THE COMPRESSIBILITY OF ICE.

By Theodore W. Richards and Clarence L. Speyers.[1]

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This investigation was conducted during the year 1909, and a preliminary report, giving the results but no details, was published in the Year-Book of the Carnegie Institution of Washington for 1910.[2] In view of the fact that the compressibility of ice is a very interesting property from many points of view, and also because no other actual experimental determination of this constant seems ever to have been made, a more complete discussion of the data and results may be expedient.

The experimental details have already been so carefully described in previous papers from the Chemical Laboratory of Harvard College that further description is perhaps unnecessary. Of course it was imperative to work at a constant temperature so far below zero that the ice would not melt under pressure. This temperature (—7.03°) was maintained by packing the compression apparatus in ice, bathed in a dilute solution of common salt, into which portions of a more concentrated solution were stirred from time to time as the ice in the bath melted. The glass piezometer was first wholly filled with mercury, and subjected to carefully measured, gradually increasing pressures; afterwards it was partly filled with ice (which of course displaced an equal volume of mercury), and again subjected to quantitative compression. The determination of volume was effected by allowing the mercury to make contact with a very finely pointed platinum wire in a capillary tube, changes in volume being determined and measured by weighed globules of mercury added through the capillary. From the curves indicating the relations of added pressure to added mercury in the two cases, the difference between the compressibility of mercury and of ice is very simply calculated. The compression of the apparatus, occurring equally in the two series, is entirely eliminated from the result.

The form of piezometer was essentially that indicated by the diagram taken from a previous paper.[3] Dilute alcohol was used in the capillary above the mercury, instead of water as usual. It was found that in this apparatus in two successive and entirely distinct trials with mercury alone in the apparatus, a variation in pressure of 398 megabars[4] corresponded to 0.365 gram of mercury, and 416.5 megabars corresponded

[1] This paper was written after the death of Dr. Speyers. The experiments were carried out by the two authors in collaboration.

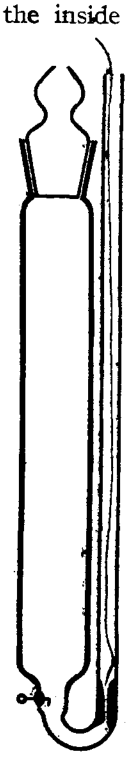
[2] Year Book, *Carnegie Institution of Washington*, 9, 221 (1910).

[3] This Journal, 34, 975 (1912).

[4] The megabar is the "atmosphere" of the c. g. s. system, being the pressure of one million dynes per square centimeter. It is about 0.987 ordinary atmosphere. See This Journal, 26, 4081 (1904). This standard of pressure has recently been adopted by the Blue Hill Observatory.

to 0.389 gram of mercury. Evidently then on the average 400 megabars correspond with 0.370 gram of added mercury. These determinations, which took place at —7.03°, were verified by two determinations at higher temperatures. The corresponding values for 0° and 20° were, respectively, 0.378 and 0.398. By extrapolating these values about the same result (0.373) is obtained as the average given above, so that (rating each determination as of equal weight) 0.371 may safely be taken as the mercury-constant of the apparatus. The pressure gauge was very carefully verified by reference to an absolute standard.

Into the apparatus thus standardized, ice was introduced in two ways. In the first place the solid was frozen as a hollow adherent cylinder in the inside of the piezometer, this having been filled with pure boiled, air-free water and packed in a mild freezing mixture. When about half of the water had been frozen, the remainder was poured out, and by carefully weighing the amount of ice clinging to the tube was determined and found to be 14.779 grams (in vacuum). While the apparatus was still packed in the freezing mixture, it was filled with cold mercury and the stopper adjusted with all the usual precautions so often described in previous papers. It was then subjected to quantitative compression at —7.03°, and the amount of mercury which must be added for 400 megabars' increase of pressure (between 100 and 500 as before) was found to be 1.079 grams, or 0.708 more than when the mercury alone was in the apparatus.



All this was done in warm weather, during the month of June, 1909. For fear that the clinging of the ring of ice to the glass piezometer might interfere with the exact determination of the compressibility, it seemed highly desirable that a free cylinder of ice also should be compressed in the same apparatus, but during the warm weather this was not easily feasible because of the melting of the ice during the weighing and transference. In the month of December, following, however, the confirmatory experiment was actually carried out in a very cold room. A cylinder of ice weighing 9.475 grams in vacuum was compressed in the same glass piezometer in the usual fashion, and the total amount of mercury added for 400 megabars was found to be 0.815 gram. Subtracting the change when mercury alone is in the receptacle, 0.444 is obtained as the difference between the mercury added in the two cases over this range of pressure. From the June experiment we should conclude that the introduction of 10 grams of ice into the vessel would cause an added mercury value of 0.479, and from the December experiment that 10 grams would produce a change of 0.470. Evidently the two determinations are essentially concordant and from their average the compressibility of ice is easily calculated by substitution in the usual equation so often used in previous work:[1]

$$\beta_{100-500} = \frac{0.474 \times 0.918}{13.64^2 \times 10 \times 400} + 0.00000398 = 0.00000120.$$

The deviation of each single result from the mean is less than 1%, which is as good an outcome as could be expected considering the difficulty of the problem.

