

Specific Heats of Oxygen at Coexistence*

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Specific heats of saturated liquid, along the coexistence path, are useful for computing thermodynamic properties throughout the compressed liquid phase. We report 86 experimental heat capacities of oxygen for the two-phase system, liquid plus vapor, from the triple-point to near the critical-point and corresponding derived values for the liquid phase. These results are represented by a formula which can be integrated for heat absorbed and for entropy. The changes in value of internal energy, enthalpy, and entropy of the saturated liquid are tabulated from the triple-point to the critical-point.

Key Words: Coexistence; experimental; heat capacity; liquid phase; oxygen; saturated liquid; specific heat.

List of Symbols

A, B, C, r	constants for eq (5.1).
A_i	coefficients for liquid density formula.
B_i	coefficients for rectilinear diameter formula.
C_i	coefficients of formula for C_b .
D_i, E_i	binomial coefficients (appendix IV).
C_a	gross heat capacity adjusted for curvature.
C_b	heat capacity of empty calorimeter bomb.
\bar{C}	specific heat, two-phase sample, adjusted for curvature.
\bar{C}_v	specific heat of two-phase sample at constant total volume.
C_σ	specific heat of liquid on coexistence path.
E	internal energy.
E_b	volt-box output potential.
E_s	potential across standard resistor for heater current.
H	enthalpy.
ΔH_v	heat of vaporization.
J	the joule.
k	conversion factor, $0.101325 \text{ J/cm}^3 \text{ atm}$.
N	total g moles of fluid in bomb plus capillary tube.
N_b	g moles of fluid in the bomb.
N_c	g moles of fluid in the capillary tube.
P	pressure, $1 \text{ atm} = 0.101325 \text{ MN/m}^2$.
Q	heat energy; also calorimetric heat input.
$Q/\Delta T$	unadjusted, gross heat capacity.
R_b	volt-box input resistance.

R_l	input lead-wire resistance.
ρ	density.
S	entropy.
t	time.
T	temperature, Kelvin.
T_1, T_2	initial and final temperatures of a heating interval.
T_a	average temperature in ΔT .
T_c	critical-point temperature, 154.77 K . [17]
T_t	triple-point temperature, 54.3507 K . [17, 18]
ΔT	calorimetric temperature increment, deg. Celsius.
v	molal volume, $1/\rho$.
V_b	volume of the calorimeter bomb.
V_l	total liquid volume.

1. Introduction

This work is part of a program on thermodynamic properties of oxygen. For gaseous states the temperature dependence of these properties may be obtained from spectroscopically derived specific heats at zero density [1]¹ combined with accurate PVT data. For compressed liquid states, however, additional data are required. Useful among these are specific heats of saturated liquid, $C_\sigma(T)$, along the coexistence path. In the present report we give experimental results from near the triple-point to near the critical-point. We give an empirical formula for temperature dependence of these results, and the integrals in analytical form which we use for calculating the heat absorbed and the change in value of entropy on this path. We tabulate also the energy and enthalpy. Our results for specific heats in single-phase domains will be reported separately. In a forthcoming publication by one of us (L.A.W.), the present results are used

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

with extensive *PVT* data to construct a complete thermodynamic network for oxygen from the triple-point to 300 K at pressures to 300 atm.

2. Apparatus and Procedures

2.1. Apparatus

The calorimeter is the same as used previously for hydrogen [2, 3], except that nearly all of the internal electric wires were replaced (following a relocation of our laboratory). In brief, the spherical sample-holder of type 316 stainless steel is about 2 in in diameter. It is filled via a stainless steel capillary tube 34 in long, $\frac{1}{8}$ in o.d. and 0.006 in i.d., terminating in a shutoff valve on top of the cryostat. A lightweight, cylindrical copper case on the sphere protects the 100 Ω electric heater (wound on the sphere) and serves as the reference temperature for two thermopiles (100 $\mu\text{V}/\text{deg C}$) controlling a guard ring and the adiabatic shield. For control of each of these shields we use a commercial, electronic "controller," giving automatic reset and rate sensitivity, in addition to our previous equipment. We observe the relative shield temperatures continuously on a recorder.

Temperature of the sample-holder is measured with the same platinum resistance thermometer (NBS 1955 scale) and 6-dial, μV potentiometer. Pressures are measured with the same dead-weight gage (piston diameters recently recalibrated), accurate to about one part in 10,000. For safety, oil of the gage is separated from the oxygen by nitrogen gas between two null-diaphragms. Filling pressures are corrected for hydrostatic pressure of cold oxygen in the capillary tube.

We obtain the calorimetric heating rate from simultaneous readings of potential and current. Potential wires are connected at the heater in a manner to account for heat developed in the current-carrying wires between shields and calorimeter [4, 5]. The potential wires lead to a potential-divider (volt-box). We correct for resistance of these potential wires, and for current drawn by the volt-box. The heater current is measured potentiometrically by means of a calibrated, standard resistor and a type K-3 potentiometer.

Time of the heating interval, Δt , is measured by an electronic counter (quartz piezoelectric oscillator) accurate to better than one part in a million. This counter is switched on and off by the potential across the calorimeter heater. An intervening transmitting circuit, of 22 megohm input impedance, gives the counter a signal independent of the heater potential.

2.2. Procedures for the Sample

The commercial high-purity oxygen (maximum nominal impurities 0.01%) is taken from a steel cylinder at about 130 atm. At this pressure the oxygen flows through a molecular sieve trap at 76 K, and is admitted slowly to the calorimeter bomb until this pressure also is near 130 atm. The amount of sample

is fixed by the selected bomb temperature. A steady state exists after 30 min, when we measure temperature and pressure. We then immediately close the cryostat valve, and begin cooling the bomb into the region of two phases for the contained oxygen.

2.3. Procedure for a Heat Measurement

We measure five temperatures, $T(t)$, in several minutes immediately preceding a heat. They are extrapolated linearly to obtain T_1 at the midtime, t_a , of the heating interval. For a temperature rise of about 5 $^\circ\text{C}$ in 10 min we use currents from 0.04 to 0.12 A, dependent on the amount of sample. We average electric power from three pairs of potential and current readings. Shield temperatures as shown on the recorder lag about 0.005 $^\circ\text{C}$ at the start, recovering to within 0.001 $^\circ\text{C}$ of the calorimeter in about a minute. The opposite behavior follows ending of a heat. We then observe temperature drift of the calorimeter on another recorder. In about 20 min the temperature no longer increases, and may begin a very slow decrease (imperfect adiabatic shielding), when we take another five values for $T(t)$ over about 5 min. They are extrapolated linearly to obtain T_2 at t_a .

3. Calculations and Adjustments

3.1. Amount of Sample

Given the filling conditions P and T , we use an equation of state, appendix V, to calculate the one-phase density with an uncertainty of about 0.1 percent. By use of our bomb volume (uncertainty 0.1%, appendix I) we then have the amount of sample in the bomb. We sum amounts over the length of the capillary tube by use of estimated temperatures in appendix II, and above equation of state. Sum of amounts in bomb and capillary is N , total gram moles in the closed system, with maximum uncertainty of 0.2 percent.

3.2. The PVT Conditions

We use the average temperature for a specific heat observation, $T_a = (T_1 + T_2)/2$, to calculate pressure P_a from the vapor-pressure equation (appendix VI). First and second derivatives of $P(T)$ also are calculated at T_a . Volume of the bomb, V_b , and dV_b/dT are calculated at T_a , P_a (appendix I). Amount of sample in the bomb is $N_b = N - N_c$ where N_c is amount in the capillary tube at T_a , P_a . The increased amount in capillary tube, δN_c , is amount at T_2 , P_2 less amount at T_1 , P_1 . Average density of the sample is defined $\rho_{av} \equiv N_b/V_b$.

Density of the liquid phase, ρ_l mole/cm³, and the derivative versus T , we obtain from the function (L.A.W.) of table 1. By use of the function for rectilinear diameter (L.A.W.) table 2, we obtain the vapor density, ρ_g . Relative volume of liquid in the bomb then is

$$V_l/V_b = (\rho_{av} - \rho_g)/(\rho_l - \rho_g), \quad (3.1)$$

where V_l is absolute (not molal) volume of the liquid phase.

