

$$\beta' = \frac{\beta\alpha'\Delta^2T'}{\alpha\Delta'^2T}$$

For example, according to Dupré's rule, sulphur should be ten times as compressible as selenium; but they are, as a matter of fact, almost alike. It is not necessary, however, to go as far afield as this to discover the uncertainty of Dupré's rule. The single case of water, having at 1° and 100° the coefficient of expansion of  $-0.000006$  and  $+0.00077$  respectively, and the compressibilities of  $0.000051$  and  $0.000048$  respectively, would prove that it is not infallible—although it takes cognizance of causes which undoubtedly affect compressibility. No surprise need be excited by this lack of parallelism, for compression always tends towards producing a smaller volume in a system, while warming does not necessarily tend to produce a greater volume. In every case it will be observed that volatility, which may be ascribed to lack of cohesive tendency, seems to be associated with increased compressibility, other things being nearly equal. This is seen most strikingly on comparing the compressibility of chlorine, bromine, and iodine, but it is manifest also in other cases; for example, in the cases of arsenic and antimony, or sulphur and selenium. This effect of decreasing the cohesive tendency is entirely in accord with principles which were laid down in the recent communications from this laboratory concerning the significance of changing atomic volume.<sup>1</sup> It is reasonable to suppose that substances already much compressed by their own great internal pressure would not be sensitive to outside pressure. Further consideration of these relationships will be taken up in the following paper.

In conclusion, it is a pleasure to acknowledge the generous support of the Carnegie Institution of Washington which alone has made this and the following investigation possible.

## THE COMPRESSIBILITIES OF THE CHLORIDES, BROMIDES, AND IODIDES OF SODIUM, POTASSIUM, SILVER AND THALLIUM.

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### Introduction.

In a recent series of papers on the significance of changing atomic volume it has been pointed out that the volumes of both solids and liquids are probably in part dependent upon both the chemical and the cohesive

<sup>1</sup> Richards, *Loc. cit.*

forces existing within them.<sup>1</sup> The interpretation of the facts was made more reasonable by the application of the following plausible assumptions:

"First, that internal pressure, due to both cohesive attraction and chemical affinity, might be expected to diminish the volume of condensed systems (*i. e.*, solids and liquids); secondly, that the greater the pressure, the greater should be the diminution of volume; and thirdly, that, other conditions being equal, a substance already much compressed by internal pressure would be expected to suffer less contraction upon subjection to additional pressure than one but little compressed." These assumptions were found to be warranted by the facts, and hence it is clear that compressibility—one of the essential data involved—becomes worthy of much more detailed study than it has heretofore received.

In order to trace completely the connection between the very important internal pressures and the external volumes of material, it is necessary to know the compressibilities of both elements and compounds through a wide range of pressure, whereas at the time when the relation was first suggested, the compressibilities of only a very few elements under comparatively small pressures were known. Nothing was known in regard to the variation of the compressibility through the great range of pressure (probably amounting to at least tens of thousands of atmospheres in many cases) necessary to produce a contraction in the elementary substances equal to that produced by chemical combinations.

The relations are further complicated by the fact that not only chemical affinity, but also cohesive attraction seems to have a marked influence on the volume of both elements and compounds, and therefore upon the change in volume accompanying chemical changes.

It seems probable that the exact mathematical expression of these very complicated relationships can hardly be expected in the near future. Nevertheless, it is by no means impossible that further careful experimental work may considerably increase qualitative knowledge of the subject; and even although it may be incomplete, such qualitative knowledge is far better than nothing. The nature and mode of action of chemical affinity is so important that no clue promising to furnish even approximate knowledge concerning its action should be neglected. Indeed, much progress has already been made in placing these ideas (and the hypothesis of compressible atoms to which they lead) upon a firmer experimental basis, through the study of the compressibilities of a majority of the solid or liquid elements.<sup>2</sup>

Obviously, the determination of the compressibilities of salts might

<sup>1</sup> Richards, *Proc. Am. Acad.*, **37**, 1 (1901); **37**, 399 (1902); **38**, 293 (1902); **39**, 581 (1904); also a paper presented to the International Electrical Conference of St. Louis, 1904. See also *Z. physik. Chem.*, **49**, 15 (1904).

<sup>2</sup> Richards, *Pub. Carnegie Inst.*, **76** (1907). *Z. physik. Chem.*, **61**, 77, 171 (1907). This monograph is condensed in the preceding paper.

help to unravel the tangled clues; accordingly the present research was undertaken. It was conceivable that a relationship might be found between the compressibilities of each element and that of its salts, taking account of the change in volume and heat evolved during the formation of the salt and other properties of the salts. The study of a series of salts containing one element in common might furnish an explanation as to the variations of the compressibility, and furnish further light upon the source of the heats of the reactions by which the salts were formed; and interesting systematic relations bearing upon the periodic system of the elements were to be anticipated.

The halogen salts of the univalent metals were selected for study, because these salts have large heats of formation, accompanied by a correspondingly large contraction during the formation of the salts; and the elements themselves are unusually compressible (except silver and thallium) and show a fairly regular variation in the properties under consideration. Moreover, the relationships are probably simpler in the case of the salts like these containing only two atoms in the molecule, than they would be in more complicated compounds.

There are no measurements of any of the compressibilities of these salts except sodium chloride to be found in the usual publications, and data on the related properties are very incomplete and often unreliable; the work lay in an almost unexplored field.

The new method of determining compressibility was used in this work, with only a few minor modifications of the apparatus and manipulation.<sup>1</sup> The apparatus was either the same as or essentially similar to that which has been described in detail in the original articles.

The essential feature of the method 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, and again noting the relationship of pressure to volume. Obviously in such a method as this, the compressibility of the apparatus itself is eliminated, occurring in both series of measurements. The relation of volume to pressure was easily determined by causing the mercury meniscus to make contact with a very fine platinum point in a tube of narrow diameter; and the decrease in volume was determined by adding weighed globules of mercury and noting the pressures needed to cause similar contact.

In general, it may be said that the method continued to give entire

<sup>1</sup> Richards and Stull, "New Method of Determining Compressibility," publication of the Carnegie Institution, No. 7. Richards, Stull, Brink and Bonnet, "The Compressibilities of the Elements and their Periodic Relations," publication of the Carnegie Institution, No. 76. This method is briefly described in *THIS JOURNAL*, 26, 399 (1904).

satisfaction, provided that air was scrupulously eliminated from the substances to be studied.

### The Compression Apparatus.

One of the Cailletet compression-pumps used in the previous investigations served well in this one also as a means of obtaining the high pressures needed. The apparatus (shown in Fig. 1) consists of a lever- and screw-compression pump (*A*) filled with oil, communicating through a stout fine copper tube with a heavy steel barrel (*B*) provided with a stout steel screw cap (*C*). The hydraulic guage (*D*) registering these pressures will be discussed under a subsequent heading.

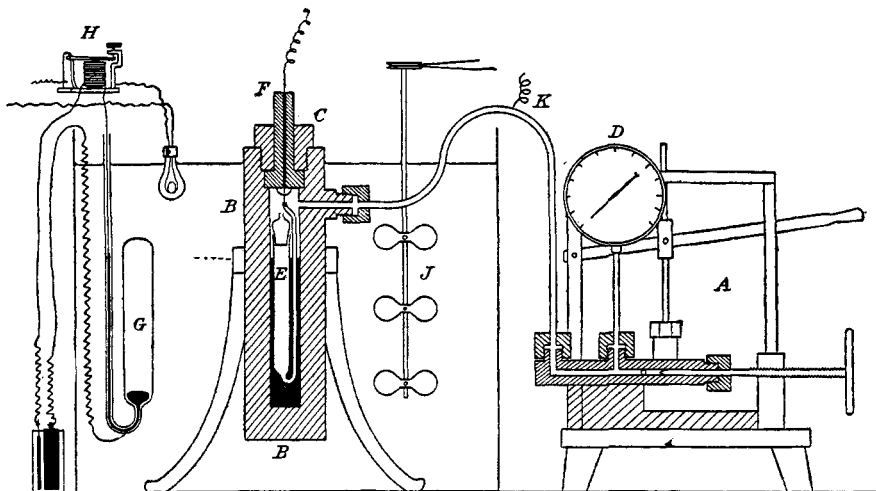


Fig. 1.

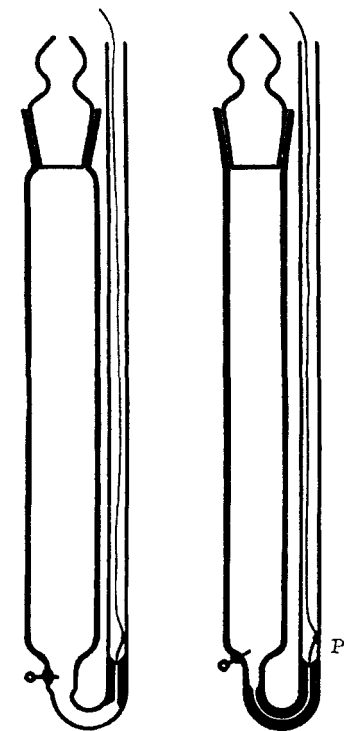
As before, the glass jacket (*E*) containing the mercury and other substance to be compressed was suspended under the oil and mercury in the steel barrel, hanging from a bronze piece (*F*) held down by the screw cap. Two forms of glass jackets are shown on a less diminutive scale, about half their actual size, in Fig. 2. In order to keep the apparatus at constant temperature, the barrel as far up as the screw cap was immersed in the water of a thermostat, which varied less than  $0.005^{\circ}$  throughout any complete determination.

It will be remembered that the tube or glass jacket was at first filled completely with mercury, and the change in volume for different pressures was measured very simply by placing the whole jacket under the liquid in the barrel of the Cailletet compression apparatus, adding successive weighed proportions of mercury, and noting each time the pressure needed just to break and then make again the electrical connection between the meniscus and the platinum point (*P*). The quantity of mercury in the glass jacket was usually so adjusted that the first constant

pressure reading was very nearly 100 atmospheres, and this first reading was taken as the starting point of the determination. Minute air-bubbles were thus disarmed of possible injurious effects. As already suggested,

a weighed quantity of mercury was now added through the open tube and pressure was again applied. The added pressure necessary to break the electrical circuit corresponds to the volume of the extra mercury introduced. This process was repeated until the highest pressure was reached, and thus were found the points on a curve which represented the difference between the compressibilities of mercury and glass.

