Entropy of Bromate Ion.—Now $Ba(BrO_3)_2 \cdot H_2O = Ba^{++} + 2BrO_3^- + H_2O$. Using the value for Ba^{++} given by Latimer and Buffington,[1a] and that for water obtained by Latimer and Greensfelder[1d] from the data of Simon and others, we find $S^{\circ}_{BrO_3^-} = {}^1/_2(80.72 + 26.48 - 15.92 - 4) = +43.6$ E. U., and the entropy of BrO_3^- at 298.1°K. = +43.6 E. U., with respect to $S^{\circ}_{H^+} = 0$.

The greatest uncertainty is the value for the heat of solution and it is planned to check this value by a direct experimental determination.

The authors wish to thank Mr. J. Elston Ahlberg of this Laboratory for assistance in the experimental work and calculations.

Summary

The specific heat of $Ba(BrO_3)_2 \cdot H_2O$ has been measured from 16 to 300°K. These values, together with the heat and free energy of solution of barium bromate, have been used to calculate the entropy of bromate ion in hypothetical one molal aqueous solution.

Berkeley, California

[Contribution from the Wolcott Gibbs Memorial Laboratory, Harvard University]

THE COMPRESSIBILITY OF THALLIUM, INDIUM AND LEAD[1]

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Introduction

Existing data on the compressibility of thallium are in apparent conflict. The first pertinent experimental work[2] on this metal (about twenty years ago) gives the value 2.85×10^{-6} for the cubic compressibility at 20° over the pressure range 100–500 megabars. Fifteen years afterwards, P. W. Bridgman published a determination[3] seeming to indicate that the cubic compressibility under the same conditions may be considerably larger—about 3.5×10^{-6}. This latter determination was based upon the linear compressibility, actually measured, which was multiplied by three on the assumption that thallium is isotropic. Bridgman pointed out that the large difference between his value and the earlier

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[1] *Note by the Editor.*—This research was completed in 1927 under the direction of Professor Theodore W. Richards but the present account of it was prepared after the death of Professor Richards by Dr. Lawrence P. Hall.

[2] Richards and Stull, *Carnegie Institution of Washington*, Pub. No. 76, **1907**, p. 65. The value there given, 2.6, after correction for the new compressibility of mercury, for slight errors in the pressure gage and to the megabar standard, becomes 2.85×10^{-6}. The value given on page 62 is wrong through typographical error—a misprint which has unfortunately been copied elsewhere (for example, This Journal, **37**, 1646 (1915)).

[3] Bridgman, *Proc. Am. Acad. Arts Sci.*, **58**, 198 (1922).

one "strongly suggested that the crystal system cannot be cubic."[4] If this were the case, of course, his determination of the linear compressibility means little unless the direction in relation to the crystal axis is known; and since the specimen was an extruded one, definiteness in this respect is unlikely.

The discrepancy prompted further experimental investigation, especially desirable since compressibility has acquired important significance in relation to internal pressure. The earlier work referred to above was of a pioneering nature and was made to discover rather the order of magnitude of various compressibilities than the precise values, although indeed the results have nearly all of them, except this one, been confirmed within a narrow limit of error by subsequent investigators. Accordingly, the present investigation was carried out with greater care.

The earlier result was in fact found to be very close to the true value. Bridgman's inference as to the cause of the discrepancy of his value and ours is supported; it has been confirmed, moreover, very recently by Terpstra, and others,[5] who have shown that the crystal structure of metallic thallium is face-centered tetragonal, similar to that of indium and gallium. Becker and Ebert state that the axial ratios are almost unity, but according to Terpstra the ratio is 1.58. This would account for the wide discrepancy in values for the compression coefficient.

The compressibility of indium also was studied; because of the fact that only a very small amount of the metal had been available for the use of previous experimenters. This outcome also, verified the earlier work at Harvard within a reasonable limit of error.

The compressibility of lead was redetermined as a test of the methods used.

Preparation of Materials

Mercury was purified in the usual fashion by passing it in fine drops through dilute nitric acid and by final distillation, according to Hulett. Toluene was purified by shaking a commercially pure sample with three successive portions of concentrated sulfuric acid, each time washing with water, dilute sodium hydroxide and again with water. After standing over anhydrous calcium chloride, it was shaken with separate quantities of clean mercury until no further tarnishing of the mercury took place; subsequently the toluene was distilled. The middle fraction (mean boiling point, 110° at 760 mm.) was preserved over sticks of sodium hydroxide in a glass-stoppered bottle and used in the determinations.

