JOURNAL OF RESEARCH of the National Bureau of Standards—A. Physics and Chemistry
Vol. 73A, No. 1, January–February 1969

Specific Heats C_v of Fluid Oxygen from the Triple Point to 300 K at Pressures to 350 Atmospheres*

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(August 15, 1968)

Experimental specific heats at constant volume for oxygen in single phase domains are reported from the triple point to 300 K at pressures to 350 atmospheres. An empirical equation with seven constants describes these specific heats over the entire domain of ρ-T coordinates to within the experimental accuracy of 1 to 2 percent. Values for the terminal slopes of PVT isochores at the coexistence boundary, $(\partial P/\partial T)_v$, are derived for the liquid.

Key Words: Compressed liquid; heat capacities; liquid; oxygen; specific heats; thermodynamic properties.

List of Symbols

C_b	heat capacity of empty calorimeter bomb.
$C_v(\rho, T)$	specific heat of the sample.
$C_v^{\circ}(T)$	specific heat in ideal gas states.
C_x	adjustment for bomb expansion.
J	the joule.
k	conversion factor, 0.101325 J/cm³ atm.
L	the liter, 1,000 cm³.
N	total moles of fluid in bomb plus capillary tube.
N_b	moles of fluid in the bomb.
N_c	moles of fluid in the capillary tube.
P	pressure. 1 atm = 0.101325 MN/m².
Q	calorimetric heat input.
$Q/\Delta T$	gross heat capacity.
ρ	density.
ρ_c	critical density, 13.62 mol/l.
σ	density reduced at the critical point.
t	time.
T	temperature, Kelvin, NBS 1955 scale.
T_1, T_2	temperature at start and end of heating interval.
T_c	critical-point temperature, 154.77 K.
$\Delta T \equiv T_2 - T_1$	calorimetric temperature increment.
v	molal volume, $1/\rho$.
V_b	volume of the calorimeter bomb.
x	temperature reduced at the critical point.

1. Introduction

Specific heats are basic data for the computation of thermodynamic properties in the compressed liquid domain, yet for oxygen these data apparently never have been measured [1].[1] In the present report we give our results for C_v over the entire fluid domain below 300 K and below 350 atm. Many details of the experimental work are given in our companion publication on specific heats along the liquid-vapor coexistence path [2]. In forthcoming reports we give thermodynamic properties based on the current measurements.

2. Experimental Method

The calorimeter and cryostat are the same as used for the two-phase observations [2]. Briefly, the calorimeter is a spherical shell of stainless steel, 2 in in diameter, surrounded by adiabatic shields maintained at the calorimeter temperature by automatic controls. The amount of sample is determined from an observed temperature T and pressure P in a single-phase domain; from the bomb volume at this T, P; and from the fluid density derived from an equation of state [1]. The method for measuring calorimetric heat is identical with that of [2] as is the tare heat capacity of the empty calorimeter bomb. The computational method of adjusting for expansion of the bomb during a heating interval also is the same except that the required pressure increase in the bomb is estimated.

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*This work was carried out at the National Bureau of Standards under the sponsorship of the National Aeronautics and Space Administration Fund Transfer R–06–006–046.

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[1] Figures in brackets indicate the literature references at the end of this paper.

3. Calculation of C_v From Laboratory Observations

To adjust for expansion of the bomb we estimate the pressure at T_1 and at T_2. An iterative method minimizes the difference $|\rho-\rho_e|$ where density ρ is obtained from contents and volume of the bomb,

$$\rho=[N-N_c(P,T)]/V_b(P,T), \qquad (1)$$

and density ρ_e is used in the equation of state $P(\rho_e, T)$ to obtain the pressure. For the capillary tube we obtain $N_c(P, T)$ by summing over both liquid and gaseous phases whenever a meniscus exists in this tube. The capillary volume is about $0.0002 \cdot V_b$.

The densities ρ_1, ρ_2 obtained in this way at T_1, T_2 already recognize fluid in the capillary tube. We therefore use them in the adjustment C_x for bomb expansion as follows (appendix I),

$$\Delta v \equiv 1/\rho_2 - 1/\rho_1,$$

$$C_x \equiv k \cdot [T_2 \cdot (\partial P/\partial T)_2 - \Delta P/2] \cdot \Delta_v/\Delta T. \qquad (2)$$

Our experimental data thus are reduced by the equation,

$$C_v = [Q/\Delta T - C_b]/N_b - C_x \qquad (3)$$

with no curvature adjustments [2]. Only for datum No. 225 near critical is the adjustment significant: this datum should be reduced to 46.4 J/mol-K in table 2. The maximum uncertainties (errors) in C_v are calculated as in [2], using the same estimates for uncertainty of individual variables.

4. Experimental Results

The locus of each specific heat observation is given by figure 1 in density-temperature coordinates. The observations extend from the coexistence envelope at low temperatures to the 350-atm boundary of pressure at high temperatures. The amount of sample for each experimental run (horizontal line on fig. 1) is calculated from the loading conditions of table 1. The total number of moles N given in the last column includes a few ten thousandths in the capillary tube.

Table 2 gives experimental results. Identification in the first column is the run number followed by two digits for the point of that run. Next are the observed temperature, the estimated pressure, and the calculated density at this pressure. The bomb volume V, BMB and DV/DT for the bomb are calculated at T, P as in [2]. The seventh column DEL T is the experimental temperature increment, ΔT. Following columns are the gross heat capacity $Q/\Delta T$, the tare heat capacity of the empty calorimeter, and the adjusted specific heat of the oxygen sample computed