3.3. Gross, Tare, and Net Heat Capacities

Corresponding to the temperature rise ΔT , the total heat absorbed is Q joules, calculated from volt-box potential E_b , potential E_s across the standard resistor (both in volts), and time Δt , seconds,

$$E_x \equiv E_b \cdot (1 + R_l/R_b)/K, \quad (3.2)$$

$$I_b = E_x/(R_b + R_l), \quad (3.3)$$

$$Q = E_x \cdot [E_s/R_s - I_b] \cdot \Delta t. \quad (3.4)$$

In (3.4), $R_s = 1.000\,004\ \Omega$, $R_b = 225,000\ \Omega$ is volt-box input resistance, $R_l = 30\ \Omega$ is resistance of the potential wires between heater and volt-box, and $K = 1/2000$ is the volt-box ratio (0.02% accuracy). Potentiometer accuracies for E_b and E_s are 0.01 percent and 0.015 percent. Uncertainty in Q therefore is about 0.05 percent.

TABLE 1. Densities ρ_l of saturated liquid oxygen

$$\rho_l = \rho_c + 10^{-6} \cdot \sum_{n=1}^7 A_n \cdot x^n$$

where $x \equiv (T_c - T)^{1/3}$.

$T_c = 154.77\ \text{K}$	$\rho_c = 0.01362\ \text{mol/cm}^3$
$A_1 = 3419.8$	$A_2 = 516.52$
$A_3 = 319.91$	$A_4 = -275.099$
$A_5 = 92.846\ 5$	$A_6 = -14.724\ 0$
$A_7 = 0.927\ 88$	

TABLE 2. Rectilinear diameter for oxygen

$$(\rho_l + \rho_g)/2 = \rho_c + 10^{-3} \cdot \sum_{n=1}^8 B_n \cdot x^n$$

where $x \equiv (T_c - T)/100$.

$T_c = 154.77\ \text{K}$	$\rho_c = 0.01362\ \text{mol/cm}^3$
$B_1 = 5.892$	$B_2 = 3.256$
$B_3 = -14.031$	$B_4 = 43.814$
$B_5 = -75.269$	$B_6 = 71.788$
$B_7 = -36.405$	$B_8 = 7.727$

As discussed below, the value of ΔT depends on the temperature scale, on extrapolations in time, and randomly on use of the potentiometer dials. We take the nominal uncertainty in ΔT to be $(0.1\%) \cdot (5/\Delta T)$. Uncertainty in the observed gross heat capacity, $Q/\Delta T$, therefore is roughly 0.15 percent.

An uncertainty in ΔT of roughly 0.05 percent is probable, based on uncertainties in slope of the temperature scale relative to the thermodynamic scale [7]. The statistical uncertainty in temperature increment, $\Delta T = T_2 - T_1$, obtained from least squares fitting of the $T(t)$ data, usually is near 0.01 percent, with rare

values of 0.03 percent. Possible uncertainties arising from accuracy of the potentiometer for $\Delta T = 5.0\ ^\circ\text{C}$, are given by the last column of table 3. Values this large arise only by chance if the uppermost dial of the potentiometer is changed in obtaining ΔT . Most frequently the uncertainties will be 0.1 to 0.01 of these values. R. E. Barieau kindly pointed out that this uncertainty could be diminished by an auto-calibration of the potentiometer.

TABLE 3. Uncertainties of temperatures derived from the potentiometer accuracy, $k = 0.01$ percent, and characteristics of the platinum resistance thermometer

$\delta T = k \cdot R \cdot dT/dR$				
T, K	R, Ω	dR/dT	δT	$(\delta T/5.0), \%$
50	1.923	0.095	0.002	0.04
100	7.305	.110	.007	.13
150	12.72	.107	.012	.24
200	17.99	.104	.017	.35
300	28.23	.101	.028	.56

We measured 68 tare heat capacities C_b of the empty calorimeter bomb from 55 to 300 K, in J/K. They were adjusted for curvature by application of a cubic expression in three separate ranges of T . After investigating various ways to utilize Debye functions, we represent these data more simply by

$$\text{Log}_e(C_b/50) = \sum_{i=1}^8 C_i \cdot (100/T)^{i-1}, \quad (3.5)$$

with an rms relative deviation of 0.11 percent. Table 4 gives values for coefficients, C_i . For this report the deviation applies to values of C_b from 20 to 67 J/K in the range $55 \leq T < 155\ \text{K}$. For any quantity of sample, therefore, absolute uncertainty in the quantity $[Q/\Delta T - C_b]$ will range from 0.02 to 0.07 J/K due to uncertainties in C_b alone over the above range of T .

TABLE 4. Constants for C_b of the empty calorimeter, eq (3.5)

$C_1 = 0.9625\ 75$	$C_2 = -2.6479\ 48$
$C_3 = 6.6945\ 41$	$C_4 = -11.5636\ 585$
$C_5 = 10.9871\ 61$	$C_6 = -6.0136\ 545$
$C_7 = 1.7776\ 616$	$C_8 = -0.2195\ 491$

3.4. Curvature Adjustment

If the specific heat is not a linear function of T , a curvature adjustment may be necessary to find its value at the average temperature T_a [5]. We have applied this adjustment to the gross heat capacities, assuming that their true behavior is represented by

$$C_a = C_1 + C_2 \cdot T_a + C_3 \cdot T_a^2 + C_4 \cdot T_a^3 + C_5/\sqrt{T_c - T_a}, \quad (3.6)$$

where T_c is the critical temperature. (The coefficients C_1, C_2 etc. are not related to those of table 4.) The experimental gross heat capacity at average temperature T_a then is

$$C_a = Q/\Delta T - \{C_3/12 + C_4 \cdot T_a/4 + (C_5/32)/(T_c - T_a)^{5/2}\} \cdot \overline{\Delta T}^2 \quad (3.7)$$

This formula is obtained by integrating (3.6), i.e., $C_a \equiv \delta Q/dT$, between the limits $(T_a - \Delta T/2)$ and $(T_a + \Delta T/2)$. Collection of terms then yields two parts for Q , $C_a(T_a)$ the desired heat capacity at T_a , and a correction term which is a function of T_a and of ΔT . Coefficients in (3.6) are found by least squares, using $C_a = Q/\Delta T$. The difference between C_a and $Q/\Delta T$ is found to be small compared with various uncertainties and therefore could be neglected in the present work. For brevity, we define results of the curvature adjustment on specific heat of the two-phase sample as follows (prior to adjustment for calorimeter volume expansion),

$$\bar{C} = (C_a - C_b)/N_b, \quad (3.8)$$

with uncertainty of roughly 0.5 percent when $C_a \approx 2 \cdot C_b$.

3.5. Expansion and Capillary Adjustments

The bomb expands during the calorimetric interval ΔT . An adjustment to find specific heat at constant volume has been described [8, 9]. The capillary tube absorbs an amount of vapor, δN_c , which must boil away from liquid in the bomb. Combining these adjustments we obtain C_v for the two-phase sample,

$$\bar{C}_v = \bar{C} - \{T_a(dP/dT)(dV_b/dT) + \delta N_c \cdot \Delta H_v/\Delta T\}/N_b. \quad (3.9)$$

For this expression, we describe the heat of vaporization in joules per mole by use of $x \equiv (1 - T_a/T_c)$,

$$\Delta H_v = x^{0.4} \cdot (1.05 - 0.2 \cdot x) \cdot 10^4. \quad (3.10)$$

For computing overall uncertainty (see below), we take the following rough estimates,

$$(dP/dT), 0.5\%, \quad (dV/dT), 2.0\%$$

$$\delta N_c, 100.0\%, \quad \Delta H_v, 2.0\%.$$

A large uncertainty is assumed for δN_c because temperature along the capillary tube is poorly defined. A portion of the total capillary volume of 0.015 cm³ is outside the cryostat, at room temperature.