The lead was a very pure specimen, most of which had previously been used for the purpose.[6]

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[4] In an anisotropic crystal there is a marked difference in linear compressibility ong its different axes. See, for example, Bridgman's values for zinc, ref. 2, p. 217.

[5] (a) P. Terpstra, *Z. Krist.*, **63**, 318 (1926), quoted in *C. A.*, **20**, 3105 (1926); (b) Becker and Ebert, *Z. Physik*, **16**, 165 (1923).

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

Thallium

The purification of the thallium offered much difficulty. Several hundred grams of crude thallium containing several per cent. of impurities (mostly lead and zinc) served as a starting point. This was dissolved in hot dilute nitric acid and the crystals of nitrate were treated with concentrated sulfuric acid in slight excess. After all of the nitric acid had been expelled at a high temperature and fumes of evaporating sulfuric acid were evolved, the sulfate paste was dissolved in excess of pure water and the residual lead sulfate was separated. Small amounts of thallic oxide formed were reduced with sulfurous acid. The sulfate was once crystallized and from its solution thallium was deposited electrolytically, having present an excess of sulfuric acid sufficient to prevent the deposition of zinc at the cathode and thallic oxide at the anode. It was necessary to make this solution very dilute to avoid the inclusion of sulfate and the current density was kept low in order that the metal should be precipitated as compact, well-defined crystals. As usual, great current density produced only a spongy product. From time to time the crystals were removed by means of a small glass fork from the cathode to a casserole, in which they were leached free of salt and acid by many successive additions of pure, boiled but cool water, and preserved in a glass-stoppered bottle filled to the neck with freshly boiled water. These precautions are necessary; otherwise the substance on subsequent fusion will contain sulfate and oxide, rendering fusion difficult and the product impure.

When ready for fusion the thallium was shaken free of all superficial water by centrifuging, dried as rapidly as possible in a vacuum desiccator and fused in a steady flow of pure hydrogen at a temperature of 400°, whereby traces of mercury and other volatile impurities were driven off. The surface of the fused and cooled mass was scraped free of most of the slag (presumably thallium oxide) and the porcelain boat which served to contain the metal was transferred to a specially designed slag funnel. On remelting by uniform heating, the thallium was quickly poured into a clean glazed boat, the slag remaining behind. Finally, the purified metal was cast into a cylinder and turned in a lathe to fit the piezometer.

Indium

The method of preparation of the allied metal, indium, was not dissimilar, although not quite identical. The source was a large quantity of material obtained in several lots as a by-product from a recent research on the atomic weight of gallium.[7] Part had been prepared in preliminary fashion during vacation by Dr. Craig, who very kindly gave it to us for the present purpose. The original source of all was the Oklahoma residues described elsewhere.

The particular specimens used had been largely freed from lead, copper, gallium and arsenic, as well as much of the zinc. Further steps were necessary, however, to obtain adequate purity. The first lot of this material was dissolved by an excess of sulfuric acid and the warm, dilute solution treated with hydrogen sulfide. The precipitate was removed; after partially neutralizing with ammonia, the filtrate was again saturated with hydrogen sulfide, and the small amount of precipitated indium sulfide mixed with impurities was again filtered off. Zinc and iron still remained to be separated, at least in part. For this purpose fractional electrolysis was tried. Neither a strongly acid nor a completely neutralized solution gave satisfactory results, but electrolytic deposition could be effected when the solution was about half normal in acid.

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[7] Richards and Craig, THIS JOURNAL, **45**, 1155 (1923).

With suitable current density (easily regulated) the indium was deposited in compact form on stout platinum wires (about 1 cm. long) sealed into soft glass tubing. At first only the tip of the cathode was covered with electrolyte. During six or seven hours, somewhat less than 1 g. per hour could conveniently be deposited on each electrode. The small pieces of indium were washed with water and preserved under freshly prepared distilled water. All the fractions contained zinc, since the current density was too great to separate this metal from indium.

These nuggets, although they had been somewhat protected against oxidation, were so much oxidized that they refused to melt together in a current of hydrogen. To effect coalescence, the drops of melted indium were rubbed together under paraffin at the temperature of about 170° (melting point of indium, 156°).[8] Stirring the material under this protecting environment caused the slag to be suspended in the paraffin, whereas the melted metal easily united into a bright, coherent globule. Some of the material is, of course, lost with the slag, but at least 70% may be recovered.

