

PVT Properties of Water and Mercury

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The PVT properties of water and mercury have been measured up to 8000 bar between 30 and 150°C with an accuracy of 0.01% of the volume by electromagnetically detecting the change in length of a column of fluid. Numerical differentiation yields thermal expansion coefficients and compressibilities accurate to 0.5% for water and 1.0% for mercury. The first and second derivatives of entropy with respect to volume for mercury are consonant with a hard sphere model, though $(\partial^2 U/\partial V^2)_T$ requires a softer repulsive potential. Water, because of its structure, only approaches such a simple model above our maximum temperature.

INTRODUCTION

The purpose of this study is twofold. First, data of sufficiently high precision to provide derivatives of the equation of state accurate to 1% or better were not available for mercury or water up to 8000 bar except along certain select isotherms or at low pressures. Thus, a good map of thermal expansion coefficients was not available at high pressures. Both thermal expansion coefficients and compressibilities are needed to compute the derivatives of entropy and energy with respect to volume which are exceedingly useful in testing theoretical equations of state.

Second, the piezometer uses a mercury seal and the measurement of the properties of mercury and water in conjunction with the already existing high precision data provides a test of the equipment to provide that no meniscus correction is required as a function of temperature and pressure. The piezometer is designed for use in our program with hydrocarbons and fused organic salts. It is required to have a small volume of only 1.5 cc and to permit the sample to be solid or liquid at room temperature.

EXPERIMENTAL

Piezometer Design

The piezometer is of a design similar to that of Doolittle, Simon, and Cornish¹ in which the volume of the liquid is determined by measuring the length of a vertical column of liquid in a sample tube of uniform bore, enclosed in a standard high-pressure tube. The sample tube of 310 stainless steel (as drawn temper 0.092 in. o.d. × 0.072 in. i.d. × 22 in., Superior Tube Co.) is closed at the top and the lower end is immersed in a mercury well of 304 stainless steel (0.120 in. o.d. × 0.106 in. i.d.). A cylindrical float 0.068 in. diam × 0.5 in. of a magnetic, heat-treated 416 stainless steel floats in the sample on the surface of the mercury seal. The position of this float is measured relative to a similar piece of 416 steel welded into the top of the sample tube by means of a linear variable differential transformer mounted on the outside of the $\frac{1}{8} \times \frac{9}{16}$ in., 304 stainless steel pressure tubing. The transformer is used as a null instrument and is moved along the pressure tubing by the leadscrew of a Monarch type E

toolroom lathe. While the detection system can see 0.0001 in., the over-all accuracy is 0.001 in. A removable 416 SS plug is inserted into the lower end of the sample tube with a breather hole above it to permit entry of the mercury into the sample tube. The distance between this plug and the top plug permits continual monitoring of the compressibility and thermal expansion of the sample tube. The whole assembly is immersed in a thermostat of GE-SF 1093 silicone oil controlled to $\pm 0.02^\circ\text{C}$ and the temperature is measured with a platinum resistance thermometer.

In constructing the sample tube, care must be taken to maintain magnetic symmetry about the 416 SS plugs. The plugs at the top and bottom are welded at their midpoints to short sections of tubing which extend at least an inch beyond them. Without this symmetry, the magnetic centers shifted of the order of 0.02 in. with a 100° temperature change. Mercury and water showed no effect on the magnetic centers. The length of the plugs between the magnetic centers was determined by measuring the distance between the magnetic centers with the transformer while a 1-in. glass spacer of known length was between them. The annular volume of the test fluid around the float was determined from the dimensions of the float and the average cross section of the sample tube. The latter was obtained from the volume of the tube calculated from the weight of the tube filled with mercury and its internal length measured with a cathetometer using a transfer standard.

Since the transformer position is measured by the rotations of the leadscrew, its thermal expansion was measured by relative measurements with a copper rod constructed similarly to the sample tube. The lead screw of AISI-C-1144 steel has a mean thermal expansion coefficient between 25 and 150°C of $(12.2 \pm 0.4) \times 10^{-6}/^\circ\text{C}$ based on copper SAE-CA 102.²

The cross sectional area of the sample tube is corrected for thermal expansion and compression. The thermal expansion of the 310 SS sample tube was measured in two ways. A direct measurement was made of the length of the tube using the magnetic plugs in the top and bottom. The second method was to measure the thermal expansion of a liquid whose expansion was known accurately at or near 1-atm pressure. Calibration with water^{3,4} and mercury⁵ between 25 and

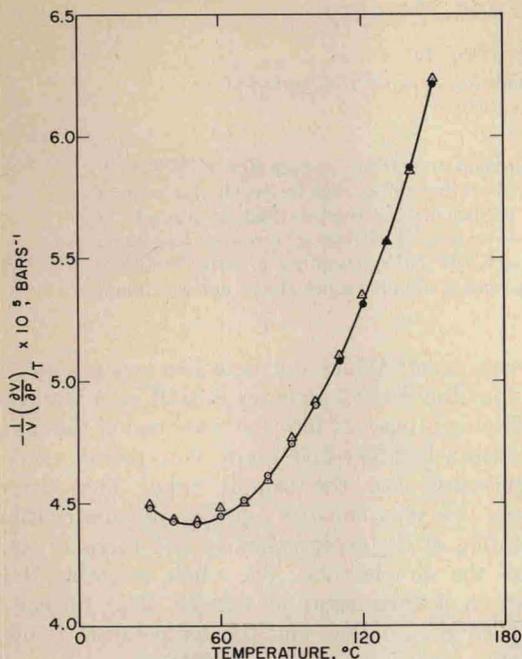


FIG. 1. Compressibility of water at 1 atm pressure. —, This work; \circ , Ref. 15; \bullet , Ref. 3.

