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

COMPRESSIBILITY, INTERNAL PRESSURE AND ATOMIC MAGNITUDES

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The problem of atomic diameters has been recently the subject of much speculation and discussion. As a contribution to this subject, attention has been called to a method of solving the problem which depends upon the compressibilities of the elements involved.[1] The method was a direct outcome of a thesis which has been emphasized for over 20 years; namely, that the volumes of solids are determined primarily by two factors, compressibilities and affinities. This thesis ascribes changes of volume of solids (and also of liquids) to the varying pressures produced by varying affinities, exerted upon atomic surfaces (or repelling tendencies) which resist compression in varying degree.

The data and arguments upon which this recently published computation of atomic diameters rests have been before the chemical public for many years.[2] Attention was specifically called to them 8 years ago,[3] but the complete computation was not performed at that time. Brief recapitulation may be made of the details and outcome as regards the present problem.

The method was as follows. When solid potassium and liquid chlorine combine to form potassium chloride, the sum of their gram atoms (70.5 cc.) contracts to form 37.5 cc. of potassium chloride at ordinary temperatures, the change of volume being 33.0 cc. The formation of sodium chloride similarly involves a contraction of 21.8 cc.; and combinations of other alkali elements and halogens give values of the same order, although of differing magnitudes.[4] The contractions thus occurring were plotted in relation to the compressibilities of the metals. They make fairly smooth curves which show, beyond reasonable doubt, that the contraction is a function of the compressibility of the elements concerned. Thus, the contractions in the case of potassium are far less than those in the case of

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[1] Richards, THIS JOURNAL, **43**, 1584 (1921).

[2] Richards, *Proc. Am. Acad. Arts. Sci.*, **37**, 1 (1901); **37**, 397 (1902); **38**, 291 (1902); **39**, 579 (1904).

[3] Richards, THIS JOURNAL, **36**, 2417 (1914).

[4] Recently Richard Lorenz and W. Herz [*Z. anorg. allgem. Chem.*, 117, 267 (1921)] have considered the contractions on combination of these elements at the absolute zero. Of course the values found by them are but little different from those at the ordinary temperatures, since volume-changes caused by temperature in these substances are so small in proportion to those caused by chemical affinity. This latter fact I have already pointed out; and Lorenz's values follow as a matter of course from my earlier investigations.

the more compressible element cesium, and the contractions in the case of iodine are far less than the contractions in the case of the more compressible element chlorine. By extrapolating these curves to an imaginary metal of zero compressibility, values were obtained which must correspond approximately to the contraction of the chlorine, bromine or iodine alone. Since the ordinary volumes of these latter halogens are known and the contraction which happens during combination is thus indicated, we have a value for the volume occupied by each halogen in the state of combination, which is simply the difference between the original volume and the contraction thus obtained by extrapolation. The volume of the halogen being known, that of the metal, as it exists in combination, is very simply found by another subtraction. The results follow.

TABLE I

ATOMIC VOLUMES OF HALOGENS AND ALKALI METALS IN COMBINATION (CC. PER GRAM ATOM)

	In chlorides	In bromides	In iodides
Halogen	12.60	17.60	23.70
Lithium	7.90	7.47	9.26
Sodium	14.45	14.53	17.21
Potassium	24.92	25.70	29.46
Rubidium	30.61	31.77	36.12
Cesium	29.74	30.39	33.90

Dividing these values by the number of atoms in a gram atom (606.2 sextillion, as found by Millikan), we obtain the actual bulk in metric measure of the atoms in combination; and by taking the cube root of this bulk, we obtain the atomic diameters. An insignificant correction for the corners of the minute cubes must be applied in some cases, since these cubes, which are imagined to be fitted together, are not exactly of the same size.

The values thus found are given roughly in the following table in comparison with similar values found by entirely different methods by two of the other investigators of this topic.[5]

As was pointed out at the time, this solution does not pretend to be complete.[6] Several subsidiary influences were arbitrarily neglected, especially the varying reaction-heats, and also the question as to the effect of the differing atomic volumes of the metals, which involve at the

[5] Davey and Wick [*Phys. Rev.*, 17, 403 (1921)] have pointed out that cesium chloride is a cube-centered and not a face-centered structure. This structure was unknown to me at the time of publishing my last paper; I had assumed with Bragg that cesium chloride is like the other chlorides. The effect of the difference in structure is nevertheless slight; far less than that caused by the various assumptions made by other investigators. Davey's values for atomic diameters, based upon a plausible, but unproved, assumption, are not far from mine [*Phys. Rev.*, 18, 102 (1921)].

[6] Ref. 1, p. 1585.

same time different bulks to be compressed and different surfaces exposed to pressure—circumstances partially counterbalancing one another.