The mercury was now wholly removed, except for a small amount in the U-tube—enough to seal the bend. The rest of the left-hand side of the apparatus was then filled with a liquid of known compressibility (usually pure xylene), and the salt was introduced in the form of a closely fitting cylinder, or else in small fused pieces free from cracks. The jacket was now placed once more in the Cailletet barrel, and once more the pressures corresponding to the successive added portions of mercury were found. These new readings define the curve of the total compression of the liquid, the metal, and the residual mercury, all



Jacket A and B.  
Fig. 2.

Jacket C.

taken together. By subtracting the corresponding values from this first curve, and also those corresponding to the known weight of xylene, results are obtained which represent the differences between the compression of the metal and a like bulk of mercury. From this the compressibility is very simply computed.

In all the measurements, great care was exercised to add the proper amounts of mercury necessary to bring the successive pressure readings near the 100, 200, 300, 400, and 500 graduations, especial pains being taken with the two extreme points. This practice requires more patience during the experiment than the introduction of irregular quantities of mercury, but gives more reliable and comparable results, since it reduces greatly or obviates entirely the possible error introduced during the plotting of the results and the estimation from the curve of the amount of mercury which must be added to correspond with a change in pressure from 100 to 500 pressure units.

The special precautions needed for manipulating this apparatus are sufficiently discussed in the preceding papers to which the reader is referred for further details.<sup>1</sup>

### Preparation and Standardization of Jackets.

The forms and details of the glass jackets or receptacles needed to contain the substances during compression are important matters, and vary with the nature of the substances. Since the substances to be investigated in the present work were expected to have small compressibilities, and since many of them could not be prepared in a form which would permit them to be closely packed and yet be essentially free from cracks and cavities, several new tubes or jackets were made, of as large capacity as the bore of the compression barrel would permit. The form of the jackets is shown in Fig. 2 already presented. Jacket A was used in only two cases. Jacket B was made from jacket A, after the latter had been accidentally broken. It contained the same ground glass stopper, but had a slightly greater volume than the original jacket. Jacket C was designed for use with substances which could be obtained in the form of a cylinder which was free from cracks or cavities. A cylinder which would fit the jacket snugly could be introduced through the stopper. Jacket V was that used in previously published work;<sup>2</sup> it resembled Jacket C in shape. These jackets were entirely satisfactory, especially in the two most important features, the perfect fit of the ground glass stoppers and the adjustment of the platinum point in the opening of the capillary glass tube. During an experiment, the stopper was held firmly in position by filling it with mercury to weigh it down, and by a stout rubber band. A definite amount of lubricant was always placed on the stopper. When the jacket contained only water or mercury as the liquids to transmit the pressure, 5 mg. of a rubber-paraffin lubricant was used. When the jacket contained xylene, 20 mg. of thick molasses was used.

The hydraulic gauge used for the measurement of the pressure was made by Schaeffer and Budenberg, of Zürich, Switzerland, and was labeled No. 3014491. Its standardization will be described in the following section of this paper. Since the gauge was graduated in kilograms per square centimeter, this unit of measure was used in recording the details of the experiments. The results are calculated in terms of atmospheres and megabars (megadynes per square centimeter) at the end of this paper. All measurements were made at 20°.

In order to eliminate the effect of the change in volume of the jacket and of mercury used to transmit the pressure, an experiment must first be made with each jacket containing mercury alone. The following

<sup>1</sup> *Carnegie Institution of Washington Publications*, 7 and 76. Also *Z. physik. Chem.*, 61, 77 1007.

<sup>2</sup> *Carnegie Inst. Pub.*, 76, 11, 18, 19 (1907).

table presents in as concise a form as possible, the results of these measurements with each of the four jackets.

## OBSERVATIONS CONCERNING THE COMPRESSION OF MERCURY IN GLASS.

Jacket.	Total weight of mercury.	Weight of mercury (in milligrams) added, with corresponding pressures beneath.								
A.....	592.9	0	53.8	108.9	203.5	295.6	383.1	1.1	...	...
		87	145	203	304	404.5	500.5	90	...	...
B.....	618.4	0	11.6	111.1	199.4	299.8	388.9	-17.9	11.2	385.1
		86	102	205.5	296.5	403	500	73	105	496
C.....	403.6	0	17.7	82.8	144.9	204.9	261	1.6	...	...
		74	98	203	304.5	404	498	76	...	...
V.....	127.6	0	54.3	89.3	30.8	...	...	...	...	...
		56	352	550	221	...	...	...	...	...

These figures show that when Jacket A contains mercury alone, 0.372 gram of mercury must be added between the pressures 100 and 500 kilograms per square centimeter. This constant for the jacket is designated  $W_0$ . For Jacket A,  $W_0 = 0.372$ .

The experiments with Jacket B give three independent determinations of  $W_0$ , 0.3792, 0.3825 and 0.3824: mean 0.381 =  $W_0$  for Jacket B. The experiments with Jacket C give two independent determinations of  $W_0$ , 0.2432 and 0.2429: mean, 0.243 =  $W_0$  for Jacket C. On the other hand, Jacket V, which was much smaller, gave  $W_0 = 0.0721$ .

The difference between the compressibilities of mercury and glass is given with sufficient approximation by the equation

$$\beta' - \beta'' = \frac{w'}{W' P}$$

where  $\beta'$  = compressibility of mercury  
 $\beta''$  = compressibility of glass  
 $W'$  = weight of mercury in jacket  
 $w'$  = mercury added  
 $P$  = change in pressure

$$\text{Jacket A. } \beta' - \beta'' = \frac{0.372}{592.9 \times 400} = 1.57 \times 10^{-6}$$

$$\text{Jacket B. } \beta' - \beta'' = \frac{0.381}{618.4 \times 400} = 1.54 \times 10^{-6}$$

$$\text{Jacket C. } \beta' - \beta'' = \frac{0.243}{403.6 \times 400} = 1.51 \times 10^{-6}$$

Thus the average difference between the compressibilities of glass and mercury was found to be 0.0000154. The individual values lie between the extremes observed in previous work.

### The Standardization of the Pressure Gauge.

It seemed probable that the greatest danger of constant error in the determination of compressibility by this method is due to an uncertainty

in regard to the absolute value of the intervals of pressure as recorded by the gauge. It has been pointed out in the previous papers that the difference between the compressibility of water and mercury at 20° is a perfectly definite quantity which can serve as a standard of pressure and a means of comparing different gauges. The value was, therefore, determined.

42.41 grams (in vacuum) of water were introduced into Jacket A with sufficient mercury to seal the bend at the bottom and make the electrical contact. The following table contains the observations.

OBSERVATIONS CONCERNING THE COMPRESSION OF WATER.

Mercury added, grams. . . .	0	1.942	4.237	6.373	8.506	-0.321
Corresponding pressures. . . .	116	198	300	397.5	496.5	101
Mercury added, grams. . . .	2.066	4.282	6.442	8.603	-0.299	
Corresponding pressures. . . .	203	300	398.5	499.5	102	

Four independent determinations of the weight of mercury added through the range 100 to 500 kilograms per square centimeter, and hence of the average compressibility through this range, can be obtained from these measurements; namely, 8.956, 8.925, 8.959, 8.960 grams.

The compressibility of water is calculated by the equation:

$$\beta = \frac{(w - w')(1 - \beta'''P_1)D}{13.546(P_1 - P_2)A} + \beta'$$

where  $\beta$  = average compressibility of water between the pressure  $P_1$  and  $P_2$ ;

$\beta'$  = compressibility of mercury between 100 and 500 pressure units =  $3.71 \times 10^{-6}$ ;

$\beta'''$  = compressibility of mercury between 0 and 500 pressure units =  $3.73 \times 10^{-6}$ ;

$w$  = weight of mercury added through the range of pressure  $P_1 - P_2$ ;

$w'$  = weight of mercury added through the range of pressure  $P_1 - P_2$ ; where the jacket contains mercury alone = 0.372;

13.546 = density of mercury at 20°;<sup>1</sup>

D = density of water at 20° = 0.9982;

A = weight of water in jacket = 42.41;

$P_1$  = the higher pressure;

$P_2$  = the lower pressure.

Giving  $W$  in turn the values 8.956, 8.925, 8.959 and 8.960, we obtain as the average compressibility of water between 100 and 500 kilograms per square centimeter,  $40.93 \times 10^{-6}$ ,  $40.80 \times 10^{-6}$ ,  $40.95 \times 10^{-6}$ ,  $40.95 \times 10^{-6}$ .

<sup>1</sup> In subsequent equations the constant factor  $\frac{1 - \beta'''P_1}{13.546}$  is usually given as  $\frac{1}{13.57}$  because  $P_1$  was always 500.  $\beta'''$  is so nearly equal to  $\beta'$  that the latter may be used instead of the former without appreciable error.



These four values of the compressibility of water indicate that the water decreases 0.01637, 0.01632, 0.01638 and 0.01638 respectively between 100 and 500 kg/cm<sup>2</sup> of its uncompressed value. The four results come within the extremes of the older work on the compressibility of water,<sup>1</sup> but are slightly below the best of the earlier work. Richards and Stull found 0.01642 three or four years ago, and two years ago Richards and Mathews found 0.01640 and 0.01639. This apparent decrease of the compressibility to the present average 0.01636 may perhaps have been due to a slight weakening of the spring of the gauge, but the change was so slight that the readings of the dial may still be accepted. The result just given will enable any one to apply a correction to all our results, if such correction proves itself to be necessary in the light of future knowledge.

The following table shows the variation of the compressibility of water with pressure, as calculated in a similar manner from these data.

CHANGE OF COMPRESSIBILITY OF WATER WITH PRESSURE; $\beta \times 10^6$ .			
Range of pressure Kg/cm <sup>2</sup> .	1st measurement.	2nd measurement.	Mean.
100-200	42.8	42.7	42.8
200-300	41.1	41.7	41.4
300-400	40.1	40.1	40.1
400-500	39.4	39.2	39.3

These figures show that the pressure gauge was still behaving well in every part of its range.

*Compressibility of Xylene.*—Owing to the high surface tension of mercury, it is not permissible to expect this liquid to make a perfect and uniform contact with the salts immersed in it. One must, therefore, surround the solids by a small amount of another liquid, which will adhere and fill up any minute cracks. Xylene was usually used for this purpose when working with salts which are soluble in water. Merck's xylene (a mixture of *o*-, *m*-, and *p*-xylene) was distilled over sodium and the fraction coming over at 137°-140° was used. The compressibility of this xylene was determined in order to supply a correction for its presence.