3.6. Calculation for C_σ

At sufficiently low temperatures one may observe directly C_σ , the heat capacity of the condensed phase at

its own (negligible) vapor pressure. Otherwise C_σ is related to \bar{C}_v of the two-phase system via PVT properties [8, 10]

$$C_\sigma = \bar{C}_v + (T/\rho) \cdot \{(-d\rho/dT)(dP/dT)/\rho - ((V_b \cdot \rho/N_b) - 1) \cdot d^2P/dT^2\}, \quad (3.11)$$

where ρ refers to the liquid phase. At the critical point $(-d\rho/dT) = \infty$. If the bomb is completely filled with liquid, $V_b \cdot \rho/N_b = 1$. For computing overall uncertainty (see below), we take the following rough estimates

$$\begin{array}{ll} \rho, 0.1\% & V_b/N_b, 0.2\% \\ d\rho/dT, 1.0\% & d^2P/dT^2, 5.0\%. \end{array}$$

4. Experimental Results

Table 5 gives loading conditions for the sample in five experimental runs. Temperature and pressure, obtained by computation from laboratory observations, in effect are direct measurements. Volume of the bomb is computed, appendix I. Density is obtained by iterating the equation of state [6]. Total g moles, N , includes a few ten-thousandths in the capillary tube.

Table 6 gives the experimental conditions, the specific heats, and the uncertainties (errors) for each measurement (point) of the five experimental runs. Under ID is given the run number, followed by two digits for the point in that run. Temperature is the average, T_a . Pressure, bomb volume, and density are calculated, section 3. This density is the defined average, $\rho_{av} = N_b/V_b$. The sixth column gives ΔT , followed by $Q/\Delta T$, its value adjusted for curvature, and the tare heat capacity from (3.5). Next is \bar{C}_v for the two-phase system, obtained via the adjustment of (3.9), and then C_σ calculated via (3.11), both in J/(mol K). The last two columns give uncertainties for \bar{C}_v and for C_σ in percent, calculated by methods of appendix III.

TABLE 5. Loading conditions for the samples

Run	T , K	P , atm	V , cm ³	ρ , 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
5	173.070	129.980	73.054	20.223	1.4775
20	180.928	123.245	73.072	16.833	1.2302
32	137.181	106.345	72.934	28.633	2.0882

TABLE 6. *Experimental specific heats, saturated liquid oxygen*

ID	Temp. K	Pres. atm.	V_b cm ³	Dens. mol/l	DEL T K	DQ/DT J/deg	$DQDTA$ J/deg	Tare J/deg	C_p J/M-K	CSAT J/M-K	Errors		Percent	
											C_V	CSAT		
201	56.948	0.003	72.669	13.214	2.754	74.096	74.096	22.910	53.307	53.243	0.580		0.587	
202	60.157	.007	72.672	13.213	3.673	76.465	76.466	25.185	53.404	53.280	.527		.541	
203	60.357	.008	72.672	13.213	3.645	76.628	76.629	25.326	53.428	53.298	.529		.543	
204	63.936	.018	72.677	13.212	3.525	79.350	79.350	27.835	53.649	53.405	.550		.577	
205	67.925	.042	72.682	13.211	4.481	82.261	82.261	30.578	53.824	53.377	.516		.566	
206	72.313	.092	72.688	13.210	4.309	85.477	85.477	33.501	54.129	53.345	.538		.626	
207	76.537	.181	72.695	13.209	4.151	88.651	88.650	36.199	54.624	53.390	.558		.697	
208	80.914	.335	72.702	13.208	4.614	92.088	92.087	38.860	55.430	53.591	.548		.756	
247	81.735	.374	72.704	13.207	.936	92.488	92.488	39.344	55.344	53.376	1.291		1.543	
209	85.426	.590	72.710	13.206	4.427	95.857	95.856	41.459	56.648	54.041	.564		.860	
248	83.340	.458	72.707	13.207	2.276	93.826	93.826	40.276	55.767	53.532	.749		1.011	
210	87.465	.745	72.714	13.205	4.377	97.515	97.513	42.585	57.201	54.201	.570		.911	
211	91.759	1.176	72.723	13.204	4.228	100.793	100.791	44.859	58.246	54.336	.585		1.032	
212	95.904	1.752	72.732	13.202	4.088	104.017	104.014	46.933	59.441	54.561	.598		1.160	
213	100.224	2.557	72.742	13.200	4.580	107.561	107.558	48.972	61.006	55.036	.578		1.266	
214	104.683	3.649	72.752	13.198	4.432	111.194	111.190	50.953	62.724	55.572	.588		1.417	
215	109.022	5.011	72.763	13.196	4.280	114.936	114.931	52.764	64.730	56.397	.597		1.567	
216	113.688	6.856	72.776	13.194	5.087	118.950	118.942	54.592	66.999	57.402	.564		1.682	
217	118.664	9.323	72.790	13.192	4.899	123.492	123.484	56.412	69.827	58.951	.569		1.847	
218	123.185	12.070	72.803	13.189	3.846	127.721	127.715	57.958	72.617	60.725	.619		2.043	
219	127.626	15.294	72.817	13.187	5.079	132.040	132.026	59.383	75.615	62.979	.558		2.091	
220	132.584	19.576	72.834	13.183	4.881	137.197	137.178	60.872	79.419	66.468	.561		2.204	
221	137.495	24.605	72.851	13.180	5.115	142.744	142.710	62.249	83.733	71.438	.547		2.265	
222	143.712	32.240	72.875	13.176	5.273	151.443	151.349	63.863	91.026	82.803	.532		2.274	
223	148.798	39.696	72.896	13.172	4.954	161.666	161.307	65.087	100.099	104.910	.529		2.174	
224	152.389	45.729	72.912	13.169	2.288	174.037	173.290	65.903	111.709	159.122	.702		2.035	
301	57.563	.004	72.669	28.793	2.150	134.441	134.440	23.348	53.094	53.080	.563		.565	
302	60.020	.007	72.672	28.792	2.769	136.329	136.328	25.089	53.164	53.142	.505		.508	
303	63.138	.015	72.676	28.790	3.473	138.737	138.735	27.279	53.268	53.229	.466		.471	
304	67.026	.035	72.681	28.788	4.309	141.548	141.546	29.966	53.327	53.259	.438		.446	
305	71.253	.077	72.687	28.786	4.146	144.316	144.314	32.805	53.293	53.179	.450		.466	
306	71.610	.082	72.687	28.786	4.145	144.308	144.307	33.041	53.177	53.059	.451		.467	
307	76.180	.171	72.694	28.783	5.008	147.560	147.559	35.975	53.329	53.146	.431		.456	
308	81.112	.344	72.703	28.780	4.874	151.277	151.277	38.978	53.671	53.407	.441		.480	
309	85.910	.624	72.711	28.776	4.757	155.073	155.074	41.729	54.170	53.827	.450		.504	
310	91.013	1.090	72.721	28.772	5.466	158.927	158.929	44.473	54.700	54.289	.436		.508	
311	96.412	1.835	72.733	28.768	5.353	162.482	162.484	47.179	55.105	54.663	.444		.535	
312	101.694	2.885	72.745	28.763	5.231	166.132	166.133	49.639	55.672	55.272	.452		.560	
313	106.854	4.290	72.758	28.758	5.115	169.825	169.823	51.873	56.367	56.113	.459		.582	
314	111.605	5.980	72.770	28.753	5.817	173.190	173.184	53.791	57.055	57.073	.445		.577	
315	117.372	8.629	72.786	28.747	5.738	177.526	177.510	55.952	58.087	58.690	.449		.587	
316	123.021	11.961	72.803	28.740	5.585	182.011	181.979	57.904	59.286	60.874	.455		.588	
501	58.515	.005	72.670	20.332	7.229	102.718	102.718	24.024	53.261	53.218	.386		.391	
502	65.588	.026	72.679	20.330	6.924	107.935	107.935	28.979	53.437	53.289	.404		.421	
503	72.387	.093	72.688	20.327	6.700	112.688	112.687	33.549	53.561	53.199	.420		.462	
504	78.969	.257	72.699	20.324	6.483	117.578	117.577	37.695	54.064	53.369	.435		.517	
505	85.485	.594	72.711	20.321	6.569	122.788	122.786	41.492	55.019	53.877	.442		.579	
506	91.909	1.194	72.723	20.317	6.302	127.571	127.569	44.936	55.924	54.261	.455		.660	
507	98.099	2.132	72.737	20.313	6.100	132.123	132.119	47.984	56.940	54.741	.466		.745	
508	104.668	3.645	72.752	20.309	5.819	137.342	137.338	50.946	58.465	55.727	.477		.840	
509	110.671	5.615	72.767	20.305	6.216	141.950	141.943	53.424	59.901	56.770	.472		.912	
510	116.768	8.318	72.784	20.300	6.012	147.003	146.994	55.734	61.753	58.421	.479		.992	
511	122.642	11.713	72.801	20.295	5.771	151.952	151.941	57.777	63.712	60.528	.486		1.060	
512	128.503	15.996	72.820	20.290	6.071	157.421	157.401	59.654	66.131	63.681	.479		1.096	
513	134.442	21.382	72.840	20.284	5.848	163.348	163.314	61.404	68.939	68.327	.483		1.122	
514	139.909	27.392	72.860	20.278	5.129	169.472	169.416	62.892	72.051	75.118	.500		1.133	
515	144.531	33.362	72.878	20.273	4.163	175.847	175.757	64.066	75.536	85.273	.532		1.133	
2001	59.127	.006	72.671	16.928	4.948	90.069	90.069	24.458	53.334	53.266	.445		.452	
2002	63.957	.018	72.677	16.927	4.748	93.761	93.761	27.849	53.578	53.414	.463		.482	
2003	68.641	.048	72.683	16.926	4.631	97.212	97.212	31.062	53.771	53.444	.479		.516	
2004	73.193	.107	72.689	16.924	4.486	100.365	100.364	34.073	53.886	53.315	.496		.561	
2005	77.601	.212	72.697	16.922	4.348	103.626	103.625	36.858	54.273	53.377	.512		.615	
2006	84.311	.505	72.708	16.920	5.535	108.880	108.878	40.729	55.396	53.858	.485		.662	
2007	89.547	.935	72.718	16.917	5.322	113.143	113.141	43.704	56.442	54.244	.499		.755	
2008	95.108	1.628	72.730	16.915	5.824	117.347	117.344	46.543	57.549	54.584	.492		.842	