150°C yielded values of the sum of the coefficient of expansion of the lead screw plus twice the coefficient of expansion of the sample tube. The results by the two methods agreed well, giving an uncertainty in subsequent density measurements of less than 0.01%. The resulting thermal expansion coefficient of 310 SS is taken as $14.6 \times 10^{-6}/^\circ\text{C}$. The compressibility found by direct measurement is accurate to 1.5% and is found to increase by 1.0% over a 120°C range from the value of $2.13_4 \times 10^{-6}/\text{bar}$ at 30°C.

Finally one must determine (1) if there is a taper to the bore of the sample tube, (2) if there is a significant change in the shape of the mercury meniscus with temperature and pressure, (3) if there is anisotropy in the physical properties of the drawn sample tube, and (4) if there is a significant film left on the walls as the mercury moves up the sample tube. The above measurement of the thermal expansion coefficient of the sample tube by two methods would have shown a discrepancy caused by any of these phenomena except anisotropy in the compressibility of the metal. However, lack of any anisotropy in the thermal expansion coefficients suggests that the compressibility should be similar. If the mercury meniscus changed shape, the density data for water with a mercury seal and mercury with a water seal should have deviated in opposite directions from existing accurate data. At 1 atm a temperature effect on the meniscus of mercury would have resulted in the metal expansion coefficients calculated by the second method differing significantly when water and mercury were used. No such deviations were observed. To test the uniformity of the bore by another method, a second sample tube was made from

304 stainless steel (Uniform Tube Co.) and a compression isotherm was run on water at 100°C. The results agreed within 0.01% with those from the 310 tube over the 8000-bar range.

Pressure Measurement

The pressure is measured on a Harwood manganin gauge with 110- Ω pressure and balancing coils. These two coils are thermostated in an oil bath at $25 \pm 0.05^\circ\text{C}$, while the other side of the Wheatstone bridge containing 2000- Ω arms has all resistors of 1 Ω or greater thermostated at 34°C . The precision of measurement is 0.2 bar at all pressures. The gauge is calibrated periodically at the freezing point of mercury at 0°C using the recent international standard of 7569 bar.⁶ The electrical resistance of a mercury filled capillary is used to locate the freezing point to ± 1.5 bar. The resistance decreases upon freezing by over a factor of 2 so that the freezing and melting can easily be followed by the drift in the resistance on the Mueller bridge. The freezing point is independent of the bridge current. The nonlinearity of the gauge was determined by calibration to 10 000 psi with a Ruska 2400 H dead weight tester. At this pressure the deviation from linearity based on the mercury freezing point is about one third of the maximum deviation of 11 bar which occurs at 4000 bar when a quadratic form is used. These deviations from linear are in the direction such that the correct pressure is greater than the pressure obtained from the assumption that the gauge is linear. The daily drift of the resistance of the manganin gauge is about 1 bar; however, the pressure coefficient of the resistivity is unaltered by the drift to higher resistances.

Samples

Water was distilled off permanganate and the mercury was the commercial triply distilled grade. Some liquid is entrapped when the sealing mercury is injected

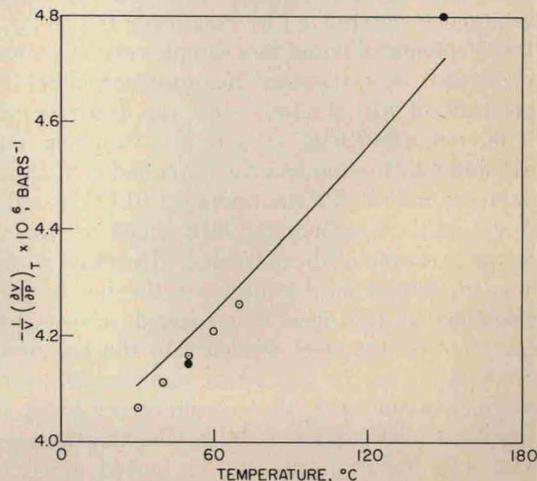


FIG. 2. Compressibility of mercury at 1 atm. pressure. —, This work; \circ , Ref. 19; \bullet , Ref. 20.

TABLE I. Specific volume of water, cm³/g.

