

# Thermodynamic Properties of Fluid Oxygen at Temperatures to 250 K and Pressures to 350 Atmospheres on Isochores at 1.3 to 3.0 Times Critical Density \*

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The starting point for these calculations is liquid oxygen at the triple point. An analytical formula is used for specific heats of saturated liquid along the coexistence path to obtain internal energies and entropies of the saturated liquid. With these initial values, the calculations next are made as a function of temperature along isochores, using an "equation of state" for the specific heats  $C_v(\rho, T)$  in the single-phase domain. Enthalpies are obtained by adding  $Pv$  to the internal energies. Results are tabulated at uniform densities and temperatures. Based on uncertainties of one percent in the specific heat data, the uncertainty of thermal properties also is taken to be 1 percent.

Key Words: Compressed liquid; enthalpy; entropy; internal energy; oxygen; saturated liquid; thermodynamic properties.

## List of Symbols

$C_\sigma(T)$	specific heat of liquid along the coexistence path.
$C_v(\rho, T)$	specific heat at constant volume in the single phase domain.
$C_v^o(T)$	specific heat at constant volume in the ideal gas states.
$D$	density, on the computer-printed tables.
$E$	internal energy. $E_0^o$ for ideal gas state at $T=0$ .
$E_t$	internal energy of liquid at the triple point.
$H$	enthalpy.
$H_t$	enthalpy of liquid at the triple point.
$J$	the Joule.
$k$	conversion factor, 0.101325 J/(cm <sup>3</sup> -atm).
$L$	the liter, 1000 cm <sup>3</sup> .
$P$	pressure. 1 atm = 0.101325 MN/m <sup>2</sup> .
$\rho$	density.
$\rho_c$	0.01362 mol/cm <sup>3</sup> at the critical point [1].
$S$	entropy.
$S_t$	entropy of liquid at the triple point.
$T$	temperature, K (NBS 1955).
$T_c$	154.77 K at the critical point [6].
$T_t$	54.3507 K at the triple point [1].
$v$	$1/\rho$ molal volume.

## 1. Introduction

We recently have completed  $PVT$  and  $C_v$  measurements on oxygen at temperatures to 300 K and pressures to 350 atm, data needed for calculating thermodynamic properties [1, 2, 3]. The computation of a self-consistent thermodynamic network is an intricate and time-consuming labor [4]. In the present report, we use specific heat data in compressed liquid states to obtain thermodynamic properties along paths at constant density (isochores), beginning at the saturated liquid. We consider these results to be preliminary because the same properties can be calculated along alternate routes, as for example on isotherms by use of  $PVT$  data, and a measure of the consistency remains to be established.

## 2. Computational Methods

Figure 1 is reproduced here to show the computational paths used in the following. This figure is a density-temperature diagram for oxygen, including the locus for a pressure of 350 atm. The small circles locate experimental  $C_v$  measurements along isochores [3]. We start our calculations with  $E=E_t$  and  $S=S_t$  at the liquid triple point, located on figure 1 near  $T=54$  K and  $\rho/\rho_c=3.0$ , calculating the change in values of  $E$  and of  $S$  with increasing  $T$  along the saturated liquid path, down to various rounded densities. We then calculate the change in values

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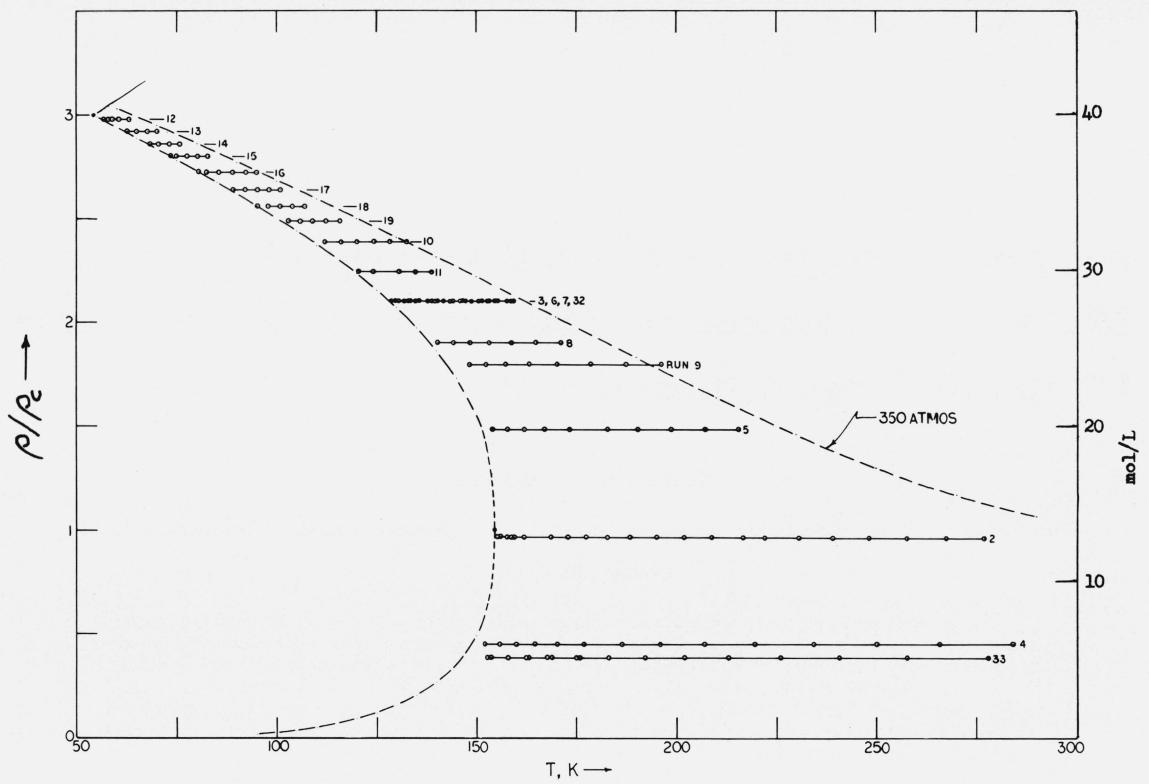


