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Equation of State of Water to 250 Kilobars*

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An equation of state for water, applicable in the pressure range 25 kilobars to 250 kilobars, is formulated in terms of experimental data obtained from shock wave measurements. This equation of state is used to calculate P-V relations for several adiabats and isotherms. Thermodynamic and hydrodynamic data along the Hugoniot curve are given as a function of shock pressure, and pressure-particle velocity relations for initial shocks followed by reflected shocks and rarefactions are given.

I. INTRODUCTION

THE purpose of this paper is to present a complete thermodynamic description of water at high pressures in the neighborhood of the Hugoniot curve. To this end, the experimental data of the preceding paper are used to formulate an equation of state applicable in the pressure range 25 to 250 kilobars (1 kilobar$\equiv 10^9$ dynes/cm^2). This equation of state is then used to calculate some specific results of interest, such as pressure-volume relations for several adiabats and isotherms neighboring the Hugoniot curve, temperatures and entropies for states on the Hugoniot curve, and changes in particle velocity due to reflected shocks and rarefactions.

II. EQUATION OF STATE

In order to obtain an equation of state, the experimental data of the previous paper are augmented by the assumption that for sufficiently high pressures the thermodynamic variable $(\partial H/\partial V)_P$ may be approximated as a function only of pressure, i.e.,

$$(\partial H/\partial V)_P \equiv C_P/(\partial V/\partial T)_P = \xi(P), \tag{1}$$

where H is the specific enthalpy, V the specific volume, and C_P the specific heat at constant pressure. In the present case Eq. (1) is assumed to hold for pressures greater than 25 kilobars. (See the appendix for a discussion of this approximation.) The assumption (1), when combined with the experimentally determined Hugoniot curve, leads to an equation of state of the form

$$H(P,V) = H_H(P) + \xi(P)[V - V_H(P)], \tag{2}$$

where H_H and V_H are the specific enthalpy and specific volume for a state on the Hugoniot curve and may be considered, of course, as functions only of pressure.

The values of H_H and V_H as a function of pressure can be obtained from the Rankine-Hugoniot relations [Eqs. (1), (2), and (3′) of previous paper] and an analytical fit of the experimental Hugoniot curve data for water initially at 20°C and 1 atmos:

$$U_s - 1.483 = 25.306 \log_{10}(1 + U_p/5.190), \tag{3}$$

where U_s and U_p are the shock and particle velocities respectively in km/sec. Equation (3) fits all the data within experimental error and also gives the correct limiting value for shock velocity as the shock strength approaches zero ($U_p \rightarrow 0$). A comparison of the specific volumes obtained from Eq. (3) with those obtained from previous calculations[1,2] using Bridgman's data shows that there is excellent agreement at 25 kilobars. For pressures below 25 kilobars, the maximum discrepancy in compression, $1 - V/V_0$, is less than 3%. Consequently, in the following calculations, Eq. (3) will be used throughout the entire pressure range 1 atmos to 450 kilobars.

Assumption (1) allows $\xi(P)$ to be obtained directly from the experimental data for $(\Delta H/\Delta V)_P$ (Sec. II of preceding paper). For convenience the following analytical fit is used in the pressure range 25 kilobars to 250 kilobars:

$$\log_{10}\xi = 2.17943 + .0030338P \tag{4}$$

for ξ and P in kilobars.

The thermodynamic description at high pressures may be completed by supplementing the equation of state [Eq. (2)] with specific heat data along some line not an isotherm. In the following calculations C_P at 25 kilobars was assumed to be constant and to have the value 36 bar cm^3/g deg or 0.86 cal/g deg. From Eqs. (1) and (4) it follows that $(\partial V/\partial T)_P$ at 25 kilobars is also constant and has the value 2.0×10^{-4} cm^3/g deg. Actually, since the lowest experimental point for $(\Delta H/\Delta V)_P$ was at a pressure of about 100 kilobars, it was necessary to make an independent evaluation of $(\partial V/\partial T)_P$ at 25 kilobars in order to obtain the value of $\xi(P)$ at this pressure. The way in which C_P and $(\partial V/\partial T)_P$ were evaluated at 25 kilobars is discussed in the appendix.

It follows from the thermodynamic identity

$$\left(\frac{\partial C_P}{\partial T}\right)_s \equiv \frac{C_P}{T} + T\left(\frac{\partial V}{\partial T}\right)_P \left\{\frac{\partial}{\partial T}\left[\frac{C_P}{T\left(\dfrac{\partial V}{\partial T}\right)_P}\right]\right\}_P \tag{5}$$

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* Work done under the auspices of the U. S. Atomic Energy Commission.

