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

THE COMPRESSIBILITIES OF THE CHLORIDES, BROMIDES AND IODIDES OF LITHIUM, RUBIDIUM AND CESIUM

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Sir Joseph J. Thomson,[1] in his recent papers and especially in his very interesting lectures, has emphasized the importance of the compressibilities of elements and simple salts as guides to a knowledge of the structure of atoms; and so, also, has Max Born.[2] The belief that the behavior of solids and liquids under pressure must throw new light on the fundamental structure of matter has indeed been, from the first, the inciting stimulus which led to the present extended series of researches. These were begun in 1902, and were marked in 1907 by the publication of results for the compressibilities of about half of the elements known at that time.[3]

Shortly after 1907 the subject was taken up independently by P. W. Bridgman of the Jefferson Physical Laboratory of Harvard University,[4] who has since studied compressibilities under much greater pressure ranges by a different method, and has obtained many interesting and highly valuable results. Nevertheless, further investigations at the lower pressure range are still desirable, especially with regard to hygroscopic substances like the lithium salts, and other substances which need very careful chemical treatment. Bridgman's method measures linear compressibility; the method used in the present series of investigations determines cubic compressibility. Thus the two methods supplement each other. Where there is a difference between the results, the difference is usually to be traced to the fact that the substance concerned is not isotropic. For the most part the two series of investigations confirm each other within their combined limits of error, and often the results are almost precisely the same. Confirmation of this sort obtained through two quite different techniques is valuable and gives confidence in each.

The chemical relations of the resulting data have proved to be even more interesting than the physical relations, and promise to develop yet greater interest in the future. The compressibilities of the halides of the alkali metals are particularly enlightening because, being merely binary

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[1] Thomson, *Phil. Mag.*, [6] **41**, 510 (1921); "The Electron in Chemistry," Franklin Institute, Philadelphia, **1923**.

[2] Born, "Der Aufbau der Materie," Julius Springer, Berlin, **1922**.

[3] Richards, Stull, Brink and Bonnet, "The Compressibilities of the Elements and their Periodic Relations," *Carnegie Inst. Pub.*, **76** (1907).

[4] Bridgman, *Proc. Am. Acad. Arts Sci.*, **44**, 253 (1908); also many later papers in these Proceedings, especially, *ibid.*, **58**, 222 (1922).

compounds and crystallizing in the regular system, these salts show behavior which is easier to interpret than that of many other more complicated substances. Therefore, it was clearly worth while to complete the series of compressibilities of chlorides, bromides and iodides begun by one of us in collaboration with Grinnell Jones many years ago.[5] That investigation included the chlorides, bromides and iodides of sodium, potassium, silver and thallium. The present investigation amplifies the data concerning univalent metals by adding to the list the chlorides, bromides and iodides of lithium, rubidium and cesium.

Method and Apparatus

The essential feature of the method used in the present work is the comparison of the unknown compressibility with the known compressibility of mercury, by first compressing mercury in a given apparatus, measuring both pressure and change of volume, and then displacing most of the mercury by the substance to be studied, again noting the relationship of pressure to volume. Obviously the compression of the apparatus itself is eliminated, since it occurs equally in both series of measurements. The relation of volume to pressure is easily determined by causing the mercury meniscus to make contact (under pure water) with a very fine platinum point in a tube of narrow diameter; and the decrease in volume is determined by adding successive weighed globules of mercury and noting the successive increased pressures needed to cause similar contact. This method was first devised in 1902. It has been improved in detail in subsequent years.[6] For the experiments to be described, a Cailletet compression pump was connected with an exact absolute pressure gage in which pressures were measured by an oscillating, precisely measured plunger, weighted with known carefully standardized weights.[7] This system was further connected with the compression cylinder containing the piezometer or glass jacket in which the substance to be determined was compressed under mercury.

The piezometer has been so often described that a very brief description will suffice in the present paper.

The older form (shown in Fig. 1), constructed of glass instead of steel, was used since it is much the easier to manipulate. It was used with confidence because many comparisons of the two forms have shown that, when properly manipulated, the glass form gives very accurate results.[8] The chief precautions necessary in its use are the following.

In the first place, the ground glass stopper must be very carefully inserted with a

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[5] Richards and Jones, THIS JOURNAL, **31**, 158 (1909).

[6] References to the earlier work are given in (a) *ibid.*, **36**, 2438 (1914). See also Richards and others, *ibid.*, **37**, (b) 470, (c) 1643, (d) 2696 (1915); (e) **38**, 989 (1916); (f) **41**, 59 (1919); (g) **42**, 49 (1920); (h) **43**, 1538 (1921); (i) *Smithsonian Report* for **1916**, p. 213.

[7] Richards and Shipley, THIS JOURNAL, **38**, 990 (1916).

[8] See especially, Richards, Bartlett and Hodges, *ibid.*, **43**, 1542 (1921).

constant quantity of lubricant (in this case 1.5 mg.) and it must be pushed very carefully into position. In the present work, the stopper, which had been ground very carefully with fine emery and smoothed by means of rouge, was rotated for each closure twelve times while it was pushed into place (thus distributing the lubricant very thinly and very evenly) until the stopper was arrested by the friction of glass on glass. If this precaution is not taken, trouble will arise from leakage as well as from a slight shift of the stopper during compression. That a satisfactory result is obtained in this way is shown by the fact that after finishing each complete experiment and removing the added mercury, the initial pressure-volume condition of the instrument was regained within 0.1 atmosphere.


Fig. 1.

The second condition which must be fulfilled is that, after the piezometer has been carefully filled and closed, the application of hydrostatic pressure in each successive trial shall be of the same duration. Under pressure, glass suffers a slight hysteresis, which causes the volume slowly to diminish under constant high pressure. This might lead to perceptible error; but if the apparatus is treated in precisely the same way every time it is used, the error is wholly eliminated.[9] In our work the pressure was always read fifteen minutes after its application—time enough to allow the heat of compression to escape, and not enough to cause serious hysteresis.