Jacket A was used, containing 36.278 grams (vac.) of xylene.

#### OBSERVATIONS CONCERNING THE COMPRESSION OF XYLENE.

Mercury added, grams.....	0	3.873	7.849	11.670	14.085	—0.002
Corresponding pressure.....	103.5	200	307	421	495	103.5

From the experiments in which mercury was added, we can calculate  $W = 14.390$ , and from the experiment in which mercury was removed  $W = 14.392$ . The compressibility of xylene is calculated by the use of the equation used for water, by substituting  $D = 0.863$ ;  $A = 36.278$ ;  $P_1 = 500$ ;  $P_2 = 100$ ;  $\beta' = 0.00000371$ ;  $W' = 0.372$  (Jacket A). From the result of the experiment made by adding mercury, we obtain

<sup>1</sup> See *Carnegie Inst. Publication*, 76, 33.

$$\beta = \frac{(14.390 - 0.372)(1 - 500 \times 0.00000373) 0.863}{13.546 \times 400 \times 36.278} + 0.00000371 = 65.14 \times 10^{-6}$$

From the first experiment made by taking out mercury, the result  $65.15 \times 10^{-6}$  is obtained. Richards and Mathews, in an investigation, as yet unpublished, found the compressibilities of ortho-, meta- and para-xylene to be respectively 64.4, 64.6 and 65.7, figures corresponding closely with our present result obtained from a mixture of the three. This value leads to the value 0.3864 to be used as the coefficient of K in the equation on p. 172.

The determinations made with Jacket V were made before the others by W. N. Stull and one of us, with the same apparatus and nearly at the same time as the work on the elements, already frequently quoted. In the first and third of these (concerning halite and sodium bromide), a sample of kerosene (paraffin oil) was used, giving the value 0.4387 for the coefficient for K; in the second (concerning halite) another sample of paraffin was used, giving the value 0.3830; and in the fourth, a sample of bromoform, giving the value 0.0820.<sup>1</sup>

#### Preparation of Materials.

*Mercury.*—The mercury used in this work was purified by dropping very small drops of the metallic liquid several times through a long column of dilute nitric acid and mercurous nitrate. It was then distilled in a current of hydrogen under a pressure of about 2 cm. of mercury.

*Potassium Chloride.*—The best commercial "C. P." material was dissolved, filtered and reprecipitated by passing hydrochloric gas into the solution. Care was taken not to make the hydrochloric acid solution very concentrated, in order to avoid, as much as possible, the precipitation of sodium chloride. The crystals were drained in the centrifugal machine. Spectroscopic examination showed a very marked concentration of the sodium in the mother liquors and only an insignificant trace in the precipitate. It is much more important for the present purpose that the material compressed should be free from cavities and water than that the last traces of other similar salts should be removed. In order to accomplish this object, the salt was fused in a large platinum dish and the dish rotated during cooling, so that the salt solidified in thin strips along the sides of the dish. If the salt is allowed to cool wholly in contact with the platinum dish, the unequal contraction of the platinum and salt produces innumerable small cracks in the salt. If the layer of salt is very thin, it is almost impossible to separate it from the dish, and thick layers of salt invariably contain cavities. It was found, however, that immediately after solidifying the salt is somewhat flexible, and by rapid work can be pulled away from the dish, and thus allowed to cool out of con-

<sup>1</sup> Richards and Stull, *Carnegie Inst. Pub.*, 76, 18, 59. For 25.39 gms. of bromoform alone 2.078 gms. extra of mercury had to be added between 100 and 500 pressure units.

tact with the platinum. Even with this precaution, usually only a part of the material is fit for use. It must be broken up in sizes small enough to enter the compression jacket, and each separate piece must be examined very carefully. Pieces containing cracks or cavities were fused again; and only perfectly clear and transparent pieces of salt used. It was preserved in a desiccator over sulphuric acid until the measurements were to be made.

*Potassium Bromide.*—The best commercial "C. P." material was crystallized once with centrifugal draining and prepared in a condition suitable for compression in exactly the same way as the chloride of potassium. An analysis of a portion of this material showed that only 0.012 per cent. had been converted into oxide or hydroxide during the fusion, which is too small an amount to have a measurable effect on the compressibility.

*Potassium Iodide.*—The best commercial "C. P." salt was recrystallized once with centrifugal drainage and fused. It was titrated with standard acid and found to be 0.2 per cent. decomposed.

*Sodium Chloride.*—The best commercial "C. P." salt was dissolved, filtered, precipitated by passing hydrochloric acid gas into the solution and drained centrifugally. A spectroscopic test proved the absence of potassium. It was then fused and pieces free from cracks were selected in exactly the same way as that described for potassium chloride. Owing to the higher melting point and more rapid cooling, a much smaller proportion of the fused mass could be used. This made this process much more tedious in this case, as it necessitated several successive fusions of the salt, but the final product was of as good a quality. Two experiments were made by W. N. Stull upon clear transparent natural halite from Germany.

*Sodium Bromide.*—The first two experiments on sodium bromide were made with material prepared by R. C. Wells for determining the transition temperature of this salt.<sup>1</sup> It was exceedingly pure. For the late experiments, sodium carbonate was dissolved, filtered and crystallized twice with centrifugal drainage and then added in solution in very slight excess to a solution of pure oxalic acid, and the precipitated sodium oxalate drained in the centrifugal machine. Bromine was dissolved in cold strong solution of potassium bromide and then distilled from this solution. A slight excess of this bromine was then added to the sodium oxalate and after the reaction was complete, the excess of bromine was boiled off, and the solution of sodium bromide evaporated to dryness. Each specimen of the salt was then fused. For the work done with Jacket V, the salt was then powdered; for the other work satisfactory pieces were selected in the manner already described.

<sup>1</sup> *Proc. Am. Acad.*, 41, 436 (1906).

*Sodium Iodide.*—Iodine which had been distilled from a solution of an iodide, was converted into hydriodic acid by means of red phosphorus and water. The excess of phosphorus was filtered out and the hydriodic acid purified by distillation and added in slight excess to sodium carbonate which had been thrice recrystallized. The solution was evaporated to dryness and the product fused in an open platinum dish with some evolution of iodine. The product, which was not transparent, was titrated with standard acid and found to be 0.6 per cent. decomposed. As the compressibility of the hydroxide is not of a different order from that of the iodide, no great error could have been caused by this impurity.

*Silver Chloride.*—Commercial "C. P." silver nitrate was dissolved, filtered, diluted very largely and poured into an excess of hydrochloric acid. The precipitate was washed very thoroughly and dried. It was then fused in a vertical hard glass tube in a vacuum and shaken until the air bubbles had escaped. Air was then admitted to the tube and the fused salt allowed to solidify from the bottom upwards. In this way was made a cylinder of silver chloride essentially free from cracks or cavities, which fitted the jacket quite closely.

*Silver Bromide.*—Silver bromide was prepared in the same manner as the silver chloride. The bromine used was the same as that used for the preparation of sodium bromide. It was converted into ammonium bromide by adding it to an excess of ammonia, and this bromide was used for precipitating the silver.

*Silver Iodide.*—We are greatly indebted to Professor Baxter for supplying us with 133 grams of very pure silver iodide remaining from his investigation on the atomic weights of silver and iodine. To this was added about 20 grams of silver iodide which was somewhat less pure but amply pure enough for the present purpose. This iodide was fused in a large glass tube, forming a cylinder which fitted the jacket very closely.

*Thallous Chloride.*—200 grams of metallic thallium prepared by Kahlbaum were dissolved in dilute nitric acid. The solution was found to be free from silver or lead. It was then diluted to four liters and poured into an excess of hydrochloric acid, and the precipitate was washed very thoroughly and dried and fused in the same way as the silver halides.

*Thallous Bromide.*—Thallium bromide was made from the thallium chloride after the compressibility measurements had been made on the latter. It was found to be impossible to wash away the mercury with which the chloride had come in contact during the compression. The thallium chloride was, therefore, boiled with water until the water was saturated, and then the water was poured off and cooled. A small amount of thallium chloride was deposited, and the mother liquor was used again to dissolve more thallium chloride. This process was re-

peated until the projecting points and irregularities of the surface had been dissolved sufficiently to make it possible to wash the pieces of thallium chloride perfectly free from adhering mercury. The thallium chloride was then treated with concentrated sulphuric acid and heated until it had all dissolved, and the heating was continued until all the hydrochloric acid had been driven off. Four liters of water were then added, and the solution was heated and poured into an excess of the pure ammonium bromide solution, already mentioned. The precipitated thallium bromide was washed, dried, and fused in a hard glass tube in the same manner as silver chloride.

*Thallous Iodide.*—Thallous iodide was made from the thallous bromide after the compressibility measurements on the latter had been completed. The thallous bromide was freed from adhering mercury by cautious heating. The pure thallium bromide was heated with concentrated sulphuric acid until all of the bromine had been expelled. The solution was then diluted and saturated with sulphur dioxide to reduce any thallic salt which might have been formed, and then the excess of sulphur dioxide boiled off. This solution was then greatly diluted and a solution of hydriodic acid added. The hydriodic acid was prepared in the manner already described under the preparation of sodium iodide. The precipitated thallous iodide was washed, dried, and fused in a hard glass tube, forming a cylinder which fitted the jacket very closely.

### **The Filling of the Compression Jacket.**

The jacket was first weighed and then the carefully selected material to be compressed was packed into the jacket as closely as possible. The amount of salt used was determined by a second weighing. 5 mg. of paraffin lubricant (or 20 mg. of thick molasses) were placed on the stopper, which was pressed firmly into position.

The liquids were introduced according to a method somewhat similar to that used by Richards and Stull.<sup>1</sup> The jacket was placed in the large test tube (G), and the rest of the apparatus was set up as shown in the diagram (Fig. 3). The bulb (A) contained ether only, all air having been expelled by boiling under reduced pressure. The funnel (D) containing mercury had been previously weighed. The funnel (E) contained xylene (or water). The apparatus was then exhausted through C by means of a Sprengel pump to a pressure of about 2 mm. of mercury. The stop-cock (C) was then closed and the stop-cock (B) opened, thus filling the apparatus with ether vapor. The stopcock (B) was then closed and the ether vapor pumped out through C as completely as is possible by a water pump. The alternate filling with ether vapor and exhausting was repeated thirty times. By this means the air in the jacket is

<sup>1</sup> *Carnegie Inst. Pub.*, 76, 32.

completely removed and replaced by ether vapor under a pressure of about 15 mm.