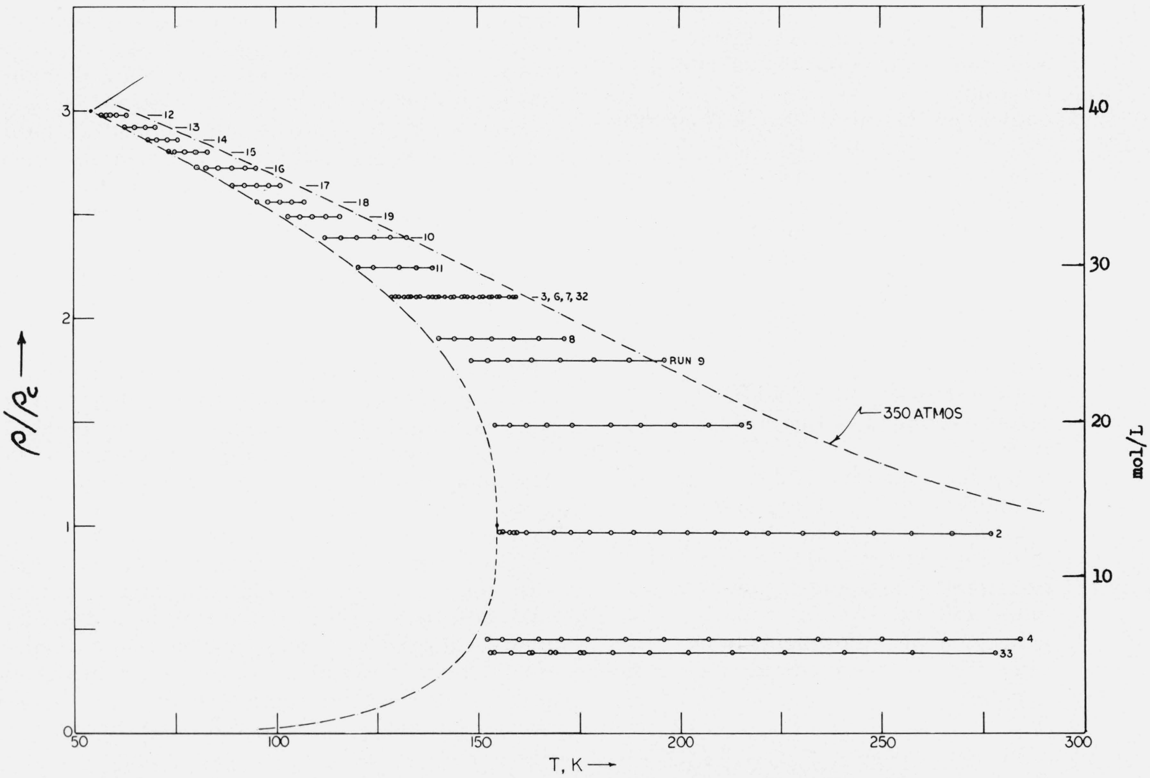

FIGURE 1. *Locus of* C_v *data in* $\rho-T$ *coordinates.*

by eq (3). The last column is estimated maximum relative uncertainty (error), in percent. This increases rapidly with diminishing interval ΔT and with diminishing amount of sample. A comparison of runs 3, 6, 7, 32, all at the same density, shows that these estimates of error are realistic.

The behavior of these specific heats is illustrated in figure 2 by plots of selected runs (isochores). For a wide range of densities about the critical density the specific heat increases sharply as temperature diminishes toward the coexistence envelope. At densities far removed from critical, however, the temperature dependence is relatively weak.

TABLE 1. *Loading conditions for the samples*

Run	*T*, K	*P*, ATM	*V*, cm³	*D*, Mol/l	*N*, Mol
2	197.279	131.432	73.133	13.128	0.9602
3	139.255	129.352	72.950	28.679	2.0924
4	200.125	76.159	73.086	6.110	0.4467
5	173.070	129.980	73.054	20.223	1.4775
6	139.083	128.514	72.949	28.696	2.0936
7	138.976	127.012	72.948	28.688	2.0929
8	148.103	96.998	72.947	25.893	1.8890
9	173.955	187.207	73.112	23.090	1.6884
10	116.705	125.967	72.884	32.557	2.3731
11	131.071	159.226	72.953	30.621	2.2341
12	59.069	122.822	72.754	40.632	2.9565
13	65.450	120.256	72.763	39.783	2.8950
14	71.341	114.230	72.769	38.974	2.8364
15	76.877	108.612	72.775	38.202	2.7805
16	85.691	138.618	72.817	37.157	2.7060
17	94.357	145.740	72.843	36.010	2.6234
18	102.979	156.273	72.873	34.875	2.5417
19	109.048	141.669	72.877	33.884	2.4696
32	137.181	106.345	72.934	28.633	2.0882
33	207.639	71.974	73.106	5.253	0.3841

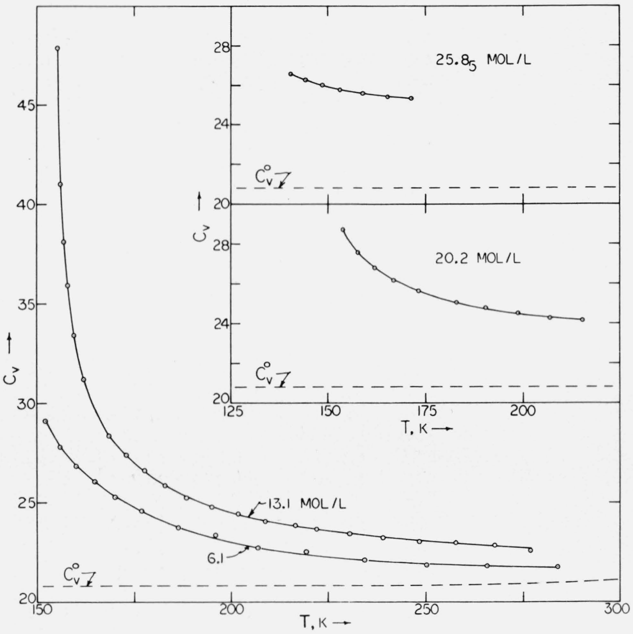

FIGURE 2. *Selected isochores of* C_v *data.*

TABLE 2. *Experimental specific heats*

ID	*T*, K	*P*, atm	Dens. mol/l	*V*, bmb cm³	DV_b/DT cm³/deg	Del *T* K	*DQ/DT* J/deg	Tare J/deg	C_v J/M-K	Error percent
225	155.297	51.144	13.166	72.925	0.0047	0.764	112.656	66.536	47.883	2.077
226	155.970	52.427	13.166	72.928	.0047	0.812	106.171	66.679	40.978	2.173
227	156.753	53.920	13.165	72.932	.0047	0.830	103.576	66.844	38.103	2.237
228	157.829	55.971	13.164	72.937	.0047	1.414	101.692	67.069	35.905	1.592
229	159.558	59.267	13.163	72.945	.0047	2.106	99.644	67.423	33.402	1.311
230	162.067	64.054	13.160	72.957	.0048	2.991	98.042	67.923	31.208	1.145
231	168.678	76.686	13.154	72.989	.0049	3.947	96.558	69.170	28.354	1.090
232	172.876	84.734	13.151	73.010	.0049	4.554	96.375	69.912	27.385	1.061
233	177.619	93.820	13.146	73.033	.0050	5.036	96.396	70.709	26.571	1.051
234	182.951	104.018	13.141	73.060	.0050	5.737	96.521	71.556	25.811	1.034
235	188.633	114.906	13.136	73.089	.0051	6.284	96.805	72.407	25.213	1.029
236	195.116	127.315	13.130	73.122	.0052	6.853	97.260	73.319	24.729	1.025
237	201.815	140.083	13.124	73.157	.0052	6.741	97.840	74.202	24.404	1.048
238	208.788	153.339	13.117	73.193	.0053	7.397	98.351	75.065	24.028	1.040
239	216.716	168.371	13.109	73.235	.0054	8.697	99.094	75.984	23.835	1.012
240	222.219	178.853	13.104	73.265	.0054	8.676	99.500	76.588	23.621	1.025
241	230.717	194.880	13.096	73.311	.0055	8.624	100.165	77.471	23.384	1.043
242	239.156	210.642	13.087	73.357	.0055	9.367	100.833	78.295	23.211	1.036
243	248.314	227.681	13.078	73.408	.0056	9.298	101.488	79.138	23.003	1.053
244	257.729	245.185	13.069	73.461	.0056	9.901	102.259	79.955	22.943	1.048
245	267.382	263.047	13.059	73.515	.0057	9.883	102.936	80.749	22.810	1.061
246	276.983	280.719	13.049	73.570	.0057	9.810	103.453	81.497	22.557	1.079
317	130.692	45.629	28.719	72.852	.0115	4.180	117.358	60.316	26.501	0.710
318	134.835	86.416	28.700	72.899	.0117	4.155	118.134	61.515	26.279	.722
319	138.945	126.677	28.680	72.947	.0119	4.115	119.032	62.638	26.149	.734
320	143.490	169.947	28.659	73.000	.0121	4.071	120.315	63.808	26.181	.745