Further, it may be noted that the platinum point for making the contact above the capillary should be very sharp, clean, firm and accurately centered. The capillary itself should have a diameter not much over 1.5 mm. Air bubbles must, of course, be carefully excluded. The mercury must be very pure and superficially clean; if it becomes contaminated on the surface, one may more conveniently clean the piezometer and start afresh, rather than attempt to dissolve the impurity with acid, which is apt to leave a film of mercurous salt. Castor oil (which was used to convey the pressure) may best be removed by pure alcohol, which is better than ordinary ether because it does not blacken the mercury.

One other point, especially emphasized by Cohen and Schut,[10] should be mentioned, namely, that the capillary should be moistened by forcing the mercury somewhat below its true level and thus allowing the supernatant water to reach its walls, before adjusting the exact electrical contact. They recommend for this purpose the temporary application of several hundred atmospheres of pressure, but it seems to us that except with very incompressible substances such an excess of pressure would overstep the mark. Drops of water are sometimes held in the capillary if too much of the glass is wetted. It is better, in order to make the individual readings as comparable as possible, to choose such a temporary excess of pressure as will always drive the mercury down about the same distance into the capillary—perhaps 3 mm. With water in the piezometer the pressure needed for this purpose would be only about one-tenth of that required for mercury. The same object may be attained if, in filling the piezometer in the first place, mercury is at first withdrawn under water until the mercury column in the capillary is several millimeters below the desired point. Subsequently enough mercury is dropped in to attain the working level. The latter of these methods has usually been adopted in our work in the past, although (as Cohen and Schut have pointed out) this fact has perhaps not been adequately emphasized.[11]

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[9] Ref. 7, p. 995.

[10] Cohen and Schut, "Piezochemie," Akademiche Verlagsgesellschaft m.b.H., Leipzig, 1919, p. 28.

[11] See for example, Ref. 5, p. 171 (five lines from the bottom of the page).

By heeding all these precautions one is able to obtain a sensitivity of 0.000002 cc. in measuring volume, and therefore a high degree of accuracy. The method has functioned very well not only with us, but also more recently in the van't Hoff Laboratory of Utrecht, with Professor Ernst Cohen and his collaborators, and is rated by them as the best of all methods.[10]

The temperature of the piezometer during the actual determination must, of course, be kept very constant and exactly the same in all determinations. Therefore the electrically regulated and heated thermostat which contained the compression bomb was kept constant within 0.001°, at 19.820°—the temperature of all the work. This was practically equivalent to making the determinations at 20.00°, since the error of experiment was far greater than the insignificant change in volume or compressibility of the salts caused by 0.18°.

Method of Filling the Piezometer

The introduction of the salt in a perfectly dry state is not easy to accomplish. Water must be scrupulously excluded, because the saturated solution is very much more compressible than any of the substances under consideration. After preliminary trials of other methods, the following procedure was finally adopted.

The salt under treatment was carefully fused (in a platinum boat) surrounded by an atmosphere of nitrogen or the appropriate hydrogen halide in the familiar "bottling apparatus," which has served in so many determinations of atomic weights. The salt was then removed from the boat in the air, broken into small pieces, and placed in a short, wide, open glass tube, which had been somewhat narrowed at one end. This receptacle was placed within the heating tube of the bottling apparatus, which now contained also the weighed piezometer and its stopper—the latter in the side pocket reserved for it. The substance in the tube was then reheated once more to about 300° in an atmosphere of dry nitrogen. When cold the smaller orifice of the glass receptacle was pushed into the mouth of the piezometer, and the salt was discharged into the latter by means of a glass rod. The stopper of the piezometer was then inserted, and after the removal of the charged piezometer from the bottling apparatus this stopper was rotated into position in the manner already described. The piezometer with its halide contents was then ready for filling with mercury, which was introduced through its narrow side tube, without displacing its stopper.

Mercury does not easily penetrate very small orifices or pores on account of its great surface tension. Hence, the surfaces of the solid salts must be covered with some other liquid in which they are not soluble. Toluene was chosen for this purpose; this liquid and mercury were added by a method essentially similar to that used by one of us in collaboration with Grinnell Jones fifteen years ago.[12] The piezometer, provided with a suitable small funnel tube was introduced into a tall cylinder, with an air-tight stopper through which ran the tubes of two dropping funnels and an exit to an air pump. On the side of this latter tube was arranged a bulb containing ether, with a suitable stopcock. After pure mercury had been placed in one of the dropping funnels and toluene in the other, the air was exhausted from the cylinder by means of a rotary air pump.

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[12] Ref. 5, p. 171.

To sweep out the last trace of air, ether vapor was admitted and that again exhausted—these two latter operations being repeated in succession twenty times in order to remove all the air and leave only a negligible amount of ether vapor in the apparatus. Finally a small quantity of toluene (from 0.1 to 1.5 g., according to the condition of the salt under examination) was admitted through the funnel tube and the side tube of the piezometer (which latter remained firmly stoppered), and mercury was run in after it. The liquid metal, of course, rose up through the pieces of salt, driving the toluene above it, until the piezometer was completely filled. The trace of ether vapor condensed and was dissolved in the toluene. Subsequently the piezometer was weighed, the gain over the weight when salt alone was within it representing the combined weight of the mercury and toluene. After the completion of the experiment, the salt was dissolved in water and every trace of mercury was washed into a dish where it was carefully freed from water and toluene and weighed. Especial care was taken to avoid loss of mercury through very small globules which may be carried away by drops of toluene floating on the salt solution. In this manner the weight of the toluene was found by difference. The algebraic calculation of the results is sufficiently indicated in previous papers.[13] The average compressibility of mercury between 100 and 500 megabars is taken as 3.95×10^{-6}. That of toluene over the same range was carefully redetermined and found to be 69.12×10^{-6}—sufficiently near to the value 69.0 found in an earlier research.[14] The density of the toluene was taken as 0.8649.

Preparation of Materials

Hydrochloric acid was prepared by diluting the purest acid of commerce with pure water and distilling, only the middle fraction of the distillate being used.