The clean metal thus prepared, after being all melted together and freed from paraffin with benzene, was re-melted and cast into a cylinder of a proper diameter to fit the piezometer. The tube for casting, of proper bore, containing the indium, was allowed to cool very slowly by being gradually lowered through a ring burner, the solidification of the metal taking place from below upward. Thus the formation of cavities within the cast metal was prevented. The cylinder thus obtained weighed approximately 35 g. and was used for preliminary determinations of compressibility.

Since neither the quantity nor the purity of this specimen was adequate for the best possible results, a larger specimen of purer material was prepared for the final determinations. The 35 g. specimen itself formed part of the raw material for the new sample. It was fractionally crystallized as metal three times, 22 g. of purer material being thus recovered. The several fractions poured off as liquid, which contained much of the zinc, were then dissolved in dilute sulfuric acid, filtered from a trace of lead sulfate, treated with hydrogen sulfide, again filtered and freed from the gas, precipitated as indium hydroxide, leached with 5 separate portions of dilute pure caustic potash to remove as much as possible of the residual gallium and zinc and then washed a number of times by decantation with water. This solution was then combined with other similar ones to be described.

The most impure of the residues were brought to a state of moderate purity before the process of further purification described above in detail was applied. In this preliminary treatment the sulfite method was used to eliminate iron. Several other specimens of indium residue were also worked up by substantially the same method, and added to the material. A number of solutions, all of about the same degree of purity and containing a total of about 105 g. of indium, were combined and electrolyzed; nearly 90 g. of metal was separated and fused together in the way already described.

The solidifying point at this stage averaged 145.1°, as found by the method commonly used for organic compounds, while a sample of the pure indium used by Richards and Sameshima[9] gave a value 156°+ by the same method. Spectrographs were now made by an accurate Féry spectrometer, in order to determine the nature and quantity of the impurities. As was expected, considerable zinc still remained, but only faint traces of gallium were to be seen and nearly all of the lead also had been eliminated.

For final purification the method described by Richards and Craig for freeing gallium from zinc was used. Indium, like gallium, has a very high boiling point, whereas zinc, even from an alloy, has considerable vapor pressure at a bright red heat. Hence,

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[8] This device was suggested by Dr. Craig, based upon his experience with the material.

[9] Richards and Sameshima, THIS JOURNAL, **42**, 49 (1920).

by heating sizable portions of the sample in a large evacuated silica test-tube, the zinc was easily distilled into the upper part of the tube, taking with it only a very small amount of indium. Determinations of the zinc in the sublimates from weighed portions (by titration with ferrocyanide standardized against pure zinc) gave an average of 2.7% of zinc in the original metal. The melting points of different almost non-volatile residues varied from 154 to 156°. A cooling curve of the combined preparations (85 g.) gave a nearly constant temperature (155°) for four minutes, during which time almost all of the melted mass solidified (or, on warming, almost all of the solidified mass melted). The specific gravity of the metal thus prepared and very carefully cooled was found to be 7.296. Richards and Wilson[10] found the density to be 7.277, but their samples had not been cooled so carefully and may have contained minute air bubbles. Spectrographs of the non-volatile metallic mass showed it to be free from zinc. The amount of gallium remaining was only a trace and other likely metals were sought for but not found. Thus, although the claim cannot be made that this 85-gram specimen was absolutely pure, it was evidently more than pure enough to serve the purpose in hand. Zinc had been the only substance really difficult to eliminate and that was wholly eliminated by the process of heating to high temperature *in vacuo*.

Standardization of Absolute Gage

Since the exactness of standardization of pressure is important, the weights used in the absolute pressure gage were all carefully compared with a weight standardized by the Bureau of Standards at Washington. A second set of weights was also calibrated for use with a second (auxiliary) absolute gage, which was used only for comparison and calibration of the first gage, as will presently be discussed.

The pistons of both gages were accurately measured with Brown and Sharpe micrometer calipers and with a Newall measuring machine at the Taft-Pierce Co. of Woonsocket, R. I. The diameters of the cylinders to hold the gages were determined by measurement of closely fitting plugs. The first piston (used throughout the experiments) had a diameter of 0.6360 cm. and its cylinder had a diameter of 0.6368 cm. Hence, the value 0.6364 cm. was indicated as the effective diameter.[11] The second piston was 1.4003 cm. in diameter and its cylinder 1.4008 cm., with an effective diameter of 1.4006 cm. Since this second gage had almost five times the area of the first, the percentage accuracy of measurement was greater.

