PROPERTIES OF WATER. PART V. PRESSURE-VOLUME-TEMPERATURE RELATIONS OF WATER IN THE RANGE 400-1000 C AND 100-1400 BARS

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Institute of Geophysics, University of California, Los Angeles, California

ABSTRACT. New measurements of specific volume of water along 11 isotherms in the range 400-900 C were correlated and extrapolated to form a smooth table of specific volumes extending to 1000 C and 1400 bars.

INTRODUCTION

Prior to 1950 the specific volume of water had been measured in only a small part of this range, to 460 C and 350 bars (Keyes, Smith, and Gerry (1936)). The measurements of Kennedy (1950) extended to 1400 bars below 600 C and to lower pressures at higher temperatures, and were extrapolated to 2500 bars and 1000 C. Subsequently it was pointed out by Hilsenrath and others (1955, p. 437) that Kennedy's data were inconsistent at higher pressures and unreliable at lower pressures. The range 1-100 bars has since been remeasured by Kennedy (1957), using CuO to remove the hydrogen generated by reaction of water with the bomb wall. In the meantime new measurements of Kirillin, Rumiantsev, and Zubarev (1956) have appeared for temperatures to 650 C and to pressures of 500 or 900 bars.

In this paper we present the results of measurements made in 1956-1957, extending to about 1400 bars and 750 C, and to lower pressures at higher temperatures (1300 bars at 810 C, 700 bars at 865 C, and 400 bars at 905 C). The data are correlated and extrapolated to 1400 bars and 1000 C.

METHOD

The apparatus used in these measurements has been described in detail in previous papers of this series (Holser and Kennedy, 1958).

Most of the measurements were made on isotherms. The method is the same as that previously described, except that in many runs the measurements were carried down to about 40 bars, so that the rate of removal of water with change of pressure could be extrapolated to zero pressure. Such measurements were therefore independent of any other values except the specific volume of water at the temperature and pressure used (usually 200 bars, 200 C) in determining the volume of the bomb. Particularly in the lower part of the temperature range, the data were not sufficiently numerous or precise to make this extrapolation, and the previous low pressure measurements of Kennedy (1957) were used to establish the mass of water in the bomb at the lowest pressure on the isotherm.

A total of 25 isotherms were run at the following temperatures: 420, 460, 500, 550, 620, 700, 750, 800, 810, 865, 905, and 950. A number of these covered the pressure range incompletely. The effect of hydrogen evolution became evident at 900 C, and necessitated the rejection of all the data for 950 C. At the latter temperature the presence of the CuO in the bomb was not sufficiently effective in reducing the hydrogen concentration during the length of time required for this type of run, although Kennedy's (1957) isometric runs at low pressures were apparently successful because they were in this region for only a brief time. Some other single measurements were also rejected on the basis of inconsistency or known operational errors.

In order to check the trend of isometric lines in the p-T plane, particularly for the purpose of extrapolation, other runs were made at approximately constant volumes of 4.71, 6.70, and 14.8 cc/g. A very long time would have been required to stabilize each temperature closely enough for measurements with the piston gauge. This would have increased the danger of errors due to slight leakage, or to creep of the bomb material near the upper limit of the runs. Therefore the pressures were read with the precision Heise Bourdon gauge.

REDUCTION AND CORRELATION OF DATA

The mass of water in the bomb at the low pressure end of an isothermal measurement was determined by the following method of extrapolation. The ratio $\Delta m / \Delta p$ for various pressure intervals from say, 500 bars, down to the lowest pressure of about 40 bars, was plotted against pressure. A smooth curve drawn through these points could then be extrapolated to find $\Delta m / \Delta p$ for the interval from zero pressure to the lowest measured pressure. These data could also be checked against the measurements of bomb volume in the following way. Assume that the ratio of differences is approximately equal to the derivative, dm/dp. Then near zero pressure the last bit of water in the bomb should be extracted under ideal gas conditions, for which

