

## The PressureVolumeTemperature Relations of the Liquid, and the Phase Diagram of Heavy Water

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## The Pressure-Volume-Temperature Relations of the Liquid, and the Phase Diagram of Heavy Water

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The pressure-volume-temperature relations of both liquid  $D_2O$  and  $H_2O$  are measured between  $-20^\circ$  and  $95^\circ C$  and up to  $12,000 \text{ kg/cm}^2$ , and the transition parameters of the liquid and solid modifications of  $D_2O$  in the range between  $-60^\circ$  and  $+20^\circ C$  and up to about  $9000 \text{ kg/cm}^2$ . An unstable modification of solid  $D_2O$ , for which the designation IV is proposed, is found in the field of stability of V. Reference to the original work on  $H_2O$  shows that the corresponding modification of  $H_2O$  also exists. In general the properties of  $H_2O$  and  $D_2O$  covered by these measurements

are very much alike, and differ in the direction suggested by the greater zero-point energy of  $H_2O$ : the molar volume of  $D_2O$  is always greater than that of  $H_2O$  at the same pressure and temperature, and the transition lines of  $D_2O$  always run at higher temperatures. In finer detail, however, the differences between the two waters do not vary regularly, and probably other considerations than of zero-point energy alone are necessary for a complete explanation.

THE following measurements of some of the simpler properties of heavy water under pressure were made on 99.9 percent heavy water which I obtained through the courtesy of Professor Urey. My conventional high pressure apparatus was used in the measurements; the pressure range was up to  $12,000 \text{ kg/cm}^2$  and the temperature range from  $-60^\circ$  to  $+95^\circ C$ .

### PRESSURE-VOLUME-TEMPERATURE RELATIONS OF THE LIQUID

The measurements of the volume of the liquid as a function of pressure and temperature were made by the sylphon method fully described in other places.<sup>1</sup> A new sylphon was used, calibrated as usual. Since the principal interest of these measurements is in the difference between the properties of ordinary and heavy water rather than in the absolute values, the

compressibility of ordinary water was redetermined in the same sylphon and with all other parts of the set-up unchanged. The order of the measurements was as follows: first, measurements with  $H_2O$  at  $0^\circ$ ,  $-5^\circ$ ,  $-10^\circ$ ,  $-15^\circ$ ,  $-20^\circ$ , and check at  $0^\circ$ ; second, measurements with  $D_2O$  at  $+30^\circ$ ,  $0^\circ$ ,  $-5^\circ$ ,  $-11^\circ$ ,  $-16^\circ$ ,  $+52.5^\circ$ ,  $+75^\circ$ ,  $+95^\circ$  and check at  $30^\circ$ ; and third, measurements with  $H_2O$  again at  $+52.5^\circ$ ,  $+95^\circ$ , and  $0^\circ$ . The smoothness of functioning of the apparatus can be estimated from a comparison of the volumes of  $H_2O$  at  $0^\circ$  with the two fillings of the sylphon. The maximum discrepancy between the two determinations of the volume was at  $4000 \text{ kg}$ , where the first run gave  $15.875$  for the molar volume and the second run  $15.892$ . At  $6000 \text{ kg}$  the difference between the two runs had dropped from  $0.017$  to  $0.009$ . In calculating the volumes listed in the tables the first step was, in principle, to draw smooth curves through the experimental points at each constant temper-

<sup>1</sup> P. W. Bridgman, *Proc. Am. Acad.* **66**, 185 (1931); **68**, 1 (1933).

TABLE I. *Molecular volume of liquid D<sub>2</sub>O.*

PRESSURE (kg/cm <sup>2</sup> )	-20°	-15°	-10°	-5°	0°	20°	40°	50°	60°	80°	100°
1					18.122	18.125	18.200	18.270	18.363	18.570	
500					17.692	17.739	17.835	17.904	17.985	18.174	18.400
1000				17.308	17.328	17.404	17.512	17.585	17.665	17.850	18.048
1500			16.974	16.994	17.014	17.110	17.235	17.306	17.385	17.562	17.753
2000		16.660	16.685	16.712	16.741	16.854	16.982	17.054	17.130	17.302	17.486
2500	16.380	16.410	16.440	16.468	16.501	16.620	16.751	16.827	16.905	17.067	17.250
3000	16.155	16.188	16.221	16.255	16.287	16.411	16.543	16.617	16.693	16.850	17.028
3500		15.987	16.025	16.061	16.094	16.215	16.353	16.428	16.503	16.657	16.824
4000		15.807	15.843	15.879	15.915	16.040	16.178	16.252	16.330	16.477	16.634
5000				15.567	15.600	15.730	15.870	15.949	16.015	16.150	16.310
6000					15.352	15.465	15.597	15.671	15.740	15.875	16.023
7000						15.215	15.358	15.427	15.494	15.625	15.763
8000						15.001	15.140	15.207	15.272	15.402	15.533
9000						14.803	14.944	15.010	15.074	15.198	15.328
10000							14.767	14.827	14.885	15.007	15.137
11000							14.606	14.663	14.718	14.835	14.961
12000							14.452	14.508	14.563	14.677	14.807