TABLE II

DIAMETERS OF INDIVIDUAL ATOMS OF ALKALI METALS AND HALOGENS (IN ÅNGSTRÖM UNITS)

	Laudé	Bragg	Richards In chlorides	Richards In bromides	Richards In iodides
Chlorine	3.3	2.1	2.8	...	...
Bromine	3.6	2.4	...	3.1	...
Iodine	4.1	2.8	...	...	3.4
Lithium	...	3.0	2.3	2.4	2.6
Sodium	2.2	3.5	2.9	2.9	3.1
Potassium	2.9	4.2	3.5	3.5	3.7
Rubidium	...	4.5	3.8	3.8	3.9
Cesium	3.2	4.7	3.8	3.7	3.8

The time has now come for a more exact treatment of the problem, based upon the same fundamental ideas, but employing more pertinent data in a wholly different fashion. The new solution to be offered to-day depends upon the actual changes of volume suffered by the elements concerned, under the application of definitely measured great external pressures. In other words the pressures necessary to compress potassium and chlorine, respectively, to the volumes which they occupy in potassium chloride are approximately found, and the relative magnitudes of these volumes, when subjected to these pressures, are simply computed from known data.

The first problem which faces the theorist in this direction is the question as to the exact forms of the volume-pressure curves of the elements under great pressures. The general trend of such curves has long been known. Many years ago it was shown that as a rule the more compressible the substance the more rapidly its compressibility decreases with increasing pressure[7]—especially as regards the three common halogens. This opinion was reiterated as regards the alkali metals 4 years later in a subsequent publication, in which it was shown that whereas the compressibility of lithium scarcely falls off at all and that of sodium decreases less than 2% for 200 atmospheres' change of pressure, the more compressible potassium might decrease as much as 4% and cesium (the most compressible of metals) more than 20% over the same range.[8] That this is to be expected, has been pointed out repeatedly. When a substance is already under great pressure due to its affinities, a small additional outside pressure would be expected to cause but a small change in the compressibility, being only a very small fraction of the total sum of the internal and external pressures to which the body is subjected. Knowledge of this rate

[7] Richards and Stull, *Carnegie Inst. Pub.*, **7**, 44 (1903).

[8] *Ibid.*, **76**, 23 (1907).

of decrease of compressibility with pressure is obviously of assistance in estimating by extrapolation the volumes of substances subjected to the exceedingly high pressures imputed to chemical affinity and cohesion, which are often far beyond our present experimental range.

Internal pressure may be defined, for the present purpose, as pressure exerted by the force of affinity, either chemical or cohesive. This pressure, added to any external pressure which may be present, is exactly balanced in all substances by the sum of the pressures produced by thermal agitation and the repelling potential present in all atoms and molecules.

Fortunately Bridgman's very careful recent experimental work[9] provides us with a basis for study of these phenomena far more adequate than was formerly possible. He has determined the compressibilities of 30 metals over a range of 12,000 atmospheres; and these metals were so varied in nature and in compressibility as to give a good idea of the performance of solids under varying stresses. His investigation (which in almost every case agrees with my own old results within the limit of error of the early experiments) ranged from tungsten, which was shown several years ago to be the least compressible of metals,[10] to potassium, which 10 years before that had been shown to be among the most compressible.[8]

Study of his results shows that a considerable consistency, although not perfect agreement, is exhibited by the metals. When they are ranked in the order of compressibility, and note is taken of the decreases in compressibility due to a change of 1000 atmospheres' pressure, it is clear that the second differential coefficient is indeed very much less where the compressibility is small than it is where the compressibility is large.

This tendency, which is thus exhibited by the several metals arranged in order, is shown also by those single metals which are compressible enough to give significant results for the third differential coefficient—notably potassium and sodium.

The study of Bridgman's results develops many points of interest in addition to those which have been brought out in his own communications. The most important of these points is the fact that the curves for potassium and sodium are very similar in character, the only important differences being such as would be caused by the existence of a much greater internal pressure in sodium than in potassium. This would indeed be inferred also from the higher melting and boiling points, and from the lower

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[9] Professor P. W. Bridgman's most recent report of work is now in process of publication in the *Proc. Am. Acad. Arts Sci.*, **58** (1922). He kindly placed at my disposal the proof of this paper, from which the data used in the present communication have been taken. An abstract was printed in *Proc. Nat. Acad. Sci.*, **8**, 361 (1922).