For comparison these two pistons were mounted in the usual way and "in parallel." The weights required to maintain an equilibrium between the two pistons were determined over a range of pressures and the effective area of the first piston was found in terms of the larger one.[12] This method of comparison proved to be an exceedingly sensitive one. By it the effective diameter of the working piston appeared to be 0.6366 cm. From a mean of these two estimates the effective area may be taken as

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[10] Richards and Wilson, *Carnegie Institution of Washington*, Pub. No. 118, 1909, p. 13.

[11] The effective diameter is taken as the mean of the diameters of cylinder and piston, cf. Richards and Shipley, THIS JOURNAL, **38**, 992 (1916).

[12] See Bridgman, *Proc. Am. Acad. Arts Sci.*, **44**, 214 (1909).

0.31824 sq. cm. One kilogram, then, on the absolute gage, would correspond to 3.0813 megabars (if based in 980.4 as the factor of gravity at Cambridge).

Method

The method employed was essentially identical with that invented twenty-five years ago and used by former workers in the Wolcott Gibbs Memorial Laboratory.[13]

The piezometer was of glass. All precautions (frequently reiterated in the past) were taken to avoid errors from hysteresis, etc. Under these circumstances the glass piezometer has appeared to yield as good results as the more complicated steel one.[14] The piezometer was filled with great care. Bubbles of air were excluded as completely as possible. At first a small amount of a lubricant of rubber and paraffin was used on the stopper of the piezometer. However, because this was so easily dissolved in the toluene, in later experiments either a sirup of phosphoric acid or a warm mixture of dextrose and glycerine[15] was substituted. The thermostat was kept at 24.840 ± 0.002°.

The piezometers were standardized with mercury. Since the metals under investigation were protected from mercury by toluene, the compressibility of toluene also had to be investigated. With piezometer No. 1 filled with mercury alone a change of 0.2685 g. of mercury was made in the side arm in going from 100 to 500 megabars. The constant at 24.84° for the toluene (density = 0.8616) was found to be 0.4219 g. Hg/g. of toluene from 100 to 500 megabars, because 26.5 g. of toluene needed 11.42 g. of mercury in the side tube over the pressure range. These values are the averages of many trials.

Hence, $w' = 0.269$ and $m = 0.4219$ for piezometer No. 1, using the equation $\beta = \frac{(w - w' - mK)}{5425\ W} D + \beta'$, where β is the compressibility sought, w the weight of mercury added in the particular case, w' the weight of mercury added when mercury alone is present, m the additional weight of mercury needed (in the side arm) when one gram of another liquid replaces an equal volume of mercury (within the piezometer), K the weight of the other liquid, D the density of the specimen, W its weight and β' is the compressibility of mercury; 5425 is 400 times the density of mercury at 25° between 100 and 500 megabars.

The value of β at 24.84° for this specimen of toluene is 70.9×10^{-6}. Richards and Shipley[16] found 69×10^{-6} at 20° for toluene.

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[13] For examples, see (a) ref. 2; (b) ref. 6; (c) a diagram of the apparatus will be found in *J. Franklin Inst.*, July, **1914**, p. 7.

[14] For comparison of glass and steel piezometers, see (a) ref. 6, p. 471; (b) Richards, Bartlett and Hodges, THIS JOURNAL, **43**, 1538 (1921).

[15] Tyrer, *J. Chem. Soc.*, **103**, 1678 (1913).

[16] Richards and Shipley, THIS JOURNAL, **38**, 998 (1916).

Compressibility of Lead

To standardize methods and to relate the results for indium and thallium with older work, the compressibility of lead was redetermined, using a cylinder which had been cast, hammered to remove possible imperfections in casting, and turned on a lathe to fit the piezometer. Its density was 11.346. Toluene was used as the confining fluid to transmit pressure to the specimen and to prevent lead from coming in contact with mercury. Sirupy phosphoric acid was used for lubrication of the stopper. The first experiment to measure the compressibility of lead was interrupted and therefore rejected. The successful experiments are recorded in Table I.

TABLE I

COMPRESSIBILITY OF LEAD AT 25°

Expt.	Wt. of toluene, g.	Wt. of lead, g.	Mercury, 100–500 meg., g.	$\beta \times 10^6$ (meg.)
1	2.663	314.140	1.153,[a] 1.153	2.41, 2.41
2	2.519	314.135	1.096, 1.084	2.43, 2.35
			Av.	2.40

[a] The two values given for each experiment are the weights of mercury required in the side arm. The first represents the weight in going from 100 *up* to 500 megabars, the second from 500 *down* to 100.