P, BARS	TEMPERATURE, °C													
	25.00	30.00	40.00	50.00	60.00	70.00	80.00	90.00	100.00	110.00	120.00	130.00	140.00	150.00
0.	1.00301	1.00442	1.00789	1.01215	1.01714	1.02279	1.02907	1.03598	1.04350	1.05165	1.06042	1.06985	1.07996	1.09080
200.	0.99419	0.99565	0.99920	1.00344	1.00830	1.01384	1.01988	1.02643	1.03360	1.04131	1.04956	1.05843	1.06789	1.07786
400.	0.98582	0.98738	0.99098	0.99523	1.00002	1.00542	1.01126	1.01755	1.02438	1.03171	1.03951	1.04790	1.05675	1.06616
600.	0.97790	0.97955	0.98322	0.98747	0.99216	0.99747	1.00312	1.00918	1.01575	1.02276	1.03023	1.03820	1.04658	1.05538
800.	0.97044	0.97213	0.97588	0.98011	0.98478	0.98996	0.99543	1.00134	1.00769	1.01445	1.02157	1.02918	1.03710	1.04548
1000.	0.96337	0.96509	0.96891	0.97315	0.97774	0.98285	0.98821	0.99393	1.00006	1.00658	1.01341	1.02073	1.02825	1.03624
1200.	0.95665	0.95841	0.96226	0.96650	0.97107	0.97604	0.98131	0.98688	0.99282	0.99915	1.00574	1.01272	1.01998	1.02759
1400.	0.95024	0.95206	0.95596	0.96016	0.96469	0.96960	0.97477	0.98019	0.98599	0.99209	0.99847	1.00520	1.01214	1.01948
1600.	0.94412	0.94596	0.94991	0.95408	0.95864	0.96344	0.96845	0.97338	0.97943	0.98537	0.99156	0.99807	1.00478	1.01183
1800.	0.93828	0.94016	0.94413	0.94832	0.95280	0.95755	0.96252	0.96775	0.97325	0.97902	0.98499	0.99134	0.99782	1.00461
2000.	0.93271	0.93460	0.93857	0.94277	0.94719	0.95192	0.95678	0.96191	0.96728	0.97288	0.97871	0.98487	0.99115	0.99772
2200.	0.92737	0.92928	0.93327	0.93747	0.94185	0.94649	0.95132	0.95630	0.96156	0.96706	0.97272	0.97870	0.98482	0.99121
2400.	0.92220	0.92414	0.92818	0.93231	0.93670	0.94130	0.94603	0.95096	0.95609	0.96150	0.96710	0.97282	0.97878	0.98495
2600.	0.91727	0.91922	0.92320	0.92738	0.93168	0.93627	0.94093	0.94578	0.95083	0.95608	0.96150	0.96715	0.97296	0.97896
2800.	0.91252	0.91446	0.91850	0.92264	0.92693	0.93142	0.93606	0.94077	0.94578	0.95091	0.95619	0.96175	0.96736	0.97323
3000.	0.90792	0.90990	0.91395	0.91805	0.92235	0.92679	0.93135	0.93601	0.94089	0.94598	0.95111	0.95652	0.96206	0.96771
3200.	0.90351	0.90547	0.90949	0.91361	0.91782	0.92227	0.92675	0.93137	0.93616	0.94113	0.94623	0.95148	0.95688	0.96248
3400.	0.89925	0.90121	0.90527	0.90928	0.91353	0.91789	0.92236	0.92689	0.93163	0.93648	0.94147	0.94668	0.95192	0.95737
3600.	0.89513	0.89710	0.90111	0.90518	0.90935	0.91371	0.91805	0.92266	0.92720	0.93204	0.93692	0.94199	0.94719	0.95244
3800.	0.89114	0.89309	0.89714	0.90116	0.90531	0.90960	0.91397	0.91836	0.92298	0.92766	0.93252	0.93749	0.94255	0.94779
4000.	0.88725	0.88923	0.89321	0.89726	0.90137	0.90565	0.90996	0.91432	0.91882	0.92349	0.92821	0.93314	0.93810	0.94316
4200.	0.88349	0.88545	0.88948	0.89349	0.89761	0.90175	0.90605	0.91037	0.91484	0.91940	0.92408	0.92887	0.93377	0.93877
4400.	0.87984	0.88184	0.88581	0.88982	0.89386	0.89807	0.90226	0.90656	0.91092	0.91546	0.92000	0.92480	0.92956	0.93448
4600.	0.87630	0.87826	0.88226	0.88622	0.89029	0.89442	0.89861	0.90281	0.90717	0.91159	0.91615	0.92076	0.92551	0.93040
4800.	0.87287	0.87484	0.87879	0.88278	0.88677	0.89089	0.89497	0.89919	0.90345	0.90786	0.91230	0.91693	0.92153	0.92629
5000.	0.86949	0.87147	0.87544	0.87937	0.88339	0.88743	0.89155	0.89564	0.89991	0.90422	0.90863	0.91313	0.91772	0.92235
5200.	0.86626	0.86820	0.87214	0.87606	0.88002	0.88411	0.88814	0.89222	0.89639	0.90070	0.90498	0.90950	0.91395	0.91858
5400.	0.86307	0.86505	0.86894	0.87285	0.87677	0.88080	0.88488	0.88886	0.89303	0.89724	0.90152	0.90589	0.91034	0.91483
5600.	0.85996	0.86194	0.86585	0.86970	0.87365	0.87762	0.88158	0.88561	0.88969	0.89387	0.89812	0.90245	0.90679	0.91126
5800.	0.85697	0.85892	0.86279	0.86667	0.87052	0.87450	0.87845	0.88240	0.88646	0.89060	0.89475	0.89905	0.90334	0.90773
6000.	0.85399	0.85596	0.85985	0.86367	0.86754	0.87145	0.87537	0.87928	0.88332	0.88737	0.89150	0.89573	0.89996	0.90433
6200.	0.85113	0.85307	0.85693	0.86075	0.86459	0.86848	0.87236	0.87626	0.88020	0.88426	0.88830	0.89253	0.89667	0.90097
6400.	0.84830	0.85026	0.85410	0.85792	0.86170	0.86559	0.86942	0.87328	0.87723	0.88120	0.88524	0.88935	0.89333	0.89770
6600.	0.84555	0.84748	0.85133	0.85512	0.85894	0.86275	0.86657	0.87036	0.87425	0.87824	0.88219	0.88629	0.89036	0.89453
6800.	0.84289	0.84478	0.84862	0.85239	0.85616	0.86000	0.86375	0.86751	0.87138	0.87529	0.87920	0.88328	0.88733	0.89139
7000.	0.84022	0.84217	0.84597	0.84971	0.85346	0.85726	0.86101	0.86474	0.86859	0.87241	0.87624	0.88032	0.88431	0.88837
7200.	0.83764	0.83958	0.84337	0.84709	0.85082	0.85458	0.85830	0.86201	0.86581	0.86965	0.87346	0.87745	0.88137	0.88537
7400.	0.83514	0.83704	0.84082	0.84454	0.84821	0.85199	0.85563	0.85938	0.86310	0.86689	0.87070	0.87461	0.87851	0.88245
7600.	0.83265	0.83456	0.83832	0.84199	0.84570	0.84942	0.85305	0.85675	0.86049	0.86419	0.86799	0.87185	0.87569	0.87963
7800.	0.83021	0.83211	0.83588	0.83954	0.84322	0.84689	0.85055	0.85419	0.85787	0.86160	0.86528	0.86913	0.87295	0.87681
8000.	0.82786	0.82975	0.83346	0.83712	0.84078	0.84446	0.84807	0.85167	0.85533	0.85901	0.86270	0.86646	0.87026	0.87409

