMORIAL LABORATORY,
HARVARD UNIVERSITY, CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

THE HYDROLYSIS OF ETHYL ACETATE BY NEUTRAL SALT SOLUTIONS.

BY WILLIAM E. HENDERSON AND DAVID R. KELLOGG.

Received January 28, 1913.

In the course of some previous work[1] one of us found that the reaction between ethyl acetate and water, represented in the equation.

$$CH_3COOC_2H_5 + H_2O = CH_3COOH + C_2H_5OH,$$

is greatly accelerated by potassium chloride, bromide, or iodide. The results obtained at that time seemed to be of sufficient interest to justify a further study of this neutral salt effect. Accordingly the investigation has been extended along two general lines, namely: (1) The catalytic effect of an additional number of salts has been studied at 100°. (2) Conductivity and viscosity data have been obtained for these salts at the concentrations and temperature employed in the hydrolysis experiments, and from these data the degree of ionization has been calculated.

Methods and Apparatus.

Measurement of Hydrolysis.—The velocity of hydrolysis was determined in the manner described in the earlier work, using the same apparatus but with the following changes: The sealing tubes were made with necks sufficiently wide to allow liquids to run in without the use of the capillary funnel. The ethyl acetate was measured with an automatic overflow pipet which added materially to the accuracy of the measurements. (At 25° this pipet delivered in three experiments, 1.2271 grams, 1.2283 grams, 1.2270 grams, or a mean of 1.2274 grams.)

The salts selected for study were the chlorides of sodium, lithium, calcium, strontium, barium, and cadmium, together with cadmium iodide. The halides of potassium were studied in the previous paper. Solutions of desired concentration were made by direct weighing of the dry salt except in the case of the chlorides of calcium and lithium. These were made up to approximately the concentration desired and their exact concentration determined by titration. The cadmium salts were crystallized several times, the others being taken from original packages of J. T. Baker's Analyzed Chemicals. Kahlbaum's ethyl acetate (1200 grams) was purified by washing with a 5% solution of sodium carbonate, no effervescence being noted. It was then washed three times with water,

---

[1] THIS JOURNAL, 31, 403, 886.