[Contribution from the Wolcott Gibbs Memorial Laboratory of Harvard University.]

THE COMPRESSIBILITY OF INDIUM.

By Theodore W. Richards and Jitsusaburo Sameshima.

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In a paper[1] collating recent values of the compressibilities of the elements, the periodic nature of compressibility was emphasized, especially in relation to the similar periodicity of other properties. In this connection, the values of these constants for indium and gallium are particularly interesting because of the low melting points of these substances. The compressibility of gallium has already been determined;[2] that of indium is recorded in the present paper.

The sample of metal used in the following determinations had been carefully purified, having been recovered by suitable electrolytic means from the amalgams used in an earlier electrochemical research.[3] It was cast in the shape of a cylindrical bar by slowly cooling liquid indium in an appropriate glass tube which had been coated with an exceedingly thin film of soft paraffin to prevent the adhesion of the metal to the glass. After cooling, the tube was broken and the ingot was removed, freed from traces of oxide and imperfections in casting at the upper end by cutting with a clean knife, and thoroughly cleansed from paraffin. The metallic rod thus obtained was 4.5 cm. long and 0.51 cm. in diameter and weighed about 6.7 g. The density of this bar was measured, in order to be sure that it contained no air cavities, by weighing first in air and then in water, suspended by a very thin wire, for which due allowance was made in the calculation. Two determinations gave the following results at room temperature:

Weight of indium	6.6928	6.6903
Volume of indium	0.9145	0.9152
Density of indium (20°)	7.318	7.310

A previous determination of this material (less carefully cast) gave the value 7.277.[4]

The method employed for the determination of the compressibility was in principle the same as that employed in most of the earlier work published from this laboratory. It has been often described, but a brief recapitulation is needful, in order that important improvements adopted in the present instance may be understood. A glass piezometer containing mercury is provided with a finely pointed platinum wire to make exact electrical contact with the meniscus forming the outer surface of the mercury in a tube of 1.5 mm. diameter. Successive weighed portions of mer-

[1] T. W. Richards, This Journal, 37, 1643 (1915).

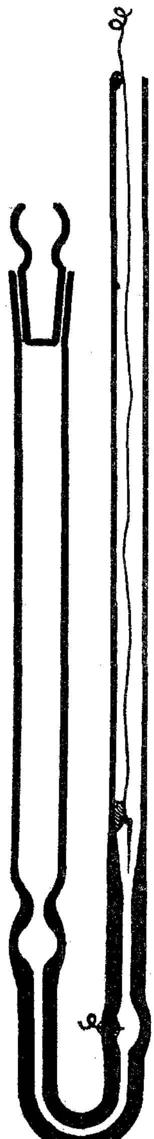
[2] Richards and Boyer, *Ibid.*, 41, 133 (1919).

[3] Richards and Wilson, *Carnegie Inst. Publications*, 118 (1909).

T. W. Richards, *Ibid.*, 118, 13 (1909).

cury added to the mass demand, of course, successively higher and higher pressures to force the mercury down to the exact contact-point.

Thus a curve, giving the relation of added weights of mercury to added pressure, is easily established. This having been done, the substance to be studied is immersed in the mercury, displacing some of that liquid, and a new similar curve is established. From these two curves the difference between the compressibility of the substance and that of mercury is readily computed. The compressibility of mercury being known, the datum sought becomes known likewise.



In the present case, since indium amalgamates vary readily, the solid metal cannot be plunged directly into the liquid one, but must be protected by an inert liquid (*e. g.*, water) which complicates the situation because of its far greater compressibility. The complication was largely neutralized with the help of an innovation introduced in the present case. By placing as nearly as possible the same amount of water in the piezometer during the initial measurements with mercury alone as is used afterwards to protect the indium, the final data were made practically independent of the compressibility of water, only a very small correction for a slight surplus or deficiency of this substance being required. Even this small correction was necessary merely because of the difficulty of making the quantities of water exactly identical. Practically, the indium simply displaced its volume of mercury, without coming into contact with it.

The consistent use of water had another even more important advantage; it made possible the employment of a much smaller piezometer, which (considering the very small quantity of indium at our disposal) greatly reduced the possible errors due to pressure-hysteresis in the glass, and to imperfections in the stopper of the piezometer. The glass vessel was made to fit closely the little bar of indium. The stopper, being only 0.55 cm. in diameter instead of over twice as much, could be fitted with great nicety. The instrument is shown in its actual dimensions, in the diagram. Such a small piezometer cannot be used with mercury alone since the compression of this quantity of the metal at 500 atmospheres is not enough to free the platinum point and obtain a satisfactory "make-and-break" contact. With a gram of water present the little instrument functioned admirably; the pressure of the "make" was only $^1/_3$ atmosphere less than that at the "break," and was doubtless much nearer than this (probably within 0.1 atmosphere) to the true value.