into the bottom of the sample tube. Therefore, the water was held overnight at 100°C to insure separation. The mercury was prepared by degassing under vacuum, and was then held under water at 100°C for several days.

RESULTS

The measured specific volumes of water are given in Table I using the known data near 1 atm.^{3,4} Pressures are expressed in bars, absolute, and temperature on the International Practical Temperature Scale of 1948. The data were taken at equal intervals assuming the pressure gauge to be linear and then the data were corrected for the nonlinearity of the gauge. Derivatives of the volumetric data for water were computed by successively fitting seven point quartics and then differentiating at the middle point, except at the edges of the block of data where the differentiation was carried out at the remaining points also. Seven point quadratics were fitted to the $(\partial V/\partial T)_P$ to obtain the pressure correction to C_p . Tables of compressibility, thermal expansion coefficients $(\partial S/\partial V)_T$, $(\partial U/\partial V)_T$, C_p and C_v are available⁷ as well as tables of S , U , and H based on the low-pressure values in the National Engineering Laboratory Steam Tables (1964).⁸ The heat capacities at 1 atm for water are those of Osborne, Stimson, and Ginnings.⁹

Our volumetric data for water can be compared with measurements made by three methods: the volumetric displacement method, the bellows method, and the method of integrating the compressibility computed from velocity of sound measurements.

The most accurate data available for water are those of Kell and Whalley^{3,4} who used the displacement method. At their maximum pressure of 1000 bar, our volumetric data lie between 0.000 and 0.010% below theirs over the whole temperature range. Much earlier Adams¹⁰ used the displacement method to much higher pressures at 25°C. The present data lie 0.02%

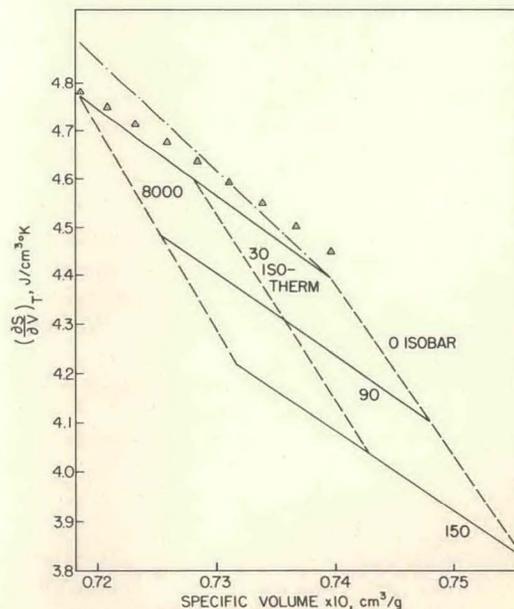


FIG. 3. Derivative of the entropy with respect to volume for mercury. Δ Reference 21; ---, hard-sphere theory.