TABLE 2. *Experimental specific heats*—Continued

ID	T, K	P, atm	Dens. mol/l	V, bmb cm³	DV_b/DT cm³/deg	Del T K	DQ/DT J/deg	Tare J/deg	C_v J/M-K	Error percent
321	147.531	208.734	28.640	73.048	.0122	4.065	121.052	64.790	26.045	.754
322	151.493	246.338	28.621	73.096	.0123	4.038	121.854	65.703	25.975	.762
323	155.489	283.838	28.602	73.144	.0123	4.010	122.640	66.577	25.917	.771
324	159.453	320.561	28.583	73.191	.0124	3.987	123.419	67.402	25.881	.779
401	152.179	42.261	6.126	72.908	.0035	3.667	78.902	65.856	29.116	1.842
402	155.794	44.979	6.124	72.921	.0036	3.654	79.105	66.642	27.809	1.932
403	160.002	48.086	6.123	72.936	.0036	4.858	79.536	67.512	26.825	1.784
404	164.797	51.575	6.122	72.954	.0036	4.830	80.129	68.450	26.050	1.851
405	170.195	55.441	6.120	72.973	.0037	6.065	80.766	69.443	25.253	1.770
406	176.883	60.164	6.118	72.998	.0037	7.453	81.616	70.588	24.586	1.719
407	186.560	66.896	6.115	73.034	.0038	8.851	82.742	72.102	23.712	1.720
408	196.057	73.392	6.112	73.070	.0038	10.315	83.926	73.446	23.349	1.704
409	207.059	80.831	6.108	73.113	.0039	11.906	85.051	74.856	22.704	1.718
410	219.594	89.217	6.104	73.162	.0040	14.076	86.411	76.303	22.502	1.703
411	234.502	99.074	6.099	73.222	.0040	16.083	87.771	77.847	22.080	1.721
412	250.222	109.382	6.093	73.285	.0041	15.818	89.133	79.307	21.849	1.768
413	265.673	119.428	6.088	73.348	.0041	15.564	90.424	80.611	21.810	1.801
414	284.186	131.436	6.082	73.425	.0042	22.098	91.825	82.036	21.743	1.743
516	154.095	54.534	20.260	72.925	.0065	3.557	109.070	66.277	28.687	0.861
517	157.860	69.185	20.253	72.950	.0066	4.052	108.211	67.075	27.548	.841
518	162.027	85.593	20.245	72.978	.0068	4.604	107.931	67.915	26.773	.821
519	167.104	105.862	20.235	73.012	.0069	5.636	108.019	68.882	26.160	.784
520	173.286	130.879	20.222	73.056	.0071	6.818	108.375	69.983	25.635	.758
521	182.885	169.899	20.203	73.125	.0073	7.424	109.089	71.546	25.030	.762
522	190.402	200.537	20.187	73.180	.0074	8.030	109.875	72.662	24.786	.759
523	198.662	233.997	20.170	73.242	.0076	8.631	110.597	73.793	24.489	.759
524	207.168	268.288	20.152	73.306	.0077	8.559	111.373	74.869	24.263	.773
525	215.586	301.941	20.134	73.371	.0078	8.488	112.233	75.857	24.159	.784
601	129.811	37.509	28.740	72.842	.0115	3.266	117.622	60.052	26.746	.776
602	133.528	74.090	28.722	72.885	.0117	4.191	118.258	61.144	26.503	.715
603	137.687	114.969	28.703	72.933	.0119	4.158	119.135	62.301	26.348	.727
604	141.772	154.822	28.683	72.981	.0120	4.123	119.959	63.374	26.208	.738
605	146.114	196.833	28.663	73.032	.0121	4.601	120.928	64.452	26.134	.718
606	150.669	239.909	28.641	73.087	.0123	4.556	121.869	65.517	26.071	.728
607	154.966	279.917	28.621	73.138	.0124	4.084	122.699	66.465	25.983	.764
608	159.013	317.536	28.601	73.187	.0124	4.056	123.490	67.312	25.941	.772
706	128.832	27.695	28.736	72.831	.0114	1.235	116.949	59.755	26.563	1.311
701	130.025	39.312	28.730	72.844	.0115	3.309	117.328	60.116	26.580	0.774
702	134.223	80.690	28.710	72.893	.0117	5.111	118.134	61.342	26.354	.672
703	139.804	135.185	28.684	72.957	.0119	6.140	119.373	62.864	26.197	.647
704	146.427	198.814	28.653	73.036	.0121	7.147	120.813	64.527	26.058	.633
705	153.498	265.658	28.619	73.120	.0123	7.036	122.247	66.147	25.940	.645
801	140.433	41.159	25.920	72.874	.0094	3.443	114.237	63.029	26.569	.800
802	144.299	69.148	25.906	72.911	.0096	4.335	114.672	64.009	26.260	.743
803	148.597	100.417	25.891	72.952	.0097	4.315	115.265	65.040	26.003	.755
804	153.298	134.674	25.874	72.998	.0099	5.247	115.933	66.103	25.769	.717
805	159.026	176.397	25.854	73.054	.0101	6.277	116.864	67.315	25.593	.690
806	165.241	221.439	25.831	73.117	.0103	6.228	117.775	68.534	25.404	.702
807	171.390	265.204	25.809	73.179	.0104	6.159	118.795	69.654	25.335	.712
901	148.563	49.065	23.158	72.904	.0078	3.472	111.380	65.032	27.063	.836
902	152.486	70.121	23.148	72.935	.0079	4.430	111.376	65.924	26.510	.775
903	157.402	96.826	23.135	72.974	.0081	5.460	111.703	66.980	26.056	.736
904	163.303	128.912	23.119	73.023	.0083	6.544	112.244	68.164	25.651	.711
905	170.379	167.584	23.100	73.082	.0085	7.701	113.034	69.475	25.311	.695
906	178.665	212.816	23.077	73.153	.0087	8.963	113.961	70.879	25.001	.684
907	187.541	261.017	23.052	73.231	.0089	8.897	114.947	72.247	24.743	.698
908	196.331	308.226	23.027	73.308	.0090	8.810	115.944	73.483	24.579	.710
1001	108.879	10.276	32.611	72.766	0.0154	2.682	144.011	52.706	37.350	0.691
1002	112.214	60.010	32.588	72.816	.0154	3.998	122.680	54.028	27.778	.670
1003	116.182	118.880	32.560	72.875	.0155	3.956	123.831	55.520	27.617	.683
1004	120.105	175.140	32.533	72.934	.0157	3.913	125.072	56.916	27.568	.695
1005	124.452	236.551	32.503	73.000	.0159	4.807	126.438	58.374	27.472	.658
1006	128.570	293.382	32.475	73.064	.0159	3.930	127.509	59.674	27.404	.711
1007	132.456	345.654	32.449	73.123	.0159	3.884	128.793	60.835	27.405	.720