TABLE 6. Experimental specific heats, saturated liquid oxygen—Continued

ID	Temp. K	Pres. atm.	V_b cm ³	Dens. mol/l	DEL T K	DQ/DT J/deg	DQDTA J/deg	Tare J/deg	C_p J/M-K	CSAT J/M-K	Errors	
											C_p	Percent CSAT
2009	101.059	2.740	72.743	16.911	6.105	122.031	122.026	49.352	59.070	55.226	.492	.952
2010	107.253	4.417	72.759	16.908	6.364	127.065	127.058	52.039	60.973	56.211	.490	1.072
2011	113.476	6.763	72.775	16.904	6.116	132.161	132.153	54.512	63.100	57.499	.498	1.206
2012	119.674	9.893	72.793	16.900	6.315	137.612	137.599	56.766	65.689	59.463	.495	1.318
2013	125.847	13.936	72.811	16.895	6.066	143.326	143.309	58.823	68.650	62.227	.500	1.424
2014	133.607	20.556	72.837	16.889	5.756	151.059	151.028	61.166	73.007	67.580	.505	1.518
2015	139.222	26.577	72.858	16.884	5.513	157.562	157.504	62.711	77.003	74.171	.507	1.546
2016	144.586	33.439	72.879	16.880	5.260	165.194	165.048	64.080	82.007	85.561	.508	1.531
2017	149.672	41.101	72.900	16.874	4.960	176.417	175.696	65.289	89.660	112.651	.506	1.442
3201	56.440	.003	72.668	28.736	3.670	133.850	133.848	22.547	53.301	53.290	.444	.446
3202	60.313	.008	72.672	28.734	4.084	136.722	136.721	25.296	53.360	53.336	.434	.437
3203	64.924	.023	72.678	28.732	4.364	140.173	140.172	28.521	53.468	53.417	.432	.439
3204	69.487	.056	72.684	28.730	4.772	143.206	143.205	31.631	53.431	53.337	.427	.440
3205	74.304	.128	72.691	28.727	4.876	146.489	146.489	34.788	53.492	53.336	.431	.453
3206	79.250	.268	72.699	28.724	5.032	150.113	150.114	37.865	53.754	53.519	.434	.468
3207	84.378	.520	72.708	28.720	5.254	154.102	154.103	40.869	54.226	53.904	.434	.483
3208	89.559	.937	72.718	28.716	5.122	157.864	157.865	43.710	54.666	54.266	.443	.510
3209	94.825	1.585	72.729	28.712	5.428	161.408	161.409	46.404	55.072	54.626	.441	.527
3210	100.347	2.583	72.742	28.707	5.635	165.171	165.171	49.029	55.616	55.187	.441	.546
3211	105.901	3.999	72.755	28.701	5.493	169.126	169.124	51.472	56.337	56.034	.448	.570
3212	111.610	5.982	72.770	28.696	5.321	173.243	173.237	53.793	57.193	57.196	.456	.590
3213	117.010	8.441	72.785	28.690	5.502	177.342	177.328	55.821	58.178	58.716	.454	.593
3214	122.534	11.642	72.801	28.683	5.572	181.691	181.663	57.741	59.331	60.791	.455	.590

UN=0.2, UA=0.15, UB=0.1, UC=2.5, UD=102.0, UE=1.6, UF=0.3, UG=5.0, UH=0.1.

5. Formulation and Comparisons With Earlier Data

An analytical description of $C_p(T)$ is required for computations. Using the reduced argument, $x \equiv (T_c - T)/(T_c - T_t)$ where T_c and T_t are critical-point and triple-point temperatures, we find that a plot of $C_p \cdot x^{1/2}$ versus T is a straight line, except for a small deviation as $T \rightarrow T_c$, figure 1. In the following

form, this deviation is described by a binomial, which can be expanded for term-by-term integration,

$$C_p = [A + B \cdot x + C \cdot (1 - r \cdot x)^n] / x^{1/2}, \quad (5.1)$$

with $n=12$. We define $r \equiv (T_c - T_t)/T_c$, such that $(1 - r \cdot x) \equiv T/T_c$.

This formula is similar to results obtained for a van der Waals fluid [16]. The weighted least squares determination of coefficients yields

$$A = 25.60277, \quad B = 27.71001, \quad C = -2.48274.$$

In table 7 the column PCNT is percent deviation of data, CSAT, from the calculated value, CALC. Weights, WT , are inversely proportional to the square of absolute errors obtained from the last column of table 6. In the last column of table 7, $D_2 \equiv (CSAT - CALC)^2$ and column entries are $D_2 \cdot WT$. For $n=86$ data, the weighted, mean-square relative deviation is

$$\left\{ \frac{\sum^n (\Delta C_p / C_p)^2 \cdot WT}{\sum^n WT} \right\}^{1/2} \cdot 100 = 0.19\%.$$

The correspondingly weighted absolute mean-square deviation is 0.11 J/mol K.

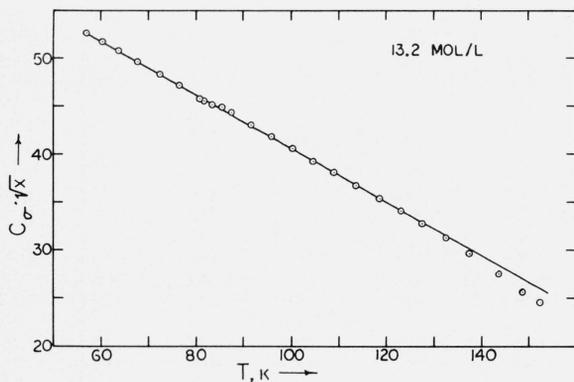


FIGURE 1. Data of run No. 2 in coordinates of eq (5.1).