TABLE II. Density of mercury, g/cm³.

P, BARS	TEMPERATURE, C												
	30.00	40.00	50.00	60.00	70.00	80.00	90.00	100.00	110.00	120.00	130.00	140.00	150.00
0.	13.5213	13.4969	13.4725	13.4482	13.4239	13.3997	13.3755	13.3514	13.3273	13.3033	13.2792	13.2553	13.2314
1000.	13.5755	13.5526	13.5279	13.5053	13.4808	13.4572	13.4325	13.4103	13.3871	13.3634	13.3389	13.3157	13.2925
2000.	13.6286	13.6052	13.5818	13.5590	13.5356	13.5127	13.4887	13.4659	13.4433	13.4200	13.3969	13.3750	13.3516
3000.	13.6797	13.6577	13.6340	13.6121	13.5882	13.5656	13.5424	13.5206	13.4986	13.4745	13.4522	13.4306	13.4085
4000.	13.7302	13.7078	13.6846	13.6630	13.6404	13.6182	13.5948	13.5731	13.5515	13.5296	13.5071	13.4856	13.4627
5000.	13.7786	13.7569	13.7345	13.7127	13.6900	13.6683	13.6459	13.6247	13.6035	13.5813	13.5590	13.5381	13.5167
6000.	13.8272	13.8044	13.7819	13.7612	13.7393	13.7175	13.6948	13.6746	13.6530	13.6325	13.6105	13.5896	13.5679
7000.	13.8729	13.8516	13.8294	13.8084	13.7865	13.7653	13.7438	13.7231	13.7028	13.6811	13.6595	13.6402	13.6188
8000.	13.9181	13.8971	13.8749	13.8547	13.8335	13.8126	13.7906	13.7705	13.7501	13.7298	13.7078	13.6877	13.6675

below Adam's specific volumes at 5000 bar and in almost exact agreement at 8000 bar. Bridgman's early displacement measurements¹¹ appear uncertain because his pressure scale was in error by 1% at 8000 bars.¹² After estimating the correction to the pressure scale, his volume at 8000 bar and 25°C is 0.17% greater than ours.

There are in general much larger discrepancies with the siphon bellows techniques. Our specific volumes lie 0.6% below Bridgman's bellows data¹³ at the same conditions as above. Similarly the data of Burnham *et al.*¹⁴ deviate from ours in the same direction over the whole temperature range with a maximum deviation of 0.6% at 8000 bar.

A truly independent check of the PVT measurements comes from the compressibility computed from the velocity of sound. Figure 1 shows our compressibilities of water at 1 atm compared with those of Greenspan and Tschigg¹⁵ from the velocity of sound. The latter have been checked by Carnvale, Bowen, Basileo, and Sprenke¹⁶ over the limited range 0.5–40°C and are in error by no more than 0.06%. The agreement with our data is quite good with only an occasional point off by 0.5%. Holton, Hagelberg, Kao, and Johnson¹⁷ have measured the velocity of sound at high pressures and have integrated their compressibilities to obtain volumetric data. At 40°C and 8000 bar they agree within 0.01% of our data while at their highest temperature of 80°C and 8000 bar their volume is 0.1% larger than ours. The latter difference is equal to the uncertainty in their volumes at this high pressure.

Thus, the data derived from the velocity of sound measurements agree with our data to between 0.01% and 0.1%; the displacement methods generally agree to within this accuracy while the bellows methods all yield volumes which are high by 0.6%. We estimate

TABLE III. Coefficients for the equation of state of mercury.

$$P = \sum_{l,m=0} C_{l,m} t^l \rho^m,^a$$

<i>m</i>	0	1	2
<i>l</i>			
0	7.421727 × 10 ⁵	-1.277089 × 10 ⁵	5.378285 × 10 ³
1	-58.65276	+5.684101	+0.1450404
2	-0.3624357	+5.464785 × 10 ⁻²	-2.129211 × 10 ⁻³

^a Units: *P*, bars; *t*, °C; *ρ*, g/cm³.

the maximum error to be no more than 0.02% for our volumetric data for water and the precision is about 0.005%. The compressibility and thermal expansion coefficients are accurate to 0.5% except for the compressibility at very high pressure where the decrease of the compressibility causes the percentage error to increase somewhat.