TABLE II. *Molecular volume of liquid H<sub>2</sub>O.*

PRESSURE (kg/cm <sup>2</sup> )	-20°	-15°	-10°	-5°	0°	20°	40°	50°	60°	80°	100°
1					18.018	18.048	(18.157)	(18.233)	(18.323)	(18.539)	(18.800)
500					17.601	17.690	17.800	17.865	17.941	18.129	18.345
1000				17.234	17.251	17.352	17.485	17.554	17.630	17.805	18.002
1500		16.880	16.898	16.924	16.951	17.072	17.204	17.275	17.352	17.518	17.701
2000	16.579	16.600	16.624	16.658	16.684	16.805	16.949	17.025	17.100	17.262	17.437
2500	16.324	16.357	16.389	16.423	16.452	16.573	16.722	16.796	16.871	17.030	17.195
3000		16.140	16.173	16.213	16.241	16.366	16.514	16.587	16.661	16.816	16.977
3500		15.948	15.982	16.019	16.050	16.185	16.326	16.397	16.469	16.620	16.776
4000			15.802	15.843	15.875	16.012	16.152	16.224	16.294	16.440	16.589
5000			15.486	15.532	15.564	15.698	15.847	15.918	15.986	16.122	16.265
6000					15.293	15.430	15.575	15.645	15.712	15.842	15.982
7000							15.340	15.405	15.469	15.599	15.730
8000							15.125	15.188	15.249	15.374	15.501
9000							14.930	14.990	15.050	15.172	15.295
10000							14.748	14.807	14.866	14.985	15.106
11000							14.575	14.636	14.695	14.812	14.930
12000							14.422	14.480	14.538	14.653	14.771

ature, and then to compute and tabulate the volume at regular pressure intervals from each of these curves. The graphical representation used was on a very large scale. To give greater accuracy, not the actual observations were plotted, but the difference between the actual observations and points computed by a simple logarithmic formula with two constants that could be so adjusted as approximately to fit the experimental curve over the entire range. At each constant pressure of this first tabulation curves were then drawn, also on a very large scale, giving volume as a function of temperature, and from these curves were constructed the final Tables I and II, of volume at regular intervals of pressure and temperature.

The quantities of water used in filling the syphon, which were of the order of 5 grams, were determined by weighing. The density of H<sub>2</sub>O at atmospheric pressure was taken from *International Critical Tables*. The molecular volume of D<sub>2</sub>O was based on the value of Taylor

and Sherwood<sup>2</sup> for the molecular volume at 25°, 18.127. The values at other temperatures below this were obtained by combining this value with the values of Lewis and Macdonald<sup>3</sup> for the thermal expansion. The molecular volumes at higher temperatures at atmospheric pressure were obtained directly from the syphon readings; these are not as accurate as the values under higher pressures, the syphon not being particularly well adapted to readings at low pressures.

#### THE PHASE DIAGRAM OF THE SOLIDS

The method and the apparatus were very similar to those used for the corresponding measurements of H<sub>2</sub>O in 1912.<sup>4</sup> The D<sub>2</sub>O, about 13.5 grams in amount, was placed in a steel shell, completely surrounded by the pressure

<sup>2</sup> H. S. Taylor and P. W. Sherwood, *J. Am. Chem. Soc.* **56**, 998 (1934).

<sup>3</sup> G. N. Lewis and R. T. Macdonald, *J. Am. Chem. Soc.* **55**, 3057 (1933).

<sup>4</sup> P. W. Bridgman, *Proc. Am. Acad.* **47**, 441 (1912).