Hydrobromic acid was prepared in a similar way, all distillates which came over below 105° being rejected. Some of it had been made from moderately pure bromine by reducing with sulfur dioxide and distilling, the small amount of sulfuric acid being removed from the distillate by barium hydroxide. All the hydrobromic acid used was redistilled twice or thrice.

Hydriodic acid was obtained by reducing fairly pure iodine with hydrogen sulfide. The product was distilled thrice. None of these acids was of the highest purity, but each was amply pure for the purpose in hand.

Lithium salts were prepared from pure lithium nitrate which had been thrice crystallized. Two successive precipitations as carbonate removed all significant impurities of the other alkali metals. In order to avoid loss during the carbonate precipitation, the mother liquors were evaporated to expel ammonium salts and then treated with more ammonium carbonate. From the twice precipitated lithium carbonate, lithium chloride and bromide were made. Neither of these salts when fused in the appropriate gas stream was found to show any trace of hydroxide. Hydrolysis had, therefore, been prevented. The lithium iodide used was a "pure" commercial preparation. Lack of time prevented more careful treatment of this substance, which served for only one determination. On dehydration, it lost a little of its iodine, but the fusion of the dry salt was accomplished without further decomposition.

Rubidium chloride was prepared by recrystallizing an already pure substance kindly loaned by Professor G. P. Baxter.

Rubidium bromide and iodide were prepared from rubidium sulfate through the precipitation of the sulfuric acid by an exactly equivalent amount of barium hydroxide and the neutralization of the resulting rubidium hydroxide by the appropriate acid. This rubidium preparation contained about 1% of cesium which, however, could not

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[13] Compare Ref. 5, p. 172.

[14] Ref. 7, p. 998.

have affected the compressibility, since the compressibilities of rubidium and cesium salts are so nearly identical.

Cesium chloride, bromide and iodide were prepared from a partially purified nitrate of cesium obtained from pollucite. After the evaporation of this nitrate to dryness with concd. hydrochloric acid, and separation of the resulting silica, the aluminum and iron present were precipitated as hydroxides by means of ammonia. The filtered solution was evaporated and heated with concd. sulfuric acid until all traces of chloride or nitrate were eliminated. The cesium sulfate (which contained sodium, but no appreciable amounts of potassium or rubidium sulfates) was exactly converted into the hydroxide by means of barium hydroxide; and this (practically free from barium or sulfuric acid) was divided into three equal parts, serving to furnish (by neutralization with the corresponding acids) the three halides. Each of the latter was thrice recrystallized. The process freed the iodide wholly from sodium, as shown by flame test and spectroscope; but it was less effective with the chloride and bromide. Hence the compressibility determinations of cesium chloride and bromide were made with preparations containing small amounts of sodium, which were determined analytically in order to be sure that the amount of impurity did not exceed permissible limits. The sodium could have been removed by precipitation of the cesium as dichloro-iodide; but this would have been a work of supererogation, since even a considerable percentage of sodium produces no appreciable error in the result. This circumstance is due to the fact that this impurity affects both the specific gravity and the compressibility of the mixture in such a way that if specific gravity of the pure cesium salt is used in the calculation, the resulting value of the compressibility corresponds, well within the experimental error, to the true value sought, even with a mixture containing several per cent. of sodium.

None of the halides of rubidium and cesium, after fusion, showed any trace of alkalinity; thus, they had not been hydrolyzed during their desiccation. Before introduction into the piezometer they were cracked into small pieces in order to open any possible air pockets; and the accompanying powder, which exposed an unduly large surface, was removed with a sieve and fused again.

Nitrogen (obtained from liquid air) was freed from its last traces of oxygen by being passed over an ammoniacal copper solution continuously and automatically renewed on the surface of copper gauze, and finally over red-hot copper. Of course, all traces of ammonia and aqueous vapor were carefully eliminated. It was found convenient to have a small quantity of pure hydrogen in the nitrogen in order to prevent any accidental trace of oxygen from causing the melted halide to attack the platinum boat.

Determination of Compressibility

With apparatus and substances prepared in this way the following determinations of compressibility were made.

Before the data are communicated and the results are discussed, the unusual behavior of rubidium bromide and iodide and cesium bromide should be mentioned. Under pressure, these salts (after they have been fused) appear at first to have an abnormally large compressibility—as much as three or four times the true value. This is not, however, a true compressibility, but is rather a definite permanent contraction, as is proved by the fact that when the pressure is removed the original volumes are not fully attained. The contraction, as measured by the weight of mercury needed to correspond to a given pressure, begins as soon as pressure is applied. Above 400 atmospheres it proceeds rapidly, and a few minutes' application of a pressure of 500 atmospheres completes the conversion, or at least produces a volume which is subsequently unvarying. Time enough (as much as a month) enables the fused salt to transform into the less bulky crystalline form without external pressure.

As an example of the abnormal performance of these salts one experiment with cesium bromide may be reported in detail.

16.481 G. of the salt was taken, and 0.5933 g. of toluene. The compression experiment was started at 95.8 kg./sq. cm. The addition of 0.3922 g. of mercury corresponded to a pressure of 280.6 kg./sq. cm.; of 0.5300 g. of mercury to 339.9 kg./sq. cm.; of 0.7058 g. of mercury to 466.6 kg./sq. cm. and of 0.7660 g. of mercury to 515.8 kg./sq. cm. Thereupon, 0.4175 g. of mercury was removed, leaving 0.3485 g. of that which had been added during the experiment; and the corresponding pressure, instead of being in the neighborhood of 250 atmospheres, was found to be only 97.6 kg./sq. cm., or about the initial pressure.

From these data it is easy to compute exactly the contraction of the salt which occurred after the first application of 100 atmospheres' pressure. It amounted to the volume of 0.345 g. mercury, or 0.33 cc. per mole (212.74 g.) of salt. Now, at 100 atmospheres' pressure, where this comparison was made, the transition had already been partly accomplished. To find the total contraction the curves must be extrapolated to zero pressure; or, better, the observations should begin there. By the former of these two methods, the amount of the contraction was found in two experiments with rubidium iodide to be about 0.28 and 0.26 cc. per mole, and in two experiments with cesium bromide to be about 0.39 and 0.38 cc. per mole. No measurement of the contraction was made with rubidium bromide, of which the unstable bulky form of the salt is even more transitory—this form having been observed on only two occasions. In most cases the salt very soon gave normal and unchanging values for the compressibility.