[10] Richards and Bartlett, THIS JOURNAL, **37**, 470 (1915).

coefficient of expansion, of sodium. Both metals are generally assumed to have monatomic molecules. Their striking similarity suggests a device for extrapolating the potassium compressibility curve. Since the tendency of each curve, as indicated by the second difference, is about the same, and since the densities are not far apart, it is reasonable to use the sodium curve as an extrapolation of the potassium curve, beginning at a point corresponding to the greater internal pressure of sodium, and using as a starting point of this section of the curve that volume of sodium which the potassium would have had if it had been compressed under the corresponding external pressure. In other words, the device is simply to reckon the excess of internal pressure which exists in sodium as added to that artificially applied. When this is done, by the method of trial and error, the locus of the sodium values giving a continuous smooth long curve is easily found. At first the exact difference in the internal pressures was not known; but fortunately this lack caused little uncertainty, because there is a rather wide range over which the sodium curve gives almost identical results. This is because at this portion of the curve, the second differential coefficient of the volume is nearly proportional to the first. Following this method it was possible to construct a curve which showed with reasonable plausibility the volumes occupied by potassium up to a pressure of 40,000 or more atmospheres.

The outcome is depicted as the longest of the curves in the accompanying diagram (Fig. 1). The corresponding volumes of potassium for different pressures are given 3 pages later in Table III. As far as 12,000 atmospheres they are simply a repetition of Bridgman's values; from 12,000 to 18,000 they are interpolated between the potassium and sodium; from 18,000 atmospheres to 30,000 they were found to be simply the Bridgman values for sodium multiplied by 0.67, the volume to which potassium is reduced at the former point. This factor enters because Bridgman's values for sodium are expressed in terms of a *unit* volume of sodium under atmospheric pressure.

This curve is of great interest, as representing approximately the behavior of a monatomic metal at high pressures. It can hardly be far from the truth, since Bridgman's results were obtained with extraordinary care and the method of extrapolation does not admit of a wide range of error, if a smooth curve is to be obtained. It will be the basis of the subsequent discussion.

The determination of the exact mathematical equation of this curve becomes a matter of great importance for the study of the volume-pressure phenomena of liquids and solids. Its especial importance over that of the vast majority of cases is due to the fact that as the element has monatomic molecules, its behavior must be more capable of direct interpretation than that of most substances.

The attempt to fit a definite curve to observations having at best inevitable errors of observation may yield a great variety of mathematical expressions which fit the case within the limit of error. The case of the pressure-volume curves of gases, which have been treated with more or less success by widely different expressions, serves to illustrate the point. That the equation of van der Waals, in spite of the probable variability of its "constant," *b*, has held its ground, is probably due to its involving sound physical conceptions of the dimensions concerned.

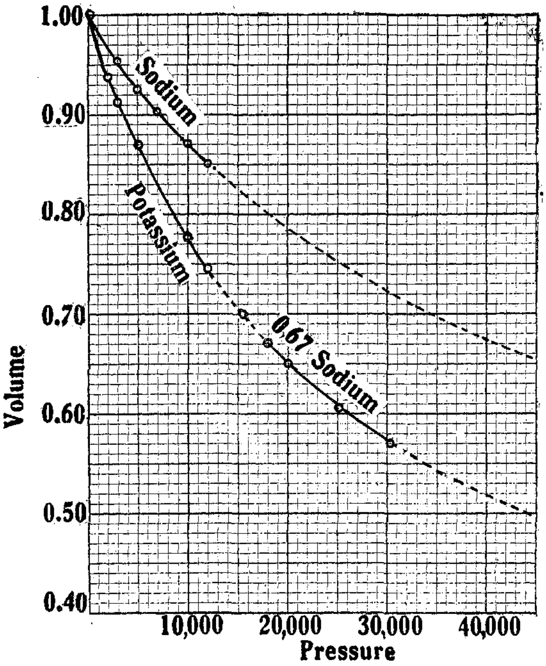

Fig. 1.—Pressure-volume curves for sodium and potassium. The volumes are plotted as ordinates, external pressures as abscissas. The data are due to Bridgman. The potassium curve is extrapolated by taking $^2/_3$ of the sodium values as referred to unit volume, and beginning this adjusted curve at 18,000 atmospheres. The sodium values are a mean of Bridgman's results and correspond to 52.5°. The potassium values correspond to 45°. The correction to 20° is probably beyond the accuracy of the extrapolation, but should be made in a final computation.

Bridgman has fitted to his experimental results equations of the familiar three-constant type, so much used by physicists. He rightly points out that such equations are not useful for extrapolation. As a rule they have no physical significance, but are simply mathematical compromises.

The conception of the probable nature of the variables and dimensions involved may advantageously precede mathematical treatment. In the present case we have to deal with pressure acting against a resisting tendency possessed by the atoms, and also with the possible change of the affinity with changing distances. Moreover, account must be taken of the great initial internal pressure under which the substance exists under normal conditions.

Since we are dealing at present with the pressure-volume curve, and since our constant, like that of the gas-law, should probably best possess the dimension of energy, obviously three methods of treatment are possible: (1) all irregularity may be put upon the pressure, leaving the volume unmodified, giving an equation of the type, $(p + fP)\, v = k$; or (2) all the irregularity may be put upon the volume, leaving the pressure simply as the sum of the external and internal pressures, giving an equation of the type, $(p + P)\, fv = k$; or (3) both volume and pressure may be supposed to be modified, as in the case of the equation of van der Waals.