TABLE 2. *Experimental specific heats* – Continued

ID	T, K	P, atm	Dens. mol/l	V, bmb cm³	DV_b/DT cm³/deg	Del T K	DQ/DT J/deg	Tare J/deg	C_v J/M-K	Error percent
1101	120.598	34.060	30.681	72.814	.0134	3.252	119.834	57.086	27.145	.750
1102	124.251	77.714	30.660	72.862	.0134	4.078	120.649	58.308	26.970	.696
1103	130.736	155.031	30.623	72.949	.0137	4.093	122.320	60.329	26.782	.710
1104	134.797	202.264	30.600	73.003	.0138	4.062	123.406	61.504	26.702	.720
1105	138.824	249.075	30.577	73.057	.0139	4.026	124.403	62.605	26.638	.730
1201	56.368	31.319	40.670	72.689	.0266	2.189	136.052	22.495	36.444	.660
1202	58.917	116.769	40.634	72.751	.0268	2.909	133.675	24.309	35.190	.602
1203	57.897	82.169	40.649	72.726	.0267	2.561	133.302	23.585	35.202	.629
1204	60.442	169.884	40.612	72.787	.0269	2.535	134.526	25.387	34.989	.642
1205	62.967	251.014	40.578	72.849	.0271	2.530	135.948	27.159	34.995	.652
1301	62.590	31.232	39.821	72.697	.0253	2.525	135.336	26.896	35.516	.640
1302	65.138	109.378	39.787	72.756	.0255	2.576	132.643	28.668	34.171	.652
1303	67.705	186.200	39.754	72.815	.0256	2.566	132.990	30.429	33.533	.665
1304	70.233	262.996	39.721	72.874	.0257	2.528	134.959	32.130	33.603	.677
1401	68.103	20.551	39.015	72.698	.0241	2.453	139.280	30.699	36.401	.654
1402	70.626	94.552	38.983	72.753	.0242	2.604	131.137	32.391	32.993	.667
1403	73.222	166.234	38.951	72.811	.0243	2.597	132.251	34.092	32.902	.678
1404	75.794	235.407	38.921	72.868	.0244	2.555	133.549	35.733	32.638	.692
1501	72.907	3.541	38.249	72.691	.0229	1.469	148.023	33.888	39.092	.840
1502	74.969	58.588	38.224	72.735	.0229	2.665	129.376	35.211	32.211	.674
1503	77.616	126.868	38.194	72.791	.0230	2.641	130.468	36.867	31.904	.687
1504	80.237	195.252	38.164	72.847	.0231	2.614	131.740	38.458	31.779	.699
1505	82.818	261.059	38.134	72.902	.0232	2.585	133.216	39.975	31.748	.710
1601	80.108	5.857	37.217	72.705	.0214	2.010	146.516	38.381	38.279	.732
1602	82.640	67.258	37.189	72.756	.0214	3.064	128.741	39.872	31.172	.659
1603	85.671	137.879	37.158	72.816	.0215	3.029	130.090	41.596	31.124	.671
1604	89.014	214.296	37.123	72.883	.0216	3.673	131.574	43.420	30.882	.634
1605	92.303	287.554	37.089	72.949	.0217	2.922	132.853	45.138	30.812	.702
1606	95.052	346.307	37.061	73.005	.0218	2.593	133.954	46.516	30.599	.747
1701	89.205	38.784	36.059	72.747	.0198	3.071	127.701	43.522	30.522	.673
1702	92.249	102.328	36.030	72,803	.0198	3.024	128.105	45.110	30.173	.689
1703	95.257	163.556	36.002	72.859	.0199	2.998	129.212	46.617	29.942	.701
1704	98.232	224.501	35.973	72.915	.0200	2.969	130.292	48.047	29.792	.713
1705	100.982	279.569	35.947	72.967	.0200	2.540	131.390	49.318	29.718	.770
1801	95.085	9.674	34.943	72.736	.0182	2.325	143.109	46.532	36.569	.720
1802	97.805	60.228	34.920	72.783	.0183	3.124	125.443	47.845	29.177	.697
1803	100.912	117.381	34.893	72.837	.0183	3.096	126.360	49.286	28.914	.709
1804	103.990	174.180	34.867	72.890	.0184	3.067	127.467	50.653	28.800	.721
1805	107.030	229.235	34.841	72.944	.0185	3.036	128.575	51.946	28.708	.732
1901	102.977	40.081	33.932	72.778	.0170	3.112	124.268	50.210	28.681	.711
1902	106.074	93.034	33.907	72.828	.0170	3.092	124.934	51.546	28.423	.723
1903	109.146	143.256	33.883	72.878	.0171	3.060	126.022	52.814	28.395	.734
1904	112.406	195.782	33.858	72.932	.0172	3.488	127.224	54.102	28.282	.705
1905	115.869	252.214	33.831	72.989	.0174	3.451	128,404	55.406	28.202	.717
3215	129.470	31.078	28.669	72.836	.0114	1.904	117.407	59.949	26.757	1.007
3216	132.006	55.993	28.657	72.865	.0115	3.216	117.856	60.704	26.613	0.788
3217	135.669	91.698	28.639	72.906	.0117	4.166	118.642	61.748	26.466	.721
3218	140.018	134.022	28.619	72.957	.0119	4.589	119.623	62.920	26.350	.706
3219	144.268	175.030	28.599	73.007	.0120	4.567	120.439	64.001	26.202	.716
3220	148.803	217.859	28.578	73.060	.0121	4.566	121.420	65.088	26.146	.724
3221	153.319	259.958	28.556	73.114	.0123	4.528	122.265	66.108	26.029	.734
3222	157.769	301.385	28.535	73.168	.0123	4.456	123.186	67.056	25.998	.744
3301	153.683	40.658	5.268	72.911	.0034	3.974	76.126	66.188	25.789	2.225
3302	157.856	43.222	5.267	72.925	.0035	4.481	76.804	67.074	25.242	2.177
3303	162.538	46.053	5.265	72.942	.0035	5.023	77.530	68.015	24.681	2.146
3304	167.824	49.204	5.264	72.960	.0035	5.670	78.393	69.015	24.324	2.104
3305	175.869	53.924	5.262	72.989	.0036	6.997	79.464	70.420	23.450	2.060
3306	183.525	58.348	5.260	73.016	.0036	8.471	80.576	71.644	23.154	2.000
3307	192.262	63.335	5.257	73.048	.0037	9.183	81.705	72.924	22.756	2.018
3308	202.057	68.848	5.255	73.085	.0037	10.605	82.915	74.233	22.494	1.999
3309	213.082	74.992	5.252	73.126	.0038	12.226	84.166	75.570	22.262	1.986