[1] H. G. Snay and J. H. Rosenbaum, NavOrd Report 2383 (1952).

[2] M. H. Rice, M. S. thesis, Iowa State College (1955).

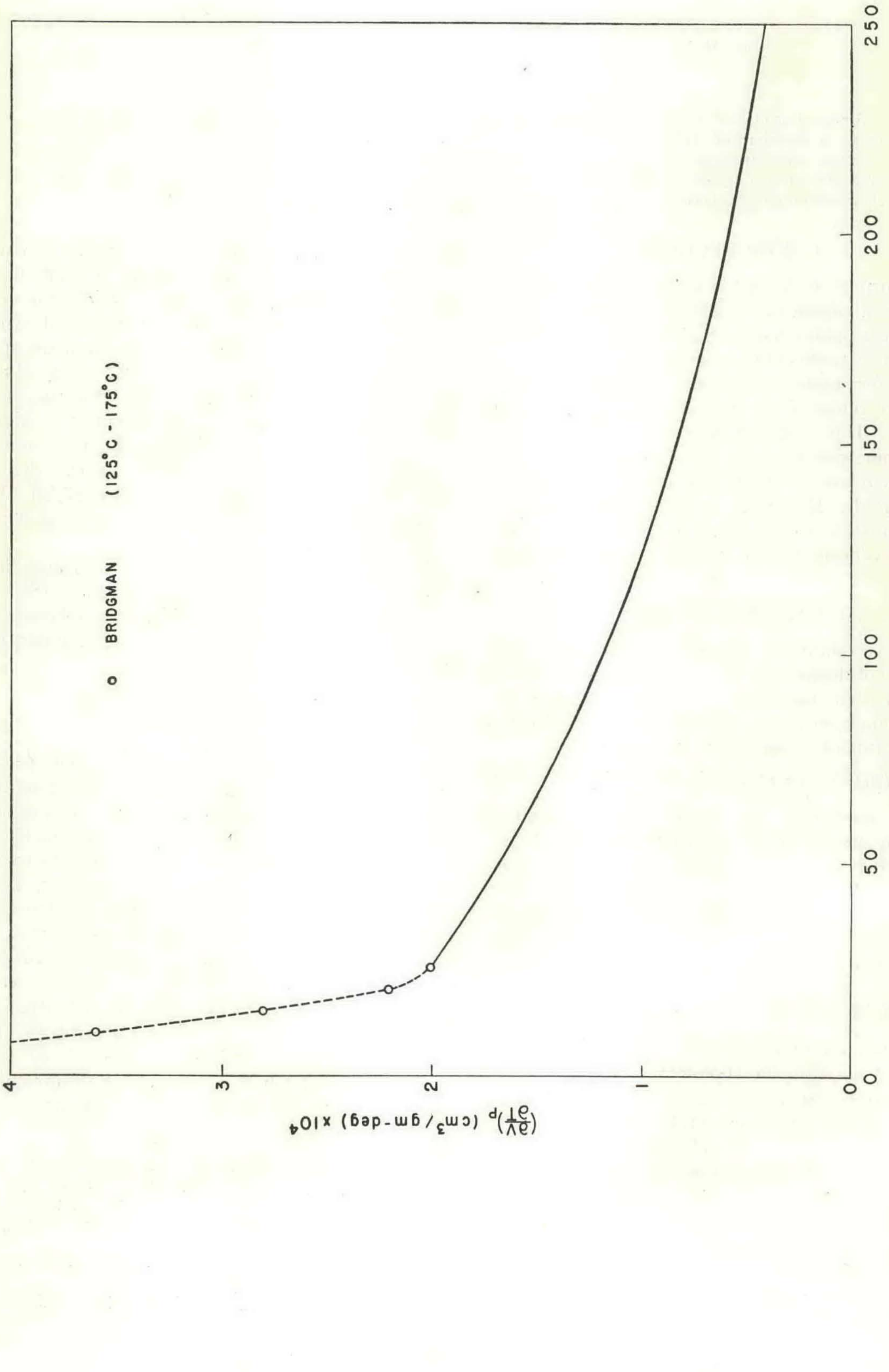

FIG. 1. Thermal expansion as a function of pressure.

TABLE I. Pressure-volume relations for several adiabats which intersect the Hugoniot curve.