TABLE 7. Comparison of experimental specific heats with values calculated from eq (5.1)

ID	Temp.	CSAT	CALC	PCNT	Weight	D2*WT	ID	Temp.	CSAT	CALC	PCNT	Weight	D2*WT
3201	56.440	53.290	53.294	-0.007	1.5956	0.002	2008	95.108	54.584	54.565	.034	.2872	.010
201	56.948	53.243	53.290	-.088	.5287	.115	212	95.904	54.561	54.645	-.154	.1675	.119
301	57.563	53.080	53.286	-.386	.5631	2.379	311	96.412	54.663	54.698	-.064	.5845	.072
501	58.515	53.218	53.280	-.117	.9487	.366	507	98.099	54.741	54.884	-.260	.3490	.712
2001	59.127	53.266	53.277	-.021	.7744	.010	213	100.224	55.036	55.143	-.194	.1418	.162
302	60.020	53.142	53.274	-.248	.6574	1.146	3210	100.347	55.187	55.159	.051	.9920	.079
202	60.157	53.280	53.274	.012	.5978	.002	2009	101.059	55.226	55.253	-.049	.2298	.017
3202	60.313	53.336	53.273	.118	1.6550	.652	312	101.694	55.272	55.340	-.123	.5364	.247
203	60.357	53.298	53.273	.047	.5929	.037	508	104.668	55.727	55.787	-.108	.2790	.102
303	63.138	53.229	53.272	-.081	.7318	.136	214	104.683	55.572	55.790	-.390	.1142	.542
204	63.936	53.405	53.274	.246	.5404	.927	3211	105.901	56.034	55.994	.071	.8828	.140
2002	63.957	53.414	53.274	.263	.7054	1.380	313	106.854	56.113	56.163	-.090	.4952	.125
3203	64.924	53.417	53.278	.261	1.6381	3.168	2010	107.253	56.211	56.237	-.045	.1823	.012
502	65.588	53.289	53.281	.014	.8563	.005	215	109.022	56.397	56.581	-.324	.0930	.313
304	67.026	53.259	53.292	-.061	.7887	.085	509	110.671	56.770	56.931	-.283	.2360	.612
205	67.925	53.377	53.300	.144	.5561	.329	314	111.605	57.073	57.143	-.123	.4881	.242
2003	68.641	53.444	53.308	.255	.6369	1.181	3212	111.610	57.196	57.145	.090	.7901	.209
3204	69.487	53.337	53.318	.035	1.6381	.058	2011	113.476	57.499	57.602	-.178	.1430	.151
305	71.253	53.179	53.345	-.310	.7449	2.043	216	113.688	57.402	57.656	-.441	.0793	.513
206	72.313	53.345	53.364	-.035	.4783	.016	510	116.768	58.421	58.528	-.183	.1950	.224
503	72.387	53.199	53.365	-.311	.7556	2.073	3213	117.010	58.716	58.603	.193	.7415	.946
2004	73.193	53.315	53.381	-.124	.5645	.247	315	117.372	58.690	58.717	-.046	.4557	.033
3205	74.304	53.336	53.406	-.131	1.5432	.753	217	118.664	58.951	59.143	-.324	.0637	.234
207	76.537	53.390	53.464	-.139	.4036	.223	2012	119.674	59.463	59.498	-.058	.1152	.014
2005	77.601	53.377	53.497	-.224	.4906	.702	3214	122.534	60.791	60.622	.278	.6991	1.988
504	78.969	53.369	53.543	-.324	.6373	1.920	511	122.642	60.528	60.669	-.232	.1637	.324
3206	79.250	53.519	53.553	-.063	1.4377	.163	316	123.021	60.874	60.834	.067	.4296	.070
208	80.914	53.591	53.617	-.048	.3559	.024	218	123.185	60.725	60.906	-.297	.0501	.164
308	81.112	53.407	53.625	-.407	.7097	3.375	2013	125.847	62.227	62.191	.058	.0926	.012
247	81.735	53.376	53.652	-.514	.1055	.802	219	127.626	62.979	63.179	-.317	.0448	.180
248	83.340	53.532	53.726	-.360	.2189	.820	512	128.603	63.681	63.711	-.047	.1474	.013
2006	84.131	53.858	53.765	.173	.4317	.373	220	132.584	66.468	66.670	-.302	.0367	.149
3207	84.378	53.904	53.778	.235	1.3263	2.112	2014	133.607	67.580	67.565	.022	.0710	.002
209	85.426	54.041	53.834	.384	.2823	1.206	513	134.442	68.327	68.354	-.039	.1199	.008
505	85.485	53.877	53.838	.073	.5302	.082	221	137.495	71.438	71.775	-.470	.0305	.347
309	85.910	53.827	53.862	-.064	.6535	.079	2015	139.222	74.171	74.199	-.038	.0579	.005
210	87.465	54.201	53.956	.455	.2555	1.538	514	139.909	75.118	75.292	-.231	.0995	.300
2007	89.547	54.244	54.096	-.273	.3468	.759	222	143.712	82.803	83.275	-.567	.0229	.510
3208	89.559	54.266	54.097	.312	1.1755	3.359	515	144.531	85.273	85.609	-.392	.0792	.892
310	91.013	54.289	54.206	.153	.6383	.441	2016	144.586	85.561	85.776	-.251	.0453	.209
211	91.759	54.336	54.265	.130	.2061	.103	223	148.798	104.910	105.396	-.461	.0159	.374
506	91.909	54.261	54.278	-.031	.4291	.012	2017	149.672	112.651	112.502	.132	.0303	.067
3209	94.825	54.626	54.538	.162	1.0881	.845	224	152.389	159.122	157.151	1.254	.0081	3.136

Comparison with earlier data, which exist at temperatures up to the boiling-point, becomes possible by use of (5.1) for interpolation. Table 8 gives such data for saturated liquid oxygen, in J/mol K [11, 12, 4, 13], and compares them with our calculated results. The mean deviation of a few tenths of 1 percent from the data of Giauque and Johnston is within our accuracy.

Values for d^2P/dT^2 at saturation can be derived from two-phase heat capacities at two or more average densities [10]. Such data may be an aid to formulating an accurate vapor pressure equation, and R. E. Barieau brought this to our attention [14] almost simultaneously

with the report of Yang and Yang [15]. For coexisting phases the relation is

$$\bar{C}_v/T = -d^2G/dT^2 + (d^2P/dT^2) \cdot v \quad (5.2)$$

where G is the Gibbs free energy per mole and v is the average molal volume. We see that d^2P/dT^2 is obtained on isotherms as the slope of plots of \bar{C}_v/T versus v . We now use this method only to show consistency between our experimental specific heats and available vapor pressure equations of high accuracy. We have compared two vapor pressure equations [6, 7] with each other, finding excellent agreement

in the second derivatives from the triple point to the boiling point.

Column 10 of table 6 gives the raw data, \bar{C}_v , for five runs at four significantly different average densities.

TABLE 8. Comparison of calculated specific heats, J/mol K, with Euken, 1; Clusius, 2; Giauque, 3; Itterbeek, 4.

ID	T, K	Refer.	Calcd.	Prcnt.
1	57.40	53.60	53.29	0.59
1	60.50	53.56	53.27	.54
1	65.10	53.39	53.28	.21
1	67.70	53.22	53.30	-.15
1	69.50	53.22	53.32	-.18
1	71.30	53.47	53.35	.23
1	73.00	52.80	53.38	-1.08
2	56.60	52.80	53.29	-.92
2	58.00	52.59	53.28	-1.30
2	59.70	52.13	53.28	-2.15
2	62.50	53.72	53.27	.84
2	65.10	54.14	53.28	1.62
2	65.50	52.47	53.28	-1.52
2	67.40	52.26	53.30	-1.94
2	67.60	53.68	53.30	.72
2	69.20	52.26	53.31	-1.98
2	70.10	53.30	53.33	-.05
2	71.00	52.43	53.34	-1.71
2	72.50	53.09	53.37	-.52
2	72.80	52.34	53.37	-1.94
3	56.95	53.38	53.29	.17
3	57.95	53.22	53.28	-.12
3	60.97	53.18	53.27	-.17
3	61.48	53.18	53.27	-.17
3	65.57	53.18	53.28	-.19
3	65.92	53.18	53.28	-.19
3	68.77	53.26	53.31	-.09
3	69.12	53.35	53.31	.07
3	70.67	53.43	53.34	.18
3	71.38	53.47	53.35	.23
3	73.31	53.60	53.38	.41
3	74.95	53.76	53.42	.63
3	75.86	53.56	53.45	.21
3	77.58	53.72	53.50	.42
3	78.68	53.68	53.53	.28
3	81.13	53.89	53.63	.49
3	82.31	53.81	53.68	.25
3	82.96	53.89	53.71	.34
3	84.79	54.10	53.80	.56
3	86.43	54.02	53.89	.24
3	86.61	54.18	53.90	.51
3	86.97	54.06	53.92	.25
3	87.32	54.02	53.95	.14
3	90.33	54.35	54.15	.36
4	70.00	53.40	53.33	.14
4	74.00	53.57	53.40	.32
4	78.00	53.73	53.51	.41
4	82.00	53.89	53.66	.42
4	86.00	54.06	53.87	.36
4	90.00	54.22	54.13	.17

For 50 points, Sumpct. = -0.08, Rmspct. = 0.81.