The value for β, 2.40×10^{-6} (in megabar units), at 25° may be compared with 2.35×10^{-6} at 20° found by Richards and Bartlett,[17] who used lead under water and mercury in a steel piezometer. When the value of these experimenters is corrected to 25°, 2.41×10^{-6} is obtained. The earlier value of Richards and Stull[2] corrected to present-day standards is also 2.4×10^{-6}. Bridgman[3] found 2.40×10^{-6} (in megabar units) at 30°.

The agreement of the values found by these new experiments on lead with the values presented in the literature indicated that the experimental method had been correctly executed and gave added weight to the significance of the new values obtained for thallium and indium.

Compressibility of Thallium

In the determination of the compressibility of thallium the value of w' for the piezometer used (No. 2) was found to be 0.2816 as the average of three experiments. The density of the casting used in the determinations was 11.85. In the first experiment a relatively large amount of toluene was used. This was lessened in the second by the addition of a small button of thallium to the piezometer. Sirupy phosphoric acid was used as a lubricant on the stopper.

Experiments 1 and 2 (Table II) were performed in June, 1925. Four months later the compressibility of this casting of thallium was redeter-

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[17] Ref. 6, p. 479.

mined (Expts. 3, 4 and 5) and essentially the same result for compressibility was obtained as before.

Table II

Compressibility of Thallium at 25°

Expt.	Toluene, g.	Thallium, g.	Mercury, 100–500 meg.		$\beta \times 10^6$
1	4.541	301.25	2.067		3.06
			2.022		2.74
2	3.913	309.70	1.772		2.89
			1.775		2.87
				Av.	2.89
3	4.650	301.59	2.090		2.89
			2.090		2.89
4	4.384	301.29	1.992		2.99
5	4.587	300.66	2.063		2.88
			2.073		2.69
				Av.	2.87
6	3.504	315.36	1.590		2.78
			1.584		2.82
7	3.398	315.35	1.541		2.79
			1.541		2.79
				Av.	2.80
				Av. of all	2.85

It was discovered during the second series of experiments that there was a minute "pipe" hole in one end of the casting. Although it did not appear that a significant error could be caused by this flaw, the metal was recast. Much experimentation was required to perfect a method of obtaining a casting free from flaws. The final procedure was to pour the melted thallium into a pyrex tube of proper bore, with a lining of magnesium oxide to prevent sticking of metal to glass. The tube had been previously heated. With its molten charge it was lowered vertically through an electric furnace. Cooling was effected from the lower tip very slowly as the tube descended. In this carefully controlled manner there was obtained a casting free from flaws. The specimen was cleaned, hammered, and fitted to the piezometer. The data for the determinations made from this specimen are found under Experiments 6 and 7. Although from these experiments β appears slightly lower than in the previous ones, the average of all the experiments (2.85×10^{-6}) cannot be far from the truth. If the mean is weighted by giving double credit to the last two experiments, since they were performed with a better cast specimen, the average 2.83×10^{-6} is obtained.

Compressibility of Indium

Indium–Zinc Alloy.—A preliminary series of determinations was carried out with a 35-g. sample of indium, containing about 3% of zinc (density 7.292). An iron cylinder was used in the lower part of the barrel of the piezometer to decrease the amount of toluene required. Although individual standardizations with the iron cylinder and also individual determinations of compressibility seemed satisfactory, there was exceedingly poor agreement of successive experiments for an unknown cause. From these preliminary experiments β for indium appeared to be about 2.4×10^{-6}.

Since part of the difficulty seemed to be in the lubricant used, Ramsay grease was used on the stopper, which necessitated the use of water as the confining liquid, although it reacts with indium very slowly, generating hydrogen. Contact of the indium with iron slightly accelerates the action. In a loaded piezometer left overnight an appreciable bubble of gas was found. However, a small amount of gas dissolves completely in the confining liquid and appears to cause no appreciable error.

A slight modification of procedure was made in starting at a pressure of 500 megabars, reducing the pressure to 100, and returning to the higher pressure. By this technique the same values of compressibility were usually obtained for "up" and "down" experiments. Standardization of the piezometer showed that 0.2045 g. of mercury was the added weight of mercury required in the side arm over the range 100 to 500 megabars due to the substitution of one gram of water for its volume of mercury within the piezometer (m in the equation), 0.4462 g. of mercury corresponding to 2.182 g. of water.