Probably the unstable (or metastable) bulky forms of these three salts, which appear as they solidify on quickly cooling from fusion, are partially amorphous, and probably in time, or under the influence of moderate pressures, the amorphous forms settle into definite crystals, with a contraction of somewhat less than 1% of the volume. If not amorphous, they must be in an unstable crystalline form very like the permanent one.

The compressibilities of these substances given in Table I all correspond to the stable forms which, either after continued pressure or after a long time, showed no further abnormalities in their compressibility curves. There was no evidence of instability in any of the six other salts investigated. Either (as is most likely) they assumed the stable crystalline condition even more promptly than rubidium bromide, or else the "metastable" substances were sufficiently stable to withstand any treatment to which we subjected them and were really the forms measured. If the exact specific gravities of crystalline and fused salts were known, intelligent choice could be made between the horns of this dilemma; but unfortunately only those of the fused salts have been accurately determined.

The full data concerning the compressibility determinations of the nine salts of lithium, rubidium and cesium under discussion are too voluminous for publication here. Their omission is the more permissible since the experimental part will soon be published in full in the *Bulletin de la Société de chimie de Belgique.* Moreover, the determinations are rather a preliminary than a final contribution to the subject. The individual data for a single salt may serve as a type of the others; these data are given in Table I.

The first column gives the number of the experiment; the second column, the weight of mercury needed by the piezometer over the range from exactly 100 to exactly 500 kg./sq. cm. when mercury alone was present; the third column, pressure readings; the fourth column, the corresponding weights of mercury added to produce these pressures; the fifth column, the mercury which was needed to cover the exact range 100 to 500 kg./sq. cm., when the piezometer contained salt and toluene in addition to mercury; the sixth column records the weight W of salt and that K of toluene (to fill the interstices of the salt) within the piezometer; and the last column the result for the compressibility (β) of cesium iodide, expressed in terms of the megabar as the unit of pressure.

TABLE I

DATA OF DETERMINATIONS OF THE COMPRESSIBILITY OF CESIUM IODIDE

Temperature 19.82°.

Expt.	w' = jacket constant	Press. in kg./sq. cm.	Wt. of Hg added G.	w = weight of Hg corr. to 100–500 kg./sq. cm.	Other data	$\beta \times 10^6$ (per megabar)
19	0.1122	97.7	0		W = 10.456	9.3
		163.4	.0696		K = 0.4807	
		235.5	.1414			
		310.7	.2122			
		391.7	.2821			
		475.3	.3537			
		562.3	.4252	0.3716		
20	.1122	77.6	....		W = 13.871	9.1
		177.6	.1048		K = 0.4903	
		277.8	.2089			
		386.8	.3131			
		500.2	.4160	.3929		
21	.1110	89.1	....		W = 21.981	9.6
		327.2	.3811		K = 0.8451	
		505.4	.6225	.5967		
					Av.	9.3

The equation[13] by means of which the results are calculated is as follows:

$$\beta = \frac{(w - w' - mK)}{5428\,w} = +\beta'.$$

In the present determinations (since toluene was used), m = 0.4020, as determined very carefully by new trials with this liquid. The result as calculated from the figures given involves the kg./sq. cm. as the unit of pressure; it was translated into the megabar standard with sufficient accuracy for the present case through simple multiplication by 1.0198.

The average result of these experiments and those of similar experiments with each of the other nine salts are recorded in Table II. In it are included also the values for the densities of the several substances.[15] These values were needful for calculating the results, and are interesting also in relation to the others. The values given for the compressibilities are represented algebraically by the equation, $\beta = \Delta V/V_0\Delta p$, in which $\Delta p = 400$ megabars, and ΔV corresponds to the range from 100 to 500 megabars. They are practically equal to the compressibilities, usually defined as $\frac{1}{V_0}\left(\frac{\partial v}{\partial p}\right)_{t^\circ}$, at the pressure of 300 megabars.

TABLE II

RESULTS OF DETERMINATIONS OF COMPRESSIBILITIES

Alkali metal	Chloride Density	Chloride Compressibility megabars × 10⁶	Bromide Density	Bromide Compressibility megabars × 10⁶	Iodide Density	Iodide Compressibility megabars × 10⁶
Li...........	2.068	3.7	3.464	5.0	4.061	7.2
Rb..........	2.798	7.3	3.349	8.2	3.550	9.3
Cs...........	3.974	5.9	4.432	7.0	4.509	9.3

Discussion of Results

First, a word concerning the probable accuracy of the values of compressibilities given above is apropos. Although the decimals are not entirely certain (as can be seen from Table I), nevertheless they probably represent in most cases very closely the true values. The determinations of the compressibilities of lithium iodide and rubidium bromide are the least accurate, since they depend upon only one determination apiece. Lack of time prevented us from attaining greater certainty by using larger amounts of material and by making a larger number of experiments; but the above values are quite accurate enough to serve, as will be seen, the main object of the research.

In order to show more clearly the significance of the new figures, they are entered in Table III, together with the earlier results of Grinnell Jones[5] and one of us for sodium and potassium halides. Since compressibility is closely related to atomic volume, and also to the contraction which occurs on combination, the values for these quantities are likewise contained in the table. Incidentally it may be noted that P. W. Bridgman has very recently redetermined the compressibilities of some of these salts and has verified the earlier results within a reasonable limit of error. These results have not yet been published.

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[15] Baxter, *Am. Chem. J.*, **31**, 559 (1904). Baxter and Wallace, THIS JOURNAL, **38**, 259 (1916).