TABLE III. *Parameters of the transition lines of D<sub>2</sub>O.*

PRESSURE (kg/cm <sup>2</sup> )	TEMPER- ATURE (°C)	$d\tau$ $dP$	VOLUME CHANGE (cm <sup>3</sup> /mole)	LATENT HEAT (kg cm/mole) (cal/mole)	
L-I					
0	+ 3.82	-.00665	1.56	-65,000	-1523
400	+ 0.82	823	1.79	59,600	1396
800	- 2.74	950	2.01	57,000	1335
1200	- 6.76	1055	2.23	56,300	1319
1600	-11.14	1135	2.45	56,600	1326
2000	-15.82	1195	2.64	56,800	1331
2400	-20.70	1238	2.774	56,600	1326
III-L					
2200	-18.90	.00409	0.860	53,500	1253
2600	-17.37	356	.730	52,400	1228
3000	-16.04	310	.620	51,400	1204
3400	-14.90	268	.530	51,100	1197
3800	-13.96	230	.460	51,800	1214
IV-L					
4000	-17.90	.00946	1.710	46,100	1080
4500	-13.40	856	1.633	49,600	1162
5000	- 9.30	790	1.556	52,000	1218
5500	- 5.50	736	1.478	53,700	1258
V-L					
3000	-18.90	.00812	1.647	51,500	1206
3500	-14.98	.00754	1.498	51,300	1202
4000	-11.34	.00698	1.372	51,500	1206
4500	- 7.99	642	1.264	52,200	1223
5000	- 4.91	590	1.173	53,300	1249
5500	- 2.09	546	1.095	54,400	1274
6000	+ 0.57	514	1.026	54,600	1279
6500	+ 3.08	494	0.967	54,100	1267
VI-L					
5000	-10.01	.00936	1.920	54,000	1265
5500	- 5.40	914	1.825	53,500	1253
6000	- 0.91	880	1.738	53,800	1260
6500	+ 3.41	848	1.659	54,100	1267
7000	7.57	812	1.589	54,900	1286
7500	11.53	769	1.528	56,500	1324
8000	15.26	721	1.475	59,000	1382
8500	18.74	668	1.430	62,500	1464

PRESSURE (kg/cm <sup>2</sup> )	TEMPER- ATURE (°C)	$d\tau$ $dP$	VOLUME CHANGE (cm <sup>3</sup> /mole)	LATENT HEAT (kg cm/mole) (cal/mole)	
I-III					
2250	-20.0	-.270	-3.553	3,330	78
2285	-30.0	-.270	3.503	3,150	74
2325	-40.0	-.270	3.453	2,980	70
2360	-50.0	-.270	3.403	2,810	66
I-II					
2295	-30.0	.1815	-3.950	5,290	124
2240	-40.0	.1815	3.925	5,040	118
2185	-50.0	.1815	3.900	4,790	112
II-III					
2400	-29.69	.01137	0.431	9,200	216
2800	-26.08	.775	.380	12,100	283
3200	-23.40	605	.344	14,200	333
3600	-21.20	520	.313	15,200	356
II-V					
3540	-21.5	-.0124	-0.712	14,500	340
3800	-24.7	-.0124	0.712	14,300	335
III-V					
3555	-14.5	.468	-.985	-540	- 12.7
3540	-21.5	.468	-1.029	-560	- 13.1
IV-VI					
5410	- 6.2	.94	0.352	-100	- 2.3
5402	-14.0	.94	0.310	-100	- 2.3
V-VI					
6405	+ 2.6	1.90	0.696	100	2.3
6401	- 5.0	1.90	0.670	95	2.2

transmitting medium, in the lower cylinder, the temperature of which was thermostatically controlled, and which was varied for these measurements from +20° to -60°. The phase diagram was not followed beyond +20° and 8600 kg because I did not want to risk the loss of such a large quantity of D<sub>2</sub>O; there is, however, no reason to think that there are any significant features beyond the range actually covered. The bath for temperatures below 0° was ethyl alcohol, about five gallons in amount, into which the temperature regulating arrangement admitted, when necessary, a stream of alcohol from a reservoir maintained at -75° by solid CO<sub>2</sub>. The commercial availability of solid CO<sub>2</sub> made the low temperature manipulations very much more convenient than in 1912. The lower cylinder connected through a heavy pipe with the upper cylinder, maintained at room temperature, in which was situated the manganin gauge. The

position of the piston by which pressure was generated in the upper cylinder was read to 0.0001 inch by two Ames dial gauges, so mounted as to compensate for any slight warping of the press. The position of the piston was determined at constant bath temperature as a function of pressure; a phase change is shown by a discontinuity in the position of the piston. The change of volume is determined at once by the amount of the discontinuity and the cross section of the piston. The cross section has to be corrected for the elastic stretch of the cylinder under pressure. This correction was calculated from the elastic constants; it is proportional to the pressure and at 10,000 kg is 1.35 percent. There is in addition a correction for the thermal expansion of the transmitting liquid, isopentane, on passing, during a phase change, from the temperature of the lower to that of the upper cylinder.