Mehl and Mair[18] found with a 25-g. sample of water the value 0.2044 at 25°. Three standardization experiments were made with approximately the same quantity of water used when the bar of indium was present. Over the pressure range of 100 to 500 megabars 0.1600 g. of mercury was required when 0.8576 g. of water was present; 0.1895 g. of mercury for 1.005 g. of water; and 0.1665 g. of mercury for 0.8838 g. of water. Hence, from the average of these results, the value of w' is 0.1605 on the basis of 0.8576 g. of water.

TABLE III

COMPRESSIBILITY OF 97% INDIUM ALLOY

Expt.	Water. g.	Indium, g.	Mercury, 100–500 meg.	$\beta \times 10^6$
1	1.1896	35.357	0.1895[a]	2.52
2	1.1584	34.215	.1845	2.53
3	1.1110	34.211	.1734	2.48
			Av.	2.51

[a] Identical values were obtained for both the "up" and "down" experiments.

Pure Indium.—The 35-g. sample was purified and combined with more indium to form a larger and purer specimen, which would not re-

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[18] Mehl and Mair, THIS JOURNAL, **50**, 55 (1928).

quire an auxiliary steel bar. The density of this larger casting was 7.296. Its density was redetermined several times during the course of the experiments, since on several occasions a slight amalgamation took place in the process of unloading the piezometer after a determination of compressibility. The spot amalgamated was immediately scraped free from mercury. Since no change in density resulted, it is unlikely that the small amount of surface amalgamation which occurred had any influence on the compressibility.

A piezometer of proper size for the cylinder of indium was standardized with mercury alone and the factor 0.1098 was found for the pressure range of 100 to 500 megabars. With 2.1820 g. of water there was required in the side arm over this pressure range 0.5560 g. of mercury; with 2.0541 g. of water, 0.5300 g. of mercury. This gives a value for m of 0.2045 and for w' a value of 0.5299 on the basis of 2.0541 g. water.

After Expt. 3 (Table IV), the indium was melted and recast, because after scraping of the amalgamated spots the cylinder fitted poorly and required a larger quantity of water. The new casting had a density of 7.297.

TABLE IV

COMPRESSIBILITY OF INDIUM

Expt.	Water, g.	Indium, g.	Mercury, 100–500 meg.	$\beta \times 10^6$
1	2.0059	81.538	0.4335	2.57
			.4375	2.64
2	2.2500	80.471	.4780	2.46
			.4780	2.46
3	2.2972	80.094	.4935	2.56
			.4935	2.56
			Av.	2.54
4	1.6500	85.070	.3540	2.52
				2.52
5	1.7102	84.727	.3700	2.58
			.3720	2.61
			Av.	2.56
			Average of all	2.55

The previous value for the compressibility of indium[9] ($\beta = 2.7 \times 10^{-6}$ at 25°) was determined with a sample of only 6.7 g. Essentially in accord with it is the value more recently determined and here presented, which was made with an 80-g. specimen.

From the value 2.55×10^{-6}, β for indium, and the value 1.7×10^{-6} for zinc, it may be calculated that an alloy of 97% indium and 3% zinc (approximately the amount indicated by analysis and density of the alloy) would have a compressibility of 2.52×10^{-6}, if the rule of mixtures holds. This calculated value is slightly higher than the value actually found for such an alloy (2.51×10^{-6}), as would be expected from the generalization that solid solutions have compressibilities somewhat lower than calculated by the rule of mixtures.[18]

Discussion

In Table V certain properties and constants of the members of the natural group which has recently been studied, together with those of

TABLE Va

COMPARISON OF PHYSICAL PROPERTIES OF CERTAIN NATURAL GROUPS

Element	At. wt.	Density at 20°	At. vol.	M. p., °A.	Scratch hardness Moh's scale	Cubic coeff. of expansion × 10^6
Cu	63.57	8.92	7.13	1356	3.0	50
Zn	65.38	7.14	9.15	693	2.5	82
Ga	69.72	5.91	11.80	303	1.5	[85]
Ge	72.38	5.36	13.50	1232	(3.0)	[22]
As (metal)	74.96	5.7	13.14	1073	(3.5)	16
Ag	107.88	10.5	10.26	1234	2.7	57
Cd	112.41	8.6	13.07	594	2.0	94
In	114.8	7.3	15.73	428	1.2	100
Sn (white)	118.70	7.31	16.24	505	1.8	67
Sb	121.77	6.68 (25°)	18.20	904	3.0	33
Au	197.2	19.3	10.21	1336	2.5	43
Hg	200.61	14.2[a]	14.15[a]	234	1.5	180[b]
Tl	204.4	11.85	17.23	577	1.2	90
Pb	207.22	11.34	18.2	601	1.5	88
Bi	209.00	9.80	21.3	544	2.5	40

[a] At melting point.