$$dm/dp = V/R'T \tag{1}$$

where V is the measured volume of the bomb, and R' is the gas constant including the molecular weight of water. Strictly speaking, T is the absolute thermodynamic temperature. Preliminary calculations suggested that our data were probably not sufficiently precise to detect any differences (Keyes, 1949, p. 927) between the thermodynamic and International scales of temperatures, therefore International temperatures were used in all calculations and reduction of data. In other words, where the extrapolation of our measurements did not intersect $p = 0$ at the values of dm/dp calculated from equation (1) and the International temperature, the difference could usually be attributed to errors of measurement. Otherwise the difference might have been attributed to the fact that the extrapolation depended on a thermodynamic temperature while equation (1) was calculated with an International temperature. Most of the differences were small and showed no general trend.

A final mass, determined either in the above fashion or by the use of Kennedy's (1957) data, was the basis for the calculation of specific volumes at each higher measured pressure.

Each isotherm was smoothed by the method of item differences described previously. Inasmuch as the function $z = pv/RT$ varied less sharply with pressure than did the specific volume, the function $\Delta z/\Delta p$ was plotted against p. This turned out to be a very satisfactory method of smoothing small irregularities in the isotherm measurements, except below 400 bars and 500 C, where $\Delta z/\Delta p$ varied sharply.

Isotherms in the unmeasured region above 750 C were determined by extrapolating the trend of isometrics in the p-T plane. In order to determine the trend of a given isometric accurately, it was necessary to make a precise interpolation at that specific volume on each isotherm. Inasmuch as a precise curve of $\Delta z/\Delta p$ (derived directly from the data) was already available for each isotherm, it was used in the following way as an aid to interpolation. Assuming that the variation of z with p is nearly linear, then near z_0, p_0

$$Z = Z_0 + \frac{\Delta z}{\Delta p} \; (p - p_0) \tag{2}$$

and also

$$Z = \frac{pv}{RT} = \frac{p_0 v}{RT} + \frac{p - p_0) v}{RT}$$

therefore

$$(p - p_0) = \frac{z_0 - p_0 v/RT}{v/RT - \Delta z/\Delta p} \tag{3}$$

Using this equation one can precisely calculate the pressure p for a given v, using known nearby values of p_0, z_0, and $\Delta z/\Delta p$. A more precise calculation may be made by assuming a quadratic form in place of equation (2), and measuring the slope of the $\Delta z/\Delta p$ vs. p curve near z_0, p_0. A solution for $(p - p_0)$ in this case requires a series expansion, of which the first term is given by equation (3) above, but even the second term is not significant for most interpolations.

Isometrics derived in this fashion seem nearly straight on a large scale plot, but differencing to get $\Delta p/\Delta T$ confirms a slight concavity towards the T axis. Plots of this function against temperature were extrapolated and reintegrated to obtain values of pressure at temperatures above the range of measurement. The combination of measurements along isotherms, and higher isotherms derived by extrapolation along isometrics, gave a set of isothermal measurements at temperatures to 1000 C. Cross-smoothing at high temperatures was then done in an analogous fashion, using a plot of $\Delta z/\Delta T$ vs. T. This same plot could also be used to interpolate temperatures between the measured isotherms. At temperatures below 700 C this method could not be used because $\Delta z/\Delta T$ varied too sharply over the temperature intervals measured. Smoothing and interpolation at these low temperatures was done on a large scale plot of z vs. T.

The final results are tabulated in terms of specific volume in table 1. These final values are most easily compared with the measurements of the

original isothermal runs in terms of z^1. For most runs the standard deviation is 0.0005 − 0.0020 in z. Both runs at 420 C below 500 bars, and one of the runs at 460 C, had standard deviations of 0.0025 − 0.0030 in z. In view of the good agreement between Keyes and Kirillin at 420 C, their measurements were used for table 1 below 500 bars in that region. At nearly all temperatures each of our runs showed greater internal consistency than the deviations from the table, indicating that the factors varying between runs (bomb volume and temperature) are probably the major source of uncertainty in table 1. Above 620 C the deviations of the measurements from table 1 are in part a reflection of the smoothing among isotherms, but at lower temperatures the isotherms were not sufficiently close for such smoothing to contribute very much to the deviations.