In Table III, "Contr." signifies the contraction in cubic centimeters which occurs when gram-atomic volumes of the several elements enter into combination. The column headed "V_M" records the molecular volume of the salt, and the column headed "β" records the average compressibility of the several salts as defined above. The total sum of the atomic volumes of the elements concerned in each case may of course be obtained by adding the number in the column headed "Contr." to the corresponding number in the following column. Thus, the added atomic volumes of solid sodium and liquid chlorine are equal to 21.8 + 27.0 = 48.8 cc., of which 23.7 cc. consists of sodium and 25.1 cc. consists of chlorine, as found from the atomic weights and densities of the elements.

Table III

Contractions on Combination, Molecular Volumes and Compressibilities of the Chlorides, Bromides and Iodides of the Alkali Metals

	Chloride			Bromide			Iodide		
Alkali metal	Contr.	V_M	β	Contr.	V_M	β	Contr.	V_M	β
Li	17.6	20.5	3.7	13.5	25.1	5.0	5.7	33.0	7.2
Na	21.8	27.0	4.3	17.2	33.1	5.3	8.5	40.9	7.1
K	33.0	37.5	5.2	27.7	43.3	6.4	17.9	53.2	8.8
Rb	37.7	43.2	7.3	32.0	49.4	8.2	21.7	59.8	9.3
Cs	53.4	42.3	5.9	48.7	48.0	7.0	38.7	57.6	9.3

Before attempting to interpret these interesting figures, let us seek to discover any relations which they may show among themselves or to other allied properties.

The most striking regularity to be seen among the values of compressibility is the fact that each bromide is more compressible than the corresponding chloride, and each iodide more compressible than the corresponding bromide.

Previous investigations have shown that compressibility is often related to molecular volume.[3] In the accompanying diagram, Fig. 2, the fifteen values are all plotted accordingly. Evidently, considering each metal separately, the points for the three halides of a given metal lie on or near a curve which, with only slight curvature, leads to the origin. The slight deviation of the sodium and lithium compounds from their curves may be due to experimental error. That these five curves should pass through the origin would indeed be expected: a hypothetical substance with zero molecular volume could have only zero compressibility. That the curvature should be so slight is nevertheless not a foregone conclusion; such a phenomenon is to be expected only among compounds of elements as similar as the halogens.

If molecular volume alone determined compressibility, all of the points for the fifteen substances should of course lie on the same curve. That the situation is by no means so simple as this is shown by the fact that a curve passing through the points representing the five chlorides, or the five bromides, or the five iodides is sometimes quite irregular, and does not tend directly towards the origin. Evidently molecular volume alone, even with these very simple compounds, is not the sole factor determining compressibility. With the three halides of a given metal the compressibility usually increases in greater proportion than the molecular volume, whereas on comparing the same halides of different metals, the opposite is seen to be the case. For example, cesium bromide is more compressible (in proportion to its molecular volume) than is cesium chloride, but less compressible (in proportion to its molecular volume) than is lithium bromide.

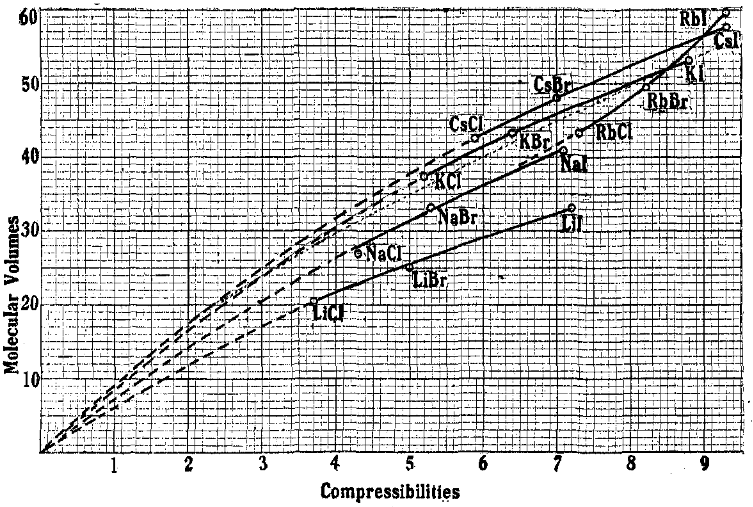

Fig. 2.

In another diagram, Fig. 3, is depicted another series of relations, namely, those of the compressibilities to the contractions which take place during the combination of gram-atomic quantities of the metals and metalloids (liquid chlorine and bromine, and solid iodine). Evidently, for any given metal the halides show greater compressibility the less the contraction which takes place during their formation; whereas usually for any given halide of different metals, the greater the contraction the greater is the compressibility. Evidently here, as in the other case, at least two influences must be at work.

Yet another diagram is worth recording, namely, the relation of these compressibilities to heats of formation (Fig. 4). The data for heats of formation are taken from the paper of M. de Forcrand;[16] they appear to be the best (in many cases the only) results at hand, and are doubtless

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[16] de Forcrand, *Compt. rend.*, **152**, 27 (1911).

accurate enough for our purpose. The values for chlorides have each had 9 kj. subtracted from them (this being the heat of evaporation of a gram atom of chlorine) and thus are referred to liquid chlorine. This was done in order to make the chlorides and bromides more strictly comparable. The latent heat of melting of iodine was not added to the values for the iodides, because the volume changes given in Fig. 3 refer to solid and not to liquid iodine.

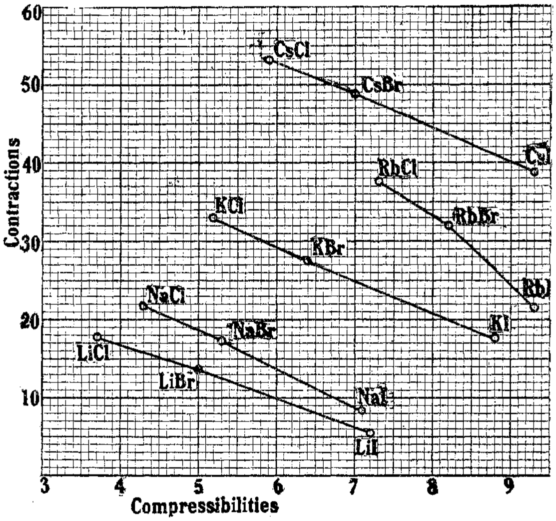

Fig. 3.