A few of the changes of volume, on the II-III

and the II-V curves, were determined by the method of varying bath temperature and plotting pressure against temperature at constant volume. This change in procedure was made necessary by the smallness of these volume changes; the method was essentially the same as followed in the previous work on H<sub>2</sub>O.

A special apparatus was made for the determination of the points on the freezing curve of the ordinary ice between 0° and +3.82°, since the high pressure apparatus is not sensitive in this range. This special apparatus was constructed of mild steel and was the same in principle as the other. Pressure was read on a Bourdon gauge, calibrated against an absolute free piston gauge. Two independent determinations of the freezing pressure at 0.00° were 496 and 497 kg/cm<sup>2</sup>. In

computing the results, the slope of the upper end of L-I curve, between 0° and +3.82°, was so determined as to be consistent with this value, 496.5, for the melting pressure; the other two points at +2° and +3° were not quite so regular, perhaps because of inferior temperature control.

The measurements were completed without accident, with a single set-up of the apparatus for all the points above 500 kg, and with a single set-up of the special low pressure apparatus for all the points below 500 kg. There was no perceptible rounding of the corners of the melting curves, indicating adequate purity. The equilibrium points (temperature as a function of pressure) are shown in Fig. 1. In Fig. 2 are shown the corresponding changes of volume, in

TABLE IV. *Triple points of the system water-ices.*

D <sub>2</sub> O						H <sub>2</sub> O				
PHASES	PRESSURE (kg/cm <sup>2</sup> )	TEMP. (°C)	VOLUME CHANGE (cm <sup>3</sup> /mole)	LATENT HEAT		PRESSURE (kg/cm <sup>2</sup> )	TEMP. (°C)	VOLUME CHANGE (cm <sup>3</sup> /mole)	LATENT HEAT	
				(kg cm/mole)	(cal/mole)				(kg cm/mole)	(cal/mole)
L-I-III										
L-I III-L III-I	2245	-18.75°	2.713 .847 3.560	-56,600 53,300 - 3,300	-1326 1249 - 77	2115	-22.0°	2.434 .839 3.273	-43,100 39,100 - 4,000	-1010 916 - 94
L-III-V										
III-L V-III V-L	3555	-14.5°	.498 .985 1.483	50,900 500 51,400	1192 12 1204	3530	-17.0°	.434 .985 1.419	47,100 700 47,800	1103 17 1120
L-IV-VI										
IV-L VI-IV VI-L	5410	- 6.2°	1.492 .352 1.844	53,500 100 53,600	1253 2.3 1255					
L-V-VI										
V-L VI-V VI-L	6405	+ 2.6°	.978 .696 1.674	54,100 - 100 54,000	1267 - 2.3 1265	6380	+ 0.16°	.949 .700 1.649	53,800 150 53,950	1260 4 1264
I-II-III										
III-I II-III II-I	2290	-31.0°	3.498 .449 3.947	- 3,100 8,400 5,300	- 73 197 124	2170	-34.7°	3.532 .387 3.919	- 1,700 9,400 7,700	- 40 220 180
II-III-V										
II-III V-II V-III	3540	-21.5°	.317 .712 1.029	15,100 -14,600 500	353 - 342 11	3510	-24.3°	.261 .721 .982	13,000 -12,300 700	304 - 288 16

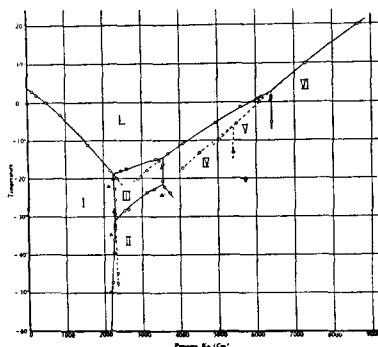


FIG. 1. The transition lines of the system  $D_2O$ . Prolongations of transition lines into regions of instability are dotted. Observed points are shown by circles. The triangles are the triple points in the  $H_2O$  system.

$cm^3$  per mole, as a function of temperature on the transition lines. The smoothed results are given in Table III; this table gives the pressure-temperature coordinates, the volume difference, the slope  $d\tau/dp$  of the transition line, the latent heat of the transition, the latter calculated by Clapeyron's equation and this latent heat in calories per mole calculated with the conversion factor,  $1 \text{ kg cm} = 0.02343 \text{ mean calorie}$ . In finding the smoothed results there are several conditions that must be met at the triple points of which there are six: namely, the three independently determined transition lines must pass through a common point, the three independently determined changes of volume must satisfy the additive relation, and the calculated latent heats must also satisfy the additive relation. These three conditions are so interrelated as to leave very little freedom in drawing the best curves through the experimental points, the latent heats being determined by the slopes which are tied down by the conditions that the curves pass through a triple point. One may therefore feel considerable confidence in the results, since any important error would be expected to manifest itself in the impossibility of satisfying the triple point conditions. In Table IV are collected the triple points parameters, with the values for  $H_2O$  also given for comparison.