A few grams of xylene were then allowed to enter the jacket from the funnel (E) and then mercury was added to the jacket from the funnel (D). As the mercury rises in the jacket, the xylene floating on its surface wets the salt, thus ensuring a good contact. In this way the jacket is filled completely. Occasionally, very small bubbles of air were present, but these soon dissolved in the liquid and could not produce any error. The ether vapor, of course, condenses completely, but so very little is present that no correction need be applied for it. The apparatus was then taken apart, and the side tube of the jacket was carefully dried, and the jacket weighed. The increase of weight of the jacket gives the weight of the mercury and xylene added to the jacket. The weight of mercury added is found by a second weighing of the funnel (D), and, therefore, the weight of the xylene added can be calculated.

The jacket was then placed in the compression barrel and a pressure of 600 atmospheres applied to it, in order to open any slight cavities in the salt which may have been overlooked and force the liquid into any minute cracks still present. The mercury above the platinum point was then removed. It was found advantageous to add a warm solution of potassium bichromate in concentrated sulphuric acid to the side tube in order to remove traces of grease (coming from the lubricant on the stopcocks of the funnels D and E) from the vicinity of the platinum point and the mercury meniscus. Very slight traces of grease make it impossible to obtain sharp readings of the making and breaking contact between the mercury meniscus and the platinum point. The oxidizing solution and a small amount of mercurous sulphate which is formed, were washed out and pure water added. Small drops of mercury were then added until the contact was broken in the neighborhood of 100 atmospheres. After this point had been found, a number of weighed drops of mercury were successively added and the pressure at which each contact was made on compression was read.

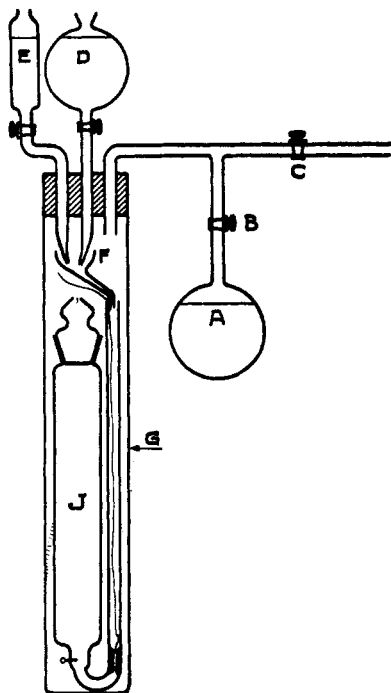


Fig. 3.

As has been said, in all the measurements, great care was exercised to add the proper amounts of mercury to bring the successive pressure readings near the 100, 200, 300, 400, and 500 graduations, special pains being taken with the two extreme points.

When water is present in the jacket around the salt, the average compressibility of the salt between 100 and 500 kilograms per square centimeter is calculated by the formula

$$\beta = \frac{(W - W_0 - 0.2025K)D}{13.57 \times 400 \times A} + 0.00000371,$$

where  $W$  = the weight of mercury added to the jacket containing the salt, mercury and water for 400 units of pressure between 100 and 500 units;

$W_0$  = the corresponding weight of mercury, added when mercury alone is present;

$K$  = the weight of water present;

$D$  = the density of the salt;<sup>1</sup>

$A$  = the weight of salt;

0.00000371 = the average compressibility of mercury between 100 and 500 pressure units;

13.57 = the density of mercury at 20.00° under a pressure of 500 kgs/cm<sup>2</sup> (see foot-note on page 165).

A detailed explanation of this equation is given on pages 22 and 36 of the "Compressibilities of the Elements and their Periodic Relations."<sup>2</sup> The slightly lower value for the coefficient of  $K$  is derived from the slightly lower value for the compressibility of water given by the measurements recorded in the present paper.

When xylene is used instead of water to ensure good contact between the salt and the compressing liquid, the corresponding formula is

$$\beta = \frac{W - W_0 - 0.3864K)D}{13.57 \times 400 \times A} + 0.00000371.$$

The value for the coefficient of  $K$  is derived from our measurements of the compressibility of xylene (see p. 167). It was found that when the jacket contained 36.278 grams of xylene, 14.019 grams more mercury must be added between 100 and 500 pressure units than when the jacket

<sup>1</sup> The authorities for the various densities given in the following tables are as follows: AgCl, Richards and Stull (unpublished); TiCl, Lamy, *Ann. chim. phys.* [3], 67, 403 (1863); NaCl, Krickmeyer, *Z. physik. Chem.*, 21, 82 (1896); NaCl, Retgers, *Z. physik. Chem.*, 3, 312 (1889); KCl, Krickmeyer, *Z. physik. Chem.*, 21, 82 (1896); AgBr, Baxter, *Am. Chem. J.*, 31, 564 (1904); TiBr, Clarke, *Am. Chem. J.*, 5, 241 (1883); NaBr, Kremers, *Jahresb. Chem.*, 10, 67 (1857); KBr, Richards and Mueller, *THIS JOURNAL*, 29, 562 (1907); AgI, Baxter, *THIS JOURNAL*, 26, 1585 (1904); TlI, Clarke, *Am. Chem. J.*, 5, 241 (1883); NaI, KI, Baxter, *THIS JOURNAL*, 30, 53 (1908).

<sup>2</sup> Richards and Stull, *Carnegie Publications*, No. 76.

contains mercury alone. Therefore, for one gram of xylene, it would be necessary to add  $\frac{14.019}{36.278} = 0.3864$  gram more mercury through this range of pressure than if the jacket contained mercury alone. As has been said, the coefficients to be used in the determinations numbered 5, 6, 7, and 8, were respectively 0.4387, 0.3830, 0.4387, and 0.0820, because different liquids were used to wet the solid in these cases.

These details will be made clearer by the complete record of one set of determinations of the compressibility of sodium bromide.

*The Compressibility of Sodium Bromide (Determination No. 9).*—The preparation of the salt has already been described. The second sample of the salt, in fused lumps, was used. The weights of materials and apparatus follow.

Jacket + sodium bromide.....	106.385
Jacket (B).....	65.745
	40.640
Vacuum correction.....	+ 0.010
	40.650 = A
Sodium bromide used.....	504.150
Mercury pipette before filling jacket.....	108.485
	395.665
Mercury added to jacket.....	395.665

Since the jacket is to contain xylene, molasses must be used as the lubricant on the stopper. The filling of the jacket was entirely satisfactory. All the air was removed.

Jacket + sodium bromide + mercury + xylene + lubricant...	504.876
Jacket + sodium bromide + 20 mg. lubricant.....	106.405
	398.471
Mercury + xylene.....	395.665
	2.806
Vacuum correction.....	+ .003
	2.809 = K
Xylene (vac.) =.....	2.809 = K

The jacket was then placed in the compression pump, and after several trials the amount of mercury was adjusted so that the contact of the platinum point should occur at about 100 atmospheres' pressure. The readings follow:

Circuit made, 103, 103, 103, 103, 103, 103, 103, 103, 103, 103.  
 Circuit broken, 103, 103, 103, 103, 103, 103, 103, 103, 103, 103.

No readings were taken until about ten minutes after the pressure was applied, in order to allow the heat of compression to be conducted away, and the readings were continued until the pressure had remained constant for at least five minutes.

After adding the first drop of additional mercury (= 0.4281 gram), the following readings were made:



Circuit made, 205, 205, 205, 205, 205, 205, 205, 205.

Circuit broken, 205, 205, 205, 205, 205, 205, 205, 205.

After adding a second quantity of mercury (= 0.3943 gram):

Circuit made, 303, 303, 302.5, 302.5, 302.5, 302.5, 302.5, 302.5, 302.5, 302.5.

Circuit broken, 303, 303, 302.5, 302.5, 302.5, 302.5, 302.5, 302.5, 302.5, 302.5.

After adding third quantity of mercury (= 0.3743 gram):

Circuit made, 403, 403, 403, 403, 402.5, 402.5, 402.5, 402.5, 402.5, 402.5, 402.5, 402.5.

Circuit broken, 403, 403, 403, 403, 402.5, 402.5, 402.5, 402.5, 402.5, 402.5, 402.5, 402.5.

Here the gauge correction was +0.5, hence the corrected reading is 403.

After adding fourth quantity of mercury (= 0.3595 grams):

Circuit made, 503, 502.5, 502.5, 502.5, 503, 503, 503, 503, 503, 503, 503.

Circuit broken, 503, 503, 503, 503, 503, 503, 503, 503, 503, 503, 503.

As before, the gauge correction was +0.5, hence the corrected reading is 503.5.

After removing 1.6763 grams of mercury by means of a very fine pipette, the following readings were made:

Circuit made, 75.5, 75, 76, 75.5, 75.5, 75.5, 75.5, 75.5, 75.5.

Circuit broken, 75.5, 75, 76, 75.5, 75.5, 75.5, 75.5, 75.5, 75.5.

After adding 0.1161 gram of mercury, calculated to bring the contact at nearly 100 atmospheres, the following results were obtained:

Circuit made, 102, 102, 102, 102, 102, 102, 102, 102, 102, 102, 102, 102.

Circuit broken, 102, 102, 102, 102, 102, 102, 102, 102, 102, 102, 102, 102.

Finally the point corresponding to the highest pressure was once more obtained by adding 1.5508 grams of mercury:

Circuit made, 500, 500, 500, 500, 500, 500, 500, 500, 500, 500, 500.

Circuit broken, 500, 500, 500, 500, 500, 500, 500, 500, 500, 500, 500.

Here again the gauge correction being +0.5, the corrected reading was 500.5.

These results may be stated in the following briefer form:

#### OBSERVATIONS CONCERNING THE COMPRESSIBILITY OF SODIUM BROMIDE.

Pressure interval kgs/cm <sup>2</sup> .	Separate drops mercury added. Grams.	Mercury per 100 kgs/cm <sup>2</sup> . Gram.	Total mercury added. Grams.
103 to 205	0.4281	0.420	0.428
205 to 302.5	0.3943	0.404	0.822
302.5 to 403	0.3743	0.372	1.197
403 to 503.5	0.3595	0.353	1.556
505.5 to 75.5	-1.6763	...	-0.120
75.5 to 102	0.1161	0.438	-0.004
102 to 500.5	1.5508	...	+1.547

The calculation of the amount of mercury which must be added between 100 and 500 pressure units is shown below. From the third column of the table above it can be estimated with sufficient accuracy that 0.0043 gram of mercury must be added for each unit of pressure through the range 100-103 pressure units, and 0.0035 gram per unit of pressure through the range 500-503.5. The calculations which follow are equivalent to the curves previously used for finding the exact amount of mercury, W, needed over the range 100-500.