To interpolate onto isotherms, we represent the data for each run with a fourth order power series ($x = T/100$),

$$\bar{C}_v = A + B \cdot x + C \cdot x^2 + D \cdot x^3 + E \cdot x^4. \quad (5.3)$$

The first row of table 9 identifies the experimental run. Second and third rows give density in mol/liter and the molal volume in cm³/mol respectively. Following rows give values for the coefficients in (5.3), followed by the rms deviation in percent. We then give selected isotherms of \bar{C}_v and of \bar{C}_v/T , interpolated by use of eqs (5.3).

We obtain coefficients of (5.2) by least squares using the form

$$\bar{C}_v/T = A + B \cdot (k \cdot v), \quad (5.2a)$$

such that $(-d^2G/dT^2) \equiv A$, and $(d^2P/dT^2) \equiv B$. Table 10 gives results on selected isotherms. The first three

TABLE 9. Interpolation of \bar{C}_v on isotherms

ID =	2	20	5	32	3
Dens =	13.21	16.92	20.31	28.72	28.78
Vol =	75.71	59.11	49.23	34.82	34.74
A =	72.0792	76.3722	78.6311	67.1128	72.2048
B =	-69.9082	-94.5828	-108.3571	-60.9817	-82.8364
C =	80.7733	133.9037	163.3518	96.4842	128.5652
D =	-34.2514	-81.4570	-107.2576	-67.6495	-87.2916
E =	12.2039	24.5486	31.0169	20.6393	24.8471
Rms =	0.22	0.16	0.12	0.12	0.17
Temp	C_v	C_v	C_v	C_v	C_v
55	53.48	53.55	53.44	53.39	53.29
60	53.40	53.41	53.28	53.32	53.15
65	53.54	53.48	53.30	53.35	53.14
70	53.90	53.73	53.48	53.45	53.24
75	54.49	54.16	53.81	53.64	53.43
80	55.31	54.75	54.28	53.89	53.70
85	56.35	55.51	54.87	54.22	54.04
90	57.63	56.43	55.58	54.61	54.46
95	59.14	57.52	56.42	55.07	54.94
100	60.90	58.78	57.39	55.61	55.49
105	62.91	60.23	58.49	56.23	56.12
110	65.19	61.88	59.75	56.96	56.84
115	67.76	63.74	61.18	57.80	57.67
120	70.62	65.84	62.80	58.77	58.62
125	73.80	68.21	64.66	59.90	59.71
Temp	C_v/T	C_v/T	C_v/T	C_v/T	C_v/T
55	0.9724	0.9737	0.9717	0.9708	0.9688
60	.8899	.8902	.8879	.8887	.8859
65	.8237	.8228	.8199	.8207	.8176
70	.7701	.7676	.7640	.7636	.7606
75	.7266	.7221	.7175	.7152	.7124
80	.6914	.6844	.6785	.6737	.6713
85	.6630	.6531	.6455	.6378	.6358
90	.6403	.6270	.6176	.6067	.6051
95	.6225	.6055	.5939	.5797	.5783
100	.6090	.5878	.5739	.5561	.5549
105	.5992	.5736	.5570	.5355	.5345
110	.5927	.5625	.5431	.5178	.5167
115	.5892	.5543	.5320	.5026	.5015
120	.5885	.5487	.5234	.4898	.4885
125	.5904	.5456	.5173	.4792	.4777

columns give T , A , B , for (5.2a). The next column, D^2PDT^2 , is the second derivative of Stewart's vapor pressure equation [6]. It is to be compared directly with the values in column B. Columns UA, UB are the absolute, statistical uncertainties in A , B , based only on deviations of the data from (5.2a). Maximum uncertainties in the \bar{C}_v data of various runs, however, are about 0.5 percent (table 6). A probable uncertainty of 0.2 percent may be assigned to each run. One then finds that uncertainties of B for (5.2a) range from about 140 percent at 55 K to about 2 percent at 125 K. Within these bounds, the vapor pressure equation [6] and our specific heats are consistent at temperatures up to 125 K.

TABLE 10. Coefficients A and B for eq (5.2a)

Equation, $C_v/T = A + B \cdot (K \cdot V)$					
Temp	A	B	D^2PDT^2	UA	UB
55	.96750	.00077	.00014	.00211	.00039
60	.88471	.00074	.00039	.00209	.00039
65	.81494	.00116	.00088	.00221	.00041
70	.75500	.00198	.00169	.00215	.00040
75	.70261	.00314	.00286	.00195	.00036
80	.65613	.00461	.00439	.00170	.00032
85	.61438	.00636	.00624	.00145	.00027
90	.57646	.00835	.00836	.00122	.00023
95	.54175	.01055	.01070	.00105	.00019
100	.50978	.01295	.01321	.00093	.00017
105	.48024	.01551	.01586	.00089	.00017
110	.45290	.01823	.01862	.00092	.00017
115	.42763	.02107	.02148	.00098	.00018
120	.40436	.02401	.02445	.00107	.00020
125	.38305	.02705	.02753	.00116	.00022

6. Derived Thermodynamic Functions

We have used (5.1) for integrations along the coexistence path from triple point to critical point, as described in appendix IV. The thermodynamic functions are calculated via the following relations:

$$\Delta S = \int [C_\sigma/T] \cdot dT, \quad Q = \int C_\sigma \cdot dT,$$

$$\Delta E = Q - \int P \cdot dv, \quad \Delta H = Q + \int v \cdot dP.$$

The pressure-volume integrals were evaluated numerically by use of the vapor-pressure equation [6] and the liquid densities of table 1.

Table 11 presents our results at integral temperatures, at which are calculated the vapor-pressure, the saturated liquid density in mol/liter, and C_σ from (5.1) in J/mol K. Following columns give the molal increase of entropy, ΔS , the heat absorbed, $C \cdot DT$, the work, $P \cdot DV$, the increase of internal energy, ΔE , the work, $V \cdot DP$, and the increase of enthalpy, ΔH , all relative to the triple-point values. Throughout this table the unit of energy is the joule. Note that

$H - H_t = E - E_t + Pv - (Pv)_t$, but at the triple point $(Pv)_t = 0.002$ J/mol, hence ΔH is numerically equal to $\Delta E + Pv$.

The probable uncertainty in these functions, obtained by integration, should not exceed that of C_σ for which we assess a probable error of 0.3 percent, as compared with maximum errors in table 6 from 0.5 to 2.2 percent.

7. Discussion

The accurate formulation of adjustment calculations for experimental specific heat measurements on a two-phase system is an exacting challenge [8, 10]. It therefore may be helpful to record the following details, pointed out by Barieau.

In eq (3.9) the adjustment for vapor entering the capillary tube is not rigorous. This vapor boils away from the liquid phase, and account should be taken of the diminished volume of liquid, an effect of increasing importance at temperatures approaching critical. In place of ΔH_v in eq (3.9) one should use ΔH_a , the heat of vaporization per mole of vapor leaving the vessel,

$$\Delta H_a = \Delta H_v \cdot \rho_l / (\rho_l - \rho_g) = T \cdot (dP/dT) / \rho_g, \quad (7.1)$$

where ρ_l , ρ_g are densities of saturated liquid and vapor. Note that ΔH_a does not vanish at the critical point. An adjustment to present data via eq (7.1), however, is not significant. At $T = 152$ K, for example, we have roughly $\Delta H_v = 2000$ J/mol, $\rho_l / (\rho_l - \rho_g) = 1.7$, and $\delta N_c / \Delta T = 2 \cdot 10^{-6}$ mol/deg for our capillary tube.