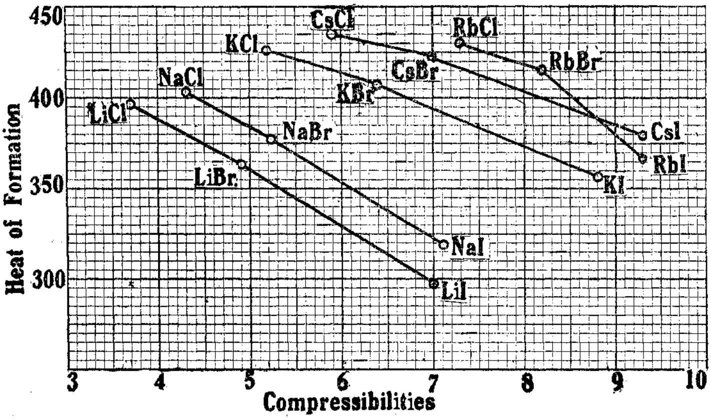

Fig. 4.

The salts of rubidium show in all three diagrams a somewhat abnormal behavior. Their molecular volumes and compressibilities are too large, and correspondingly the contractions which occur during their formation are too small to fit into the expected positions between potassium and cesium. No complete explanation has been found for this latter peculiarity.

The interpretation of the results may perhaps best be approached by considering first a recent interesting attempt in this direction by Max Born.[17] His calculation or prediction rests upon the concept of the electronic structure of the atom. The attracting force is supposed to act according to Coulomb's law (inversely as the square of the distance). The calculation of the resisting tendency (which gives to solids and liquids their property of occupying space) was at first based upon Bohr's electronic orbits. The equation thus took the form

$$\beta = \frac{9\,\delta_0^4}{13.94\,(n-1)e^2} \tag{1}$$

in which $\delta_0 = \sqrt[3]{\frac{4V_M}{N}}$, (if the molecular volume, M/D, of the salt is designated as V_M, and N is Avogadro's number) and e is the electron value in electrostatic units. According to the original reasoning, $n = 5$; but because this number gave values for the compressibilities almost twice too great, the number 9 was later chosen empirically for n. The final outcome of these considerations may be represented by the following equation, which is partly theoretical and partly empirical.

$$\beta = 4.26\,(10^{-14})\,V_M^{4/3} \tag{2}$$

where β is the compressibility in terms of the *bar* (or *barie*, which is the pressure of one dyne per square centimeter).

Substituting Millikan's more recent values,[18] 6.062×10^{23} and 4.774×10^{-10}, respectively, for N and e (instead of the old values, 6.2×10^{23} and 4.76×10^{-10} used by Born) and reckoning the pressures in *megabars* instead of in *bars*, Born's equation becomes

$$\beta = 4.41\,(10^{-8})\,V_M^{4/3} \tag{3}$$

This equation represents, then, Born's idea based partly upon the Bohr atom and partly upon known facts, in terms of the best extant values of the constants concerned. Since the problem has excited considerable interest, the predictions of this equation may be compared with the facts as found in the present investigation, in order to show the extent of agreement.

Table IV gives values for the salts discussed by Born, and also values for the nine salts dealt with in the present paper, for which compressibilities were unknown at the time of his writing. All these values have been recalculated, using the corrected form of Born's equation given above, and more accurate data for the properties of the individual salts. This

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[17] Born and Landé, *Ber. physik. Ges.*, **20,** 210 (1918); Ref. 2, p. 50.

[18] Millikan, *Phil. Mag.*, [6] **34,** 1 (1917).

was needful, because many of the data used in the original publication were not so accurate as those now available. In particular, many of the specific gravities of salts used by Born were in error,[19] (in the case of sodium bromide by over 6%) and the observed compressibilities were quoted from an early paper in which they were based upon a somewhat inaccurate value for the compressibility of mercury—the best available at that time. To each of the old compressibility data 0.16 should be added.[6c] These lacks were doubtless not the fault of Born, who was prevented by the war from obtaining access to the recent American publications.

In Table IV, the first column designates the substances; the second, their molecular weights (M); the third, the specific gravities used by Born (D_1); the fourth, the corrected specific gravities of the salts (D_2); the fifth, the molecular volumes (V_M) of the salts; the sixth, the results for the compressibilities (β_1) calculated by Born; the seventh, these same quantities (β_2) correctly calculated; the eighth (β_3), the correct observed values; and the ninth, the difference between β_2 and β_3 in each case.

TABLE IV

RECALCULATION OF BORN'S RESULTS FOR COMPRESSIBILITIES

With values also for the salts herewith discussed.

Salt	M	Density used by Born D_1	Density (correct value) D_2	V_M	$\beta_1 \times 10^6$ calc. by Born	$\beta_2 \times 10^6$ from Born's equation (corr.)	$\beta_3 \times 10^6$ obs.	Error of Born's value (corr.)
LiCl	42.40	..	2.068	20.50	..	2.46	3.7	−1.2
LiBr	86.96	..	3.464	25.07	..	3.22	5.0	−1.8
LiI	133.96	..	4.061	32.96	..	4.62	7.2	−2.6
NaCl	58.46	2.17	2.161	27.05	3.46	3.56	4.3	−0.7
NaBr	102.92	3.01	3.203	32.13	4.73	4.47	5.3	− .8
NaI	149.92	3.55	3.665	40.91	6.30	6.17	7.1	− .9
KCl	74.56	1.98	1.987	37.52	5.36	5.50	5.2	+ .3
KBr	119.02	2.70	2.749	43.30	6.64	6.68	6.4	+ .5
KI	166.02	3.07	3.123	53.16	8.68	8.75	8.8	+ .0
RbCl	120.91	..	2.798	43.21	..	6.64	7.3	− .7
RbBr	165.37	..	3.349	49.37	..	7.94	8.2	− .3
RbI	212.37	..	3.550	59.82	..	10.23	9.3	+ .9
CsCl	168.27	..	3.974	42.34	..	6.47	5.9	+ .6
CsBr	212.73	..	4.433	47.99	..	7.65	7.0	+ .7
CsI	259.74	..	4.509	57.60	..	9.75	9.3	+ .4
							Av. error (irrespective of sign)	0.83

The fact that the general order of magnitude of these results is correct is of little significance, since the quantity n was so chosen that this should be the case. The errors should, therefore, be considered irrespective of sign. The average error is 0.83 (in a quantity which averages about 6.7), or about 12.5%. The errors in the case of lithium are very large (about 33%), and in the cases of sodium, rubidium and cesium by no means

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[19] See papers by Baxter and collaborators, the results of which are summarized in THIS JOURNAL, **43**, 1586 (1921).

negligible. When it is borne in mind that the sodium and potassium salts were used as part of the empirical basis of the equation, the showing is not particularly satisfactory.