Pressure interval.	Mercury added.
100 -103	0.0129 (calc.)
103 -205	0.4281
205 -302.5	0.3943
302.5-403	0.3743
403 -503.5	0.3595
503.5-500	-0.0122 (calc.)
<hr/>	
100 -500	1.5569 = W
<hr/>	
500 -503.5	+ 0.0122 (calc.)
503.5- 75.5	- 1.6763
75.5-102	+ 0.1151
102 -100	- 0.0086 (calc.)
<hr/>	
500 -100	- 1.5566 = - W
<hr/>	
100 -102	+ 0.0086 (calc.)
102 -500.5	+ 1.5508
500.5-500	- 0.0017 (calc.)
<hr/>	
100 -500	1.5577 = W

Thus three values for W, 1.5569, 1.5566 and 1.5577, were obtained. The difference between the extremes of these three values is only 0.0011, which corresponds to only 0.3 pressure unit. The mean is  $W = 1.557$ . The compressibility of sodium bromide is calculated from this average with the help of the formula already given on p. 103 by substituting  $W = 1.557$ ,  $W_0 = 0.381$  (for jacket B),  $K = 2.809$ ,  $A = 40.65$ ,  $D = 3.08$ .

$$\beta = \frac{(1.557 - 0.381 - 0.3863 \times 2.809) 3.08}{400 \times 13.57 \times 40.65} + 0.00000371 = 0.00000498.$$

$\beta = 4.98 \times 10^{-6}$  = the average compressibility of sodium bromide over the range 100-500 kilograms per square centimeter.

Two other preliminary sets of determinations on sodium bromide, by W. N. Stull on another sample of powdered material gave the values 4.88 and 4.91, respectively. This close agreement is very satisfactory. The result 4.98 is probably the most trustworthy because made on a much larger scale.

### Data and Results Concerning Twelve Salts, the Chlorides, Bromides, and Iodides of Sodium, Potassium, Silver and Thallium.

The determinations were all carried out in essentially the same way, except for such slight differences of detail as was demanded by the slightly different condition or behavior of the substances.

In the following table the data for twelve salts are given in a much more condensed form. Xylene was usually used with the potassium and sodium salts, and water with the thallium and silver salts. Mercury could not be allowed to come in contact with the silver salts, as a reaction takes place under the great pressure with the formation of free silver and mercurous salts. There is no danger in allowing the mercury to come in contact with the thallium salts. In the first experiment with

thallium chloride, in which the material was used in the form of a cylinder, it was feared that mercury was being forced into cracks or internal cavities. The experiment was therefore repeated, after breaking the cylinder into many pieces in order to open any internal cavities, but the result was essentially unchanged. The result for thallium chloride is probably not as reliable as for the others with the possible exception of potassium and sodium iodides, which may be in error on account of the slight decomposition which took place when these salts were fused.

The last column of this table contains the values of the several compressibilities. For convenient reference, these new data are tabulated below by reference to each of the three units of pressure, the kilogram per square centimeter, the megabar<sup>1</sup> and the atmosphere. These values are based on 0.00000371 for the average compressibility of mercury between 100 and 500 kilograms per square centimeter, or 0.00000383 for its compressibility for each atmosphere over about the same range. The numbers in the table must be multiplied by  $10^{-6}$  to obtain the true value.

COMPRESSIBILITIES $\times 10^6$ AT 20.00° C.			
	Kgs/cm <sup>2</sup> .	Megabars.	Atmospheres.
Hg standard....	[3.71]	[3.79]	[3.83]
KCl.....	4.93	5.03	5.09
NaCl.....	4.03	4.11	4.17
TlCl.....	4.6	4.7	4.8
AgCl.....	2.18	2.22	2.25
KBr.....	6.11	6.23	6.35
NaBr.....	4.98	5.08	5.15
TlBr.....	5.0	5.1	5.2
AgBr.....	2.54	2.59	2.62
KI.....	8.4	8.6	8.7
NaI.....	6.8	6.9	7.0
TlI.....	6.57	6.70	6.79
AgI.....	3.85	3.93	3.98

Attention should be called to the possibility that each of these figures may need to have a small constant correction added to it, in order to equal the true absolute value. The uncertainty is due to our lack of certain knowledge of the absolute compressibility of any single substance. The present investigation gives merely the difference between the compressibility of the substance under investigation and that of mercury. As stated above, the compressibility of mercury, Amagat's value, slightly corrected for its probable decrease with rising pressure, namely, 0.00000383 between 100 and 500 atmospheres, has been assumed. This value has received support in several directions, but it does not seem to be consistent with Amagat's calculated values for iron and copper. Our work has shown that the difference between the compressibility of iron and mercury is 0.00000343 for each atmosphere, which would

<sup>1</sup> A megabar is 1,000,000 dynes per square centimeter, or 0.987 atmosphere.





make iron only 0.00000040, whereas Amagat calculates it to be 0.00000068. If Amagat's value for iron (or his value for copper, which shows similar relations) is correct, evidently about 0.00000030 should be added to each value, including that of mercury, and mercury would become about 0.000000410. Very recently, E. Grüneisen has brought forward further arguments in support of a higher value, obtaining (by an indirect method resting upon several assumptions) values for a number of substances which correspond very closely to the values found at Harvard, provided that a small quantity be added to each of the latter. In the course of this paper, Grüneisen criticizes quite erroneously one feature of the Harvard apparatus, but has afterwards withdrawn his criticism<sup>1</sup> and corrected his own error.

Amagat's work on mercury is supported by some approximate determinations of the linear compressibility of iron and copper made at Harvard, but this work had no pretense to great precision, as was clearly indicated in the original paper, and does not add any very important evidence.

From these statements, it is clear that no certain knowledge of any absolute value is at hand. As soon as any one of the substances mentioned in the present series of papers is known, that of mercury can easily be calculated, and all the other values may be immediately computed by simply adding to them the increment which the value for mercury suffers on account of the new knowledge.

For the present purpose, the absolute values are of little importance, as will be seen in the discussion which follows. We are concerned here as in the previous monograph upon this subject merely with the relative values, and the results as tabulated above will serve amply as a basis for the discussion of the matter in hand. It is hoped that before long, however, either here or elsewhere, a really reliable determination of the absolute value of some one of the substances may be made, so that all the values may be reduced to the proper standard. It is needless to say that this determination of the absolute value is a matter of great difficulty, but it will amply repay the expenditure of much time and labor.

The **only compound** in the above table concerning which we have found previously published data is rock salt, for which Voigt<sup>2</sup> found 0.0000042, identical with our value, and Röntgen and Schneider<sup>3</sup> 0.000005.

#### **Comparison and Interpretation of the Results.**

It now becomes a matter of great interest to compare these results for the compressibilities of twelve salts with each other, as well as with

<sup>1</sup> *Ann. der phys.* [4], 25, 849 (1908); withdrawal of criticism, *Ibid.* [4], 26, 397 (1908) (foot-note).

<sup>2</sup> *Volgt, Wied. Ann.*, 31, 479 (1887).

<sup>3</sup> Röntgen and Schneider, *Ibid.*, 34, 531 (1888).

the compressibilities of the elements concerned. In order to simplify the comparison, the several results are tabulated in the accompanying table, which contains the compressibilities of the seven elements as well as those of the twelve salts made from them. The values given represent the fractional decrease in the original volume of the salt produced by the pressure of one megabar, and for convenience in tabulation, each value is multiplied by one million.

COMPRESSIBILITIES OF SEVEN ELEMENTS AND THEIR SIMPLEST COMPOUNDS, BETWEEN 100 AND 500 MEGABARS. EACH FIGURE IS MULTIPLIED BY 1,000,000.

Element	Chlorine.	Bromine.	Iodine.
Potassium.....	31.5	51.8	13.0
Sodium.....	15.4	6.2	8.6
Thallium.....	2.1	5.1	6.9
Silver.....	0.8	4.7	5.1
		2.2	2.6
			3.9

Before comparing these results it may be worth while to present the same facts in another form, giving the decrease in the atomic or molecular volume (instead of the decrease in a unit volume) corresponding to each unit of pressure. By analogy, these new figures may be called the atomic or molecular compressibilities of the several substances. For some purposes, these are more rationally comparable than are the specific compressibilities. They are calculated from the latter by simply multiplying them by the atomic volumes. The following table contains atomic and molecular compressibilities thus calculated.

ATOMIC COMPRESSIBILITIES OF SEVEN ELEMENTS AND MOLECULAR COMPRESSIBILITIES OF THEIR SIMPLEST COMPOUNDS, BETWEEN 100 AND 500 MEGABARS.

EACH FIGURE IS MULTIPLIED BY 1,000,000.

Element.	Chlorine.	Bromine.	Iodine.
Potassium.....	1430	2400	1330
Sodium.....	365	188	271
Thallium.....	35.5	111	170
Silver.....	8.6	160	192
		57	75
			163

Several regularities are immediately apparent in these results. In the first place it is clear from the first table that each salt has a compressibility smaller than the average compressibility of the two elements concerned. From the second table, which takes account of the fact that the elements do not exist in the compounds in equal weights, one finds the almost equivalent rule that the molecular compressibility of each of these salts is less than the sum of the atomic compressibilities of the elements constituting it. This smaller compressibility of the two elements after they have reacted upon one another is exactly what one would have expected. The reaction with its decrease of free energy in the reacting system implies development of new affinities before latent.

These new affinities would be expected to cause greater internal compression on the average than was previously present, and substances which are under greater compression, are almost always less compressible. Hence the elements in this new condition would be expected to be less compressible than they were in the free state under less internal pressure; the facts are thus wholly consistent with the hypothesis of compressible atoms.

In the next place, one is at once struck by the fact that the potassium salts are, in each compound with halogen, the most compressible, and the silver salts in each case, the least compressible, sodium and thallium both lying between. One would have been inclined to predict this fact from the compressibilities of the elements concerned; because, as may be seen at a glance through the table, potassium is the most compressible of the four metals, and silver the least. But the matter is by no means so simple in every case, for the thallium salts are much more compressible in proportion to the sodium than one would have expected from the relative compressibilities of the metals. The salts of the two elements are almost alike in this respect, while metallic thallium is only about one-sixth as compressible as sodium.