P (kbars)	V (cm³/g)				
1	0.998	1.085	1.213	1.400	1.633
5	0.908	0.954	1.028	1.108	1.194
10	0.848	0.882	0.925	0.972	1.020
15	0.806	0.837	0.870	0.906	0.942
20	0.775	0.805	0.835	0.866	0.895
25	0.7513	0.7808	0.8099	0.8382	0.8658
30	0.7316	0.7609	0.7898	0.8178	0.8452
40	0.6995	0.7282	0.7566	0.7841	0.8110
50	0.6735	0.7016	0.7294	0.7563	0.7826
60		0.6781	0.7052	0.7315	0.7571
70		0.6575	0.6838	0.7094	0.7343
80		0.6391	0.6646	0.6894	0.7136
90		0.6225	0.6472	0.6712	0.6945
100		0.6075	0.6313	0.6544	0.6770
110			0.6163	0.6385	0.6602
120			0.6024	0.6238	0.6447
130			0.5897	0.6101	0.6301
140			0.5780	0.5976	0.6167
150			0.5668	0.5855	0.6038
170				0.5639	0,5805
190				0.5450	0.5600
200				0.5363	0.5505
210					0.5418
230					0.5257
250					0.5112

that the assumption (1) requires C_P to be a function only of entropy. The additional assumption that C_P is constant at 25 kilobars is equivalent to assuming C_P independent of pressure above 25 kilobars. The value of $(\partial V/\partial T)_P$ as a function of pressure then follows immediately from Eq. (4).

The resulting variation of $(\partial V/\partial T)_P$ with pressure is shown in Fig. 1.

The remaining sections of this paper are devoted to the use of the above equation of state in the calculation of some specific results of interest.

III. ADIABATS ABOVE 25 KILOBARS

Given an arbitrary pressure-volume point, one may obtain volume as a function of pressure along the adiabat passing through this point by solving the first-order differential equation obtained by differentiating Eq. (2) with respect to pressure at constant entropy:

$$\left(\frac{\partial H}{\partial P}\right)_s \equiv V = \frac{dH_H}{dP} + \frac{d\xi}{dP}[V - V_H] + \xi\left[\left(\frac{\partial V}{\partial P}\right)_s - \frac{dV_H}{dP}\right]. \quad (6)$$

This equation was integrated numerically to obtain the pressure-volume relations for five adiabats which intersect the measured Hugoniot curve at 50, 100, 150, 200, and 250 kilobars, respectively. Pressure-volume points for these adiabats are tabulated in Table I, the highest pressure listed for each adiabat being the point of intersection with the Hugoniot curve. The curves are plotted as Fig. 2.

The specific volumes listed in Table I for pressures below 25 kilobars are approximate values obtained from a graphical interpolation utilizing Kennedy's data.[3] The manner in which this interpolation was done will be indicated in Sec. V.

IV. ISOTHERMS

The temperature as a function of pressure along an adiabat may be obtained by integrating the expression

$$TdS \equiv C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP = 0 \quad (7)$$

to obtain

$$T(P,S) = T(P_0,S) \exp \int_{P_0}^{P} dP/\xi(P). \quad (8)$$

The temperature at 25 kilobars ($P_0 = 25$ kilobars) on each of the adiabats given in Sec. III was obtained from the value of $(\partial V/\partial T)_P$ at this pressure and the volume offset between the adiabat and the 175°C isotherm as determined by Bridgman[4] (see Appendix). The pressure-volume relations for the adiabats and the temperatures obtained from Eq. (8) then permitted the immediate construction of isotherms in the pressure interval 25 kilobars to 250 kilobars. Several isotherms so obtained are plotted in Fig. 3 along with the 175°C isothermal

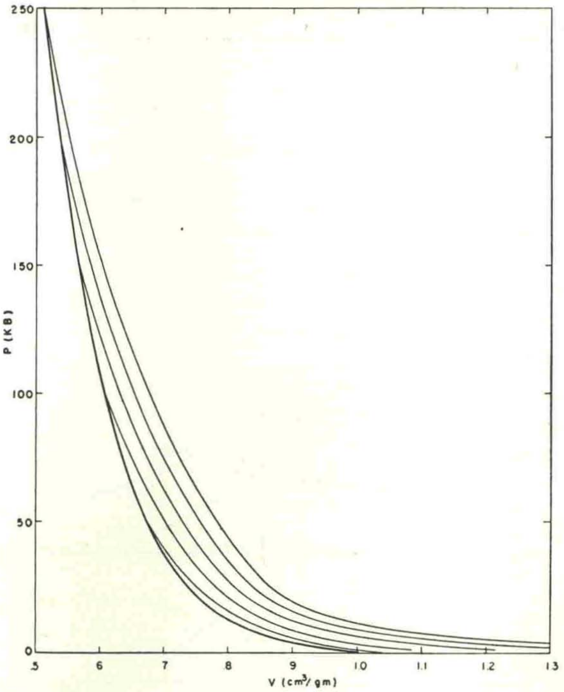

FIG. 2. Pressure-volume relations for the Hugoniot and five adiabats.