FIGURE 1. Locus of  $C_v$  data in  $\rho$ - $T$  coordinates.

of  $E$  and of  $S$  with increasing  $T$  at constant density up to 350 atm. On either of these paths we have

$$E = E_t + \int C \cdot dT + \int [P/\rho^2]_\sigma \cdot d\rho, \quad (1)$$

$$H = E + P/\rho, \quad (2)$$

$$S = S_t + \int C \cdot dT/T, \quad (3)$$

where  $C \equiv C_\sigma(T)$  for the saturated liquid path, and  $C \equiv C_v(\rho, T)$  on the isochores ( $\rho = \text{constant}$ ).

Whereas  $E_t$  and  $S_t$  may be set at zero, we believe the results will be more useful if they are on the basis of ideal gas states. We therefore take values for  $E_t$  and for  $S_t$  derived in [1] via *PVT* data and specific heats relative to data of Woolley for the ideal gas states [5],

$$E_t \equiv E_{tp} - E_0^\circ = -6189.6 \text{ J/mol},$$

$$H_t = E_t, \quad S_t = 67.00 \text{ J/mol deg},$$

where  $E_{tp}$  refers to liquid at the triple point. Note that  $H_t = E_t$  within uncertainty of the data due to the very low triple point value of the  $P \cdot v$  product.

On the saturated liquid path we perform the calculations of (1), (2), and (3) by use of the analytical formula for  $C_\sigma(T)$  in [2], the vapor pressure equation  $P(T)$  reproduced in [2] from [6], and the formula for densities of saturated liquid  $\rho(T)$ , table 1 in [2]. Along the isochores we perform the calculations of (1) and (3)

by use of the analytical formula for  $C_v(\rho, T)$  in [3]. For the calculation (2) we used pressures tabulated for us by Lloyd A. Weber from his *PVT* interpolation programs [1].

### 3. Description of the Tables

Each table describes a surface in three dimensions. Independent variables are density increasing to the right and temperature increasing downwards. Uniform values of these variables are the same in corresponding tables for pressure, internal energy, enthalpy and entropy. The range of densities from 18.00 to 40.00 mol/liter is broken into three tables, a, b, c due to printing limitations. In every table the first row gives the isochore density,  $D$ , in mol/liter, and the second row gives the temperature at saturation TSAT in K for this liquid density. This temperature is found by trial to minimize the difference between the isochore density  $D$  and that calculated by the formula  $\rho(T)$  for saturated liquid. The first column in every table gives temperatures, K (NBS 1955) along the isochores.

In table 1 for pressures, the third row gives the vapor pressure PS in atmospheres at TSAT, and table entries are the pressure in atmospheres. As all experimental data for *PVT* and for  $C_v$  terminate at a pressure near 350 atm, all entries in tables 2, 3, and 4 which correspond to a table 1 pressure greater than 350 atm necessarily are extrapolated and therefore are subject to unknown error. Horizontal lines in the tables help to locate this limit.