TABLE 2. *Experimental specific heats*—Concluded

ID	T, K	P, atm	Dens. mol/l	V, bmb cm^3	DV_b/DT cm^3/deg	Del T K	DQ/DT J/deg	Tare J/deg	C_v J/M-K	Error percent
3310	226.034	82.147	5.248	73.176	.0038	13.984	85.532	76.991	22.111	1.979
3311	240.759	90.217	5.244	73.233	.0039	15.816	86.903	78.446	21.885	1.986
3312	257.791	99.456	5.239	73.300	.0040	18.628	88.403	79.961	21.834	1.973
3313	278.133	110.390	5.233	73.381	.0040	22.722	89.996	81.585	21.743	1.964
3314	157.576	43.049	5.267	72.924	.0035	4.964	76.716	67.016	25.166	2.095
3315	162.898	46.267	5.265	72.943	.0035	5.785	77.539	68.085	24.524	2.051
3316	168.890	49.834	5.264	72.964	.0035	6.325	78.540	69.208	24.203	2.041
3317	175.475	53.694	5.262	72.987	.0036	6.999	79.473	70.354	23.645	2.043

UN=0.20, UQ=0.05, UT=0.10, UB=0.10, UP=0.10, UPP=1.00. UV=0.20.

5. Representation of the Data

These C_v data will be useful for computations only if they can be interpolated. This is difficult with two independent variables, and is exceptionally difficult when these variables do not fill a rectangular array, as at present (fig. 1). We have developed an "equation of state" for these oxygen C_v data, using density and temperature as arguments. We postulate a temperature dependence on isochores, allowing behavior of the density dependent parameters in the equation to be imposed by the data. We first present the proposed equation, discussing its genesis later on.

As seen below, the equation has at least five exponents, α, β, γ, δ, ϵ, all of which must be selected. There remain eight arbitrary constants. Define $x \equiv T/T_c$, $\sigma \equiv \rho/\rho_c$. Let $A(\sigma)$ and $B(\sigma)$ be density dependent parameters, and let $W(\sigma, T)$ give nonanalytic behavior at the critical point. The equation then is

$$C_v = C_v^\circ + A \cdot [(1-B)\cdot x^\alpha + B \cdot W \cdot x^\beta]\cdot \tag{4}$$

From [6] we use

$$C_v^\circ(T) = 20.8 + 0.04 \cdot x^3, \text{ J/mol deg.}$$

We find the descriptions,

$$A(\sigma) \equiv A_1 \cdot \sigma + A_2 \cdot \sigma^2 + A_3 \cdot \sigma^3 + A_4 \cdot \sigma^4 + A_5 \cdot \sigma^5, \tag{4–a}$$

$$B(\sigma) \equiv \exp[-B_1 - B_2 \cdot \sigma^\gamma]\cdot \tag{4–b}$$

Defined functions in (4) are

$$T_0(\sigma) \equiv T_c \cdot \exp[-C_1 \cdot (\sigma-1)^\delta \cdot \ln(\sigma)], \tag{4–c}$$

$$W(\sigma, T) \equiv [T/T_0 - 1]^{-\epsilon}. \tag{4–d}$$

Following are values of the constants for eq (4):

$\alpha=-1/4$ $A_1= 13.3714$ $B_1=0$
$\beta=-3$ $A_2=-12.91756$ $B_2=1/4$
$\gamma=+3$ $A_3= 5.05488$ $C_1=4/3\cdot$
$\delta=+3$ $A_4=-0.761749$
$\epsilon=+1/3$ $A_5= 0.052853$

Table 3 gives the proof of this practical pudding, a comparison of experimental and calculated values for $C_v(\rho, T)$ over the entire $\rho-T$ domain. The mean relative deviation of 0.47 percent for 151 data is comparable with uncertainty of the data (table 2). In this table 3 the experimental data for C_v have been adjusted to a constant density on each run by use of eq (4). The adjustments are smaller than the uncertainty in each point.

A linear form is obtained from eq (4) upon multiplying by $x^{1/4}$. Figure 3 illustrates data of run No. 2 at near critical density in these coordinates. We substitute $(x-1)^{-1/3}$ for $W(\rho, T)$ at this density. Temperature decreases to the right, with critical temperature at infinity. Vertical uncertainties shown for three points at the right arise from the C_v data. Horizontal uncertainties correspond to 0.2 K difference between our value for T_c and that of Voronel' et al. [8].

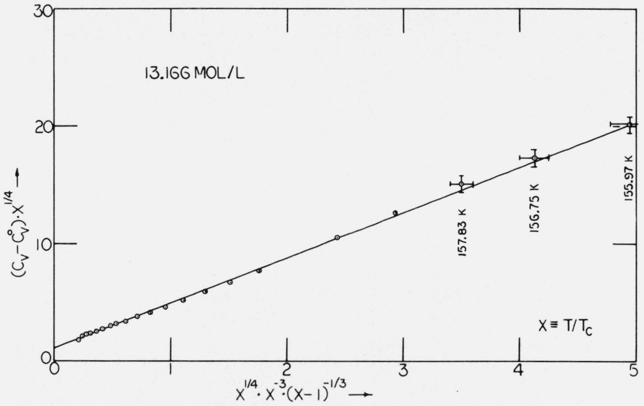

FIGURE 3. *Data of run No. 2 in coordinates of eq (4).*

Briefly, we arrived at eq (4) as follows. As the equation must be relatively simple, due to disposition of the data, we seek a mixture of weak and strong temperature dependencies only. For the former we may take $T^{-1/4}$ from the Lennard-Jones description of the second virial coefficient [7]. For the latter we include T^β, finding $\beta=-3$ by trial, in agreement with the Beattie-Bridgeman equation of state for domains away from critical [7]. For the nonanalytic part of the latter we at first explored