The qualitative characteristics of the transitions are very much like those of  $H_2O$ . Perhaps the most striking characteristic is the enormous velocity of the transitions between the solid

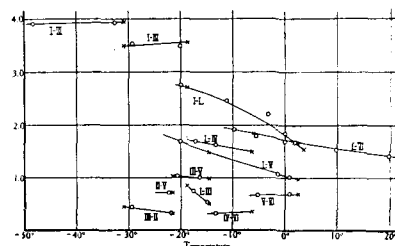


FIG. 2. The change of volume for the various transitions of the  $D_2O$  system, plotted as ordinates in  $cm^3$  per mole, against temperature as abscissa. The observed values are shown as circles; the crosses are the values computed at the triple points.

phases I-III, III-V and V-VI at the upper end of the range, immediately below the triple points with the liquid, and the enormously rapid decrease of this velocity with falling temperature. The phenomena with regard to subcooling and prolongation of transition lines into regions of instability are essentially the same as for  $H_2O$ ; as indicated in Fig. 1 the line L-I may be unstably prolonged into the region of instability of III, the line L-V into the region of III, the line L-VI into that of IV or V, and I-III into that of II. The reluctance of V to appear from the liquid phase is again noteworthy, making possible the very marked extension of the L-VI line into the region of V. But just as in the case of  $H_2O$ , if V had been recently present in the apparatus it was easy to make it appear again, even if in the meantime the system had been completely melted. The probable explanation is the persistence in the liquid phase of some sort of nuclei from which V is readily formed. A difference compared with the  $H_2O$  system is that the prolongation of the I-III line into the region of II apparently does not have a vertical tangent; in fact the I-III line is straight within the limits of error instead of being markedly curved toward the temperature axis as in the  $H_2O$  system.

In one important respect Fig. 1 differs from the phase diagram published for  $H_2O$ , namely, in the presence of the phase IV and the two transition lines L-IV and IV-VI. IV is totally unstable with respect to V, and once V has been produced, IV disappears. IV was found in the early part of these measurements, after the determination of points on the L-VI line at  $0^\circ$  and  $+10^\circ$ , and before V had yet appeared. The

first point found involving IV was on the IV-VI line. Since there was no analog for this in the diagram of  $\text{H}_2\text{O}$ , it appeared at first as if the phase diagram of  $\text{D}_2\text{O}$  must be entirely different from that of  $\text{H}_2\text{O}$ , and for a while there was considerable confusion in identifying the transitions as they were found. The confusion was increased by the fact that the melting line L-IV is not greatly different from the unstable prolongation of L-VI. The decisive factor in fixing the identification was the volume changes, the change L-IV plus IV-VI adding to L-VI, as it should, and the change L-IV being markedly different from L-VI.

After the phase diagram of  $\text{D}_2\text{O}$  was completed it was found on consulting again the original work on  $\text{H}_2\text{O}$  that the phase IV had also been found in the  $\text{H}_2\text{O}$  system, and in fact on page 529 of my 1912 paper will be found an explicit statement of the probability of the existence of another unstable form. The existence of this form was made probable both by the location of the pressure-temperature points, and by the values of the change of volume. The reason that the existence of the phase was not regarded as a certainty and the phase listed in the final results was that the transition IV-VI was not found. With the discovery of this transition for  $\text{D}_2\text{O}$ , however, the whole situation is cleared up, and the phase diagrams of  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$  appear very similar in all respects.

The designation IV is given to the new unstable phase, thus completing the sequence I to VI. When I chose the designations V and VI for the new high pressure ices beyond II and III, which had been previously found and named by Tammann, I left the designation IV blank because of uncertainty with regard to some unstable forms, the existence of which was suspected by Tammann. None of the suspected forms of Tammann have turned up, however, in the 40 years or more since he did his work, so that there seems no reason for holding this designation open any longer, and it is now employed to complete the scheme of nomenclature.