As noted by H. J. Hoge, several difficult adjustments are eliminated by performing experiments with relatively large and also with relatively small amounts of liquid in the calorimeter [8]. When two phases are present,

$$C_{\text{total}} = \text{Lim} (Q/\Delta T) = C_b - (N - N_c) \cdot T \cdot \frac{d^2G}{dT^2} + V_b \cdot T \cdot \frac{d^2P}{dT^2} + T \cdot \frac{dV_b}{dT} \cdot \frac{dP}{dT} + \Delta H_a \cdot \frac{dN_c}{dT}, \quad (7.2)$$

where G is the Gibbs free energy per mole. The difference of eq (7.2) for two amounts of sample, N_2 and N_1 , is

$$C_2 - C_1 = -(N_2 - N_1) \cdot T \cdot d^2G/dT^2. \quad (7.3)$$

From eq (7.3) may be obtained the heat capacity of liquid along the coexistence path by use of PVT data whenever the latter are available,

$$C_\sigma = T \cdot dS/dT = -T \frac{d^2G}{dT^2} + \frac{T}{\rho} \left(\frac{d^2P}{dT^2} \right) - \frac{T}{\rho^2} \frac{d\rho}{dT} \cdot \frac{dP}{dT}, \quad (7.4)$$

where ρ and S refer to liquid.

In planning the present work we elected not to follow the above very attractive method. At temperatures approaching the critical temperature, the two

different filling densities eventually must approach the same value. In this region, d^2G/dT^2 from eq (7.3) might suffer the low accuracy expected in the difference of two large experimental values. Another practical impediment to eq (7.3) is the isothermal condition,

which cannot be enforced experimentally for the two different fillings. Interpolation is required along each experimental run. Finally, for specific heats of the liquid at very low temperatures, the above filling densities are not optimum.

TABLE 11. Thermodynamic properties, saturated liquid oxygen

T, K	P, atm	Mol/l	CSAT	ΔS	$C \cdot DT$	$P \cdot DV$	ΔE	$V \cdot DP$	ΔH
54.351	0.001	40.842	53.313	0.000	0.00	0.000	0.00	0.000	0.00
55.000	.002	40.752	53.306	.633	34.61	.000	34.61	.001	34.61
60.000	.007	40.057	53.274	5.270	301.05	.000	301.05	.014	301.06
65.000	.023	39.359	53.278	9.534	567.42	.001	567.41	.055	567.47
70.000	.061	38.652	53.325	13.484	833.90	.003	833.90	.155	834.06
75.000	.143	37.936	53.423	17.166	1100.75	.008	1100.74	.371	1101.12
80.000	.297	37.208	53.581	20.618	1368.23	.019	1368.21	.786	1369.02
85.000	.561	36.463	53.811	23.873	1636.68	.042	1636.64	1.573	1638.19
90.000	.981	35.700	54.129	26.957	1906.49	.087	1906.40	2.694	1909.18
90.180	1.000	35.672	54.142	27.065	1916.23	.089	1916.14	2.748	1918.98
95.000	1.611	34.914	54.555	29.895	2178.15	.169	2177.98	4.504	2182.65
100.000	2.509	34.100	55.114	32.707	2452.26	.310	2451.95	7.142	2459.40
105.000	3.738	33.253	55.842	35.413	2729.57	.545	2729.02	10.840	2740.41
110.000	5.363	32.367	56.785	38.031	3011.03	.923	3010.11	15.862	3026.90
115.000	7.454	31.433	58.010	40.581	3297.89	1.517	3296.37	22.506	3320.39
120.000	10.082	30.439	59.617	43.082	3591.77	2.437	3589.33	31.118	3622.89
122.000	11.300	30.022	60.398	44.074	3711.77	2.932	3708.84	35.202	3746.97
124.000	12.621	29.592	61.277	45.063	3833.42	3.518	3829.91	39.692	3873.12
126.000	14.049	29.147	62.272	46.051	3956.95	4.215	3952.74	44.621	4001.57
128.000	15.591	28.686	63.402	47.041	4082.60	5.043	4077.56	50.022	4132.62
130.000	17.249	28.207	64.696	48.034	4210.67	6.029	4204.64	55.931	4266.60
132.000	19.031	27.706	66.189	49.032	4341.52	7.207	4334.31	62.390	4403.91
134.000	20.942	27.181	67.930	50.040	4475.59	8.618	4466.97	69.443	4545.04
136.000	22.986	26.628	69.982	51.062	4613.45	10.318	4603.13	77.143	4690.59
138.000	25.170	26.042	72.441	52.101	4755.79	12.381	4743.41	85.548	4841.34
140.000	27.501	25.416	75.443	53.164	4903.57	14.908	4888.66	94.727	4998.30
142.000	29.986	24.740	79.200	54.259	5058.06	18.041	5040.02	104.765	5162.83
144.000	32.631	24.000	84.063	55.399	5221.10	21.995	5199.11	115.766	5336.87
146.000	35.448	23.177	90.653	56.602	5395.45	27.105	5368.35	127.864	5523.32
148.000	38.446	22.236	100.210	57.896	5585.66	33.950	5551.71	141.239	5726.90
150.000	41.638	21.113	115.688	59.335	5800.13	43.669	5756.46	156.158	5956.29
151.000	43.312	20.445	127.975	60.142	5921.59	50.335	5871.25	164.319	6085.91
152.000	45.041	19.662	146.721	61.043	6058.19	59.059	5999.13	173.052	6231.24
153.000	46.828	18.688	180.235	62.103	6219.75	71.412	6148.34	182.485	6402.24
154.000	48.675	17.292	268.103	63.503	6434.78	92.343	6342.43	192.863	6627.64
154.770	50.140	13.620		66.148	6843.48	170.977	6672.50	202.000	7045.48

9. Appendix I. Volumes of the Calorimeter

$$l/l_0 = 1 + f(T).$$

For a spherical shell,

$$V/V_{1,0} = (l/l_1)^3 \cdot [1 + g(T) \cdot P]^3, \quad (1)$$

where $V_{1,0}$ is our reference volume at $T=100$ K, $P=0$ atm. Length, l , may be a diameter (l_0 at $T=0$, l_1 at $T=100$ K) at $P=0$. Function $g(T)$ includes the modulus of elasticity. We developed an approximation formula for thermal expansivity of type 316 stainless steel in the form

Dropping higher order terms from (1) we then have

$$V/V_R = 1 + 3 \cdot f(T) + 3 \cdot g(T) \cdot P, \quad (2)$$

where

$$V_R = V_{1,0} / [1 + 3 \cdot f(100)].$$

For the elasticity, we use six unpublished values of $(\Delta V/\Delta P)/V$ obtained by Younglove and Diller for this

calorimeter from 40 to 300 K [3]. They are represented within their precision of a few percent by

$$(\Delta V/\Delta P)/V = k \cdot x^{1/3}, \text{ atm}^{-1},$$

where $x \equiv T/100$. Our description for the calorimeter volumes therefore is

$$V/V_R = 1 + 3 \cdot f(T) + k \cdot x^{1/3} \cdot P, \quad (3)$$

where

$$f(T) = [C_1 + C_2 \cdot x] \cdot \exp [\alpha \cdot (1 - 1/x)],$$

with constants,

$$V_R = 72.657 \text{ cm}^3, \quad C_1 = -0.0002 \text{ 1461},$$

$$C_2 = +0.0005 \text{ 9455}, \quad \alpha = 1.01062,$$

$$k = 0.0000111 \text{ atm}^{-1}.$$

The reference volume measured by Younglove and Diller was $V_{1,0} = 72.74 \text{ cm}^3$. We checked this volume at room temperature by expanding oxygen from the bomb at 3 atm into a calibrated, 130 cm^3 glass flask, observing pressures on a commercial, helical-quartz *bourdon* gage. We used the equation of state derived by L.A.W. for these conditions, $Pv/RT = 1 - 0.195 \cdot P/T$, with units of atmospheres and degrees Kelvin. Our volume of $73.19 \pm 0.1 \text{ cm}^3$ at 297.3 K adjusts to $V_{1,0} = 72.6 \pm 0.1 \text{ cm}^3$. In our specific heat calculations we have used $V_{1,0} = 72.74 \text{ cm}^3$, assigning an uncertainty of 0.1 percent.