The densities of mercury based on Biggs' values⁴ at 1 atm are also given in Table II. Because the compressibility is about a tenth that of water, measurements were made at only 1000-bar intervals. Since the first derivatives of the mercury data have a precision of 1% and are slowly varying functions, all the data were fitted by a single equation of state given in Table III. Our calculated compressibilities at 1 atm are compared in Fig. 2 with the isothermal compressibilities derived from the velocity of sound data of Hubbard and Loomis¹⁸ after Bett, Weale, and Newitt.¹⁹ Our compressibilities lie about 1% above these values and are straddled by Kleppa's data.²⁰ Since the compressi-

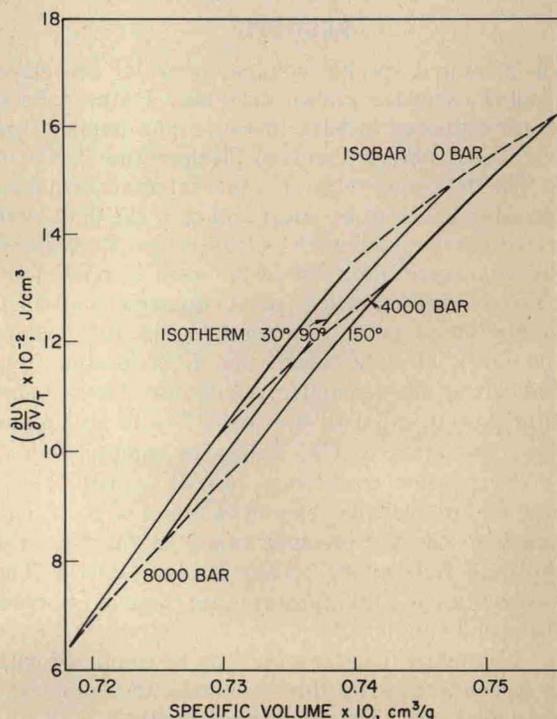


FIG. 4. Derivative of the internal energy with respect to volume for mercury.

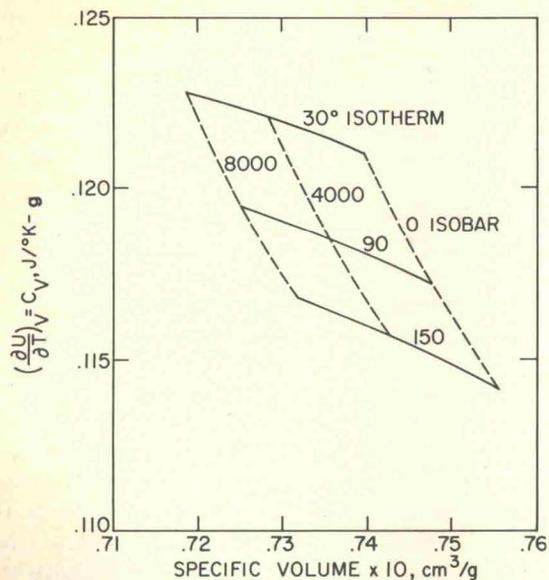


FIG. 5. Heat capacity of mercury at constant volume.

bilities of Davis and Gordon²¹ depend on the velocity of sound at 1 atm of Hubbard and Loomis, their high-pressure compressibilities are low by the same amount. Their volumes obtained by integration of the compressibility are larger than ours and the two sets of data diverge uniformly to a maximum difference of 0.03% at 8000 bar.

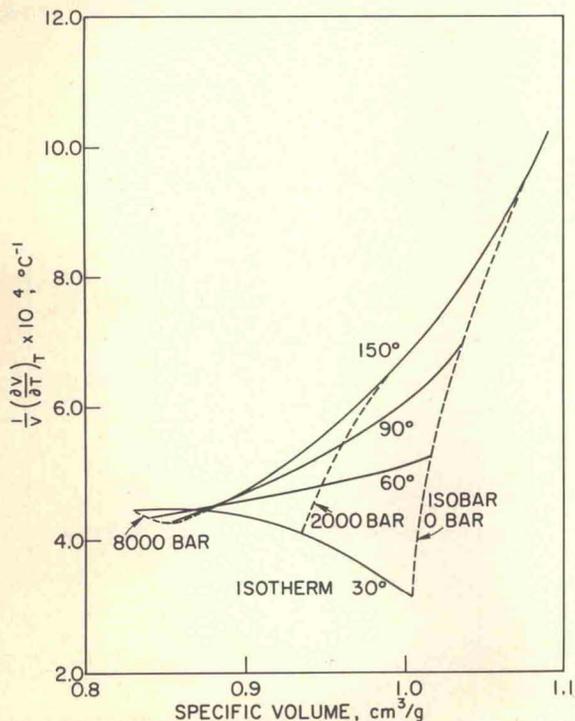


FIG. 6. Thermal expansion coefficient of water.