## DISCUSSION

### Accuracy of the results

The absolute accuracy of the volumes of the liquid phase listed in Tables I and II is not as

high as could be desired for a substance like water for which very slight departures from regularity are significant in disclosing conditions of varying association. Five different determination of the  $p$ - $\tau$ - $v$  surface of liquid  $\text{H}_2\text{O}$  have now been made in this laboratory, either by myself or by others using my apparatus, utilizing three different methods: the Aimé piezometer, the piston displacement method, both in 1912,<sup>4</sup> and the sylphon method in 1931,<sup>5</sup> 1934,<sup>6</sup> and now again in 1935. The maximum discrepancy between any of these determinations at any pressure is about 0.002 on the relative volume; for example, for the relative volumes at 3000 kg and 0° the values 0.901 and 0.899 occur. The maximum discrepancy occurs at an intermediate pressure and tends to become less at the highest pressures. A great deal more work would be necessary before the  $p$ - $\tau$ - $v$  surface of water is known with an accuracy corresponding to the accuracy of our knowledge of volume as a function of temperature at atmospheric pressure. With regard to the values below 0°, this is the first time since 1912 that the volume has been measured in this region. The results now found do not check in fine detail with those found before; in particular the minimum and maximum of volume as a function of temperature on the isobar at 1500 kg found in 1912 and shown in Fig. 40 of the 1912 paper, has not been found this time. Irregularities are now found suggesting the maximum and minimum, but not so pronounced. The sylphon method is not particularly accurate at the lower pressures, and in the present case suffers from the additional disadvantage that it is not safe to carry the liquid into the subcooled region because of danger of destroying the sylphon if freezing should occur. The measurements of 1912 represent considerable excursions into the subcooled regions, so that the chance of losing a maximum or minimum by the smoothing process at the end of the range was less. On the other hand, these new measurements, both on  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ , are the first in which the same apparatus and the same filling of the apparatus has been used to make measurements both above and below 0°. The present

<sup>4</sup> Second part of reference 1.

<sup>6</sup> P. W. Bridgman and R. B. Dow, J. Chem. Phys. 3, 35 (1935).

measurements should give a more reliable picture of the complete range of the phenomena than the former measurements. Further, the present measurements should give considerably greater accuracy for the comparative volumes of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  than can be claimed for the absolute accuracy of either. In making any comparative study of the properties of  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$  from the volumes of Tables I and II it must be remembered that the volumes of  $\text{H}_2\text{O}$  at  $0^\circ$ ,  $50^\circ$ , and  $100^\circ$  are doubtless somewhat more accurate than the values at  $20^\circ$ ,  $40^\circ$ ,  $60^\circ$ , and  $80^\circ$ , since the observations were made only at  $0^\circ$ ,  $52.5^\circ$ , and  $95^\circ$ , and the volumes at other temperatures were obtained by a graphical interpolation, which may have been subject in some cases to slight doubt because of lack of linearity. The measurements for  $\text{D}_2\text{O}$  on the other hand, were made at four temperatures above  $0^\circ$ , and so the interpolation is more certain.

The accuracy of the phase diagram is perhaps sufficiently indicated by the smoothness of the experimental points in Figs. 1 and 2. All the  $p$ - $\tau$  points obtained are shown, but not all the  $\Delta v$  points, since a perfectly satisfactory value of  $\Delta v$  cannot be obtained unless the transition is allowed to run to completion in both directions, and this was frequently inconvenient, either because of slowness of the transition, as on the lower end of the I-II and I-III lines, or because of the probability of completely losing one of the phases, as at some points on the melting curves of III and V. The measurements of the volume changes of the two transitions I-II and I-III were the most difficult, and are open to the greatest possibility of error. In the tables more significant figures are given for the temperatures, for  $dr/dp$ , and sometimes for  $\Delta v$  than are justified by the direct measurements. However, the differences of temperature and pressure could often be obtained with a greater accuracy than the absolute values themselves. Furthermore, the conditions at the triple points give a greater certainty than could be obtained from the absolute values; the values listed in the tables with a greater number of significant figures than apparently are justified have been smoothed and adjusted to satisfy the conditions at the triple points and give relative accuracy of the order suggested.

A word should be said about the normal melting parameters of  $\text{D}_2\text{O}$ . The melting temperature (triple point with the vapor) was taken as  $3.82^\circ$ , as given by Bartholomé and Clusius.<sup>7</sup> The latent heat given above, 64,950 kg cm per mole is equivalent to 1523 g cal. per mole, against 1522 recently determined by Bartholomé and Clusius. The agreement is in part fortuitous, since my measurements could hardly distinguish between a volume change at atmospheric pressure of 1.56 (the value used) and 1.57. Bartholomé and Clusius quote in their paper for the volume change 1.58, determined by Megaw from measurements of the lattice spacing in the crystals by x-rays.