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[3] G. C. Kennedy, Am. J. Sci. **248**, 540 (1950).

[4] P. W. Bridgman, Am. Acad. Arts. Sci. **74**, 399 (1942).

data of Bridgman and the lower pressure data of Kennedy,[3] who reported complete P-V-T data in the temperature range 200°C to 1000°C for pressures up to 2.5 kilobars. An examination of Fig. 3 shows that it is possible to make reasonable interpolations between the high-pressure results and those of Kennedy; also, the 175°C isotherm represents a reasonable extension of Bridgman's data. Pressure-specific volume points for these isotherms are tabulated in Table II. The points for pressures below 25 kilobars are approximate values obtained from the interpolations shown in Fig. 3. In Fig. 4 the isotherms are plotted along with the Hugoniot curve and the water-ice VII phase line as extrapolated by Snay and Rosenbaum[1] from Bridgman's data to 40 kilobars.[5] From Fig. 4 it is seen that considerable portions of the isotherms lie to the left of the phase line and hence correspond to states super-cooled with respect to ice VII. The Hugoniot curve itself lies to the left of the phase line only in the small pressure interval from about 30 to 35 kilobars; hence the effects of possible partial freezing behind a shock front will be small and will not be considered here.

V. THERMODYNAMIC DATA ALONG THE HUGONIOT

Shock-wave and thermodynamic data pertaining to the Hugoniot centered at 20°C and 1 atmos are tabulated in Table III as functions of shock pressure. The specific volume, V, shock velocity, U_s, particle velocity U_p, internal energy, ΔE, and enthalpy, ΔH, were obtained directly from the analytical fit [Eq. (3)] and the Rankine-Hugoniot relations [Eqs. (1), (2), (3), and (3′) of preceding paper].

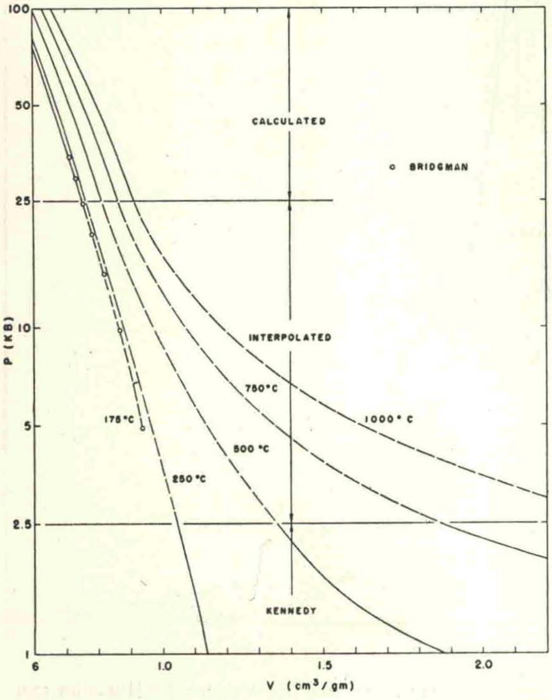

FIG. 3. Pressure-volume relations for five isotherms showing the interpolations between 2.5 and 25 kilobars.

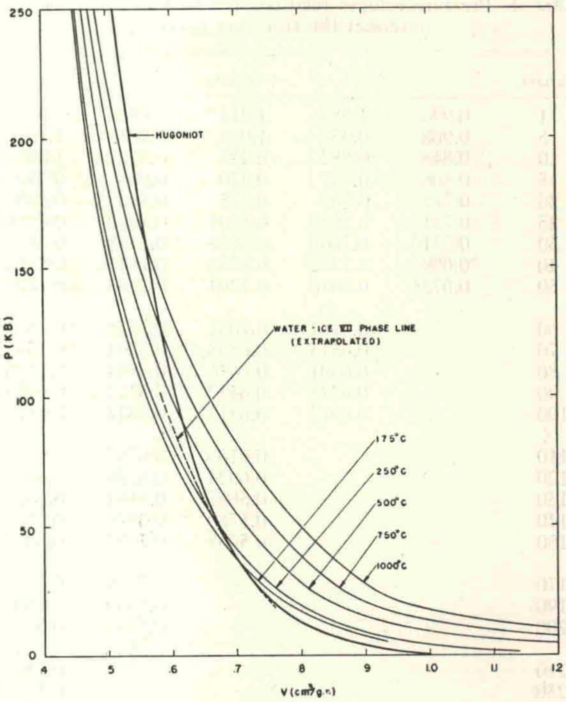

FIG. 4. Pressure-volume relations for the Hugoniot and five isotherms.