The first method was tried and found wanting. On the assumptions that the initial internal pressure of the potassium is about 25,000 atmospheres (calculated by the equation, $L/V = P$, of Dupré)[11] the curve is found to agree closely with the equation $V(p + nP) = K$, where p equals the external pressure, P the original internal pressure, and $n = 1 - k\left(\frac{P + p}{P}\right)^3$. This expression, although it fits the curve within 1% of the pressure values throughout the observed range, is not altogether satisfactory. With very high pressures it would lead to impossible results. Therefore, it is probably to be rejected.

The second method is more satisfactory. Careful study showed that both the sodium and potassium curves conform rather closely to the simple formula $(V-B)(p+P) = K$. In other words, it appears that a portion (B) acts as if it were relatively incompressible, and that the relation of the total pressure (external plus internal) to volume is simply hyperbolic. This general equation fits almost the whole joint curve for potassium and sodium very closely when $P = 25{,}800$ atmospheres; and $B_1 = 0.20$; and it fits the curve for sodium alone very closely when $P = 43{,}800$ atmospheres, and $B_1 = 0.30$. These values of B_1 correspond to unit initial volumes of metal in each case; for gram-atomic considerations they must be multiplied by 45.4 and 23.7, respectively, and are designated B without subscript. Both of these curves depart slightly from the equation given above at low values of p, but the deviations (which probably indicate a slight change in P) are unimportant for the present purpose.

The differences between fact and theory are too small to be shown on the scale of the diagram, and they are, therefore, given in Table III.

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[11] The latent heat of evaporation of potassium was taken as 97 kilojoules at the boiling point (perhaps 114 at 20°?) and $V = 45.4$.

The curves may probably be approximately extrapolated with assurance for a considerable distance.

TABLE III

VOLUMES OF K CALCULATED ACCORDING TO THE ABOVE EQUATION

POTASSIUM

Pressure p	Calc. V	Found V	Pressure p	Calc. V	Found V
0	1.000	...	20,000	0.652	0.649[a]
5,000	0.870	0.870	30,000	0.570	0.570[a]
10,000	0.778	0.778	40,000	0.514	...
15,000	0.706	[0.705]	50,000	0.472	...

[a] These two values for V are simply Bridgman's volumes for sodium under pressures of 2,000 and 12,000, respectively, multiplied by the constant factor 0.67, which represents the volume of potassium at the point where its pressure characteristics are identical with those of sodium.

Much stronger reasons are thus seen to exist for placing of the sodium curve exactly in the spot indicated than the mere smoothing of the curve. The first is that at this point the value of $B_{0.67}$ for 0.67 cc. of sodium is almost equal to that of the value of B_1 for the amount of potassium which can occupy this space under 18,000 kg./sq. cm. pressure. The difference between the values of P for sodium and potassium is 18,000, which gives another indication that the sodium curve should be annexed at this point. Correspondingly, the compressibility of that amount of sodium and its decrease with pressure is identical at this point with the extrapolated compressibility of that amount of potassium under a pressure of 18,000; and the second differential coefficients also are approximately identical under these circumstances.

The comparison of these estimates of pressure with those given by Dupré's rule is interesting. This simple rule,[11a] $Pv_m = L_m$ (in which P indicates internal pressure, v_m molecular volume and L_m molecular latent heat of evaporation) leads to values of about 25,000 and 45,000 atmospheres, respectively, instead of 25,800 and 43,800, as given above, for these two internal pressures. Thus Dupré's rule and the present new method of determining internal pressures agree as to the order of magnitude of these important quantities.

As, indeed, Dupré himself realized, his rule is incomplete. It would appear that the energy used by a nascent vapor in displacing the atmosphere should be subtracted from the molecular heat of evaporation in calculating the internal pressure. Thus the equation should read, $P = L_m/v_m - RT/v_m$, in which the first term of the second member refers to the

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[11a] A. Dupré, "Théorie Mécanique de la Chaleur," Paris, **1869**, p. 158. Attention should be called to the valuable papers of Hildebrand, THIS JOURNAL, **38**, 1452 (1916); **39**, 2297 (1917); **41**, 1067 (1919); **43**, 500 (1921). Many references to the work of others on this subject are recorded there.

liquid and the second to the vapor; at 20° this equation becomes $P = P_m/v_m - 2.43/v_m$ kj. Although the correction is not very important, the equation is used in this form throughout this paper.

Evidently the third method of treatment proposed above is not necessary at present. The curve as given is quite consistent enough to correspond to immediate needs. When still more accurate data are available it may need slight revision, in the sense indicated above.