Attention should be called also to the fact that the isotherms plotted from the observations showed but little curvature—indicating that the change in the compressibility of ice with increasing pressure is not large. The average compressibility of between 300 and 500 is probably not over 3% less than that between 100 and 300 megabars. Thus in the first experiment the change of pressure from 85 to 306 megabars needed an addition of 0.5970 gram of mercury, while the further rise of pressure to 500 megabars needed the almost proportional amount, 0.5140 gram more.

The compressibility of ice, 0.0000120, as thus found at 7.03°, appears, as has been said, to be the only value for this constant which has ever been found by direct experiment. It is about one quarter of the compressibility of water at neighboring temperatures, about five times the compressibility of glass, and somewhat less than that of metallic sodium. Bridgman, in his important and interesting work upon the various forms of ice, calculated by a somewhat elaborate thermodynamic treatment the compressibility of common ice (Ice I) at 0° as 0.000036, a value three times as large as that found in these experiments. Higher pressures yielded lower results, but not correspondingly low. He admits, however, that the figures are not very trustworthy. For Ice VI, a less bulky form, he determined the compressibility at pressures above 6500 atmospheres and at temperatures above 0°, finding it to vary from 0.0000055 to 0.0000037.[3] These values seem to be much more in accord with the present work than the result of his calculation, because Ice VI at high pressures might be supposed to have a compressibility about this much smaller than Ice I. Possibly the compressibility of common ice has an abnormally high temperature coefficient which might explain a part of the discrepancy.[4]

[1] *Loc. cit.*, p. 980. See also Stähler, *Arbeitsmethoden*, 3, 246–61 (1912). The value 0.00000398 is the compressibility of mercury over this range as computed from Bridgman's results together with some as yet unpublished results of Richards and Shipley. The preliminary adoption of this value is the reason for the fact that the values for ice given in this paper are slightly larger than in the preliminary publication.

[2] This is the density of mercury under 500 megabars' pressure at —7°.

[3] Bridgman, *Proc. Am. Acad.*, 47, 536 (1912). A later calculation gives 0.000045. Bridgman, *Ibid.*, 48, 362 (1912).

[4] Bridgman's computation of the compressibility of common ice is to be found in

It should be noted that Bridgman's method of experimentation, while admirably adapted for work under high pressures and constituting a really epoch-making contribution to this kind of work, is not particularly adapted to accurate work under comparatively low pressures, such as are considered in the present discussion. In view of the fact that work precisely similar to this present research, carried out with other solids in the Chemical Laboratory of Harvard College, has yielded results admirably concordant with the other most satisfactory work upon compressibility (taking into account the modern value of the compressibility of mercury); and also in view of the fact that our work upon liquids also agrees with Bridgman's, insofar as they are comparable, one can hardly escape the conclusion that the compressibility of ice is really as low as that found here. Incidentally it may be stated that the great apparent disagreement between certain of our results on liquids and the best work of others, as suspected by Bridgman,[1] really does not exist. In making the comparison, he overlooked the fact that our values are all given between 100 and 500 atmospheres, and therefore should not be immediately compared with the work of others over the whole range between the atmospheric pressure and 500 atmospheres.

In conclusion, it is a pleasure to acknowledge our indebtedness to the Carnegie Institution of Washington for generous pecuniary assistance in the conduct of this investigation.

Summary.

The compressibility of ice between 100 and 500 megabars is found to be 0.0000120 at —7.03° C., or about one-quarter of the compressibility of water at neighboring temperatures. It is found not to decrease remarkably as the pressure increases. This is probably the first direct determination of the compressibility of common ice which has ever been made. The difference between the low result and the higher value obtained by Bridgman through indirect calculation is probably due, at least, in part, to the existence of a large temperature coefficient.

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Proc. Am. Acad., **47**, 473 (1912). After the present paper had been sent to the press, upon having his attention called to its contents, he was able to verify the above prediction that the compressibility of common ice probably has an abnormally high temperature coefficient. With the help of his and other data, he has calculated that the average compressibility of ice between the zero of pressure and the melting pressure would be 0.000033 at 0°, 0.000023 at —5°, 0.000021 at —7°, 0.000019 at —10°, 0.000018 at —15°. The compressibility at —7° is still found to be higher than that given in the present paper, but nevertheless the agreement is much better than that of Bridgman's published results. He agrees with me in thinking that the remainder of the discrepancy may possibly be due to a considerable softening of the ice just before melting. This point is one of great interest, and will receive further experimental study here.

[1] *Proc. Am. Acad.*, **49**, 48, 74.