The temperatures in the pressure range 25 kilobars to 250 kilobars were obtained from the calculations indicated in Sec. IV. For pressures above 250 kilobars

TABLE II. Pressure-volume relations for several isotherms.

	V (cm³/g)				
P (kbars)	175°C	250°C	500°C	750°C	1000°C
5	0.934	0.966	1.139	1.350	1.616
10	0.864	0.882	0.975	1.077	1.189
15	0.814	0.830	0.896	0.966	1.040
20	0.777	0.794	0.848	0.903	0.959
25	0.7487	0.7635	0.8135	0.8635	0.9135
30	0.7266	0.7411	0.7894	0.8377	0.8860
40	0.6902	0.7037	0.7487	0.7937	0.8387
50	0.6607	0.6733	0.7153	0.7573	0.7993
60	0.6349	0.6466	0.6857	0.7248	0.7639
70	0.6127	0.6236	0.6601	0.6966	0.7331
80	0.5932	0.6034	0.6375	0.6716	0.7057
90	0.5759	0.5854	0.6172	0.6490	0.6808
100	0.5608	0.5690	0.5986	0.6282	0.6578
110	0.5468	0.5551	0.5827	0.6103	0.6379
120	0.5343	0.5420	0.5677	0.5935	0.6192
130	0.5230	0.5302	0.5542	0.5782	0.6022
140	0.5132	0.5199	0.5423	0.5647	0.5871
150	0.5040	0.5103	0.5312	0.5521	0.5730
170	0.4885	0.4939	0.5121	0.5303	0.5485
190	0.4758	0.4805	0.4963	0.5121	0.5279
210	0.4653	0.4694	0.4831	0.4968	0.5105
230	0.4567	0.4603	0.4722	0.4841	0.4960
250	0.4492	0.4523	0.4627	0.4731	0.4835

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[5] P. W. Bridgman, J. Chem. Phys. 5, 964 (1937).

TABLE III. Shock-wave and thermodynamic data for the water Hugoniot centered at 20°C and 1 atmos.

P (kbars)	V (cm^3/g)	T (°C)	U_s (km/sec)	U_p (km/sec)	C (km/sec)	ΔS (cal/g/deg)	ΔE (cal/g)	ΔH (cal/g)
0	1.0018	20	1.483	0	1.483	0	0	0
5	0.8773	36	2.008	0.250	2.350	0.005	7.4	112
10	0.8204	54	2.352	0.426	2.800	0.018	21.7	218
15	0.7845	74	2.632	0.571	3.130	0.038	38.9	320
20	0.7583	96	2.871	0.698	3.390	0.062	58.2	420
25	0.7378	121	3.083	0.812	3.611	0.087	78.8	519
30	0.7207	145	3.273	0.918	3.810	0.114	100.7	617
40	0.6940	196	3.611	1.110	4.114	0.169	147.0	810
50	0.6735	251	3.910	1.281	4.330	0.224	196.0	1000
60	0.6561	310	4.173	1.440	4.513	0.276	247.7	1188
70	0.6414	372	4.415	1.588	4.666	0.326	301.2	1373
80	0.6287	436	4.639	1.728	4.795	0.374	356.4	1558
90	0.6175	502	4.848	1.860	4.907	0.420	413.0	1740
100	0.6075	570	5.045	1.986	5.015	0.463	470.8	1922
110	0.5980	638	5.228	2.108	5.113	0.504	530.4	2101
120	0.5893	710	5.404	2.225	5.214	0.543	591.1	2280
130	0.5813	781	5.570	2.338	5.295	0.580	652.7	2457
140	0.5740	854	5.731	2.447	5.380	0.615	715.2	2634
150	0.5668	927	5.883	2.554	5.462	0.649	779.1	2810
170	0.5538	1074	6.160	2.760	5.626	0.712	909.4	3158
190	0.5420	1223	6.428	2.956	5.781	0.771	1043.2	3503
200	0.5363	1297	6.567	3.051	5.856	0.798	1111.7	3673
210	0.5310	1371	6.679	3.144	5.928	0.825	1180.6	3844
230	0.5209	1520	6.916	3.326	6.072	0.876	1320.7	4182
250	0.5112	1667	7.151	3.502	6.211	0.923	1464.5	4517
300	0.4897	2037	7.668	3.920	···	1.031	1834.5	5343
350	0.4705	2407	8.131	4.312	···	1.127	2220.5	6153
400	0.4530	2777	8.552	4.685	···	1.212	2621.3	6949
450	0.4371	3147	8.943	5.041	···	1.290	3034.3	7732

approximate temperatures were obtained by extrapolation, since temperature turned out to be almost linear in pressure. For pressures below 25 kilobars sufficient data is available from Bridgman[4,6] to fix the temperatures.