TABLE 3. *Experimental and calculated* C_v

ID	DEN	TEMP	C_v	CALC	PCNT
3301	5.268	153.683	25.79	26.01	−0.86
3314	5.268	157.576	25.17	25.49	−1.28
3302	5.268	157.856	25.24	25.46	−.85
3303	5.268	162.538	24.68	24.93	−1.01
3315	5.268	162.898	24.53	24.90	−1.49
3304	5.268	167.824	24.33	24.44	−.47
3316	5.268	168.890	24.21	24.35	−.60
3317	5.268	175.475	23.65	23.87	−.91
3305	5.268	175.869	23.45	23.84	−1.62
3306	5.268	183.525	23.16	23.40	−1.02
3307	5.268	192.262	22.76	23.00	−1.03
3308	5.268	202.057	22.50	22.65	−.67
3309	5.268	213.082	22.27	22.36	−.40
3310	5.268	226.034	22.12	22.10	.07
3311	5.268	240.759	21.89	21.89	−.01
3312	5.268	257.791	21.84	21.73	.50
3313	5.268	278.133	21.75	21.61	.64
402	6.124	155.794	27.81	27.18	2.32
403	6.124	160.002	26.83	26.42	1.53
404	6.124	164.797	26.05	25.72	1.29
405	6.124	170.195	25.26	25.08	.69
406	6.124	176.883	24.59	24.45	.56
407	6.124	186.560	23.72	23.76	−.20
408	6.124	196.057	23.35	23.26	.39
409	6.124	207.059	22.71	22.83	−.54
410	6.124	219.594	22.51	22.47	.15
411	6.124	234.502	22.09	22.17	−.39
412	6.124	250.222	21.85	21.95	−.45
413	6.124	265.673	21.82	21.81	.04
414	6.124	284.186	21.75	21.69	.26
225	13.166	155.297	46.40	47.01	−1.29
226	13.166	155.970	40.98	40.72	.64
227	13.166	156.753	38.10	37.56	1.44
228	13.166	157.829	35.90	35.17	2.10
229	13.166	159.558	33.40	32.94	1.40
230	13.166	162.067	31.21	31.04	.54
231	13.166	168.678	28.35	28.41	−.19
232	13.166	172.876	27.38	27.42	−.13
233	13.166	177.619	26.57	26.59	−.08
234	13.166	182.951	25.81	25.89	−.29
235	13.166	188.633	25.21	25.31	−.36
236	13.166	195.116	24.73	24.79	−.23
237	13.166	201.815	24.41	24.37	.17
238	13.166	208.788	24.03	24.01	.08
239	13.166	216.716	23.84	23.69	.62
240	13.166	222.219	23.63	23.51	.50
241	13.166	230.717	23.39	23.28	.50
242	13.166	239.156	23.22	23.09	.58
243	13.166	248.314	23.02	22.92	.40
244	13.166	257.729	22.96	22.79	.74
245	13.166	267.382	22.83	22.68	.65
246	13.166	276.983	22.57	22.59	−.08
516	20.260	154.095	28.69	28.69	−0.02
517	20.260	157.860	27.54	27.75	−.74
518	20.260	162.027	26.77	27.04	−1.00
519	20.260	167.104	26.15	26.42	−.99
520	20.260	173.286	25.63	25.87	−.92
521	20.260	182.885	25.03	25.27	−.96
522	20.260	190.402	24.78	24.93	−.59
523	20.260	198.662	24.49	24.65	−.63
524	20.260	207.168	24.27	24.42	−.61
525	20.260	215.586	24.17	24.24	−.29
901	23.158	148.563	27.06	26.66	1.52
902	23.158	152.486	26.51	26.35	.61
903	23.158	157.402	26.05	26.03	.10
904	23.158	163.303	25.65	25.71	−.27
905	23.158	170.379	25.31	25.42	−.44
906	23.158	178.665	25.00	25.15	−.59
907	23.158	187.541	24.74	24.92	−.70
908	23.158	196.331	24.58	24.74	−.64
801	25.920	140.433	26.57	26.19	1.44
802	25.920	144.299	26.26	26.04	.84
803	25.920	148.597	26.00	25.89	.42
804	25.920	153.298	25.77	25.75	.07
805	25.920	159.026	25.59	25.60	−.03
806	25.920	165.241	25.40	25.46	−.21
807	25.920	171.390	25.34	25.34	−.01
3215	28.669	129.470	26.76	26.49	1.01
3216	28.669	132.006	26.61	26.42	.73
3217	28.669	135.669	26.47	26.33	.51
3218	28.669	140.018	26.35	26.24	.44
3219	28.669	144.268	26.21	26.15	.21
3220	28.669	148.803	26.16	26.07	.32
3221	28.669	153.319	26.04	26.00	.17
3222	28.669	157.769	26.02	25.93	.32
317	28.719	130.692	26.50	26.46	.15
318	28.719	134.835	26.28	26.36	−.30
319	28.719	138.945	26.15	26.27	−.44
320	28.719	143.490	26.19	26.18	.04
321	28.719	147.531	26.05	26.10	−.19
322	28.719	151.493	25.99	26.04	−.19
323	28.719	155.489	25.93	25.97	−.17
324	28.719	159.453	25.90	25.92	−.07
706	28.736	128.832	26.56	26.51	.19
701	28.736	130.025	26.58	26.48	.38
702	28.736	134.223	26.36	26.37	−.07
703	28.736	139.804	26.20	26.25	−.19
704	28.736	146.427	26.07	26.12	−.22
705	28.736	153.498	25.95	26.01	−.21
601	28.740	129.811	26.75	26.49	.98
602	28.740	133.528	26.50	26.39	.42
603	28.740	137.687	26.35	26.30	.20
604	28.740	141.772	26.21	26.21	.00
605	28.740	146.114	26.14	26.13	.04
606	28.740	150.669	26.08	26.05	.11
607	28.740	154.966	26.00	25.99	.04
608	28.740	159.013	25.96	25.93	.12
1101	30.681	120.598	27.15	27.04	0.39
1102	30.681	124.251	26.97	26.96	.05
1103	30.681	130.736	26.79	26.83	−.15
1104	30.681	134.797	26.72	26.76	−.17
1105	30.681	138.824	26.66	26.70	−.15
1002	32.588	112.214	27.78	27.81	−.11
1003	32.588	116.182	27.63	27.73	−.37
1004	32.588	120.105	27.58	27.65	−.25
1005	32.588	124.452	27.50	27.58	−.29
1006	32.588	128.570	27.44	27.51	−.25
1007	32.588	132.456	27.45	27.45	.00
1901	33.932	102.977	28.68	28.58	.35
1902	33.932	106.074	28.43	28.51	−.28
1903	33.932	109.146	28.41	28.45	−.11
1904	33.932	112.406	28.31	28.38	−.24
1905	33.932	115.869	28.24	28.32	−.25
1802	34.920	97.805	29.18	29.20	−.09
1803	34.920	100.912	28.93	29.13	−.70
1804	34.920	103.990	28.83	29.06	−.81
1805	34.920	107.030	28.75	29.00	−.86