Clearly, the compressibility of the elements is not the only factor determining the compressibility of a compound, a fact which will be appreciated yet more clearly when the subject is amplified. We shall see that the compressibilities of the elements are rather a subordinate matter; far more essential are the conditions governing the nature of the compound itself.

In order to interpret the phenomena, a moment's thought must be given to the circumstances which determine the volumes occupied by substances in the solid and liquid states. It has been shown that we must imagine the existence of at least two kinds of internal pressure in all solids or liquids except those elementary substances which may have monatomic molecules.<sup>1</sup> These two kinds of pressure may be called respectively *chemical pressure* and *cohesive pressure*, the first being produced by chemical affinity and the second by cohesion; and there is good reason to believe that each form of pressure exerts an effect in diminishing the volume of the material. Whether or not cohesion is effected by the same sort of attraction as that which causes chemical action is unimportant here. It has not, as yet, been possible to determine in any given case exactly what proportion of the total change in volume during a chemical change is due to the chemical affinity and what proportion is due to the change in the cohesion, nor has it been possible to separate the heat effect into its two corresponding components; but the quali-

<sup>1</sup> Richards, *Proc. Am. Acad.*, 39, 581 (1904). *Z. physik. Chem.*, 49, 15 (1904).



tative study of numerous cases strongly supports the consideration given above.

Now, almost if not quite without exception, it has been found, as has been said, that compressibility diminishes with increasing pressure; that is to say, the addition of an atmosphere's pressure causes a smaller change of volume when a substance is already under great pressure than when it is not. Thus, when a substance is comparatively incompressible, we have some right to infer that it is already under great pressure. Conversely, coming to the case in hand, we have a right to guess that the salts of thallium, which are much more compressible than one would have expected, must be under small internal pressure, either chemical, cohesive, or both. But the chemical affinity of chlorine for thallium is not far from the average affinity of chlorine for other metals, judging from the amount of heat given out by the reaction; hence, the deficiency of internal pressure must be due rather to feeble cohesion than to the chemical cause. Accordingly, the inference may be drawn that thallium chloride has less *cohesive* affinity than the other chlorides now under consideration.

In a previous paper<sup>1</sup> it has been shown that in general, the more volatile the substance, the greater the compressibility, other things being equal. This seems to be entirely reasonable, because volatility implies slight cohesive affinity, and slight cohesive affinity would be expected to exert only a slight internal pressure. Hence, one would predict that thallium chloride ought to be more volatile than the other chlorides. The prediction was made before the relative volatility of the various salts was known to the experimenters, and the facts entirely justify it. Carnelley and Carleton-Williams<sup>2</sup> found that thallium chloride boils under an atmosphere's pressure at 720°, and the iodide at 810°, the bromide presumably lying between the two, in this as in most other respects. These temperatures are far below those at which the other halides volatilize. The boiling points of the alkaline salts (the halogen salts of sodium and potassium) have not been accurately determined, but qualitative experiments in tubes of fused quartz have shown that all the chlorides boil considerably over 1200°, and not far apart.<sup>3</sup> Silver chloride, a substance of quite another kind, was found by Biltz and Victor Meyer<sup>4</sup> to boil at even a higher temperature. They reported it to be non-volatile at 1400° and only slightly volatile at 1700°. Thus the thallium halides boil at a temperature much below the others, and it is clearly reasonable to ascribe the unexpectedly great compressibility of these thallium salts at least in part to their comparatively small cohesive tendency.

<sup>1</sup> See page 158, line 13.

<sup>2</sup> Carnelley and Carleton-Williams, *J. Chem. Soc.*, 33, 284 (1878).

<sup>3</sup> Richards, *Proc. Am. Acad.*, 39, 589 (1904). *Z. physik. Chem.*, 49, 24 (1904).

<sup>4</sup> Biltz and Victor Meyer, *Ber.*, 22, 727 (1889).

The slight volatility of silver chloride has already led to the suspicion that it must possess high cohesive affinity.<sup>1</sup> The comparatively small compressibility of the salt is quite in accord with this indication of great cohesive pressure.

The bromides are immediately seen to fall between the chlorides and iodides as we should expect according to the periodic system, but another fact that at once impresses the student of these results is the excess in compressibility of the bromide over the chloride, and of the iodide over the bromide. This shows once more that the compressibility of the free elements cannot serve as a certain clue to the compressibility of the compound formed from them, for chlorine is more compressible than bromine, and bromine more compressible than iodine, while their salts differ in exactly the opposite direction. A moment's thought serves to explain the anomaly, however. Evidently at least a part of the difference in the compressibilities of the elementary halogens is due to the difference in the cohesive affinity which exists in them. Chlorine is much more volatile than bromine, and bromine much more volatile than iodine. It is reasonable to suppose that if these elements had all been subjected to the same internal cohesive pressure in the free state, they would not be so far apart in compressibility. In this case there is no difficulty in explaining why the bromides should be more compressible than the chlorides and the iodides more compressible than the bromides, for in the bromides the chemical affinity seems to be in every case less than in the chlorides, and in the iodides less than in the bromides, while in most cases the cohesive affinities vary in the same way. The chemical affinity is best gauged in simple reactions of this kind by the heat of reaction, and this is known to decrease greatly as the atomic weight of the halogen increases. The facts are given in the following table, from which the reader may verify the statements just made.

HEATS OF FORMATION OF THE TWELVE HALIDES IN KILOJOULES PER GRAM MOLECULE.

	Chloride. <sup>2</sup>	Bromide.	Iodide.
Potassium.....	433	398	335
Sodium.....	399	359	289
Thallium.....	194	173	126
Silver.....	114	95	58

Of course these results given above signify changes in total energy,

<sup>1</sup> Richards, *Proc. Am. Acad.*, 39, 589 (1904). *Z. physik. Chem.*, 49, 24 (1904).

<sup>2</sup> The heats of formation of the chlorides are calculated as from liquid chlorine, by subtracting the latent heat of vaporization of chlorine (9 kilojoules per gram atom) from the usual values based on chlorine gas. Incidentally, attention may be called to the fact that this value for the heat of vaporization (due to Knietzsch, *Z. Elektrochem.*, 9, 847 (1903) is not far from that calculated by Richards from the change of vapor pressure with the temperature, 10.2 kilojoules (*Proc. Am. Acad.*, 37, 400, (1902)).

not in free energy, but few would be disposed to deny that the figures are here a safe guide; and that in every case the affinity of bromine for the metals is less than that of chlorine, and iodine less than that of bromine.

The cohesive affinity is less accurately known, but if the melting point is taken as a guide, the *alkaline* halides at least have their cohesive affinities ranked in the same order as their chemical affinities.

MELTING POINTS OF THE HALIDES.

	Chloride.	Bromide.	Iodide.
Potassium.....	736°	700°	636°
Sodium.....	774°	710°	630°
Thallium.....	440°	460°	442°
Silver.....	454°	430°	528°

Although this latter table is not wholly without bearing upon the question, it is by no means a perfectly safe guide to the relative cohesive affinities of the several substances. The facts already stated concerning thallium and silver salts point to the danger of inferring cohesiveness from melting point—for the thallium salts are far more volatile than the silver salts, and yet all six melt at nearly the same point. The melting point is too much affected by the exigencies which determine crystal form to be a sure guide to internal pressure.

Unquestionably the heat of vaporization of a salt is a far better guide to its cohesive affinity than the melting point; and because boiling points show a regular relation to heats of vaporization, these too are better than melting points for this purpose. Unfortunately, however, there are no exact data for the heats of vaporization or boiling points of the alkali and silver bromides and iodides from which safe conclusions in regard to their relative cohesive affinity can be drawn. This lack of information is fortunately partially compensated by the measurements of Quincke<sup>1</sup> on the surface tension of several fused salts. Richards and Mathews<sup>2</sup> have shown that surface tension is connected with all the other properties



Fig. 4.

indicating cohesive affinity, hence these measurements are directly pertinent to the case in hand. Quincke poured the fused salts on a flat surface, so as to produce large drops with plane upper surfaces. The difference in height between the plane of the upper surface and the plane of the maximum diameter is a constant for any substance, which depends only on the surface tension and density of the liquid and therefore can be

<sup>1</sup> Quincke, *Pogg. Ann.*, 138, 141 (1869).

<sup>2</sup> Richards and Mathews, *THIS JOURNAL*, 30, 8 (1908). *Z. physik. Chem.*, 61, 449 (1908).

used to measure the surface tension. The surface tension is calculated by the formula  $\gamma = a^2 dg/2$  (due to Gauss) where  $\gamma$  = surface tension in dynes per centimeter;  $a$  = difference in height between the upper plane surface and the plane of the greatest diameter (in centimeters);  $g$  = acceleration of gravity (980.6); and  $d$  = density of liquid.

Quincke determined the densities of the fused salts by finding the loss in weight of a sphere of platinum on immersion in the fused salt. The dimensions of the drop were not determined while it remained liquid, but only after solidification and cooling to room temperature. It is probable that a slight distortion occurs during the solidification and cooling. Moreover, the method only measures the surface tension at the melting point, whereas a knowledge of the cohesion at 20° is desired for the present purpose. However, in spite of these sources of error, we can accept these results as an approximate indication of the relative cohesive affinities of the salts, because the deviations are probably similar for all of the salts and only relative values are needed.

The following table gives Quincke's results for the salts under consideration.

	<i>d.</i>	<i>a.</i>	Surface tension.
KCl.....	1.612	0.296	69
NaCl.....	1.612	0.290	66
LiCl.....	1.515	0.292	63
AgCl.....	5.3	0.286	210
KBr.....	2.199	0.212	48
NaBr.....	2.448	0.202	49
AgBr.....	6.2	0.2	120
KI <sup>1</sup> .....	2.497	0.220	59 <sup>1</sup>

It will be noticed that the surface tensions of potassium, sodium, and lithium chloride are nearly the same, and that the slightly lower value of the surface tension of lithium chloride agrees with a recent observation that lithium chloride is somewhat more volatile than the others.<sup>2</sup> The large value for the surface tension of the silver salts accords with their small compressibility and high boiling points. The most important point to be noticed in this table is that in each case the surface tensions of the bromides are much less than the surface tensions of the corresponding chlorides. Thus everything points toward affinities, both chemical and cohesive, less in the cases of the bromides than in those of the chlorides; and this probable existence of less internal pressure in the bromides is quite enough to explain the fact that the bromides are more compressible than the chlorides.

Similarly the compressibility of the iodide is in every case greater than

<sup>1</sup> This experiment is unreliable because potassium iodide is partially decomposed by fusion in air.

