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THERMODYNAMIC DATA FOR WATER

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ABSTRACT

Thermodynamic data for liquid and gaseous water have been compiled and extended to limits of pressure and temperature imposed by Hugoniot, adiabat, and Thomas-Fermi model considerations. The internal energy variation is discussed.

INTRODUCTION

In general, liquids do not differ much from gases in their fundamental behavior at high temperatures, while at their freezing points they resemble the crystalline phases with which they are in equilibrium. The most marked differences occur in the middle portion of the temperature ranges over which the liquids can exist. Thermodynamic properties of water in its various phases determined from measurements by static and shock-wave methods exist in the literature.¹⁻⁶ As shown in Fig. 1, a fairly wide range of pressures and temperatures has been covered. Pressure-volume-temperature (P-V-T) data of individual investigators do not always overlap each other, however, and there are usually numerous discrepancies when they do. In order to properly describe the thermodynamic behavior of water* over the complete range it is first necessary to smooth the published results after reducing them to a

* For all temperatures greater than the critical temperature water may be regarded as "compressed water", if the specific volume is less than the critical value; otherwise, "diluted vapor".

common system of units. Then a certain amount of interpolation and extrapolation is required if the limits of one megabar in pressure, set by a density transition to the Thomas-Fermi domain, and one electron volt in temperature, set by the Hugoniot curve starting at 20°C and one atmosphere, are to be reached. However, for pressures less than one megabar the upper temperature limits can be arbitrarily set by the decreasing adiabatic relaxation temperatures.

P-V-T DATA

Sources of the experimental data have been given. In these, volume is usually tabulated as a function of pressure for different temperatures. Matching the data across both sides of boundaries shown in Fig. 1, as well as interpolation between Kennedy's and Rice's results, were done graphically from isotherms. Some isobaric adjustment also was required at ten kilobars.

The basis for extrapolation to higher pressures was the assumed linearity of $(\partial V/\partial P)_T$ vs. $1/P$ above 250 kilobars along the 175°C isotherm (see Fig. 2). Values of this function up to 250 kilobars are from Bridgman's work^{1,3} and shock-wave data calculations of Rice and Walsh.⁶ Agreement with Thomas-Fermi theory according to Jensen⁷ was imposed at five megabars. Extrapolation to higher temperatures was based on $(\partial V/\partial T)_P$ being a function of P only above 25 kilobars as shown by Rice and Walsh. Between 10 and 25 kilobars and for $T \geq 1000^\circ\text{C}$ it was assumed to be so to a sufficiently good approximation. Figure 3 shows the variation of this quantity with pressure. Again a fit with Thomas-Fermi model results has been imposed in the megabar region.⁸

EQUATION OF STATE

When the data are sufficiently complete to map out the P-V-T surface over a region, the thermodynamic description of a substance is complete,

assuming the specific heat at some pressure, e.g., one atmosphere, is known for all temperatures. Several attempts were made to find a functional relationship, $V = V(P,T)$, by least squares. The virial form

$$PV = a + b P + c P^2 + \dots$$

where

$$a = a_0 T$$

$$b = b_0 + \frac{b_1}{T} + \frac{b_2}{T^2} + \dots$$

was chosen both for its computational convenience and possible physical interpretation of the coefficients. Such a function would be quite useful in providing a relatively simple means for obtaining thermodynamic properties of water. Unfortunately, only between comparatively narrow limits of pressure and temperature was agreement with the tabulated data possible to less than 10% without using an impracticably large number of coefficients.

Statistical mechanical treatments indicate that the virial equation of state for liquids would, indeed, involve a very large number of terms.⁹ The failure of a general equation to exist for water is partly due to the absence of molecular isotropy. As in a gas the structure of the individual molecules largely determines the equation of state at small intermolecular distances. In liquid water each oxygen atom is bonded tetrahedrally to four others by a proton on the line of centers, though not at the midpoint, between each pair. The hydrogen bonds are not all completed about all oxygen atoms at any instant, and they are constantly being broken and reformed between other atoms giving rise to "molecular associations." This type of hydrogen bonding is greatly diminished at higher temperatures, water vapor consisting of single H_2O molecules for the most part. This tendency for water molecules not to exert

van der Waals type attractive forces contributes towards its abnormal thermodynamic behavior. Thus, for example, the isothermal compressibility factor, $(\partial V/\partial P)_T$, shows a minimum in its temperature variation, and at least seven different water-ice phase transitions occur.

There are a number of analytical equations of state for water which frequently may be found useful despite their limitations. Some of these are given below.