10. Appendix II. Estimated Temperatures Along the Capillary Tube

For a capillary tube which is thermally isolated except at its two ends, we may estimate temperatures by use of the temperature-dependent thermal conductivity, K , of stainless steel. We developed the approximation formula,

$$K/K_{100} = \exp [1.2 \cdot (1 - 10/T^{1/2})]. \quad (1)$$

We placed (1) in the heat-flow equation, integrated numerically by computer, and developed an approximation formula for the results,

$$T_x = T_0 \cdot [1 + a \cdot x]^{2/3},$$

$$a \equiv [(T_1/T_0)^{3/2} - 1]. \quad (2)$$

Here $x \equiv l/l_1$ is fraction of the distance from the cold end of a capillary tube of length l_1 . Temperature at the cold end is T_0 , at the hot end is T_1 , and at position x it is T_x .

11. Appendix III. Method for Estimating Uncertainties (Errors)

We express the saturated liquid heat capacity in the following form,

$$C_\sigma = (A - B - C - D)/N_b + [E - (F - 1) \cdot G] \cdot H,$$

where

$$A \equiv C_a, \quad B \equiv C_b, \quad C \equiv k \cdot T \cdot (dP/dT) \cdot (dV_b/dT),$$

$$D \equiv \delta N_c \cdot \Delta H_v/\Delta T, \quad E \equiv (-d\rho/dT) \cdot (dP/dT)/\rho,$$

$$F \equiv V_b \cdot \rho/N_b, \quad G \equiv d^2P/dT^2, \quad H \equiv k \cdot T/\rho,$$

$$k = 0.101325 \text{ J/mol-deg}, \quad \rho \text{ refers to the liquid phase.}$$

Wherever a sum of terms occurs in brackets we sum absolute errors. For each product or ratio we sum relative errors. Uncertainties in A , B , etc., are symbolized UA , UB , etc., given in percent at the bottom of table 6. For A , alone, we introduce dependence on the interval, ΔT , $U_a = 0.05 + 0.10 \cdot (5/\Delta T)$. Results are given in the last two columns of table 6.

12. Appendix IV. Definite Integrals Used for Thermal Functions

Given A , B , C , r , and n for eq (5.1), define—

$$T_d \equiv (T_c - T_t), \quad q \equiv r^{1/2}.$$

$$x \equiv (T_c - T)/T_d, \quad z \equiv x^{1/2}.$$

The heat absorbed upon heating from the triple point is—

$$\int_{T_t}^T C_\sigma \cdot dT = T_d \cdot \{2A \cdot (1 - z) + 2B \cdot (1 - z^3)/3 + C \cdot \sigma_D\},$$

where

$$\sigma_D \equiv \sum_{i=1}^{n+1} 2D_i \cdot (1 - z^j)/j, \quad j \equiv 2i - 1,$$

and the binomial coefficients are—

$$D_1 \equiv 1, \quad D_{i+1} \equiv -D_i \cdot r \cdot (n + 1 - i)/i.$$

The increase of entropy upon heating from the triple point is—

$$\int_{T_t}^T (C_\sigma/T) \cdot dT = r \cdot [A \cdot F_a + B \cdot F_b + C \cdot \sigma_E],$$

where

$$F_a \equiv \lambda/q, \quad F_b \equiv [\lambda - 2q \cdot (1 - z)]/q^3,$$

$$\lambda \equiv \ln \left[\frac{1+q}{1-q} \cdot \frac{1-q \cdot z}{1+q \cdot z} \right],$$

$$\sigma_E \equiv \sum_{i=1}^n 2E_i \cdot (1-z^j)/j, \quad j \equiv 2i-1,$$

and the binomial coefficients are—

$$E_1 \equiv 1, \quad E_{i+1} \equiv -E_i \cdot r \cdot (n-i)/i.$$

13. Appendix V

The equation of state from reference [6] is

$$\begin{aligned} P = & \rho RT + (n_1 T + n_2 + n_3/T^2 + n_4/T^4 + n_5/T^6) \rho^2 \\ & + (n_6 T^2 + n_7 T + n_8 + n_9/T + n_{10}/T^2) \rho^3 \\ & + (n_{11} T + n_{12}) \rho^4 + (n_{13} + n_{14}/T) \rho^5 \\ & + \rho^3 (n_{15}/T^2 + n_{16}/T^3 + n_{17}/T^4) \exp(n_{25} \rho^2) \\ & + \rho^5 (n_{18}/T^2 + n_{19}/T^3 + n_{20}/T^4) \exp(n_{25} \rho^2) \\ & + \rho^7 (n_{21}/T^2 + n_{22}/T^3 + n_{23}/T^4) \exp(n_{25} \rho^2) \\ & + n_{24} \rho^{n_{28}+1} (\rho^{n_{28}} - \rho_c^{n_{28}}) \exp[n_{26} (\rho^{n_{28}} - \rho_c^{n_{28}})] \\ & + n_{27} (T - T_c)^2. \end{aligned}$$

The coefficients of the equation of state, n_1 through n_{28} , taken from [6], are given in table 12. These coefficients were determined by a weighted least squares fit of the input experimental data. In this least squares fit, constraints for the critical point were imposed upon the equation of state. These constraints are listed in table 13; the fixed points are listed in table 14.

TABLE 12. Coefficients for the equation

T in K, P in atm, ρ in mol/liter		
$R = 0.0820535$	$n_{10} = -3.59419602 \times 10$	$n_{19} = -2.67817667 \times 10^2$
$n_1 = 3.38759078 \times 10^{-3}$	$n_{11} = 1.02209557 \times 10^{-6}$	$n_{20} = 1.05670904 \times 10^6$
$n_2 = -1.31606223$	$n_{12} = 1.90454505 \times 10^{-4}$	$n_{21} = 5.63771075 \times 10^{-3}$
$n_3 = -7.38828523 \times 10^3$	$n_{13} = 1.21708394 \times 10^{-5}$	$n_{22} = -1.12012813$
$n_4 = 1.92049067 \times 10^7$	$n_{14} = 2.44255945 \times 10^{-3}$	$n_{23} = 1.46829491 \times 10^2$
$n_5 = -2.90260005 \times 10^{10}$	$n_{15} = 1.73655508 \times 10^2$	$n_{24} = 9.98868924 \times 10^{-4}$
$n_6 = -5.70101162 \times 10^{-8}$	$n_{16} = 3.01752841 \times 10^5$	$n_{25} = -0.00560$
$n_7 = 7.96822375 \times 10^{-5}$	$n_{17} = -3.49528517 \times 10^7$	$n_{26} = -0.157$
$n_8 = 6.07022502 \times 10^{-3}$	$n_{18} = 8.86724004 \times 10^{-1}$	$n_{27} = -0.350$
$n_9 = -2.71019658$		$n_{28} = 0.90$

TABLE 13. Constraints imposed on the equation of state [6]

P - ρ - T at the critical point	$\left\{ \begin{array}{l} P = 50.14 \text{ atm} \\ \rho = 13.333 \text{ mol/liter} \\ T = 154.77 \text{ K} \end{array} \right.$
$(\partial P/\partial \rho)_T = 0$ at the critical point	
$(\partial^2 P/\partial \rho^2)_T = 0$ at the critical point	
$(\partial P/\partial T)_\rho = dP/dT$ from appendix 6 at the critical point	
$= 1.928386 \text{ atm/K}$	

TABLE 14. Fixed point data [6]

Critical pressure	50.14 atm
Critical temperature	154.77 K
Critical density	13.333 mol/liter
Normal boiling temperature (IPTS, fixed point)	90.18 K
Density saturated vapor at nbp	0.1396 mol/liter
Density saturated liquid at nbp	35.65 mol/liter
Triple point pressure	0.00150 atm
Triple point temperature	54.353 K

14. Appendix VI. The Vapor Pressure Equation from [6]

The vapor pressure equation is [P in atm, T in K]:

$$\ln P = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4 + a_5 T^5 + a_6 T^6 + a_7 T^7.$$

TABLE 15. Coefficients for the vapor pressure equation

$a_0 = -6.25967185 \times 10$	$a_4 = -4.09349868 \times 10^{-6}$
$a_1 = 2.47450429$	$a_5 = 1.91471914 \times 10^{-8}$
$a_2 = -4.68973315 \times 10^{-2}$	$a_6 = -5.13113688 \times 10^{-11}$
$a_3 = 5.48202337 \times 10^{-4}$	$a_7 = 6.02656934 \times 10^{-14}$

8. References

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