### Relative behavior of $\text{D}_2\text{O}$ and $\text{H}_2\text{O}$

The molecular volume of liquid  $\text{D}_2\text{O}$  is greater at all pressures and temperatures than that of  $\text{H}_2\text{O}$  at the same pressure and temperature. This is consistent with the frequently expressed idea that "association" is greater in liquid  $\text{D}_2\text{O}$  than  $\text{H}_2\text{O}$ . The general tendency is for the volume excess to become less with both rising temperature and pressure, the maximum difference, 0.104, occurring at  $0^\circ\text{C}$  and atmospheric pressure. This again is what would be expected, because it is known that  $\text{H}_2\text{O}$  becomes more normal both with increasing temperature and pressure. However, the details of the variation of the volume excess are not altogether regular. If the excess is plotted as a function of pressure at constant temperature, a flat minimum will be found at the higher temperatures, the pressure of the minimum rising with increasing temperature. Thus at  $40^\circ$  the minimum is about 0.015 at 8000 kg, while at  $100^\circ$  the minimum is 0.030 at 10,000 or 11,000 kg. On the other hand, if the excess is plotted as a function of temperature at different constant pressures, a minimum will be found not far from  $40^\circ$  at all pressures up to about 8000, the depth of the minimum decreasing to about 0.015 at 8000, but beyond 8000 the temperature of the minimum increases to perhaps  $70^\circ$  at 12,000, where the depth of the minimum is of the order of 0.025. This complication in fine detail is doubtless indicative of slight differences

<sup>7</sup> E. Bartholomé and K. Clusius, *Zeits. f. physik. Chemie* **B28**, 167 (1935).



in the details of the "association." This is further indicated by the fact that the greatest departures from smoothness in the isotherms of  $\text{H}_2\text{O}$  are found in the general neighborhood of  $0^\circ$  and at low pressures, whereas the greatest irregularities in liquid  $\text{D}_2\text{O}$  are found at 5000 kg in the neighborhood of  $50^\circ$ .

Perhaps the most sweeping characterization that can be made with regard to the phase diagrams is that the triple points in the  $\text{D}_2\text{O}$  diagram all occur at higher temperatures, and the transition lines, except those running approximately vertical, all run at higher temperatures than in the  $\text{H}_2\text{O}$  diagram. This is what would be expected in view of the usual explanation of the higher melting point of  $\text{D}_2\text{O}$  in terms of its lower zero-point energy; the  $\nu_0$  of  $\text{D}_2\text{O}$  is less than that of  $\text{H}_2\text{O}$  in consequence of the greater mass of the  $\text{D}_2\text{O}$  molecule, so that a greater temperature energy must be added to shake the molecule of solid  $\text{D}_2\text{O}$  out of its trough into the liquid phase, the implication being that zero-point energies have largely disappeared in the liquid phase. This explanation demands the approximate equality of the specific heats of solid  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$ , and this does seem to be the fact experimentally.

Going now to finer details of the phase diagrams, the differences at the triple points are not uniform, but in general the differences become less at higher pressures. Thus the excesses of the absolute temperatures of transition in the  $\text{D}_2\text{O}$  system over the  $\text{H}_2\text{O}$  system for the successive triple points L-I-Vap, L-I-III, L-III-V, and L-V-VI are, respectively, 1.40, 1.40, 1.02 and 0.86 percent. The variations of the ratio of pressures at the triple points are greater than the variations of temperature; the pressure in the  $\text{D}_2\text{O}$  system is always greater, the excess varying from 6.0 percent at the I-II-III triple point to only 0.31 percent at the L-V-VI triple point. The fact that the variations of pressure and temperature at the triple points are irregular shows that there can be no law of corresponding states for corresponding phases in the two systems. This is perhaps not surprising when the liquid phase is involved, but one might perhaps expect a closer approximation in the solid phases. The pressure in the  $\text{D}_2\text{O}$  system exceeds that in the  $\text{H}_2\text{O}$  system at the I-II-III triple point by 6 percent,

whereas at the II-III-V triple point the excess is only 1.14 percent.