The sound speeds were determined from the expression

$$C^2 = -V^2(\partial P/\partial V)_s. \tag{9}$$

The value of $(\partial P/\partial V)_s$ was obtained from Eq. (6) which, for a point on the Hugoniot, becomes

$$V_H = \frac{dH_H}{dP} + \xi\left[\left(\frac{\partial V}{\partial P}\right)_s - \frac{dV_H}{dP}\right]. \tag{10}$$

Approximate sound speeds for pressures below 25 kilobars were obtained by extrapolating the curve of c *versus* P to the value 1.483 at 1 atmos. No sound speeds are given for pressures greater than 250 kilobars, since $\xi(P)$ is not known at higher pressures.

The entropy along the Hugoniot curve was determined by integrating the expression

$$TdS = dH - VdP \tag{11}$$

to obtain

$$\Delta S = \int_0^P \frac{1}{T}\left[\frac{dH_H}{dP} - V_H\right] dP, \tag{12}$$

the integral being taken along the locus of equilibrium states defined as the Hugoniot curve. The values of the entropy so obtained were used in a graphical interpolation mentioned in Sec. III to obtain approximate volumes below 25 kilobars for each of the adiabats given in Sec. III. The entropy on each adiabat was used to find

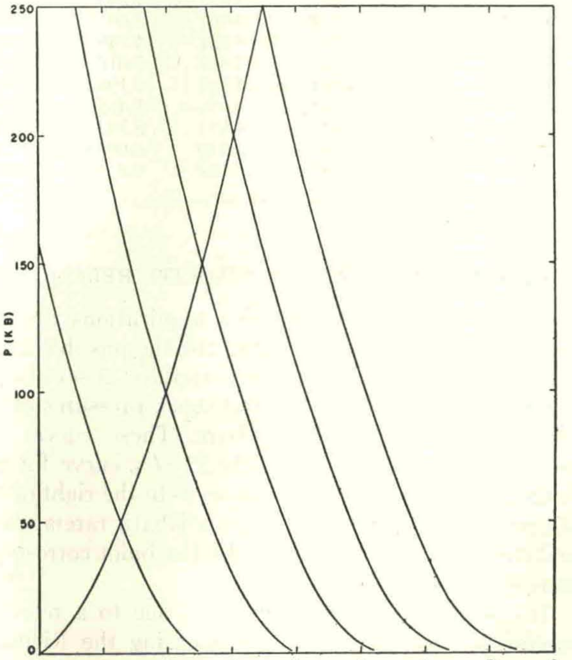

FIG. 5. Pressure-particle velocity relations for an initial shock followed by a reflected shock or rarefaction.

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[6] P. W. Bridgman, J. Chem. Phys. 3, 597 (1935).

the P, V, T point of its intersection with the water-steam phase line, complete thermodynamic data along the phase line being given by Keenan and Keyes.[7] Then temperature as a function of pressure along each adiabat was extrapolated from the value at 25 kilobars to the value at the phase line. The temperatures obtained were used with the isothermal data of Kennedy[3] to find the pressure-volume relations for each adiabat for pressures up to 2.5 kilobars. A graphical interpolation similar to that shown for the isotherms in Fig. 3 was used to obtain specific volumes from 2.5 kilobars to 25 kilobars. These results have already been given in Table I.

TABLE IV. Pressure-particle velocity relations for reflected shocks and rarefactions.

P (kbars)	U_p (km/sec)				
250		0.603	1.676	2.627	3.502[a]
240		0.675	1.752	2.707	3.586
230		0.750	1.830	2.789	3.672
220		0.826	1.910	2.874	3.760
210		0.905	1.993	2.961	3.852
200		0.986	2.079	3.051[a]	3.946
190		1.071	2.168	3.144	4.043
180		1.158	2.260	3.240	4.143
170		1.248	2.354	3.340	4.247
160		1.341	2.451	3.442	4.353
150	0.086	1.438	2.554[a]	3.548	4.463
140	0.183	1.540	2.660	3.658	4.577
130	0.283	1.644	2.769	3.771	4.694
120	0.387	1.753	2.882	3.889	4.815
110	0.497	1.867	3.000	4.010	4.940
100	0.612	1.986[a]	3.122	4.136	5.069
90	0.731	2.110	3.250	4.266	5.202
80	0.856	2.239	3.382	4.402	5.341
70	0.989	2.375	3.521	4.543	5.485
60	1.130	2.518	3.667	4.691	5.635
50	1.281[a]	2.670	3.821	4.848	5.794
40	1.443	2.834	3.987	5.016	5.963
30	1.622	3.013	4.168	5.198	6.147
20	1.830	3.222	4.380	5.415	6.368
10	2.099	3.497	4.681	5.742	6.722
5	2.274	3.687	4.910	6.006	7.011
1	2.466	3.915	5.184	6.351	7.414