<sup>2</sup> Richards, *Proc. Am. Acad.*, 39, 590, foot-note (1904). *Z. physik. Chem.*, 49, 24 (1904).

the compressibility of the bromide of the same metal in spite of the smaller compressibility of iodine, indicating that the iodides are in a less compressed condition than the bromides. The decrease in the chemical compression probably plays a greater part in this case than in the former. The heats of formation of the bromides of these four metals are on the average 11 per cent. less than the heats of formation of the corresponding chlorides, whereas the heats of formation of the iodides are on the average 26 per cent. less than the heats of formation of the bromides. Unfortunately there are no data available which are capable of furnishing reliable indications of the relative intensity of the cohesive attractions. The single measurement of the surface tension of potassium iodide by Quincke, which gave a result intermediate between the surface tensions of potassium chloride and bromide, must be considered very unreliable because potassium iodide is decomposed by fusion in the presence of air, and the oxide or hydroxide would probably increase the surface tension of the mixture.

In the case of silver iodide, one of the most abnormal of all solids, the melting point can be of no service; but here the experience of Baxter<sup>1</sup> is available, showing that it is distinctly more volatile than the chloride.

Another, but somewhat more hypothetical method of drawing conclusions concerning the magnitude of internal pressure in a substance is from its coefficient of expansion. If the assumption<sup>2</sup> is made that the affinities do not change greatly with temperature, the increase of volume caused by rise of temperature must be supposed to be accomplished only by work done against these affinities. Some of the energy added may be supposed to exist simply in the form of increased kinetic energy in the molecules, but this in similar salts may be nearly constant. Hence, it is not unreasonable to draw inferences concerning the relative internal pressures in several similar substances from the obvious distending effect of definite amounts of energy in the form of heat.

The changing of a gram molecule of a simple substance from  $t^\circ$  to  $t^\circ + \Delta t^\circ$  Centigrade involves the addition to it of an amount of energy represented by the rise of temperature,  $(\Delta t^\circ)$  multiplied by the molecular heat capacity of the substance ( $C$ ), or  $C\Delta t$ . If this energy is all used in increasing the volume of the substance, we may write  $C\Delta T = P\Delta v$  in which  $P$  is the internal stress against which the heat-energy is doing work, and  $\Delta v$  the increase in volume. Dividing by  $\Delta v$ :—  $P = C\Delta t / \Delta v$ .

While this pressure (represented by the quotient of the added energy divided by change of volume, caused by the energy) can hardly represent anything very definite, it must nevertheless be supposed in a general

<sup>1</sup> Baxter, *THIS JOURNAL*, 27, 885 (1905).

<sup>2</sup> This idea has been expressed in other words in an article by one of us in *Proc. Am. Acad.*, 37, 8 (1901). *Z. physik. Chem.*, 40, 174 (1902).

way to increase when the self-affinity increases. Hence, while giving no certain knowledge, its study may give an indication of affinity, especially in the case of similar salts.

This principle is less applicable to the case of salts than to the simpler case of elements, but its application to the salts whose compressibility has been determined, is not without interest. Concerning seven of the salts, there are data available for the specific heat and coefficient of expansion. For the specific heats the results of Regnault<sup>1</sup> may be accepted since he is the only experimenter who has determined all seven of the specific heats needed, and here it is more important to have the data relatively correct than absolutely accurate. The measurements of the coefficients of expansion were made by Fizeau<sup>2</sup> by an optical method. The data are given in the following table, and there compared with the molecular compressibility.

The last three columns in this table are the results to be compared, the so-called "energy quotient," representing the supposed internal pressure.

Salt.	Sp. heat in calories = $C_p$ .	Molecular heat capacity in mayers $C_p M$ . 4.181.	Linear coefficient of expansion = $\alpha$ .	Molecular cubic expansion = $3V\alpha$ .	Energy quotient $C_p M / 3V\alpha = P$ .	Specific compressibility $\times 10^6$ .	$P^{4/3}\beta$ .
KI...	0.1819	56.9	0.0000427	0.00684	8300	8.6	1.4
KBr.	0.113	56.3	0.0000420	0.00548	10300	6.2	1.4
KCl. .	0.171	53.3	0.0000380	0.00426	12500	5.0	1.5
NaCl.	0.214	52.3	0.0000404	0.00327	16000	4.1	1.7
AgBr	0.0739	58.1	0.0000347	0.00302	19200	2.6	1.3
AgCl.	0.0911	54.6	0.0000329	0.00255	21400	2.2	1.3
AgI..	0.0616	60.5	-0.0000139	-0.000173	...	3.9	...

The salts are arranged in this table in the order of increasing internal pressure, except in the single case of silver iodide. It will be observed at once that this is in the order of decreasing compressibility, excepting again the case of silver iodide, which is wholly abnormal and will be considered later. The regularity can hardly be the result of chance alone. In so far, these facts support in a qualitative fashion the conclusion already suggested, for it would be expected that those salts possessing the highest internal pressure would be the least affected by the addition of further outside pressure. The last column in the table contains an approximate constant, calculated by multiplying the  $4/3$  power of the internal pressure by the compressibility  $K = P^{4/3}\beta$ . While this value is not strictly constant, it ranges nevertheless between very much smaller limits than either of the data from which it is calculated, and is sufficiently constant to indicate an approximate rule in the order of sequence. It is not without interest to call attention to the fact that this function

<sup>1</sup> Regnault, *Ann. de Chim. et Phys.* [3], 46, 278 (1858).

<sup>2</sup> Fizeau, *Pogg Ann.*, 132, 292 (1867)

found empirically in this case is similar in the mathematical form to the empirical function found by Richards and Mathews,<sup>1</sup> namely  $\gamma^{4/3}/\beta = \text{constant}$ . The surface tension ( $\gamma$ ) may be supposed to be due to the internal pressure  $P$  which we are considering at present, and it is conceivable that the similarity of the mathematical form is not the result of accident.

As has been said, the case of silver iodide is abnormal in many respects and does not correspond with the other halides given in the table. The existence of a single exception of this kind among numerous other examples pointing unanimously in another direction usually does not imply that the relations are all of them wholly fortuitous, or invalidate a rule inferred from the large majority. It is more likely that the exception is due to some other superposed influence which conceals in this single case the general rule without invalidating it for the others. On this account an exception is especially interesting, because it may be expected to afford entirely new intelligence; and the case of silver iodide is therefore worthy of further study.

Silver iodide is, as has been said, anomalous in many respects. In the first place it is one of the very few solid substances possessing a negative coefficient of expansion. Previously fused quartz below  $-80^{\circ}\text{C}$ . is said to behave in this way,<sup>2</sup> but beside this substance and silver iodide no other pure solid substance contracting with increasing temperature is known to us.<sup>3</sup> As will be shown in another paper, this rare property of silver iodide does not necessarily connect itself with the other abnormalities that the salt exhibits, but it is nevertheless worthy of notice here. The negative coefficient of expansion leads to the calculation of an internal pressure by the foregoing method of  $-350,000$ —an absurd result which shows that at least in some cases the assumptions made in the calculation of  $P$  are at fault. This matter will receive further discussion in another place; it will be shown that the faulty assumption is probably the assumption that the affinity is unchanging with the temperature.

In the next place silver iodide is one of the very few substances which expands on going from a high temperature phase to a low temperature phase. A comprehensive qualitative investigation of Rodwell<sup>4</sup> has shown that while silver iodide contracts on solidifying to a transparent solid and this transparent solid contracts on cooling to a temperature of about  $120^{\circ}$  in the usual way, a low temperature variety is formed below

<sup>1</sup> Richards and Mathews, *THIS JOURNAL*, 30, 8 (1908).

<sup>2</sup> Dorsey, *Physical Rev.*, 25, 10 (1907). Scheel, *Ber. physik. Ges.*, 5, 3.

<sup>3</sup> Water between  $0^{\circ}$  and  $4^{\circ}\text{C}$ ., and liquid bismuth for eight degrees above its melting point [see Lüdeking, *Wied. Ann.*, 34, 21 (1888)] have negative coefficients of expansion, also the mixture nickel-steel [see Guillaume, *C. R.*, 136, 303 (1903)].

<sup>4</sup> Rodwell, *Chem. News*, 30, 288 (1874); 31, 4 (1875).

this point with considerable expansion. It is this low temperature variety (whose true transition temperature has since been found by Mallard and LeChatelier<sup>1</sup> to be  $146^{\circ}$ ) which manifests the negative coefficient of expansion, that is to say, which increases still more in size as it cools down to room temperature. Clearly the act of transition into the low temperature variety is that which takes the silver iodide from the ranks of the usual into those of the abnormal; only very few substances expand on passing from a high temperature phase to a low temperature one. This low temperature phase has an altogether abnormally large molecular volume, as may be seen by comparison with the iodide and bromide of silver. The bromide has a molecular volume only a little more than 3 cm. greater than the chloride, while the difference between the iodide and bromide is almost four times as great. The three values are 25.79, 29.01, and 41.40, respectively.<sup>2</sup> This abnormal molecular volume of silver iodide causes the substance to manifest yet another unusual characteristic, namely, it expands in volume when it is formed from the elements, although the reaction is one which evolves heat, and which manifestly also involves the expenditure of free energy, as it takes place of itself.

Thus silver iodide, a substance which we should expect (from its great compressibility and small heat of formation) to have a larger molecular volume than the bromide or chloride, not only confirms but exceeds these expectations to such an extent that it forms an exception to other rules which govern the vast majority of material substances.

As has been said, a careful study of the behavior of the salt shows that this contradiction occurs at the moment it changes from the high-temperature variety to that hexagonal crystalline form which is most stable below  $146^{\circ}$ . The infraction of the rules applicable to most other substances, therefore, must be traced to the tendency which causes the appearance of a definite form of crystals and the further analysis of this matter would take one too far afield in the present paper. It is enough to call attention to the similarity of this case to that of ice and of gray tin, for whose abnormalities an explanation has already been offered.<sup>3</sup>

In this connection we may recall the fact shown earlier in this paper that silver iodide is less compressible than the elements from which it is made. This is very singular, considering the fact that it occupies more space than they occupy. As a general rule the less bulky form of any substance is the less compressible, but this rule also is broken by this peculiar compound.

It is interesting to note that Mallard and LeChatelier found silver

<sup>1</sup> Mallard and Le Chatelier, *C. R.*, **97**, 102 (1883); **99**, 157 (1884).

