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indicates that the latter figure is probably more representative of the general accuracy of the results.

On comparing the two methods of this paper as regards uniformity of procedure and completeness of data, the piston displacement method is to be preferred for studying melting at high pressure. For the observance of poly- morphic changes in solids, it seems unlikely that the dynamic method of this paper could be used satisfactorily to fix transition pressures since the procedure would tend to widen regions of instability. However, for a rapid survey of possible solid-solid transitions, the dynamic method should prove to be useful for preliminary studies.

The Phase Diagram of Water to 45,000 kg/cm²

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ABOUT two years ago I found that ice VI is transformed into a new high pressure modification, ice VII, at pressures between 20,000 and 25,000 kg/cm². Although various incidental references have been made to this in print I have not yet published any numerical data on the transition because I wanted at the same time to present data for the melting curve of VII and for the compressibility. Values of these have now been obtained and are given in the following. The melting curve has been carried up to 190° and 40,000 kg/cm², and the parameters for it are fairly good. The compressibilities are much more difficult to obtain, and I have only rough values for the compressibility of VII. It would probably be possible to considerably improve the compressibility measurements with a new apparatus now under construction. However, I did not want to hold up publication of the data already at hand indefinitely until the new apparatus could be made to function, but I intend to publish later improved and more extensive compressibilities if it proves possible to obtain them. Because of the interest in all the properties of water it has seemed desirable to present these results in a paper by themselves, and in a journal somewhat more accessible than that in which most of my results for other phase diagrams have been published.

The new technique by which it has been possible to considerably extend my previous pressure range and to measure the parameters of polymorphic transitions has been sufficiently described in previous papers.[1] By a refinement of the same technique it is also possible to obtain rough values for compressibilities. It is, however, much more difficult to get a good value for compressibility at high pressures than it is to get the volume change at a transition, because there are various corrections for distortion and creep which do not enter into the measurement of the volume change at a transition. I do not propose to discuss here the various precautions which have to be taken in measuring com- pressibility, but shall reserve this for another paper, probably in *Proceedings of the American Academy of Arts and Sciences*, in which I shall give the compressibility of a number of sub- stances. It is sufficient here to remark that fairly consistent compressibilities can be obtained for the more compressible substances, but that the compressibility of the ordinary metals must be determined by some other method.

The chief technical difficulty in measuring water is the leak which occurs when it is in the liquid phase; this leak must be avoided if accurate values of the volume change on melting are to be obtained. The method adopted after a number of trials was to seal the water into a heavy lead capsule with Wood's metal. Even this is not entirely satisfactory, but the walls of

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[1] P. W. Bridgman, Phys. Rev. **48**, 893 (1935); Proc. Am. Acad. **72**, 46 (1937).

the capsule are likely to be pulled apart after pressure has been applied and released because of the large volume changes, the volume under 45,000 being of the order of 0.6 of the initial volume. Half a dozen different set-ups were made, terminated by leak or by rupture of the apparatus, in getting the final results. The actual pressure on the carboloy piston was pushed beyond 50,000 in exploring for still other possible modifications and in measuring the compressibility of VII at room temperature, but friction, which could be calculated from the difference between readings with increasing and decreasing pressure, cut down the actual maximum pressure inside the apparatus to the neighborhood of 45,000. No other modification of the solid was found up to this pressure.

The experimental results are collected in Figs. 1 and 2, and the numerical values of the various parameters in Table I. The triple point L–VI–VII is at 22,400 kg/cm² and 81.6°; the triple point parameters are included in the table. The various curves were so adjusted as to satisfy the various additive relations at the triple point. The fact that it was possible to do this without doing violence to the independently determined parameters on the various transition lines, as shown in Fig. 1, is presumptive evidence that the values cannot be far wrong. The parameters on the melt-
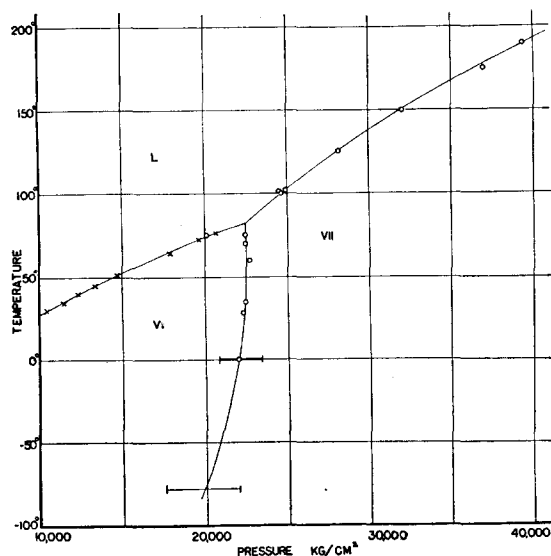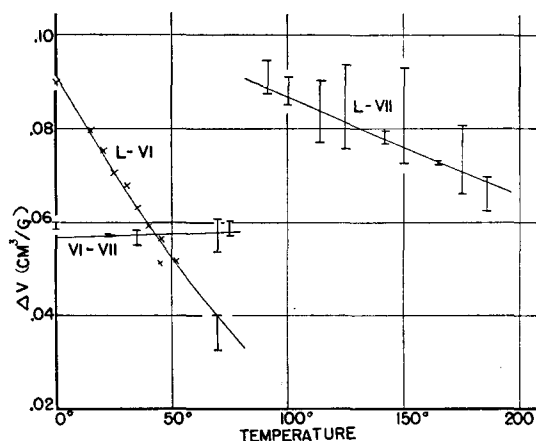

FIG. 2. The volume changes for the several high pressure transition in the water system. The crosses represent data obtained in 1912.

ing curve of VI were determined at only a single point. Previous measurements had been made to a maximum temperature of 76.4° on the melting curve and to a maximum temperature of 55.5° for the change of volume. The parameters given in the table were obtained by fitting the new single point in smoothly with those previously determined, also taking due account of the additive relations at the triple point. In Fig. 1 the previously determined temperatures on the melting curve are indicated by crosses; these are seen to lie consistently with the point now found; this incidentally confirms the validity of extrapolating the manganin gauge measurements from 13,000 to 20,700 in the previous work.