This curve may be taken as typical of the normal behavior of a monatomic molecule. Although in the case of sodium and potassium, the values of B_1 are identical at a given state of total compression, this equality does not necessarily apply to other elements, or especially to other series: the values of B_1 are doubtless different in different cases. The equation is probably always of the same general character, however, the differences being chiefly in the position of the element on the curve:—the alkali metals are far up on the left-hand branch of the curve, corresponding to small pressures, whereas such metals as copper, silver and gold are far out on the right-hand branch of the curve, having their atomic volumes reduced nearly to their B. Copper may have $P = 270{,}000$, $B_1 = 0.80$, for example. More detailed study shows that B itself changes somewhat under very great pressure, but there is no evidence that the change is important up to 30,000 atmospheres, since the equation holds so well. That P should not be widely variable was a surprise. When the problem was undertaken, I expected to face the task of discovering some modifying variable coefficient for this quantity. The method appears to afford an approximate means of evaluating internal pressures. Where pressure involves change of molecular aggregation, as for example, with water or phosphorus, modifying provisions must be introduced.

The equation reminds one of the gas law and the equation of van der Waals, and the early equations for hydrogen of Hirn, of Dupré, and of Budde.

The curve just discussed carries us far toward the solution of the problem of the contraction which occurs during the formation of potassium chloride. The volume of potassium chloride is somewhat over half that of the sum of the separate elements, and chlorine has an average compressibility over the range in question not far from that of potassium, as roughly estimated from the results published nearly 20 years ago. Hence, it is evident that because potassium at 44,000 atmospheres is reduced to half its initial volume, the average pressure which exists in potassium chloride must be of this order.

The next step in the solution of the problem is evidently the evaluation of the chlorine. This is a far less simple problem. Evidently in such cases one side of each atom must be compressed to a greater extent than the other. The more compressed part of the molecule must be less compressible than the less compressed part. With our present knowledge it is impossible to determine exactly how this difference of compressibility in the different sides of an atom is distributed throughout its substance; but the general type of volume-pressure curve which would result from such a situation is easily conceived. It would be a curve in which the second differential quotient is much larger than that in the case of the monatomic molecule. In other words, plotted on the same scale, the curve would be more sharply concave upwards. As a matter of fact this is the case with all of Bridgman's curves of compounds.

The complete mathematical solution of such a curve for polyatomic molecules involves not only the considerations discussed with regard to monatomic molecules, but also the consideration of the just mentioned fact that in polyatomic molecules two or more internal pressures must exist—those caused by cohesion, and those caused by chemical affinity, which, after all, are probably manifestations in different degrees of the same attracting tendencies. Thus the polyatomic curve must be depicted with ordinates composed of the *sums* of the ordinates of two hyperbolas, one an almost horizontal curve corresponding to the highly compressed part of the atoms and the other an hyperbola more like that of potassium. The result is a larger value for B than belongs to a monatomic substance of identical initial compressibility. The nature of each of these curves makes it possible to represent their combined effect rather roughly by another hyperbola; for example, the equation, $(p + 6200)\ (V - 0.67) = 2050$, represents closely the behavior of a milliliter of phosphorus trichloride as far as 12,000 atmospheres. The large value 0.67 in this case for B_1 corresponds, as before, to unit initial volume. Doubtless all the other curves found by Bridgman may be similarly represented roughly by hyperbolic equations; but time has not yet been available to test many of them. Under low external pressures, P and B are much more variable with polyatomic molecules than with monatomic ones, for reasons which will be made clear in a later paper.

Taking up now the case of chlorine (which must have a curve of this type), we find no direct data whatever for our calculation, since working with chlorine in apparatus strong enough to stand the great stress of high pressure is a difficult matter. There is, however, a variety of data pertinent to the question—data which enable us to compute with a considerable degree of plausibility about what the compressibility of chlorine must be for the whole range in question.

From the study of the compressibilities of chloroform and carbon tetrachloride long ago conclusions were drawn as to the compressibility of liquid chlorine, chiefly by the comparison of chloroform with bromoform.[7] Since the difference between the boiling points of these two substances is about the same as the differences between the boiling points of chlorine and bromine, it seemed reasonable to make a linear comparison such as indicated by the equation, $\beta_{Cl} = \beta_{CHCl_3} \times \beta_{Br}/\beta_{CHBr_3}$. The figures dependent upon direct determination cover the range from 100 to 500 kg. per sq. cm., and the values for the compressibility of chlorine thus calculated for the successive four ranges of 100 atmospheres each were 106, 96, 87 and 81, respectively. These values, while not very accurate, are probably sound enough to give an approximate idea of the compressibility of liquid chlorine under low pressures. In this case as in that of potassium, great assistance can be obtained from other substances. The compressibility of bromine also was determined in 1903; evidently the corresponding volume-pressure curve for this element may reasonably be annexed to that of the chlorine, after the successful fashion of the annexing of the sodium curve to that of potassium. According to the rule of Dupré, the internal pressure in chlorine is 3000 megabars at 20° and that in bromine is 5,400 megabars, a difference of 2400 megabars or 2450 kg. per sq. cm.; in other words, the bromine curve must be joined to the chlorine at a pressure of about 2,500 atmospheres. Unfortunately, we have thus extended only slightly the range of the curve, and the next halogen, iodine, has an internal pressure so much greater as to leave a great gap to be bridged.