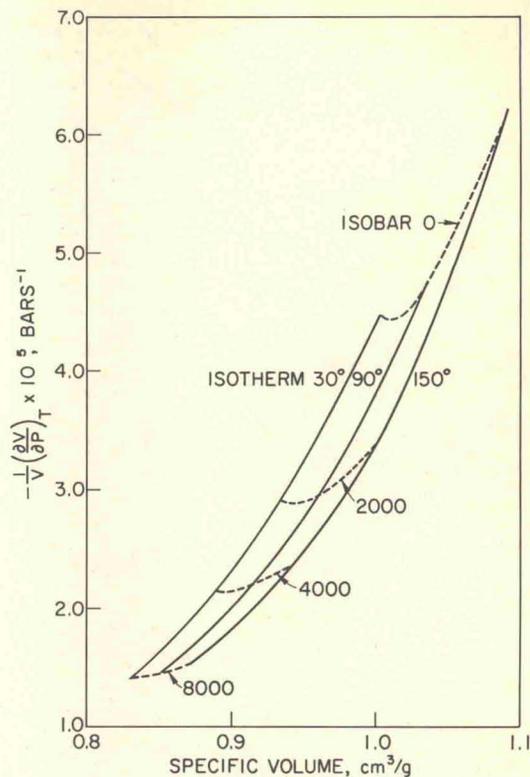


FIG. 7. Compressibility of water.

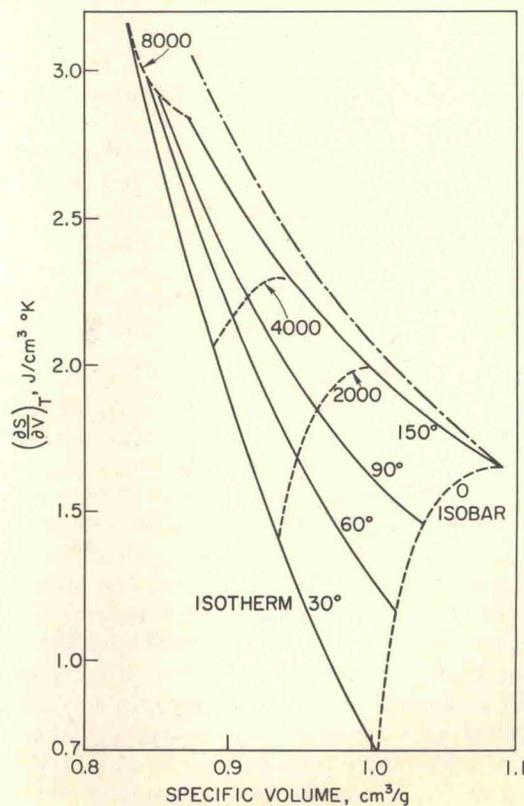


FIG. 8. Derivative of entropy with respect to volume of water. ---, hard-sphere theory.

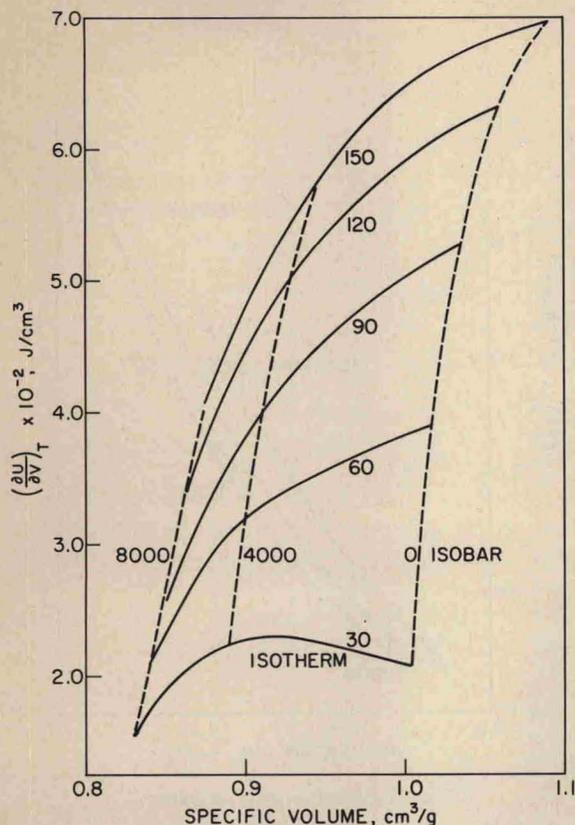


FIG. 9. Derivative of energy with respect to volume of water.

DISCUSSION

A convenient, simple model against which real systems can be tested is the hard-sphere model. This model represents the very density-sensitive phenomena arising from the packing of molecules in a dense fluid. Real systems can then be modeled by the addition of terms related to the potential energy which are slowly varying functions of the density. Ascarelli,²² in describing the compressibility and the velocity of sound in mercury, used such an equation of state

$$P = \frac{2}{3} Z E_F (N/V) - (B/V^{1/3}) + P_H, \quad (1)$$

where P is the total pressure and (N/V) is the number of atoms per unit volume. Here the hard-sphere pressure P_H has been modified by two energy terms which are temperature independent. The first term accounts for the contribution to the pressure from the Fermi energy E_F of the electron gas while the second accounts for the Coulomb, exchange, and correlation energies as well as the energy of the lowest state of the Z valence electrons per atom. The derivative $(\partial S/\partial V)_T$ for this equation of state is simply that of the hard core system. Figure 3 shows this derivative for mercury compared with the temperature-independent isotherm for the hard core system fitted to the data at 30° and zero pressure. The hard-sphere equation of state used was the (3, 3) Pade approximant of Ree and Hoover.²³