Several trials were made for the compressibilities of the various phases, but with indifferent success. Consistent values were not obtained for the compressibility of liquid or of VI. The two best runs gave fairly consistent values for the compressibility of VII, however. Between 20,000 and 45,000 kg/cm², two independent measurements gave for the total proportional volume change 0.041 and 0.037 cm³/g, mean 0.039 cm³/g. It was also possible to definitely establish the normal decrease of compressibility with rising pressure; the mean compressibility in the range 45,000–50,000 is about three quarters of that in the range 20,000–25,000. Although consistent values for the compressibility of VI were not obtained, it is highly probable that my

FIG. 1. The phase diagram of water in the region of the new high pressure solid. Crosses are determinations on the melting curve of VI made in 1912.

TABLE I. *Transition parameters of the high pressure forms of water.*

PRESSURE kg/cm²	TEMPERATURE °C	$\frac{d\tau}{dp}$	ΔV cm³/g	LATENT HEAT		pΔV
				kg cm/g	cal./g	
VI–liquid						
15,000	52.5	0.00486	0.0508	3,400	79.7	762
16,000	57.2	460	478	3,430	80.4	764
18,000	66.0	412	424	3,490	81.8	762
20,000	73.8	370	376	3,520	82.5	753
22,000	80.8	330	335	3,590	84.1	737
22,400	81.6	324	330	3,610	84.7	738
VII–liquid						
22,400	81.6	.00892	.0910	3,620	84.7	2,040
24,000	95.3	796	879	4,060	95.1	2,110
26,000	110.3	718	847	4,530	106.2	2,200
28,000	124.1	670	817	4,840	113.4	2,290
30,000	137.1	634	789	5,100	119.5	2,360
32,000	149.5	600	763	5,370	125.9	2,440
34,000	161.1	567	738	5,650	132.4	2,510
36,000	172.1	536	715	5,940	139.2	2,580
38,000	182.5	507	694	6,220	145.8	2,640
40,000	192.3	479	674	6,550	153.5	2,700
VII–VI						
19,680	−80.0	.0278				
20,370	−60.0	0303				
21,000	−40.0	0339				
21,550	−20.0	0400				
22,000	0.0	054	.0567	287	6.7	1,250
22,250	20.0	118	570	142	3.3	1,270
22,350	40.0	286	573	63	1.5	1,280
22,390	60.0	1.000	576	19	.5	1,290
22,400	80.0	∞	580	0		1,300
22,400	81.6	∞	580	0		1,300

previously published values were too high.[2] It is also highly probable that at the triple point the compressibility of VII is a few percent greater than that of VI in spite of its smaller volume; this state of affairs is not at all unusual. At 50,000 kg/cm² and room temperature the volume of VII is approximately 0.60 cm³/g. This value is indicated both by a summation of the changes of volume occurring during the several phase changes and the compressions of the several pure phases, and also by a direct measurement of the total over-all change of volume.

In general comment on the results, one may notice in the first place that the decrement of volume when the liquid freezes to VII at the

² P. W. Bridgman, Proc. Am. Acad. **47**, 535 (1912).

triple point VI–VII–L at 22,400 kg is practically the same as the volume decrement when liquid freezes to VI at the triple point V–VI–L at 6380 kg, being 0.0910 against 0.0916 cm³/g. The decrease along the melting line of the volume decrement L–VI is very large, dropping from 0.0916 at the lower triple point to 0.0330 at the upper triple point. This in itself might perhaps be taken as a suggestion of the imminence of a new phase. Along the melting line of VII the decrease of the volume decrement L–VII is at a much lower rate, so that an application of the same argument would not demand the speedy appearance of yet another modification of the solid. It was a surprise to me that the change of volume of the liquid on freezing to VII at the triple point at 22,400 was so high; one might perhaps expect the volumes of the different phases to be squeezed down into a closer approach to equality at such high pressures.

The curvature of the melting curve of VII is in the normal direction. On the other hand, there is an abnormally great increase in the latent heat. This increase is so much greater than the increase in absolute temperature that the entropy difference between liquid and solid increases by more than 40 percent from 22,400 to 40,000 kg on the melting curve. Not only does the entropy difference between liquid and VII increase at high pressures along the melting curve, but the energy difference also increases, as may be seen from the table by subtracting the values of $p\Delta v$ from the latent heat. Extrapolation of this melting line therefore certainly gives no indication of either an approaching maximum or of a critical point.

As far as the two solids VI and VII are concerned, the normal relations were found. The transition runs with very high velocity at temperatures near the triple point, but becomes rapidly less at lower temperatures. Even 160° below the triple point, however, the velocity is still very appreciable outside the limits of indifference indicated in Fig. 1.

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