COMPARISON WITH THE RESULTS OF OTHER INVESTIGATORS

This series of measurements overlaps those of Keyes, Smith, and Gerry (1936) only at 420 and 460 C, up to 360 bars. In view of the low precision of some of our runs at these temperatures, a special series of 4 single measurements were made at 460 C and 350 bars, to determine whether there was any fundamental disagreement with the data of Keyes and the equivalent data of Kirillin. The average difference between these experiments and Keyes-Kirillin was 0.0005 in z, which cannot be considered significant.

The 20 isotherms of Kirillin, Rumiantsev, and Zubarev (1956) deviate from table 1 not more than $\pm$ 0.002 in z, except as shown in table 2. Thus the greatest discrepancy between Kirillin and ourselves is at the high temperature end of his series, above 600 C. His data at 650 C are internally inconsistent, and therefore our measurements are probably to be preferred in this range until an independent check has been made.

The earlier table by Kennedy (1950) deviates considerably from table 1. At 1400 bars the difference in z decreases with temperature to a minimum of −0.006 at 500-550 C, then increases through zero at 630 C to +0.020 at 800 C and +0.025 at 1000 C. Below 1000 bars the differences are substantially less: at 500 bars the minimum is −0.002 at 500 C, zero at 560 C, a maximum of +0.004 at 750 C, and drops to +0.001 at 1000 C. Below 300 bars the early results are very erratic and mostly low.

[1] Available as document no. 5803, American Documentation Institute, Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

TABLE 1

Specific Volume of Water in cc/g

Pressure Bars	420	440	460	480	500	520	540	560	580	600	620	640	660	680	700
150	16.86	17.95	18.97	19.92	20.82	21.68	22.50	23.31	24.10	24.88	25.64	26.40	27.14	27.87	28.59
200	11.203	12.232	13.161	14.008	14.783	15.52	16.21	16.88	17.52	18.16	18.77	19.38	19.97	20.55	21.12
250	7.579	8.675	9.604	10.414	11.141	11.803	12.425	13.015	13.581	14.125	14.655	15.17	15.67	16.16	16.64
300	4.917	6.221	7.178	7.991	8.703	9.322	9.899	10.437	10.947	11.435	11.907	12.365	12.809	13.238	13.653
350	3.084	4.397	5.419	6.247	6.953	7.545	8.091	8.593	9.066	9.516	9.947	10.364	10.767	11.152	11.526
400	2.368	3.215	4.153	4.953	5.639	6.217	6.726	7.213	7.659	8.081	8.482	8.869	9.239	9.594	9.937
450	2.089	2.564	3.278	4.005	4.660	5.210	5.703	6.154	6.575	6.974	7.352	7.711	8.055	8.386	8.704
500	1.942	2.271	2.750	3.337	3.906	4.426	4.896	5.326	5.727	6.102	6.457	6.793	7.116	7.427	7.726
600	1.774	1.975	2.239	2.573	2.963	3.365	3.758	4.133	4.489	4.823	5.141	5.443	5.731	6.007	6.272
700	1.675	1.815	1.995	2.217	2.476	2.764	3.068	3.372	3.671	3.962	4.244	4.515	4.774	5.020	5.257
800	1.607	1.716	1.850	2.010	2.195	2.405	2.636	2.880	3.128	3.375	3.620	3.857	4.085	4.305	4.518
900	1.554	1.645	1.750	1.874	2.018	2.179	2.358	2.553	2.757	2.965	3.174	3.380	3.580	3.775	3.964
1000	1.512	1.589	1.677	1.779	1.895	2.026	2.170	2.327	2.494	2.669	2.848	3.026	3.201	3.373	3.541
1100	1.477	1.544	1.619	1.705	1.802	1.910	2.030	2.162	2.303	2.451	2.604	2.758	2.911	3.063	3.213
1200	1.447	1.506	1.572	1.646	1.729	1.822	1.925	2.037	2.158	2.285	2.417	2.550	2.684	2.819	2.953
1300	1.421	1.475	1.533	1.598	1.671	1.752	1.840	1.938	2.043	2.153	2.268	2.385	2.503	2.623	2.744
1400	1.398	1.448	1.501	1.559	1.624	1.695	1.772	1.858	1.949	2.047	2.148	2.251	2.356	2.464	2.574