[b] Cubic coefficient for solid mercury is 125.

TABLE Vb

COMPARISON OF PHYSICAL PROPERTIES OF CERTAIN NATURAL GROUPS

Element	Av. compress. × 10^6 at 20° 100–500 megabars	Latent heat of vap. in Kj. per g. atom	n'	$P\theta$ megabars	Π kilomegabars	Space lattice
Cu	0.75	467	5.64	19,390	376	FCC
Zn	1.7	99	5.3	14,130	178	HCP
Ga	2.0	...	[6.0]	[12,350]	[125]	FCT
Ge	1.4 (30°)	500(?)	2.6?	[4,600]	376	Dia C
As (metal)	4.5	139	...	1,040	104	H not CP
Ag	1.01	249	6.76	16,130	208	FCC
Cd	2.1	96(?)	7.03	13,120	117	HCP
In	2.55 (25°)	...	7.42	11,470	72.5	FCT or H?
Sn (white)	1.9	325	6.9	10,320	108	T not FC
Sb	2.4	190	..	4,025	109	H not CP
Au	0.65	368	9.10	21,800	243	FCC
Hg	3.1[a]	59	7.91	13,100	41.3	H or FCT?
Tl	2.85 (25°)	120(?)	6.55	9,420	77	FCT or HCP
Pb	2.40 (25°)	193	7.75	10,340	72	FCC
Bi	3.0	176	..	3,920	77.5	H not CP

[a] At melting point.

neighboring groups in the periodic table of elements, are summarized. Most of these data are taken from "International Critical Tables," Vols. I and III. The values for cubic compressibilities and coefficients of expansion are, however, with the exception of germanium and mercury, those compiled by one of us some years ago.[19] The compressibilities of germanium and mercury have been calculated from Bridgman's data.[3,20]

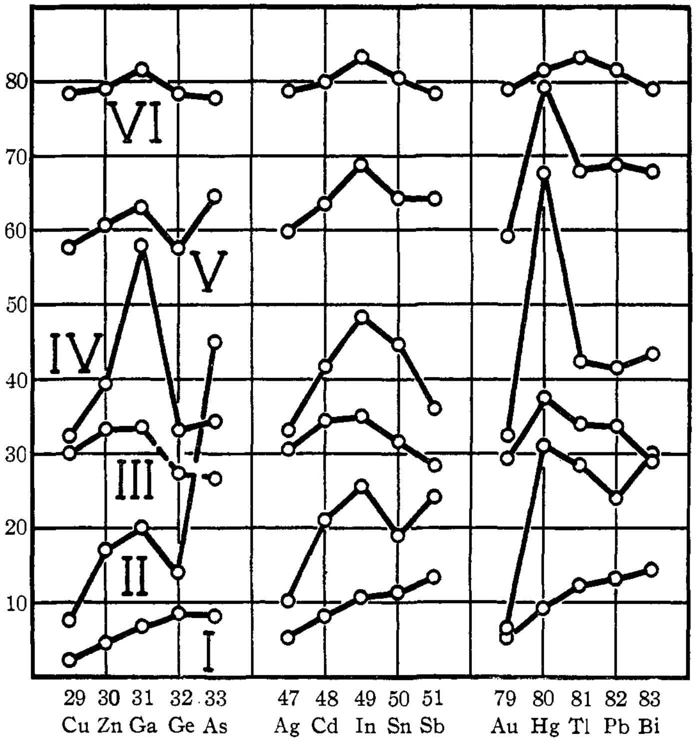

Fig. 1.—Curve I, atomic volume; II, compressibility ($\beta \times 10^7$); III, cubic coefficient of expansion ($\alpha \times 10^5 + 25$); IV, reciprocal of absolute melting point ($^1/_{T_m} \times 10^3 + 40$); V, reciprocal of internal pressure ($^1/_\pi \times 10^3 + 55$); VI, reciprocal of hardness ($\times$ 10 + 75).