Among the 14 liquids studied by Bridgman was a compound capable of throwing much light upon the immediate problem. Phosphorus trichloride, with molecular weight 137.4, density at 20° 1.575, and molecular volume 87.3, contains more than $^3/_4$ of its weight of chlorine. The phosphorus in it is undoubtedly compressed by its affinity to chlorine to a smaller bulk than that of white phosphorus, and probably to a somewhat smaller bulk than that of red phosphorus. Evidently, no great error would be committed if the atomic volume of phosphorus in this combination were taken as 13 cc. per mol (white phosphorus being 16.6, red phosphorus 14.4, and the black phosphorus of Bridgman 11.5). Subtracting 13 from 87.3 we have 74.3 cc. as the volume of the chlorine as actually combined in phosphorus trichloride, with a probable error not exceeding 1 or 2 cc. This value is not far from the volume in the liquid state of that amount of chlorine—namely, 75.3. We may infer, then, that the chlorine as combined in the phosphorus trichloride is not in a very different condition from that in liquid chlorine.

From these varied data a provisional curve representing the volume of liquid chlorine under pressure may be constructed. The gram molecular heat of evaporation of chlorine is about 2.0 Cal. per atom, and of phosphorus trichloride about 7.0 per mole at 20°. According to the modified equation of Dupré, as given, the internal pressure of chlorine and of the 74.3 cc. of chlorine in a mole of phosphorus trichloride may then be taken as 3,000 and 4,000 atmospheres, respectively. The collective verdict of all the data indicates that chlorine under 1,000 atmospheres should be compressed to about 0.9 of its original volume. Attaching the curve for chlorine derived from phosphorus trichloride at this point (each ordinate being multiplied by 0.9 for the same reason that the sodium values were multiplied by 0.67) a reasonable curve for chlorine may be constructed. The curve thus constructed is shown approximately in the diagram. It is extrapolated by the equation of its lower portion (naturally that safest to extrapolate), namely, $(p + 5{,}300)\ (v - 0.50) = 2{,}650$. The extrapolated values which especially concern us are as follows: for $p = 40{,}000$, $v = 0.558$; $p = 50{,}000$, $v = 0.548$; $p = 60{,}000$, $v - 0.541$.

This curve is confirmed by the compressibilities of both bromine and iodine. The values for bromine, as found by Stull and myself in 1903 fit the curve almost exactly, if interpolated at the proper place (2,500 metric atmospheres) indicated by its internal pressure as calculated from its heat of evaporation. The iodine value, which was less accurately determined, does not agree quite so well, but nevertheless affords confirmatory evidence. In iodine the *atoms* are not bound together so firmly and, therefore, with so great a pressure as in the case of bromine and chlorine. This would cause greater proportionate compressibility; but the deviation would be more than balanced by the greater density of iodine, which would tend toward a larger value for B and therefore less compressibility. The molecular latent heat of iodine, 63 Cal. at 20° as found by Baxter, Hickey and Holmes,[12] indicates an internal pressure of about 12,000 kg./sq. cm. or about 9,000 atmospheres more than the probable initial value of P for chlorine.

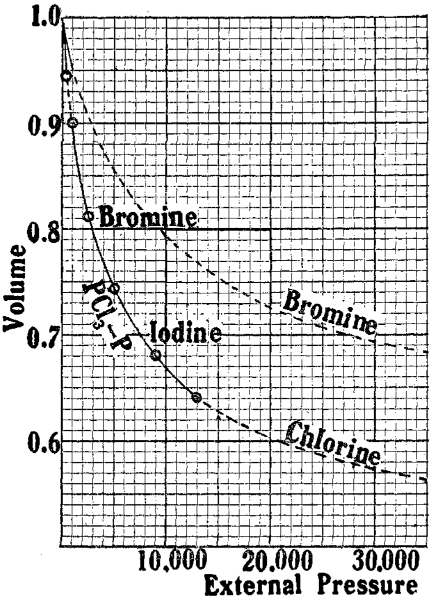

Fig. 2.—Pressure-volume curve for chlorine. The ordinates are the same as those in Fig. 1. The value for chlorine is extrapolated by means of phosphorus trichloride, bromine and iodine, which are shown to be very similar in their compressibility relations. The curve derived from phosphorus trichloride begins at 1000 and the curve for bromine at 2,500 atmospheres.