Nevertheless there is a general tendency in the right direction. The compressibilities of the chloride, bromide and iodide of a given metal always show the proper order of magnitude, the chlorides showing the smallest and the iodides the largest compressibilities. This is in accord with the facts. Moreover the lithium salts are given the smallest compressibilities, sodium the next, potassium the next, cesium the next and rubidium the largest compressibilities. This likewise is in accord with the facts. Evidently there is, in Born's assumption, an element of truth, which seems to us to lie in the following circumstances. In the first place, Born's equation assumes two opposing forces, of which the distending tendency increases more rapidly as the distance diminishes than does the compressing tendency. This is indeed an assumption absolutely necessary as a basis of a conception of the attainment of definite volume by a solid, although it is very doubtful if Coulomb's law really applies to the attracting force.[20] In the next place, Born's equation demands that a substance with great molecular volume should have a great compressibility, which also is reasonable if other circumstances are similar. Indeed both of these points of view are entirely in accord with the theory of atomic compressibility, concerning which one of us has from time to time written for the last twenty-two years. In 1907 molecular volume was shown to be closely related to compressibility;[3] and with regard to the distending tendency the following sentence was written nine years ago: "The present research shows that the (repellent) effect increases inversely as the very high power of the distance."[21]

The defect in Born's equation is also manifest in Fig. 2. According to it, compressibility should be a function of molecular volume *alone*. All of his results may, therefore, be plotted on a single curve in Fig. 2—the curve indicated by a fine dotted line. That the dotted line should be about in the right position is not surprising, for the reasons already stated. That the assumptions, however, are too simple to represent the facts, is shown by a wide scattering of the actually observed points—a scattering far too wide to be the result of experimental error. Evidently these deviations must lead to a somewhat complicated conception of the circumstances involved in determining the volume of any one of these salts, as has indeed been pointed out more than once in previous communications.[22] Molecular volumes may be large on account of at least two circumstances. On the one hand, they may be large because of the

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[20] Richards and Richards, *Proc. Nat. Acad. Sci.*, **9**, 379 (1923).

[21] Ref. 6a, p. 2437.

[22] Richards, This Journal, **45**, 422 (1923).

structure of the atoms. On the other hand, they may be large because the affinities (which bind the atoms together to make the solid) may be small. The second of these causes determining volume (which forms an essential feature of the theory of compressible atoms) is not adequately taken into account in Born's equation. Bridgman,[4] after an elaborate mathematical analysis of this equation (1922) in relation to the change of compressibility with pressure, has also concluded that, although suggestive, the equation is incomplete—without, however, intimating a reason.

Since the theory of atomic compressibility is perhaps not very generally understood (in spite of the occasional publications concerning it), a brief reiteration of the main principles and assumptions involved may be presented here. The main idea, fundamental in all these considerations of changing atomic volume, is that chemical affinity and cohesion must be assumed to cause pressure, and that the pressure thus produced must be assumed to act, together with any external pressure which may be present, in diminishing the volumes of the substances concerned, because it must act on the atoms constituting these substances. Such pressures we may call "internal pressures." The two compressing tendencies (external and internal pressure) are opposed simultaneously by two distending tendencies: first, thermal pressure (which is usually comparatively slight), and secondly, the pressure exerted by the inherent distending tendency of atoms (which alone determines the distention of substance at the absolute zero). Thus the pressure equilibrium which fixes the bulk of a solid may be very simply conceived in the form of the following equation: $p + P = P_\theta + P_z$, in which p and P are, respectively, the external pressure and the internal (attracting) pressure, whereas P_θ and P_z are, respectively, the thermal pressure and the pressure exerted by the inherent distending tendency of the atoms.[23] The repelling or distending tendency, P_z, which resists compression in solids, undoubtedly increases enormously as the attracting atoms approach one another. Therefore, the compressibility must diminish very rapidly as the volume decreases. This change would be especially noticeable in volatile substances where the cohesive affinity is slight. In such cases we should expect to find very great compressibility on the first application of pressure, and rapid decrease both in the first and second differential coefficients of the volume-pressure curve as the pressure is increased—predictions which are amply verified by experience. Thus the greater the total pressure, the less the compressibility diminishes with increasing pressure, other things being equal.[24]

That the line of thought is fruitful and significant, one may easily show.

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[23] Ref. 22, p. 425. The equation is there expressed in words, identical in significance with the algebraic expression above.

[24] Ref. 6a, p. 2425.

Even superficial study of the diagram in Fig. 2 shows that substances with small affinities tend to exhibit large compressibilities,[25] as would be expected from the theory of atomic compressibility. This tendency doubtless affects molecular volume, and is, therefore, in part implicitly recognized in Born's equation. But molecular volume depends partly upon other circumstances, as already stated, and inspection shows that affinity needs yet further weight in the equation. The simple expression $\beta = kV_M/U$, fits the case more satisfactorily, although it cannot pretend to be a final solution of the problem. In this equation, U, the heat of combination of metal and halogen, is taken as approximately representing, at least as regards order of sequence, the affinity of the pair of substances. Of course, since all the relations of the variables are not linear, but are really to be represented by curves, the outcome of the equation above can be only approximate. Nevertheless, Table V which depicts the theoretical values of the compressibility obtained by this new equation (taking for the constant k the value 0.00006) is interesting. The equation probably will not fit so well other series of substances of widely different nature. It represents the same ideas as an approximate equation for elements, recently proposed,[26] except that heat of combination takes the place of melting point, since the latter obviously furnishes little clue as to the intensity of chemical affinity.