<sup>2</sup> See Baxter, *Am. Chem. J.*, **31**, 563 (1904); also *THIS JOURNAL*, **26**, 1585 (1904).

<sup>3</sup> Richards, *Proc. Am. Acad.*, **39**, 594-6 (1904); *Z. physik. Chem.*, **49**, 28-30 (1904).



iodide at  $20^{\circ}$  under 2500 atmospheres to turn into a variety having a molecular volume 16 per cent. smaller than the hexagonal volume. The decrease in volume due to the pressure alone could not exceed 1 per cent., as calculated from the compressibility, 0.000004, hence this great change must be due to the appearance of a much denser phase, possessing a specific gravity of as much as 6.8 and a molecular volume of only 35, instead of the values observed under ordinary pressures—namely, 5.674 and 41.4, respectively. This denser form, judging from its simpler refractivity, is much more allied in its structure to the chloride and bromide of silver than the hexagonal iodide, and is probably the form which ought to be considered in any systematic comparison of the properties of the salts. Its molecular volume being less than the sum of the atomic volumes of the elements composing it ( $35 < [25.75 + 10.49 = 36.04]$ ), this variety behaves as the great majority of other substances do, contracting during its exothermic formation.

Ice, also, one of the very few other substances abnormal as to volume, exists in a much denser form under similar high pressures, as Tammann has shown.<sup>1</sup> Here again the hexagonal crystal-making tendency seems to be the cause of the abnormality, and both of these striking exceptions cease to be abnormal when the substances are subjected to a pressure great relatively to atmospheric pressure, but probably small compared with the pressures already existing in the substances.

#### Relation of Compressibility to Heat of Reaction.

In conclusion, it is worth while to point out the fact that the results on the compressibilities of salts discussed in this paper throw further light upon the relation of volume change during the reaction and the heat of reaction. In a recent paper it was shown that the contraction concerned in a chemical reaction exhibits under favorable conditions a parallelism with the contraction of volume taking place during this reaction. The conditions favorable for showing this parallelism are the combinations of a variety of elements with a single very compressible one, and the chlorides furnish an especially striking series. Two curves were drawn giving on the one the heat evolved when the various chlorides are formed and the change in volume in cubic centimeters which occurs on the change of these compounds from the elements.<sup>2</sup>

A copy of these curves is shown on the opposite page. The figures correspond to two gram atoms of chlorine. It will be noticed that the curves are in large degree parallel, and that the greatest deviations from

<sup>1</sup> Tammann, *Kryst. und Schmelz*, p. 315, Leipzig, 1903.

<sup>2</sup> See Richards, *Proc. Am. Acad.*, 37, 402 (1902). *Z. physik. Chem.*, 40, 600 (1902). In the original the heat of formation of silver chloride corresponding to one gram atom of chlorine is given instead of double this quantity to correspond with the other salts. This error has been corrected in the present diagram.

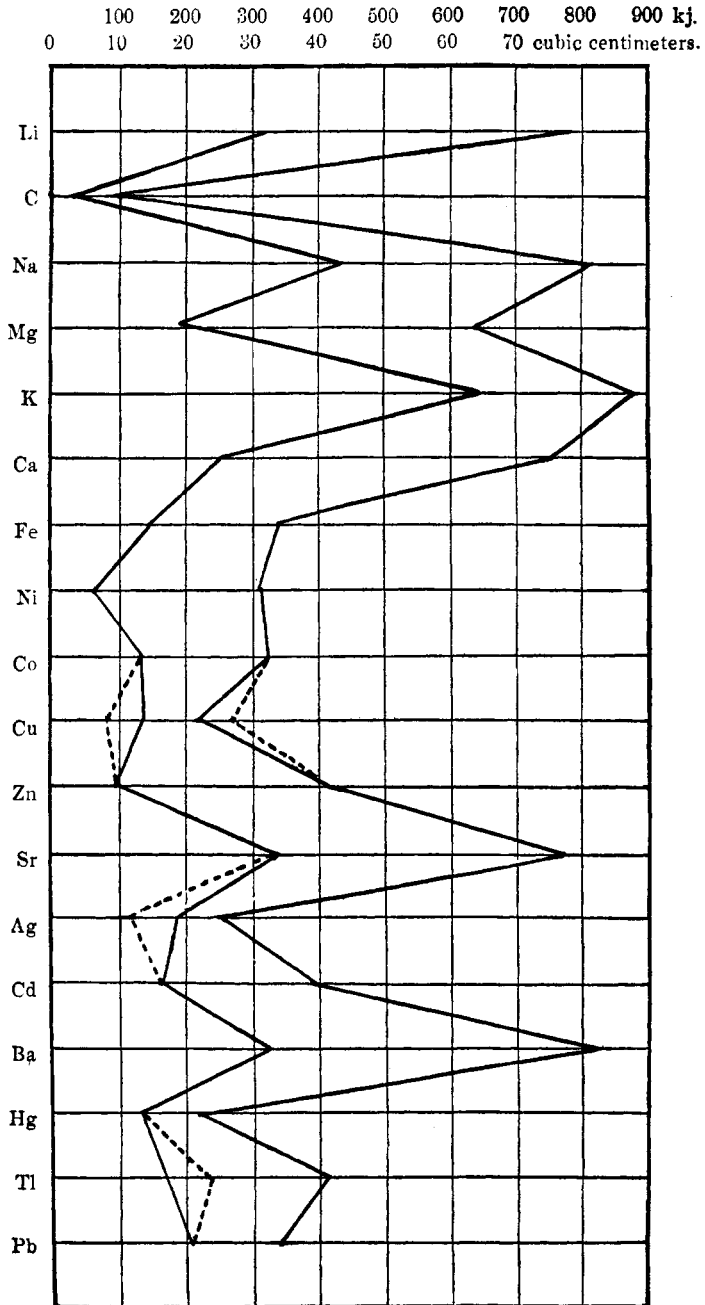


Fig. 5.

Chlorides.—Parallelism of contraction with heat of formation.

the parallelism are exhibited by copper, silver, and thallium chlorides. In order to show these deviations more clearly, the contractions which would be necessary in these cases to preserve the parallelism are indicated by dotted lines. The case of copper is a complicated one, not immediately coming under our present discussion, because the chloride given in the table is the cupric salt, and we are at present considering only the simplest kind of salts containing two atoms to the molecule. Therefore no attempt will be made here to explain the deviation of copper chloride, although incidentally it may be interesting to know that cuprous chloride, whose data correspond to the dotted lines, is no exception to the more general rule.

Turning now to the two other exceptions, namely, silver and thallium chlorides, it is clear that the results found in the present paper entirely explain their anomaly. The deviation from the parallelism of the two curves in the case of silver chloride is clearly due to the highly compressed state of this salt. In a previous paper<sup>1</sup> this was suspected from its high boiling point, and the present data confirm this suspicion by pointing out the high surface tension and low compressibility of silver chloride—both of which would be expected from a substance with considerable cohesive pressure. This cohesive pressure, in addition to the chemical affinity, would be expected to produce an abnormally large contraction, not accompanied by a correspondingly large heat effect. It has already been shown that changes in volume due to cohesive energy probably develop less heat than the same changes in volume due to chemical affinity.<sup>2</sup>

The deviation in the case of thalious chloride is exactly opposite to that in the case of silver chloride, the contraction during the formation of thalious chloride being less than is necessary to produce parallelism in the two curves. This opposite behavior can now be explained by the unusually low cohesion of thalious chloride, as shown by its comparatively large compressibility and low boiling point.

If silver and thallium chlorides possessed the same degree of cohesive affinity as the chlorides of the alkali metals, there is every reason to believe that silver chloride would suffer less contraction during its formation and thallium chloride more contraction. The dotted lines in the diagram are drawn to indicate this supposition and illustrate the present explanation of the deviation of the actual properties of these substances from the general rule of parallelism between contraction and energy change.

It is clear, therefore, that the present work upon compressibility, with its closer study of the volume relations of solid substances, affords

<sup>1</sup> Richards, *Proc. Am. Acad.*, 39, 589 (1904). *Z. physik. Chem.*, 49, 23 (1904).

<sup>2</sup> Richards, *Proc. Am. Acad.*, 39, 588 (1904). *Z. physik. Chem.*, 49, 22 (1904).

support for the hypothesis that the volume of material is essentially dependent upon the internal pressures existing within that material, because it explains some of the most palpable exceptions shown by the first crude test of that hypothesis.

### Summary.

1. The compressibilities of twelve salts have been determined—the chlorides, bromides, and iodides of sodium, potassium, silver, and thallium. The values between 100 and 500 megabars (*c. g. s.* "atmospheres") pressure are as follows:

Sodium chloride, 0.0000041; sodium bromide, 0.0000051; sodium iodide, 0.0000069; potassium chloride, 0.0000050; potassium bromide, 0.0000062; potassium iodide, 0.0000086; silver chloride, 0.0000022; silver bromide, 0.0000026; silver iodide, 0.0000039; thalious chloride, 0.0000047; thalious bromide, 0.0000051; thalious iodide, 0.0000067.

2. The relative values of the compressibilities of these salts have been correlated systematically with the volatility, surface tension, internal stress and heat of formation of the salts, as well as with the compressibility of the elements and the contraction which occurs during the formation of the salts from their elements.

3. It is shown that the new facts support the hypothesis that the volumes of liquids and solids are essentially dependent upon the chemical and cohesive affinities existing within them, and hence afford new evidence of the significance of changing atomic volume.

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## AN EXPLANATION OF THE NEGATIVE COEFFICIENT OF EXPANSION OF SILVER IODIDE.

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Silver iodide has the remarkable and almost unique property of decreasing in volume when its temperature is raised. Fizeau<sup>1</sup> has measured the coefficient of expansion of three different varieties, by a reliable optical method, and found the coefficient to be negative in every case. A cylinder of silver iodide, which had been previously fused and therefore consisted of closely-packed small crystals, was found to have a linear coefficient of expansion  $-0.00000139$  (mean temperature  $40^{\circ}$ ). Precipitated silver iodide which had been compressed until it was compact and coherent and took a good polish, but still retained its amorphous structure, was found to have the same linear coefficient of expansion  $-0.00000137$  (mean temperature  $40^{\circ}$ ). The linear coefficient of expansion of a single large hexagonal crystal was found to be  $-0.000003966$  in the direction of the principal axis and  $+0.000000647$  in a direction at

<sup>1</sup> Fizeau, *Pogg. Ann.*, 132, 292 (1867).