TABLE 3. *Experimental and calculated* C_v – Continued

ID	DEN	TEMP	C_v	CALC	PCNT
1701	36.059	89.205	30.52	30.10	1.41
1702	36.059	92.249	30.19	30.02	.58
1703	36.059	95.257	29.98	29.94	.13
1704	36.059	98.232	29.84	29.86	−.07
1705	36.059	100.982	29.78	29.80	−.04
1602	37.189	82.640	31.17	31.06	.35
1603	37.189	85.671	31.15	30.97	.57
1604	37.189	89.014	30.93	30.87	.19
1605	37.189	92.303	30.88	30.77	.35
1606	37.189	95.052	30.69	30.70	−.04
1502	38.224	74.969	32.21	32.13	.24
1503	38.224	77.616	31.93	32.03	−.33
1504	38.224	80.237	31.83	31.94	−.35
1505	38.224	82.818	31.82	31.85	−.09
1402	38.983	70.626	32.99	32.96	.10
1403	38.983	73.222	32.93	32.85	.25
1404	38.983	75.794	32.69	32.74	−.15
1302	39.787	65.138	34.17	33.96	.61
1303	39.787	67.705	33.57	33.83	−.79
1304	39.787	70.233	33.67	33.72	−.13
1203	40.649	57.897	35.20	35.24	−.12
1202	40.649	58.917	35.21	35.18	.07
1204	40.649	60.442	35.03	35.09	−.17
1205	40.649	62.967	35.08	34.94	.38

NPP = 151, Pct = 0.47.

the logarithmic form suggested by Voronel' et al., for oxygen near the critical point [8]. When this failed, we used a power ϵ in the expression

$$W \equiv (T/T_c - 1)^{-\epsilon},$$

as discussed by Fisher [9]. In this expression we obviously cannot use T_c on isochores departing from the critical density. Instead we must use $T_0(\sigma)$, a locus inside the coexistence envelope (fig. 1), touching it at the critical point. Through eq (4–c) the shape of this locus is adjusted by constant C_1. The first three derivatives vanish at the critical density (we explored $\delta = 1, 3, 5$). We hope soon to report on a *PVT* equation of state incorporating eq (4–d) for nonanalyticity at the critical point.

When coefficients for the two temperature dependent terms in eq (4) are found by least squares, they are worthless because they have large amplitudes mostly of opposite sign and their density dependence is irregular. We therefore seek data for B by trial on each isochore, obtaining A as an average. Equations (4–a), and (4–b) result from an examination of these data. As a final step, we iterate simultaneously for ϵ, B_2, and C_1, with $A(\sigma)$ constrained to eq (4–a) by least squares. Rounding these constants to the final values has an insignificant effect on the mean deviation. Constant B_1 must exceed zero if the second virial coefficient vanishes at high temperature by a $T^{-1/4}$ dependence, but our computer experiments with the present data give $B_1 = 0$. Equation (4) gives a finite value for $(\partial P/\partial T)_\rho$ at the critical point, a result derived from the thermodynamic relation

$$(\partial^2 P/\partial T^2)_\rho = -\rho^2 \cdot (\partial C_v/\partial \rho)_T/T\cdot$$

Simplification of eq (4) is possible at the cost of increased deviations on low-density isochores near saturation. A plot of the data for $A(\sigma)$ is qualitatively a cubic in σ. The expression for $T_0(\sigma)$, eq (4–c), has the most simple, acceptable behavior at the origin when constant $C_1 = 1$. In this case C_1 is not an arbitrary constant. With these considerations we present the following results to show that $C_v(\sigma, T)$ might be described with fewer arbitrary constants than for eq (4) above. More accurate data are required at the low densities for a test of this possibility.

Constants for simplified eq (4)

Assuming these values –
$\alpha = -1/4$ $A_4 = 0$
$\beta = -3$ $A_5 = 0$
$\gamma = +3$ $B_1 = 0$
$\delta = +3$ $C_1 = 1$
We find the following values –
$\epsilon = 0.360$ $A_1 = 10.2672$
$B_2 = 0.331$ $A_2 = -7.39130$
$A_3 = 1.75627$
Mean relative deviation for 152 C_v data is 0.63 percent.

These constants are *not* used in the following calculations

Data of Voronel' et al. [8], are given in table 4 on an isochore near critical density, and are compared with calculated values from eq (4). Our experimental data from table 2 agree better with Voronel' et al., than do our calculated values, suggesting that $W(\sigma, T)$ is not optimized for densities near critical. Necessary accuracy is lacking, however, for a critical comparison, because the respective critical point constants do not agree, and our experiments were not designed for high precision near the critical point.

TABLE 4. *Comparisons of* C_v *on a near-critical isochore*

T, K	Dens Mol/l	C_v, J/mol-K		
		Vrnl	Calc	Pcnt
155.000	12.7625	51.60	55.64	−7.26
155.120	12.7625	49.90	51.19	−2.52
155.130	12.7625	51.70	50.91	1.55
155.270	12.7625	50.10	47.84	4.73
155.380	12.7625	48.00	46.12	4.08
155.450	12.7625	46.90	45.23	3.70
155.640	12.7625	44.20	43.30	2.08
155.830	12.7625	44.60	41.86	6.55
156.860	12.7625	39.00	37.48	4.07
158.910	12.7625	32.80	33.79	−2.93
159.600	12.7625	34.50	33.04	4.42
160.140	12.7625	33.30	32.54	2.35

6. Derived Values for $(\partial P/\partial T)_v$ at Saturation

An interesting and valuable calculation can be performed now that we have analytical descriptions for C_σ, the specific heat of liquid along the coexistence path [2], and for C_v in one-phase domains. The thermodynamic relation [10],

$$C_\sigma = C_v + k \cdot T \cdot (-d\rho/dT)_\sigma \cdot (\partial P/\partial T)_v/\rho^2, \tag{5}$$

contains temperature dependence of liquid density on the coexistence path $(d\rho/dT)_\sigma$ given in [2], and $(\partial P/\partial T)_v$ the terminal slopes of PVT isochores at the coexistence boundary. These slopes cannot be estimated with confidence by extrapolating PVT data because in just this terminal region the isochores may have maximum curvature. Yet these slopes are required data for thermal computations on isotherms extending from saturated liquid states into compressed liquid states.