The latent heat of melting of all the ices at the low pressure end of the range is greater in the  $\text{D}_2\text{O}$  system than in the  $\text{H}_2\text{O}$  system. The sign of the difference is again what would be expected in view of the difference of zero-point energies discussed above; the magnitude of the difference is, however, somewhat surprising. The melting heat of I at the triple point with the vapor is 6 percent greater in the  $\text{D}_2\text{O}$  system than in  $\text{H}_2\text{O}$ . This difference rapidly increases with increasing pressure along the melting curve of I, and at the triple point L-I-III the excess of latent heat in the  $\text{D}_2\text{O}$  system has become 31 percent. At the same triple point the latent heat of L-III is 37 percent greater for  $\text{D}_2\text{O}$  than for  $\text{H}_2\text{O}$ . This marks the extreme—from here on with increasing pressure the differences become smaller, until at the L-V-VI triple point the latent heats in the two systems are the same within experimental error. Exact equality of the latent heats in the two systems would not be expected according to the simple zero-point energy explanation, for ice VI in the two systems must differ in the same direction with regard to zero-point energy as ice I. Another consideration also suggests that other factors besides zero-point energy must be of importance, because it is usual experience that those substances with the higher natural frequency (higher characteristic temperature) have the higher melting temperatures, whereas here it is the  $\text{D}_2\text{O}$  system, with the lower natural frequency, which has the higher melting temperature.

The relative volume changes in the two systems are significant. In general, the volume change on melting is greatest in the  $\text{D}_2\text{O}$  system; it is greater by about 4 percent at the atmospheric melting point, increases to about 12 percent at the L-I-III triple point, and from here decreases with increasing pressure, remaining 1.5 percent for VI-L at the L-V-VI triple point. In finer detail, the difference of volume between VI and the liquid in the  $\text{H}_2\text{O}$  system when plotted against temperature is concave toward the temperature axis up to  $20^\circ$ . This is abnormal. Above  $20^\circ$ , the curvature reverses, and  $\text{H}_2\text{O}$  becomes convex toward the temperature axis like other liquids. The abnormality does

not occur at all in the  $D_2O$  system, but the difference of volume between L and VI is convex toward the temperature axis over the entire measured range. The situation is reversed with regard to the phase I. In the  $H_2O$  system  $\Delta v$  is linear against temperature, whereas in the  $D_2O$  system it is abnormally concave toward the temperature axis. It is to be questioned, however, whether  $H_2O$  is not really more abnormal on its L-I line than  $D_2O$ , since the numerical magnitude of the variation of  $\Delta v$  is very much greater in  $H_2O$ . An accompaniment of this is a much greater variation of the latent heat along the L-I line for  $H_2O$  than for  $D_2O$ .

The greatest qualitative difference with regard to volume is shown by the phases I and III. At the triple point L-I-III the decrease of volume when I changes to III is 9 percent greater in the  $D_2O$  system, whereas at the I-II-III triple point, only 12° lower, it is 1 percent less. The variation is perhaps in small part due to experimental error, the volume determinations on the I-III line being the most uncertain of the measurements, but the triple point conditions did not seem to allow any important divergence from the values given, and the difference must be mostly real.

The conclusion seems forced, I believe, by this detailed examination of the differences in the two systems that abnormalities occur not only in the liquid but also in the solid phases, and particularly in the phases I and III. In fact, I have been of the opinion ever since making the original measurements in 1912 on the  $H_2O$  system that the  $p$ - $\tau$ - $v$  surface of ice I would be found to deviate markedly from that of a normal solid, particularly in the neighborhood of the L-I-III triple point. This subject has never been investigated experimentally, and would, I believe, be well worth while. Measurements should be made if possible on single crystals. Not only is it highly probable that the ices I and III are abnormal, but the abnormalities must differ in the  $D_2O$  and the  $H_2O$  systems. More elaborate considerations than simply zero-point energy appear to be necessary to satisfactorily explain the situation.

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## Precision Determination of Lattice Constants

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In Part I the theoretical and experimental conditions which must be satisfied in order to determine lattice constants with a precision of a few parts per hundred thousand are discussed with particular application to the symmetrical focusing type of camera. Cohen's method of calculation of lattice constants for the elimination of "drift" and experimental errors is applied. Methods are developed for the evaluation of standard errors and fiduciary limits of results from a single film and from a set of films. The usefulness of x-ray targets made of alloys rather than pure elements for the purpose of securing a

larger number and better distribution of lines is indicated. The influence of the number and Miller indices of diffraction lines on the values of lattice constants in noncubic systems is shown. The importance of the methods of sample preparation for precision work is emphasized. In Part II, precision measurements on Al, Ni, Ag, Au, Si, Fe, Mo, W, Mg, Zn, Cd, Sb, Bi and Sn are reported for materials of a high degree of purity. The fiduciary limits of these lattice constants vary between 2 and 7 parts per hundred thousand and are so chosen that the probability of the correct value lying between the stated limits is 19 out of 20.

### Part I. Theoretical and Experimental Conditions

#### INTRODUCTION

**D**URING the last few years the determination of precise values of lattice constants has become more and more important. In many

cases the problem consists mainly in determining comparatively small changes in lattice constants due to changes in the compositions or nature of the sample investigated. This is the case in one