(a) Keyes, Smith, and Gerry¹:

$$V = \frac{RT}{P} + a(T)$$

$$10^{-3} \text{ kb} < P < 0.5 \text{ kb},$$

$$100^\circ \text{C} < T < 550^\circ \text{C},$$

(vapor phase only).

(b) Tait⁵:

$$V = a - \frac{1}{n(T)} \ln \left[\frac{P + B(T)}{b + B(T)} \right]$$

$$1 \text{ kb} < P < 10 \text{ kb},$$

$$0^\circ \text{C} < T < 374^\circ \text{C}.$$

(c) Rice⁵:

$$V = a(T) \ln P + b(T)$$

$$10 \text{ kb} < P < 100 \text{ kb},$$

$$100^\circ \text{C} < T < 1000^\circ \text{C}.$$

(d) Schall¹⁰:

$$P = \rho f(\rho) T + k(\rho)$$

$$4 \text{ kb} < P < 190 \text{ kb},$$

$$0^\circ \text{C} < T < 600^\circ \text{C}.$$

In lieu of an equation the tabulated P-V-T data can, of course, be directly employed in machine computations.

HUGONIOT AND ADIABATS: DISSOCIATION

The Hugoniot curve has been experimentally determined to 420 kilobars by Walsh and Rice and to 800 kilobars by Al'tshuler et al.¹¹ A possible phase transformation to ice near 115 kilobars is discussed in the Russian paper. However, the estimated volume effect associated with freezing would be negligible. No other phase changes have been observed. This curve was

extended in the present report so as to join the Thomas-Fermi Hugoniot given in reference (8).

The temperature associated with one megabar on the Hugoniot was then used as a starting point to numerically integrate the expression for $T(P)$ assuming an adiabatic expansion, i.e.,

$$T dS = C_P dT - T (\partial V / \partial T)_P dP = 0.$$

The purpose of this calculation was to obtain an approximate upper temperature limit for the tabulated isobars.

At temperatures of about one-half electron volt and greater one would like to know to what degree thermal dissociation of H_2O has taken place. Because specific heats of gases at these high temperatures are poorly known the dissociation constant is given only up to $\sim 5000^\circ C$. At this value the corresponding pressure on the adiabat is 200 kilobars, for which the dissociation would be $\ll 10\%$ according to estimates made from formulae and tables given in Dorsey.¹ Extrapolation to one ev at one megabar also yield $< 10\%$. Therefore, as shown in Fig. 4, where the Hugoniot and several adiabats are plotted together with the 10% dissociation curve, one might expect dissociation to be small in the region to the right of the dashed curve.

INTERNAL ENERGY

At sufficiently high pressures the energy stored up in structural deformation of the molecules should more than counterbalance the work done by attractive forces, and the internal energy, ϵ , increase rather than decrease along an isotherm. Defining internal pressure as being that which arises from forces of attraction and repulsion between molecules and thermal pressure as that from their motions, it must be true that the sum of internal and thermal must equal the externally applied pressure. It is of interest to

see how the internal pressure, $(\partial \epsilon / \partial v)_T$, varies with the external pressure, P , as calculated from the assembled data. Writing

$$(\partial \epsilon / \partial v)_T = T (\partial P / \partial T)_V - P$$

one may solve for the pressure, P_0 , for which the left member of the equation changes sign at a given temperature.

The curve in Fig. 5 shows this pressure as a function of temperature. $(\partial \epsilon / \partial v)_T$ is negative above the curve and positive below. A less regular transition can be expected at lower temperatures than those shown because of the non-uniform change in hydrogen bonding energy with volume remarked on earlier.

APPENDIX P-V-T DATA

The following units have been used for the data tabulated here:

Pressure in kg/cm^2

Volume in cm^3/g

Temperature in $^\circ\text{K}$.

It is frequently desirable to express pressure in kilobars, where

$$1 \text{ kg}/\text{cm}^2 = 0.980665 \times 10^{-3} \text{ kb.}$$

NOTE: A somewhat irregular variation in the number of significant figures, or digits, given will be observed. Where more than three occurred in the references cited they have been retained. Only three figures should be used for the interpolated and extrapolated specific volumes even though more appear in the tables.