TABLE 1 (Continued)

Pressure Bars	720	740	760	780	800	820	840	860	880	900	920	940	960	980	1000
150	29.30	30.00	30.68	31.36	32.04	32.72	33.40	34.07	34.74	35.41	36.08	36.74	37.41	38.07	38.74
200	21.67	22.22	22.75	23.28	23.81	24.33	24.85	25.37	25.89	26.40	26.91	27.42	27.93	28.44	28.96
250	17.10	17.55	18.00	18.44	18.87	19.30	19.73	20.16	20.58	21.00	21.42	21.84	22.26	22.68	23.09
300	14.056	14.450	14.837	15.22	15.59	15.96	16.33	16.69	17.05	17.41	17.76	18.12	18.48	18.83	19.19
350	11.888	12.240	12.584	12.919	13.249	13.575	13.897	14.216	14.533	14.848	15.16	15.47	15.78	16.10	16.41
400	10.267	10.587	10.899	11.202	11.499	11.793	12.082	12.367	12.651	12.933	13.212	13.490	13.769	14.048	14.327
450	9.010	9.306	9.592	9.871	10.143	10.411	10.674	10.935	11.193	11.448	11.702	11.954	12.206	12.458	12.710
500	8.011	8.286	8.552	8.810	9.061	9.309	9.552	9.793	10.031	10.266	10.498	10.729	10.960	11.191	11.421
600	6.525	6.769	7.004	7.231	7.452	7.669	7.881	8.091	8.299	8.502	8.704	8.903	9.102	9.301	9.497
700	5.484	5.702	5.912	6.117	6.316	6.509	6.700	6.887	7.073	7.254	7.434	7.611	7.786	7.961	8.134
800	4.722	4.920	5.111	5.296	5.476	5.652	5.825	5.996	6.163	6.328	6.490	6.650	6.809	6.965	7.120
900	4.149	4.328	4.501	4.670	4.835	4.997	5.156	5.312	5.465	5.616	5.765	5.911	6.055	6.197	6.338
1000	3.707	3.870	4.028	4.183	4.334	4.483	4.629	4.773	4.914	5.053	5.190	5.325	5.457	5.588	5.717
1100	3.362	3.509	3.654	3.796	3.935	4.072	4.207	4.340	4.471	4.599	4.726	4.851	4.974	5.094	5.213
1200	3.087	3.220	3.352	3.482	3.611	3.738	3.863	3.986	4.107	4.227	4.345	4.461	4.575	4.688	4.798
1300	2.865	2.986	3.107	3.227	3.345	3.462	3.578	3.692	3.805	3.916	4.026	4.135	4.242	4.347	4.450
1400	2.684	2.795	2.905	3.016	3.125	3.233	3.340	3.446	3.550	3.654	3.757	3.858	3.959	4.058	4.155

TABLE 2

Comparison with Data of Kirillin, Rumiantsev, and Zubarev (1956)

All other differences less than ± 0.002 in z

Kirillin isotherm deg C	Pressure range bars	Difference of compressibility factor Kirillin less table 1
410.00	300	+0.004
431.34	450-500	+0.003 to 0.004
437.00	450	+0.004
461.65	350-450	−0.003 to 0.006
500.00	450-500	−0.003
500.27	450-600	−0.003
501.31	350-500	−0.003
551.45	300	−0.003
620.00	200-300	−0.004 to 0.005
650.00	150	+0.004
650.00	250-500	−0.004 to 0.008

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