At 9,000 atmospheres the compressibility, read from the tangent of the curve, is 1.1×10^{-5}, whereas the actual volume-change per atmos-

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[12] Baxter, Hickey and Holmes, This Journal, 29, 127 (1907).

phere of the appropriate volume (0.68) at this pressure is 0.9×10^{-5}. Therefore, all the data bearing upon the substance are reasonably, although not perfectly, consistent.

All the curves described in this paper and the conclusions based upon them are to be regarded only as a preliminary attempt and not as a final exact solution of the problem. In spite of the great extrapolation they seem to yield an outcome of the right order of magnitude, as regards the present question, especially since the curves, being constructed in similar fashion, may all be supposed to err more or less in the same direction, and, therefore, to have their errors compensate one another as regards the diameters of the atoms. For a final exact estimate much more study of the existing curves, and much further experimentation at even higher pressures are necessary. I propose in the near future to continue to attack the problem from every possible angle. Already further light on the nature of the influences at work during compression has been obtained, and there is hope of solving even the most difficult question, namely the apportionment (as regards change of volume) of the shares borne by chemical affinity on the one hand, and cohesive affinity on the other hand. The somewhat changeable quantity *B* is especially interesting in its periodic relations in the several elements, and in its probable partial dependence upon density. This quantity, too, will receive especial attention in the near future.

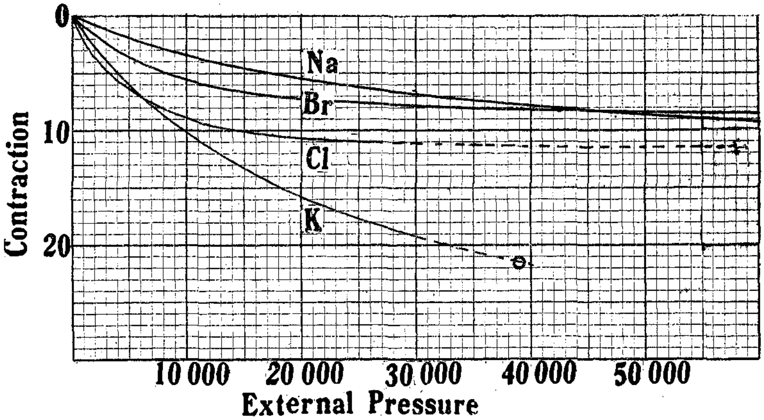

Fig. 3.—Contraction of atomic volumes of sodium, potassium, chlorine and bromine. Contractions are expressed as ordinates in cubic centimeters; external pressures as abscissas.

Having then plausible pressure-volume curves for unit volumes of both potassium and chlorine, the relative volumes which these substances occupy in potassium chloride are easily computed. The computation is most clearly explained by a diagram, although, of course it may be carried out more exactly by numerical interpolation. In the accompanying figure are plotted the decrease in volume of a gram atom each of sodium, bromine, chlorine and potassium with increasing pressure. These values serve as the basis of the following calculation.

Obviously, since the structure of the potassium chloride crystal is undoubtedly that of a face-centered cube, the chlorine and potassium in it must both be under *the same total pressures* exerted by their mutual affinities, cohesive and chemical. As indicated by Figs. 1 and 2, the average internal pressure in metallic potassium is 20,500 kg./sq. cm. ($=25,800 - 5,300$) more than in chlorine. Equilibrium must be attained approximately under conditions for which the sum of the contraction of potassium under an external pressure p and that of chlorine under an external pressure of ($p + 20,500$) amounts to the total observed contraction of 33.0 cc. per mole. This may be found from the equations of the curves, or more conveniently by inspection of Fig. 3. Under a total pressure, $(p + P) = 65,000$, where potassium attains the volume of $45.4-21.5 = 23.9$ cc., chlorine attains the volume of 13.6 cc. This result is probably not exact, because of the simultaneous presence in chlorine (and possibly also in potassium chloride) of two kinds of pressure; but it is probably not far from the truth, and gives the best idea thus far attainable of the sought. The corresponding values for the metal and halogen in potassium bromide are similarly found to be 26.0 and 17.3 with $p + P = 53,000\pm$. The values for sodium salts show much greater pressures, which involve extrapolation so excessive as to make only a rough estimate possible. The fact that the halogens' curves at high pressures are so nearly horizontal diminishes the inaccuracy of the result. It appears that the average pressure in sodium chloride is almost 100,000 atmospheres and that the sodium loses about 10 cc. and the chlorine about 12 cc. on combination. The corresponding values with sodium bromide are about 85,000, 8.6, and 8.7 cc.