The hardness values are after Rydberg.[21] The numbers in brackets have been calculated from insufficiently supported data. The values for n', $P\theta$ (thermal pressure) and π (internal pressure) are obtained from calculations making use of Richards' equations of state for solids and liquids.[22] A value of 2 has been assumed for m throughout. The symbols m and n' are the exponents representing, respectively, the rate of increase of the

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[19] (a) Richards, This Journal, **37**, 1646 (1915); (b) *ibid.*, **43**, 285 (1921).

[20] Bridgman, *Proc. Am. Acad. Arts Sci.*, **47**, 347 (1911).

[21] Rydberg, *Z. physik. Chem.*, **33**, 353 (1900).

[22] (a) Richards, This Journal, **46**, 1419 (1924); (b) *ibid.*, **48**, 3064 (1926).

internal cohesive pressure and of the internal distending pressure with decreasing volume. Values for π for all the elements listed, except germanium, arsenic, antimony and bismuth, were calculated from coefficients of compressibility and expansion data. These four were, for good reasons, calculated from latent heats of vaporization data. The coefficient of expansion for germanium is not known; while the calculation of internal pressures for the anisotropic crystals of the other three elements would lead to only approximate if not very erroneous values. The expansion and compression coefficients for arsenic, antimony and bismuth vary according to the direction chosen in the crystal, which indicates that their internal pressures are distributed very unevenly.[23] This fact applies to members of other groups appearing in Table V but not so rigorously. Consequently it seemed justifiable for qualitative considerations to proceed with the calculations as outlined above. In Fig. 1 are plotted various properties of the members of the groups indicated in Table V in relation to their atomic numbers. In the diagram the lowest curve represents atomic volumes (Curve I) and the one just above it compressibilities (Curve II). In addition, are curves for cubic coefficients of expansion (Curve III), reciprocals of the melting points in degrees absolute (Curve IV), reciprocals of internal pressures in kilomegabars (Curve V), and the reciprocals of hardness (Curve VI).

An examination of the curves in the diagram shows with but few exceptions an approximate proportionality between atomic volumes of the elements of any one family and their other properties. Thus, if the succeeding elements in the group have larger atomic volumes than the first one, then their other properties also have larger values.

On the other hand, an examination of the two lowest curves shows that although the atomic volumes of the elements in the gallium–indium–thallium group are intermediate between the atomic volumes for neighboring elements in the periodic table, the compressibilities are greater than those for either the preceding or succeeding neighbor except for mercury which, being a liquid, has an anomalous behavior. The same relations hold when atomic volumes are compared with coefficients of expansion, reciprocals of melting points and (excepting a reversed relationship between thallium and lead) reciprocals of internal pressure. In other words the members of the gallium family seem to occupy sub-maximum points on the upward slope of the completed periodic curves given in an earlier publication from this Laboratory.[24] This is remarkable in view of the generally accepted conclusion that there is an approximate proportionality between atomic volumes and related properties. The peculiar behavior of the gallium family may be explained in the following

[23] Richards, This Journal, **47**, 739 (1925).

[24] Ref. 19 a, p. 1649.

manner. Whereas the atomic volumes of its members are intermediate between their neighbors, their compressibilities show a decided maximum because other factors overbalance the effect of atomic volume. That is, their coefficients of expansion are larger, their melting points lower, and their degree of hardness much less.[25] These properties depend upon the important fact that the net internal pressure (that is, the resultant of the cohesive pressure, inherent distending pressure and thermal pressure) of these three metals is decidedly less than the net internal pressures of either the zinc or germanium family.

Acknowledgment is made for essential financial assistance from the Carnegie Institution of Washington and an anonymous benefactor of this Laboratory.

Summary

The compressibility from 100 to 500 megabars at 25° has been measured for lead ($\beta = 2.40 \times 10^{-6}$), thallium ($\beta = 2.83 \times 10^{-6}$), indium ($\beta = 2.55 \times 10^{-6}$) and an indium–zinc alloy containing 97% indium ($\beta = 2.51 \times 10^{-6}$).

The preparation of the pure metals is described. The special precautions and modifications in procedure for determining the compressibility of these specimens are presented in detail.

The thermal pressure ($P\theta$), the internal pressure (Π), and the coefficient (n') of rate of change of the internal distending pressure have been calculated according to Richards' equation of state. The periodic variation of properties is discussed with particular bearing on the gallium, indium, thallium group, which occupies a sub-maximum position.

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[25] For a discussion of the relation of compressibility and hardness, see Mehl, *Am. Inst. Min. Met.*, Tech. Pub. No. 57.