For small amounts of material, this device is perhaps even better than the elaborate steel piezometer[1] used in other recent work. The latter, to be sure, overcomes entirely the possible error due to hysteresis, but is no less subject to difficulties as regards the stopper than the glass piezometers, and can hardly be constructed on a diminutive scale commensurate with the small quantity of available indium.

The pressure gage was an absolute one,[2] of which the perfectly cylindrical plunger was found by careful measurement to possess a diameter of 0.25045 in., corresponding to an area of cross section of 0.31784 sq. cm. Thus, for example, a total weight on the piston of 166.820 kg. indicated a pressure of 514.7 megabars.[3]

The initial pressure used in the calculation was as usual 100 megabars—which is high enough to deprive possible minute air bubbles of most of their deleterious effect; and the final pressure was 500 megabars. In order to find the exact amount of added mercury needed between these limits, each curve showing the relation of pressure to weight of mercury was plotted on a large scale. The exact delineation of the curve near its extremities—usually a somewhat uncertain matter—was accomplished by a convenient device which may be of use in other cases.

A long, straight, flexible, uniform, rubber spline was bent, *by means of forces applied at the extreme ends*, so as to fit all the points. The curve being different in curvature at the two ends, the needful forces were of course different. Thus tendencies producing curvature, which cannot be very different from those causing the known part of the curve, were carried out beyond the extreme known points. The spline was light in weight, and with care was guarded against any considerable deforming effect of friction on the coördinate paper. The method was satisfactorily tested with known almost linear curves of the type at present concerned; with curves much more strongly bent it still yields fairly good results;[4] and for interpolated points near the ends of the curve it appears to be the best graphic method. Even when the two ends of the curve are quite different in curvature, the method serves well, provided, of course, that at least 4 points are known. With curves of a definite type, like these, 3 points serve sufficiently well if the extrapolation is moderate in extent and the relative forces needed for the ends are known empirically. The idea of exerting different bending forces on the two ends is essentially similar to

[1] Richards and Bartlett, This Journal, 37, 470 (1915).

[2] Richards and Shipley, *Ibid.*, 38, 989 (1916).

[3] A megabar is the pressure of a megadyne per sq. cm. or 0.987 "atmosphere."

[4] For example, the logarithms of 2.500, 3.000, 3.500 and 4.000 were plotted in relation to the numbers. Extrapolation by this method gave the value 0.611 as the logarithm of 4.1 instead of the true value, 0.613.

that of the excellent curve-ruler of Lord Berkeley;[1] but he did not emphasize the usefulness of the device for extrapolation Possibly others have done so, but we have not found reference to this point.

The readings on the coördinate paper were verified by calculation based upon the slopes of tangents to the curves at appropriate points midway in the stretches to be spanned.

The compressibility of indium was computed as follows:

let w = weight of added mercury needed for the range 100–500 megabars when indium, water and mercury were all present.

w' = weight of added mercury for the same range when only water and mercury were present.

w_2 = difference in weights of water present under these two circumstances.

W = weight of indium.

D = density of indium.

0.2069 = constant increase in the weight of added mercury over this range, due to the substitution of 1.000 g. of water for its volume of mercury.

5425 = 400 times the density of mercury at 25° under 500 megabars pressure.

β = the compressibility of indium.

β' = 0.0000400, = the compressibility of mercury at 25° between 100 and 500 megabars.[2]

Then

$$\beta = \frac{(w - w' - Kw_2)D}{5425 \times W} + \beta'.$$

Taking for example the first pair of measurements below (Expts. 1 and 2)

$$= \frac{(0.1973 - 0.2082 - [-0.207 \times 0.0216])\ 7.31}{5425 \times 6.693} + 0.00000400 = 0.00000270.$$

There follow all the necessary data, and the corresponding results are recorded in the last column.

Thus the compressibility of indium at 25° is seen to be 0.0000027, or about $^2/_3$ of that of mercury.

The experimental work may be verified by comparing the trials in which no indium was present, and among which therefore the differences should be due solely to the varying amounts of water. This comparison is reasonably satisfactory. The respective weights of water present in Expts. 1, 3, 5, 7 were 0.9463, 0.9309, 0.9235 and 1.0025; that is to say, the excesses of water above that in Expt. 5 (which contained least) were, respectively, 0.0228, 0.0074, 0.0000 and 0.0890. Multiplying each of these figures by the quantity 0.207 (the necessary amount of added mercury for one gram of water) and subtracting the products from the amounts of

[1] Lord Berkeley, *Phil. Mag.*, 24, 664 (1912).