TABLE IV

ATOMIC VOLUMES OF METAL AND HALOGEN IN COMBINATION IN FOUR RELATED SALTS

Salt	Sum of at. vols. of elements	Mol. volume of compound	Total contraction	At. vol. of metal in comp.	At. vol. of halogen in comp.	Average P kg./sq. cm.
KCl	70.5	37.5	33.0	23.9	13.6	65,000±
KBr	70.6	43.3	27.3	26.0	17.3	54,000±
NaCl	48.8	27.0	21.8	13.9	13.1	100,000±
NaBr	49.3	32.1	17.2	15.3	16.8	85,000±

Consistently, as would be expected from the heats of formation, the average internal pressure in the bromides is less than that in the chlorides. On the other hand, the average internal pressure is greater in the sodium salts than in the homologous potassium salts, although the heats of formation show the opposite order. The reason for this apparent paradox lies doubtless in the fact that the *work* involved in compression (the integral product of pressure and appropriate volume-changes) not the *pressure* is the quantity to be compared with heats of formation. The exact evaluation of this work is not possible until the distribution of the pressure as regards cohesion and affinity is definitely decided in both factors and products; each substance must be considered on its own account. Only in the case of a monatomic element such as potassium is the exact computation of the work at present possible; nevertheless, an approximate evaluation may be obtained from the average pressures given in Table IV. The details may be deferred to a subsequent publication which will soon follow. It is enough to state now that about the same amount of work is involved in each case, the two values differing in the same sense as do the heats of formation.

The compressibilities of the potassium and chlorine as they occur in the potassium chloride are given by the tangents (about 0.47 and 0.07) of the respective curves at the total pressure 65,000, which represents the average internal pressure in potassium chloride (in kg./sq. cm.). Hence the compressibility of potassium chloride may be calculated by a sufficiently obvious procedure, which gives about 6.3×10^{-6}. The compressibility of potassium chloride has been actually found to be 5.1, as corrected for the new value of the compressibility of mercury.[13] In the same way, the compressiblity of potassium bromide is calculated as 7.6, instead of 6.3, the observed value.

For the first time the compressibility of a compound is thus calculated approximately from the compressibility of its component elements. The agreement with the observed value is almost within the limit of experimental error and affords confirmation of the method of attack and of the related results of other kinds, as well as of the fundamental conceptions. It is as good an agreement as could be expected, considering the complication caused by the presence of two kinds of internal pressures.

Table V

Atomic Diameters

	New values	Old values
Potassium, in chloride	3.46	3.5
Potassium, in bromide	3.56	
Sodium, in chloride	2.85	2.9
Sodium, in bromide	2.92	
Chlorine, with potassium	2.82	2.8
Chlorine, with sodium	2.78	
Bromine, with potassium	3.04	3.1
Bromine, with sodium	3.03	

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[13] The correction should be applied as it has been applied to those of the elements given in This Journal, **37**, 1646 (1915). The original value, 4.93, is given by Richards and Jones, *ibid.*, **31**, 176 (1909).

From the values given above for the proportions in cubic centimeters occupied by the several elements, the atomic diameters are easily computed by the method used in the previous paper. The results are not far from those previously found, that for potassium chloride being almost exactly identical with the previous one, and are recorded in Table V. The present method, however, rests on a sounder basis and is open to fewer objections than the earlier attempt.

The application of the method to more complicated salts is less simple, but the underlying principles seem now to be clear, and to be placed upon a firm foundation. These principles are simply those indicated by the theory of atomic compressibility as outlined during the last 23 years and summarized in the Faraday Lecture of 1911 and the Presidential Address of the American Chemical Society in 1914. The present results enforce those conclusions without change in the ideas involved.

Many aspects of the behavior of solids and liquids seems to be clarified by these considerations. Some of them will receive further discussion in the near future.

Summary

The object of this paper is to evaluate the respective bulks of the elements in combination from the study of the compressibilities of the individual elements, and the contraction which occurs during combination. With the help of Bridgman's accurately determined pressure-volume curves for sodium and potassium, and my own earlier study of the compressibilities of bromine and chlorine, extrapolated by careful study of the nature of the curves (for which surprisingly concordant equations of the type $(p + P)(v-B)=K$ are derived), the values of the average internal pressures existing in these salts, as well as the relative volumes of the components and the atomic diameters in combination were computed. Many conclusions are drawn from the outcome, and it is pointed out that the methods employed have wide applications and may lead to interesting results in these as well as in many other directions.

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NOTES

A Lecture Experiment Demonstrating Adsorption.—A quantity of a solution of malachite green oxalate is poured into a clean glass beaker of about 1 liter capacity, and immediately poured out. The beaker is then washed with a copious supply of cold water until the dye apparently has been completely washed away. The beaker is finally rinsed with 5 to 10 cc. of water which is transferred to a test-tube. Not a trace of color can be observed in the water

That an adsorbed film of dye does exist on the glass surface is shown