Table V

Results of New Equation for Compressibility

Salt	V_M	U	$\beta/10^6$ by new equation	$\beta/10^6$ observed	Error of new value
LiCl	20.50	397	3.10	3.7	−0.6
LiBr	25.07	364	4.13	5.0	− .9
LiI	32.96	298	6.64	7.2	− .5
NaCl	27.05	403	4.02	4.3	− .3
NaBr	32.13	378	5.10	5.3	− .2
NaI	40.91	319	7.69	7.1	+ .6
KCl	37.52	426	5.28	5.2	+ .1
KBr	43.30	408	6.37	6.4	± .0
KI	53.16	356	8.96	8.8	+ .2
RbCl	43.21	430	6.03	7.3	−1.3
RbBr	49.37	415	7.13	8.2	−1.1
RbI	59.82	366	9.80	9.3	+0.5
CsCl	42.34	436	5.82	5.9	− .1
CsBr	47.99	423	6.81	7.0	− .2
CsI	57.60	378	9.15	9.3	− .1
			Av. error (irrespective of sign)		0.45

This equation, although primarily empirical, rests partly on theoretical conclusions; it is evidently about twice as accurate as that of Born, at

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[25] Ref. 5, p. 183.

[26] Ref. 6c, p. 1652.

least as regards this series of compounds. The difference lies chiefly in the fact that the new equation takes more suitable account of the mutual affinities of the elements than does the equation of Born. Whether or not his equation could be altered by the introduction of another term in such a way as to obtain as good an agreement as that just shown by the new equation, it would be difficult to say. At least we have attempted such a modification in vain.

The foregoing considerations show that the compressibilities of the fifteen salts concerned are all explicable, at least qualitatively, on the basis of the principles of atomic compressibility. They give a reasonable picture of the resultant effect of the several affinities acting in opposition to the distending tendencies which give to solids their volume. The point of view adopted has the advantage of involving primarily the consideration of pressure—the prime influence capable of producing change of volume. The unavoidable incompleteness of the outcome seems to lie not in any lack of reasonableness of the principles involved, but rather in lack of experimental knowledge of the exact law which determines the volume-pressure relations of condensed matter. In making a more complete analysis of the compressibilities of compounds, one may not forget that they represent a combined or added effect, constituted of a number of simultaneous distinct partial effects. Each of the salts under consideration contains two elementary substances, in a far more contracted condition than in their respective elementary states. These compressed entities are not equal to each other in volume, nor can their compressibilities be alike, except by chance in a few cases. Thus, the compressibility of a binary salt must be looked upon as made up of at least two added quantities, one due to compression of the combined metal, the other due to the compression of the combined halogen. In a recent paper, a preliminary attempt was made to take account of all these inevitable conditions.[22] Although the outcome was promising, it cannot be (and was not) considered as definitive. A much more extended knowledge of the data, including data at present beyond our experimental ability, is needed before the final result can be attained. The approximate solution above, which at least takes into account two most important variables, must suffice for the present.

Sir J. J. Thomson's interesting equation for the compressibility of elements is similar to Born's in that it is based on an electronic atomic structure, but in this case the structure is rather on the "octet" plan.[27] The equation is very similar to Born's, containing the same dimensions, but with a somewhat different coefficient. Without further modification

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[27] Thomson, *Phil. Mag.*, [6] **27**, 757 (1914). See also G. N. Lewis, THIS JOURNAL, **38**, 762 (1916) and I. Langmuir, *ibid.*, **41**, 868 (1919).

it gives for several elements (especially the alkali metals and calcium) better agreement with the facts than does Born's equation.[28]

The outcome of further work in this direction is to be awaited with great interest. If atoms really consist of nuclei and surrounding electrons, the attracting and repelling effects of their electric charges must, of course, be among the potent factors (if not the only factors) in determining compressibility as well as many other properties. These effects must then be (at least in part) the cause of the quantities P and P_z in the pressure equation which determines the volume of solids. The proof of their existence would be entirely compatible with the theory of compressible atoms; it would indeed supply a *raison d'être* for the opposing forces (or pressures) which are indicated in all the recent study of change of atomic volume. The present paper seems to show, however, that (at least as regards compounds) the present assumptions of the electronic theory are not adequate fully to account for all the diversities of magnitude to be observed in the actual values of compressibilities of the several halides under discussion.

We are indebted to the Carnegie Institution of Washington and to an anonymous benefactor for some of the apparatus used in this investigation.

Summary

Preliminary results giving the compressibilities of nine halides of the rarer alkali metals are recorded in this paper, namely: LiCl, 3.7; LiBr, 5.0; LiI 7.2; RbCl, 7.3; RbBr, 8.2; RbI, 9.3; CsCl, 5.9; CsBr, 7.0; CsI, 9.3; (per megabar, each quantity being multiplied by 10^{-6}). The results, together with those for sodium and potassium halides from a previous investigation, are compared with the corrected equation of Born. It is shown that while this equation in a general way depicts the tendencies of these compressibilities, it is inadequate to explain their detailed values, because it appears not sufficiently to take into account the varying mutual affinities possessed by the elements in question. A simple equation ($\beta = kV_M/U$), which takes account of varying affinity in terms of heat of combination, is found to predict the values about twice as correctly as Born's equation. Born's idea, even if incomplete, and Sir J. J. Thomson's are seen to be (as far as they go) entirely consistent with the theory of atomic compressibility as advanced during the last twenty years.

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[28] Ref. 1, p. 121. It has long been known that the compressibilities are nearly proportional to atomic volumes in the case of the alkali metals, but not in many other cases. See Ref. 3, p. 23; also *Z. physik. chem.* **61**, 97 (1907).