[2] Bridgman has shown that the diminutions of volume of mercury caused by 1000 kg./cm^2. pressure at 0° and 22° are, respectively, 0.374 and 0.391% (*Proc. Am. Acad.*, 47, 380 (1911)). Hence the compressibility of mercury changes nearly 0.2% of its value per degree centigrade. Taking the compressibility of mercury at 20° over the range 100–500 megabars as 0.00000396 (Richards and Bartlett, THIS JOURNAL, **37**, 477 (1915)), its value at 25° must then be 0.00000400.

mercury actually added in the 4 cases, we obtain the figures 0.2035, 0.2043, 0.2048 and 0.2028. The departure of these figures from the mean 0.2039 indicates the actual error of experimentation. It is seen, then, that one can fairly count on the errors not exceeding one mg. of mercury in any given case, corresponding to a volume of less than 0.0001 cc.

No. of expt.	Wt. H_2O. G.	Wt. Indium. G.	Successive totals of added mercury. Mg.	Successive pressures. Megabars.	(w or w'.) Wt. of added Hg from 100 to 500 megabars. G.	Mean compressibility of indium $\times 10^6$.
1........	0.9463	0	0	60.0		
			29.8	113.9		
			76.2	119.6	0.2082	
			127.3	296.3		
			230.0	499.2		2.70
2........	0.9247	6.693	0	111.5		
			96.8	306.3	0.1973	
			198.1	514.7		
3........	0.9309	0	0	101.6		
			99.5	289.3	0.2058	
			204.2	498.5		2.57
4........	0.9295	6.690	0	114.7		
			99.1	309.0	0.1984	
			187.7	493.1		
5........	0.9235	0	0	87.4		
			100.4	276.1	0.2049	
			208.5	491.3		
6........	0.9222	6.690	0	84.4		2.73
			11.9	106.7		
			110.4	300.3	0.1988	
			215.3	519.0		
7........	1.0025	0	0	87.7		
			129.5	315.4	0.2212	
			232.0	506.8		2.75
8........	0.9963	6.238	0	99.0		
			120.2	317.9	0.2141	
			215.2	501.2		
Total average mean compressibility of indium...............						2.69

The actual error of any given pair of trials was doubtless even less than this, since especial care was taken to have each determination in a pair made under precisely similar conditions.

We are glad to express our indebtedness to the Carnegie Institution of Washington for financial assistance in this research.

Summary.

1. A modification of the usual piezometer was employed which allowed of accurate determination with very small amounts of solid material.

2. A convenient graphic method of extrapolating (for short distances) certain types of curves was employed.

3. The compressibility of indium at 25° over the range 100–500 megabars was found to be 0.0000027, or about $^2/_3$ that of mercury.

CAMBRIDGE, MASS.

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ON THE ESTABLISHING OF THE ABSOLUTE TEMPERATURE SCALE.

BY FREDERICK G. KEYES.

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A new equation of state was published[1] by the author, in 1917, based on an attempt to use the atom essentially as conceived by Bohr. The simplest form of the equation is that which would be valid for a system of one type of molecules, which is to say, substantially completely unassociated. The equation is as follows where p is the pressure, v the volume and T the temperature on the absolute scale,

$$p = \frac{RT}{v - \delta} - \frac{A}{(v - l)^2}.$$

In this equation δ is a function of the volume for polyatomic molecules and a constant for monatomic gases. Since, however, δ is equal to $\beta e^{-\alpha/v}$, where β and α are constants, the term δ reduces to β at large volumes.

In the paper referred to above the fundamental difference in the constant δ corresponding to van der Waals' (b) constant was predicted for a monatomic system as compared to a diatomic system of molecules. Argon and atmospheric nitrogen were chosen as examples, to test the prediction derived from the physical basis used to obtain the equation, the data for the former gas being due to Onnes. For the latter gas, data due to Amagat was employed. The constant δ was found to be constant in the case of argon and a function of the volume for atmospheric nitrogen. The agreement of the calculated pressures with the pressures recorded by Amagat for atmospheric nitrogen at temperatures from 0° to 200° is so close even up to 1000 atm. that it is interesting to investigate what comes out of the application of the atmospheric nitrogen equation to the problem of establishing the absolute temperature scale.

The usual mode of computing the corrections which a gas temperature scale requires has involved the use of Joule-Thomson data for the particular gas used. E. Buckingham reviewing the available data in 1907 completed an investigation which leaves nothing to be desired as regards completeness and skill. Recently more precise data has been supplied by L. G. Hoxton, but the temperature range has not yet been extended sufficiently to affect materially the conclusions reached by Buckingham.

[1] *Proc. Nat. Acad. Sci.*, 3, 323 (1917).