The hard-sphere density ($\pi\sigma^3N/6V$) is 0.4212, just slightly lower than the value of 0.45 found by Ashcroft and Lekner²⁴ for sodium from compressibility at 100° using the Percus-Yevick equation. This latter value has been used extensively for correlating properties of many liquid metals including mercury at their melting points. The diameter resulting from the density of 0.4212 is 2.706 Å. The absolute value of $(\partial^2 S/\partial V^2)_T$ is greater for the hard-sphere system than for mercury. An exact fit at all volumes and temperatures would require the diameter to decrease 0.01 to 0.02 Å with increasing temperature and pressure, thus indicating that a very steep continuous repulsive potential is necessary.

If the absolute entropy of mercury, given by Douglas, Ball, and Ginnings,²⁵ is calculated from the ideal gas entropy plus a correction for the gas imperfections of the hard spheres, the gas imperfections must contribute a decrease of the entropy of 2.4 R to 1.9 R as the temperature increases from 30 to 150°C. The hard-sphere densities of 0.42 and 0.45 quoted above will yield more than half this correction²⁶ and a density of 0.47 to 0.50 is required for the full corrections. Thus, the entropy suggests that the mercury atoms are more constrained than the hard-sphere system at the densities of 0.42 to 0.45 suggested by the other properties.

Figure 4 shows $(\partial U/\partial V)_T$ as a function of volume. This derivative depends only on the first two terms of Eq. (1). By using the Fermi energy given by Ascarelli²² to fit B empirically at 30° and zero pressure, $(\partial^2 U/\partial V^2)_T$ is found to be of opposite sign to that observed. This again suggests the need of a steep repulsive potential with a large curvature. For completeness $(\partial U/\partial T)_V$

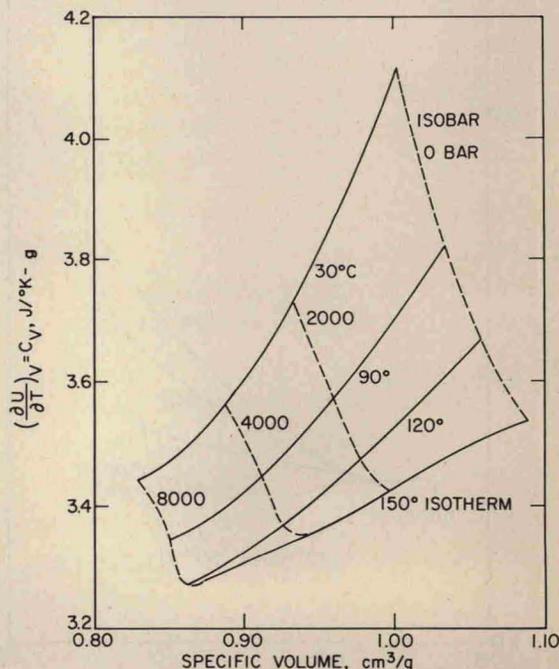


FIG. 10. Heat capacity of water at constant volume.

or the heat capacity at constant volume is shown in Fig. 5. It is based on the data of Douglas, Ball, and Ginnings²⁵ at 1 atm.

The isotherms for almost all of the properties of water are in inverted order from those of mercury. Figures 6 and 7 show the thermal expansion and compressibility surfaces. The former only achieves the order of the mercury isotherms at pressures near 8000 bar. Only at the highest temperatures does $(\partial S/\partial V)_T$ for hard spheres approximate the experimental data shown in Fig. 8 with a decrease of only 0.03 Å in the hard-sphere diameter over the 8000-bar range. At low temperatures a hard-sphere model would require the unreasonable picture of the size decreasing with decreasing temperature, and the hard-sphere $(\partial^2 S/\partial V^2)_T$ would be much too small. The isotherms in Fig. 9 for $(\partial U/\partial V)_T$ are inverted from those of mercury. The maximum in the 30° isotherm represents an inflection in the energy as a function of volume. This inflection is destroyed at higher temperatures with any such inflection having moved to volumes greater than the zero pressure volumes. No such phenomenon could be obtained from a spherically symmetric pair potential. For simple hydrocarbons all isotherms of $(\partial U/\partial V)_T$ would nearly coincide²⁷ and show a maximum at the inflection in the energy curve. The positive values of $(\partial^2 U/\partial V^2)$ at temperatures somewhat above 30° present the necessity of a sharply rising repulsive potential to give a positive curvature to the potential energy curve as is the case with mercury.

Finally, C_v for water, given in Fig. 10, shows a marked decrease at low temperatures as the volume is decreased. This result is in contrast to mercury where it rises with decreased volume. In the case of water the decrease of C_v presumably reflects the partial breakdown of the normal hydrogen-bonded structure as the fluid is compressed.

A closer analysis of water requires a detailed model of its specific structure. We hope that this data will provide a test for these models as they are developed.

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