P	V _{273°}	V _{373°}	V _{453°}	V _{493°}	V _{533°}	V _{563°}	V _{583°}	V _{633°}
1	1.0001	1.1729.6	2120	2311.	2502	2644	2738	2975
10	.9997	1.0435	193.8	221.3	242.7	258.2	268.3	293.1
10.33		1.0431	1.1275					
25				83.07	91.41	98.68	103.3	114.2
25.83	.9991	1.0421	1.1262	1.1897				
50					42.15	43.11	47.75	54.31
51.66	.9980	1.0408	1.1241	1.1866	1.2747			
75						25.52	28.63	34.13
77.19	.9968	1.0396	1.1221	1.1836	1.2694	1.3649		
100							18.30	23.83
103.32	.9957	1.0383	1.1200	1.1806	1.2644	1.3559	1.4457	6.963
206.65	.9914	1.0334	1.1123	1.1694	1.2461	1.3257	1.3975	1.8140
310	.9873	1.0286	1.1050	1.1592	1.2302	1.3014	1.3626	1.6232
362	.9853	1.0264	1.1015	1.1544	1.2230	1.2909	1.3481	1.5758
400	.9814	1.0247	1.1008	1.1538	1.2215	1.2816	1.3359	1.5448
500	.9770	1.0183	1.0953	1.1490	1.2179	1.2697	1.3327	1.5618
1000	.9576	.9993	1.0647	1.1075	1.1603	1.1999	1.2362	1.3518
1500	.9409	.9826	1.0392	1.0754	1.1197	1.1528	1.1804	1.2626
2000	.9261	.9679	1.0142	1.0458	1.0857	1.1157	1.1390	1.2057
2500	.9132	.9545	.9931	1.0211	1.0578	1.0854	1.1061	1.1634
3000	.9015	.9424	.9807	1.0116	1.0431	1.0672	1.0855	1.132
4000	.8812	.9208	.9556	.9822	1.0092	1.0293	1.0446	1.078
5000	.8639	.9028	.9406	.9624	.9872	1.0058	1.0150	1.038
6000	.8489	.8871	.9174	.9379	.9592	.9744	.9860	1.006
7000	(ICE-VI)	.8731	.9021	.9203	.9396	.9532	.9635	.980
8000	.8397	.8604	.8886	.9048	.9224	.9347	.9439	.958
9000	.8351	.8490	.8765	.8909	.9072	.9183	.9266	.939
10000	.8305	.839	.864	.876	.889	.899	.904	.920
12000		.819	.841	.852	.863	.871	.877	.890
15000		.794	.814	.824	.834	.842	.847	.860
20000		.759	.777	.786	.795	.802	.807	.818
25000		.7315	.7487	.7573	.7659	.7723	.7766	.7874
30000		.7106	.7266	.7346	.7426	.7486	.7526	.7626
40000		.6757	.6902	.6974	.7047	.7101	.7137	.7228
50000		.6472	.6607	.6675	.6742	.6793	.6827	.6911
60000		.6223	.6349	.6412	.6475	.6523	.6554	.6633
80000		.5822	.5932	.5987	.6042	.6083	.6111	.6180
100000		.5512	.5608	.5656	.5704	.5740	.5764	.5824
200000		.4657	.4705	.4729	.4753	.4772	.4784	.4814
300000		.428	.431	.432	.434	.435	.435	.437
400000		.402	.404	.405	.406	.406	.407	.408
600000		.368	.369	.369	.370	.370	.370	.371
800000		.346	.346	.346	.346	.347	.347	.347
1000000		.328	.328	.328	.328	.328	.329	.329

