

TABLE I. Specific volume of water, cm<sup>3</sup>/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	0.97383	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	0.96701	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	0.96244
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	0.89792	0.90206	0.90626	0.91056	0.91492	0.91940	0.92408	0.92887	0.93377
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	0.87877	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	0.86947	0.87328	0.87723	0.88120	0.88524	0.88935	0.89353	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	0.84211	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.<sup>3,4</sup> 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 available<sup>7</sup> as well as tables of  $S$ ,  $U$ , and  $H$  based on the low-pressure values in the National Engineering Laboratory Steam Tables (1964).<sup>8</sup> The heat capacities at 1 atm for water are those of Osborne, Stimson, and Ginnings.<sup>9</sup>

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<sup>3,4</sup> 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 Adams<sup>10</sup> used the displacement method to much higher pressures at 25°C. The present data lie 0.02%

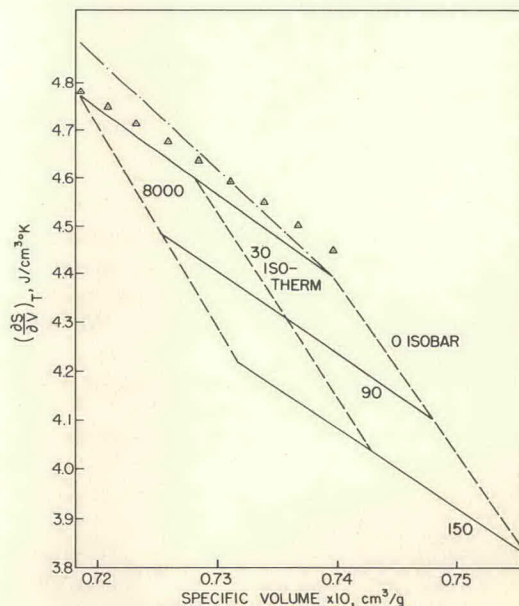


FIG. 3. Derivative of the entropy with respect to volume for mercury.  $\Delta$  Reference 21; ---, hard-sphere theory.

TABLE II. Density of mercury, g/cm<sup>3</sup>.

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 measurements<sup>11</sup> appear uncertain because his pressure scale was in error by 1% at 8000 bars.<sup>12</sup> After estimating the correction for 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 data<sup>13</sup> at the same conditions as above. Similarly the data of Burnham *et al.*<sup>14</sup> 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 Tschigg<sup>15</sup> from the velocity of sound. The latter have been checked by Carnvale, Bowen, Basileo, and Sprenke<sup>16</sup> 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 Johnson<sup>17</sup> 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 <sup>5</sup>	-1.277089 × 10 <sup>5</sup>	5.378285 × 10 <sup>3</sup>
1	-58.65276	+5.684101	+0.1450404
2	-0.3624357	+5.464785 × 10 <sup>-2</sup>	-2.129211 × 10 <sup>-3</sup>

<sup>a</sup> Units: *P*, bars; *t*, °C; *ρ*, g/cm<sup>3</sup>.

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' values<sup>4</sup> 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 Loomis<sup>18</sup> after Bett, Weale, and Newitt.<sup>19</sup> Our compressibilities lie about 1% above these values and are straddled by Kleppa's data.<sup>20</sup> Since the compressi-

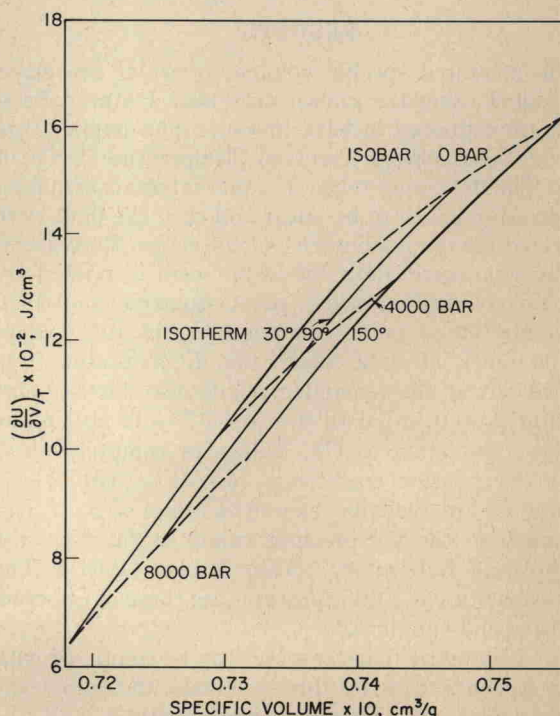


FIG. 4. Derivative of the internal energy with respect to volume for mercury.