Table 5 gives our computation of $(\partial P/\partial T)_v$ for liquid at the coexistence boundary under the heading CALCD. In column WEBER are values derived from *PVT* data [3], and in column ROWLN are some earlier values derived by J. S. Rowlinson [10]. With uncertainties of about 1 percent each in C_σ and in C_v, the uncertainty in $(C_\sigma - C_v)$ is about 3 percent when $C_\sigma \approx 2 \cdot C_v$. To this, add 1 percent uncertainty in $(d\rho/dT)_\sigma$ to obtain about 4 percent total uncertainty in the derived values for $(\partial P/\partial T)_v$. Agreement among the last three columns of table 5 is excellent.

TABLE 5. *Derived terminal values of* $(\partial P/\partial T)_v$ *for liquid*

T, *K*	*P*, atm	Mol/l	*Dρ/DT* Mol/lK	CSAT J/mol-K	C_v J/mol-K	*DP/DT*, atm/K		
						CALCD	WEBER	ROWLN
54.351	0.001	40.842	−0.1384	53.31	35.69	38.57	38.93	....
55.000	.002	40.752	−.1385	53.31	35.54	38.22	38.56	....
60.000	.007	40.057	−.1392	53.27	34.51	35.58	35.77	36.60
65.000	.023	39.359	−.1404	53.28	33.56	33.02	33.14	33.90
70.000	.061	38.652	−.1421	53.33	32.70	30.57	30.65	31.20
75.000	.143	37.936	−.1444	53.42	31.90	28.23	28.30	28.80
80.000	.297	37.208	−.1472	53.58	31.17	26.01	26.09	26.50
85.000	.561	36.463	−.1506	53.81	30.49	23.90	24.00	24.50
90.000	.981	35.700	−.1548	54.13	29.85	21.91	22.03	22.30
90.180	1.000	35.672	−.1550	54.14	29.83	21.84	21.96	22.20
95.000	1.611	34.914	−.1598	54.55	29.27	20.03	20.17	....
100.000	2.509	34.100	−.1659	55.11	28.73	18.26	18.42	....
105.000	3.738	33.253	−.1730	55.84	28.23	16.58	16.75	....
110.000	5.363	32.367	−.1817	56.78	27.78	15.00	15.17	....
115.000	7.454	31.433	−.1923	58.01	27.37	13.51	13.67	....
120.000	10.082	30.439	−.2055	59.62	27.00	12.09	12.23	....
125.000	13.321	29.372	−.2224	61.76	26.69	10.74	10.84	....
130.000	17.249	28.207	−.2448	64.70	26.44	9.44	9.61	....
135.000	21.947	26.909	−.2763	68.91	26.29	8.16	8.25	....
140.000	27.501	25.416	−.3247	75.44	26.31	6.89	6.90	....
145.000	34.018	23.601	−.4110	87.09	26.71	5.57	5.58	....
150.000	41.638	21.113	−.6247	115.69	28.50	4.09	4.14	....
151.000	43.312	20.445	−.7174	127.97	29.48	3.75		
152.000	45.041	19.662	−.8600	146.72	31.14	3.37	3.51	....
153.000	46.828	18.688	−1.1189	180.23	34.64	2.93		
154.000	48.675	17.292	−1.8252	268.10	49.22	2.30	2.72	....

7. Appendix I. Adjustment for Expansion of the Calorimeter Bomb

This derivation is similar to that of P. A. Walker [4]. With reference to figure 4, we want Q_{AB} at constant volume for a given $\Delta T = T_2 - T_1$, but we observe Q_{AC} due to the increase ΔV of bomb volume. From thermodynamics,

$$\Delta E_{AC} = Q_{AC} - \int_A^C P \cdot dV. \tag{a–1}$$

Along path ABC, however,

$$\Delta E_{AC} = \int_A^B \left(\frac{\partial E}{\partial T}\right)_{V_1} dT + \int_B^C \left(\frac{\partial E}{\partial V}\right)_{T_2} \cdot dV. \tag{a–2}$$

Combining (a–1) and (a–2) with the thermodynamic equation of state,

$$(\partial E/\partial V)_T = T \cdot (\partial P/\partial T)_v - P, \tag{a–3}$$

we obtain

$$Q_{AB} - Q_{AC} = \int_B^C P \cdot dV_{T_2} - \int_A^C P dV - T_2 \cdot \int_B^C \left(\frac{\partial P}{\partial T}\right)_V dV. \tag{a–4}$$

Sum of the first two terms on the right of (a–4) is the area of triangle ABC, which is approximately $\Delta P \cdot \Delta V/2$. Hence

$$Q_{AB} = Q_{AC} + \left[\Delta P/2 - T_2 \cdot \left(\frac{\partial P}{\partial T}\right)_V\right] \cdot \Delta V \tag{a–5}$$

where $(\partial P/\partial T)_V$ at T_2 is a mean over ΔV. For sufficiently small interval about T, however, (a–5) becomes simply

$$(Q/\Delta T)_{AB} = (Q/\Delta T)_{AC} - T \cdot (\partial P/\partial T)_V \cdot \Delta V/\Delta T. \tag{a–6}$$

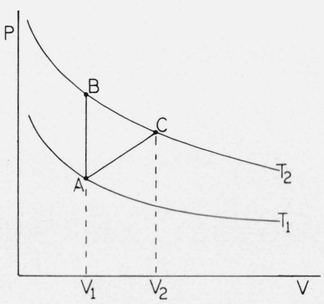

FIGURE 4. P – V *diagram for appendix I.*

We accounted for fluid forced into the capillary tube as described in the main text above eq (2). R. E. Barieau subsequently has given a careful derivation for these adjustments with the following result

$$C_v=\left[\mathrm{Lim}\left(\frac{Q}{\Delta T}\right)-C_b\right]\frac{1}{N_b}-T\cdot\left(\frac{\partial P}{\partial T}\right)_\rho\cdot\frac{dv}{dT}\cdot \tag{a–7}$$

where

$$\frac{dv}{dT}=\frac{1}{N_b}\left[\frac{dV_b}{dT}+\frac{V_b}{N_b}\cdot\frac{dN_c}{dT}\right]. \tag{a–8}$$

For our eq (2) we calculated density in the bomb as

$$\rho=(N-N_c)/V_b, \tag{a–9}$$

and the value of Δv for eq (2) as

$$\Delta v=1/\rho_2-1/\rho_1. \tag{a–10}$$

From (a–9) and (a–10) one obtains

$$\Delta v=[N\cdot\Delta V_b+V_b\cdot\Delta N_c]/(N-N_{c_2})(N-N_{c_1}), \tag{a–11}$$

or very closely for a small capillary tube,

$$\Delta v/\Delta T\approx\frac{1}{N_b}\,[\Delta V_b+V_b\cdot\Delta N_c/N_b]/\Delta T. \tag{a–12}$$

This is the same as (a–8) for small intervals.

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(Paper 73A1–530)