P	V _{673°}	V _{773°}	V _{873°}	V _{973°}	V _{1073°}	V _{1173°}	V _{1273°}	V _{2273°}	V _{3273°}
1	3164	3636						10499	15118
1.03			4109	4579	5050	5520	5991	1050	1512
10	312.7	361.1		441.7	488.8	534.7	580.3	420	605
10.33			395.7						
25	122.6	142.7							
25.83			157.0	175.8	194.5	213.9	232.1		
50	59.05	69.92						210	302
51.66			77.52	87.19	96.72	106.9	116.1		
75	37.78	45.62						140	202
77.49			51.12	57.77	64.29	71.30	77.37		
100	27.05	33.45						105	151
103.32			37.78	42.52	47.0	52.0	57.08		
200	10.31	15.11						52.5	75.6
206.65			18.11	20.97	23.39	25.74	27.84		
300	3.02	8.898						34.9	50.4
310			11.51	13.64	15.43	17.20	18.90		
350		7.108						30.0	43.2
362	2.096		9.65	11.57	13.16	14.53	16.20		
400		5.774						26.2	37.8
408	1.921	5.623	8.172	10.0	11.60	12.90	14.10		
500								21.0	30.2
510	1.745	3.890	6.114	7.7651	9.092	10.28	11.30		
1000								10.5	15.1
1020	1.4443	1.8794	2.6802	3.5829	4.434	5.208	5.900		
1500								6.75	9.75
1530	1.3284	1.5653	1.9496	2.449	2.994	3.531	4.035		
2000								4.95	7.10
2039	1.2591	1.4402	1.6630	1.980	2.350	2.738	3.123		
2500								3.97	5.60
2549	1.2092	1.3566	1.5252	1.7346	2.000	2.296	2.589		
3000	1.175	1.300	1.432	1.590				3.33	4.60
3059					1.800	2.030	2.270		
4000	1.115	1.203	1.288	1.389	1.543	1.709	1.895	2.58	3.44
5000	1.070	1.133	1.192	1.270	1.382	1.497	1.630	2.17	2.82
6000	1.033	1.080	1.130	1.190	1.274	1.360	1.454	1.90	2.43
7000	1.003	1.040	1.080	1.130	1.195	1.260	1.335	1.72	2.16
8000	.976	1.010	1.040	1.085	1.133	1.184	1.238	1.59	1.98
9000	.955	.987	1.014	1.052	1.087	1.123	1.161	1.50	1.84
10000	.932	.963	.994	1.025	1.055	1.086	1.117	1.426	1.735
12000	.901	.929	.956	.983	1.011	1.038	1.065	1.339	1.612
15000	.870	.895	.921	.946	.972	.997	1.023	1.277	1.531
20000	.828	.851	.874	.897	.920	.943	.966	1.196	1.426
25000	.7960	.8175	.8390	.8605	.8820	.9035	.9250	1.140	1.355
30000	.7706	.7906	.8106	.8306	.8506	.8706	.8906	1.091	1.291
40000	.7300	.7482	.7663	.7844	.8025	.8206	.8387	1.020	1.201
50000	.6979	.7148	.7317	.7486	.7655	.7825	.7994	.968	1.138
60000	.6696	.6854	.7012	.7170	.7328	.7486	.7644	.922	1.080
300000	.6235	.6373	.6510	.6648	.6786	.6923	.7061	.844	.982
1000000	.5872	.5992	.6112	.6232	.6352	.6472	.6592	.779	.899
2000000	.4838	.4899	.4959	.5020	.5080	.5141	.5201	.581	.641
3000000	.438	.441	.445	.448	.451	.455	.458	.491	.523
4000000	.408	.410	.412	.415	.417	.419	.421	.441	.461
6000000	.371	.372	.373	.374	.375	.376	.377	.387	.397
8000000	.347	.348	.349	.349	.350	.350	.351	.357	.363
10000000	.329	.329	.330	.330	.331	.331	.332	.336	.340

P	V_{4273°	V_{5273°	V_{6273°	V_{7273°	V_{8273°	V_{9273°	$V_{10,273^\circ}$
10000	2.044	2.353	2.662	2.971	3.280	3.589	3.898
12000	1.886	2.159	2.433	2.706	2.980	3.253	3.527
15000	1.786	2.040	2.295	2.549	2.803	3.058	3.312
20000	1.656	1.886	2.116	2.346	2.576	2.806	3.036
25000	1.570	1.785	2.000	2.215	2.430	2.645	2.860
30000	1.491	1.691	1.891	2.091	2.291	2.491	2.691
40000	1.382	1.563	1.744	1.925	2.106	2.288	2.469
50000	1.307	1.476	1.645	1.814	1.983	2.152	2.321
60000	1.238	1.396	1.554	1.712	1.870	2.028	2.185
80000	1.119	1.257	1.395	1.532	1.670	1.808	1.945
100000	1.019	1.139	1.259	1.379	1.499	1.619	1.739
200000	.702	.762	.823	.883	.944	1.004	1.065
300000	.556	.589	.622	.655	.687	.720	.753
400000	.481	.501	.522	.542	.562	.582	.602
600000	.408	.418	.428	.438	.448	.458	.468
800000	.369	.376	.382	.388	.394	.400	.406
1000000	.345	.349	.354	.358	.362	.367	.371

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Fig. 1. Sources and coverage of P-V-T data on water.

Fig. 2. $V(P)$ extrapolation curve at 175°C .

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Fig. 3. $V(T)$ extrapolation curve.

ML-13394

Fig. 4. P-T dependence of Hugoniot, adiabats and dissociation.

MUL-13395

Fig. 5. Variation of the internal pressure zero point.

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