[a] Initial water shock pressure.

VI. PRESSURE-PARTICLE VELOCITY RELATIONS

Of interest in hydrodynamic applications are the pressure-particle velocity curves for the possible interactions of a water shock with an interface. A set of such curves was calculated for initial shock pressures of 50, 100, 150, 200, and 250 kilobars. These curves are plotted in Fig. 5 along with the $P-U_p$ curve for the Hugoniot. The portions of the curves to the right of the Hugoniot correspond to reflected adiabatic rarefactions, and the portions to the left of the Hugoniot correspond to reflected shocks.

TABLE V. Interface data for a shock from water into air.

Initial water shock pressure (kbars)	Air shock pressure (kbars)	Interface velocity (km/sec)
50	0.092	2.50
100	0.228	3.98
150	0.394	5.24
200	0.590	6.42
250	0.795	7.46

The increase in particle velocity due to a reflected rarefaction was obtained by evaluating the Riemann integral along the adiabat appropriate to the state behind the initial shock:

$$\Delta U_p = \int \frac{c}{\rho} d\rho \equiv \int \left(-\frac{dV}{dP}\right)^{\frac{1}{2}} dP. \tag{13}$$

The adiabats used are given in Sec. III. The decrease in particle velocity due to a reflected shock was obtained by a direct application of the Rankine-Hugoniot relations to the state behind the initial shock. Numerical data pertaining to the curves in Fig. 5 are tabulated in Table IV.

A special interaction of interest is that at a water-air interface. In this case, a shock is propagated into the air, and a rarefaction is propagated back into the water. The pressure and particle velocity at the interface are given by the intersection of the appropriate curve in Fig. 5 with the $P-U_p$ curve corresponding to the Hugoniot of air. The results obtained by treating air initially at 20°C and 1 atmos as a perfect gas with a ratio of specific heats 1.4 are given in Table V. The experimental

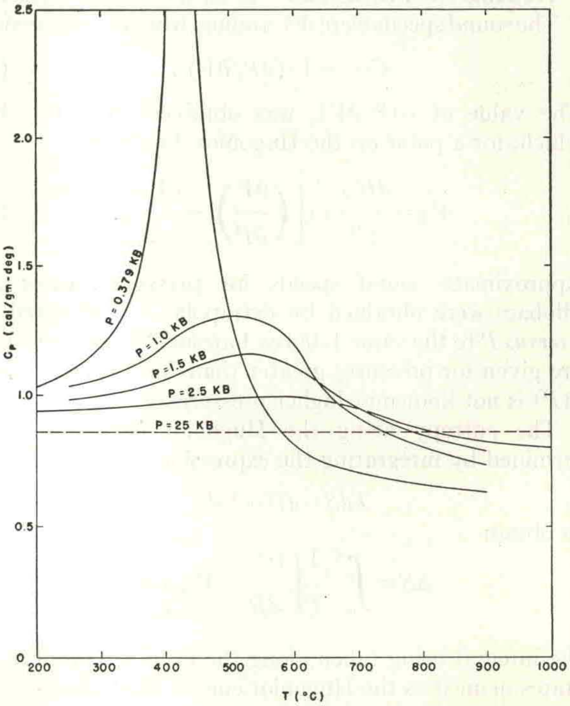

FIG. 6. Approximate dependence of the specific heat upon temperature and pressure.

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[7] J. H. Keenan and F. G. Keyes, *Thermodynamic Properties of Steam* (John Wiley and Sons, Inc., New York, 1936).

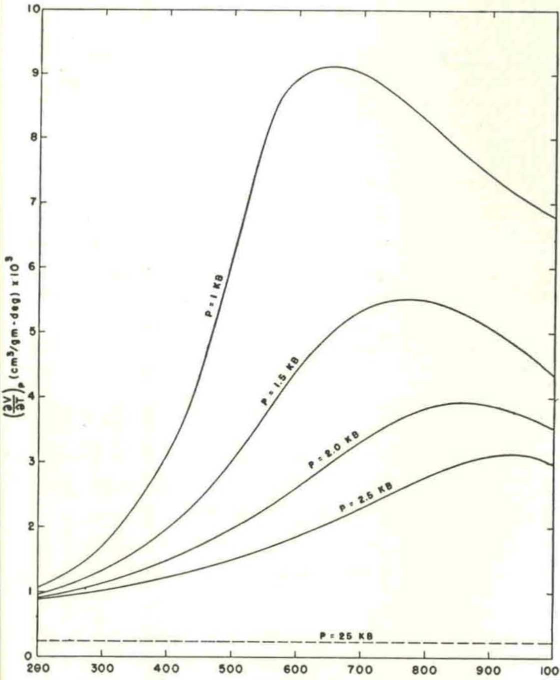

FIG. 7. Dependence of the thermal expansion upon temperature and pressure.

Hugoniot for air[8] gives air shock pressures that are about 7% lower than those listed and gives interface velocities which are about 0.3% higher. In either case, however, pressures ahead of the water free surface are sufficiently great to keep the water from boiling at the interface.

APPENDIX. A. THE APPROXIMATION $(\partial H/\partial V)_P=\xi(P)$

Sufficient conditions for the thermodynamic variable $(\partial H/\partial V)_P\equiv C_P/(\partial V/\partial T)_P$ to be a function only of pressure are that C_P and $(\partial V/\partial T)_P$ separately be functions only of pressure. Figures 6 and 7 show the temperature dependence of these two quantities as obtained from available data at low pressures. The C_P curves were obtained from enthalpies calculated from the data in Keenan and Keyes and the isothermal data of Kennedy. The $(\partial V/\partial T)_P$ curves were obtained directly from Kennedy's data by taking first differences. The rapid decrease with pressure of the temperature variations of C_P and $(\partial V/\partial T)_P$ suggests that no serious errors will be introduced by neglecting temperature variations at pressures above 25 kilobars, especially since the volume offsets between the calculated P-V curves and the measured Hugoniot are small. Also, it does not seem that the experimental data for $(\Delta H/\Delta V)_P$ are precise enough to warrant a consideration of small temperature variations. Some confidence in the calculated results is established by noting that the slope of the calculated 175°C isotherm at 25 kilobars is in excellent agreement with Bridgman's data (see Fig. 3).

B. EVALUATION OF $(\partial V/\partial T)_P$ AND C_P AT 25 KILOBARS

The value of $(\partial V/\partial T)_P$ at 25 kilobars was obtained from a consideration of Bridgman's data for the 125°C and 175°C isotherms, the only two he measured along which water is still in the liquid phase above 25 kilobars. Since Bridgman's data for these isotherms consist of volume decrements as a function of pressure above 5000 kg/cm², it was necessary to estimate the initial volumes at 5000 kg/cm² in order to fix their positions. Resulting specific volumes obtained from Bridgman by estimating the initial volumes at 125°C and 175°C are given in Table VI. Within the accuracy of the data given in Table VI, the value of $(\partial V/\partial T)_P$ at 25 kilobars is the same as that at 25 000 kg/cm², i.e., 2.0×10^{-4} cm³/g deg. This value for $(\partial V/\partial T)_P$ is plotted as the dashed line in Fig. 7.

TABLE VI.

	V (cm³/g)			
P (kg/cm²)	25°C	75°C	125°C	175°C
5000	0.873	0.893	0.914[a]	0.936[a]
10 000		0.830	0.848	0.866
15 000		0.788	0.802	0.816
20 000		0.757	0.768	0.779
25 000			0.741	0.751
30 000				0.729
35 000				0.710

[a] These volumes are estimated. The rest then follow from Bridgman's measurements.

The value of C_P at 25 kilobars, shown as the dashed line in Fig. 6, was estimated from the data at 2.5 kilobars and the thermodynamic relation

$$\Delta C_P=-\int T\left(\frac{\partial^2 V}{\partial T^2}\right)_P dP.$$

Values of $(\partial^2 V/\partial T^2)_P$ in the pressure interval 2.5 to 25 kilobars were obtained by extrapolating curves of $(\partial^2 V/\partial T^2)_P$ *versus* pressure (evaluated up to 2.5 kilobars from Kennedy's data) to zero at 25 kilobars. The resulting value of C_P at 25 kilobars is 36 bar cm³/g deg or 0.86 cal/g deg.

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[8] R. H. Christian and F. L. Yarger (private communication).

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