TABLE 1-a. Pressures

$D$ , mol/l =	18.00	19.00	20.00	21.00	22.00	23.00	24.00	25.00	26.00
TSAT, K =	153.55	152.71	151.59	150.18	148.45	146.40	144.00	141.25	138.14
PS, atm =	47.842	46.300	44.326	41.934	39.153	36.031	32.632	29.035	25.328
Temp., K	Pressure, atm								
140.00									39.085
145.00								53.788	76.333
150.00								87.137	113.724
155.00	52.070	53.789	56.857	61.919	69.778	81.395	97.905	120.627	151.077
160.00	67.121	70.660	75.825	83.266	93.786	108.352	128.105	154.366	188.622
165.00	82.689	88.035	95.253	105.005	118.099	135.510	158.386	188.051	225.989
170.00	98.539	105.694	114.946	126.969	142.589	162.791	188.731	221.726	263.238
175.00	114.552	123.522	134.802	149.078	167.186	190.123	219.057	255.323	300.395
180.00	130.694	141.473	154.761	171.263	191.831	217.481	249.383	288.815	337.050
185.00	146.902	159.492	174.797	193.534	216.552	244.852	279.615	322.220	374.285
190.00	163.162	177.573	194.888	215.828	241.248	272.165	309.794	355.611	411.425
195.00	179.478	195.702	215.002	238.108	265.890	299.410	339.991	389.318	
200.00	195.788	213.819	235.111	260.398	290.533	326.516		369.535	
205.00	212.117	231.947	255.203	282.615	315.005	353.305	398.571		
210.00	228.445	250.074	275.295	304.831	339.477	380.094			
215.00	244.750	268.123	295.340	327.444	365.949				
220.00	261.055	286.173	315.385	350.056	392.421				
225.00	277.352	304.190	335.157	371.495					
230.00	293.649	322.207	354.929	392.934					
235.00	309.873	339.837	373.251						
240.00	326.096	357.468							
245.00	343.070	377.886							
250.00	360.045								
255.00	376.286								

TABLE 1-b. *Pressures*

<i>D</i> , mol/l =	27.00	28.00	29.00	30.00	31.00	32.00	33.00	34.00
TSAT, K =	134.67	130.84	126.65	122.11	117.22	112.00	106.45	100.60
PS, atm =	21.609	17.979	14.535	11.367	8.550	6.139	4.166	2.638
Temp., K	Pressure, atm							
102.00								29.667
104.00								65.752
106.00								101.527
108.00								136.999
110.00								172.177
112.00								207.070
114.00								241.685
116.00								276.030
118.00								310.115
120.00								343.946
122.00								377.533
124.00								410.883
126.00								444.004
128.00								
130.00								
132.00								
134.00								
136.00	32.682	66.191	111.835	171.819	248.862	346.201		
138.00	49.366	84.800	132.456	194.604	273.920	373.487		
140.00	66.033	103.378	153.066	217.373	298.911	400.622		
142.00	82.733	121.927	173.573	240.040	324.046	428.652		
144.00	99.404	140.436	193.999	262.348	347.989			
146.00	116.047	159.041	214.665	284.943	372.019			
148.00	132.754	177.509	235.041	307.518	397.287			
150.00	149.391	195.957	255.415	329.926	421.828			
152.00	165.976	214.305	275.633	352.120				
154.00	182.682	232.815	296.056	374.560				
156.00	199.220	251.279	316.041	393.321				
158.00	215.870	269.464	336.581	420.240				
160.00	232.482	287.542	355.111					
162.00	248.994	305.660	374.735					
164.00	265.507	323.779	394.359					
166.00	281.981	341.913	414.344					
168.00	298.415	360.064						
170.00	314.848	378.216						
172.00	331.239	396.189						
174.00	347.630	414.162						
176.00	363.687							

In table 2 for internal energies the third row gives  $E_s$ , the change in value of internal energy of saturated liquid from the triple point temperature up to the saturation temperature TSAT for each isochore. Total  $E$  at each such point is  $E_t + E_s$ . Table entries are the internal energy,  $\bar{E}$  in J/(mol).

In table 3 for enthalpies the third row gives  $H_s$ , the change in value of enthalpy of saturated liquid from  $T_t$  up to TSAT. Total  $H$  at each such point is  $H_t + H_s$ . Table entries are the enthalpy,  $\bar{H}$  in J/(mol).

In table 4 for entropies, the third row gives  $S_s$ , the change in value of entropy of saturated liquid from  $T_t$  up to TSAT. Total  $S$  at each such point is  $S_t + S_s$ . Table entries are the entropy,  $\bar{S}$  in J/(mol deg).

#### 4. Comparisons and Estimate of Accuracy

The compendium of thermal properties of oxygen by R. B. Stewart [6] is invaluable because it provides

independent computations with which to compare our results. Stewart used an analytical equation of state to effect the computations using, among other data, Woolley's ideal gas (thermal) functions and early PVT data of L. A. Weber [1]. Our specific heat data, however, had not then been obtained.

Table 5 gives comparisons with results interpolated from Stewart's tabulations on isobars. The first two columns give density on three isochores and two temperatures on each. The rounded pressure is included for convenience in the third column. The last three columns give the relative deviation in percent of Stewart's values for  $E$ ,  $H$ , and  $S$  from our values. The excellent agreement of entropies is conspicuous. All deviations of  $E$  and of  $H$  are positive, such that a small change in our (or his) assigned value for  $E_t$  would suffice to diminish the mean of these deviations. Note that the relative deviations at  $\rho=26$  mol/l,  $T=175$  K appear large because both  $E$  and  $H$  have small values, tables 2, 3.

TABLE 1-c. Pressures

<i>D</i> , mol/l =	35.00	36.00	37.00	38.00	39.00	40.00
TSAT, K =	94.46	88.05	81.41	74.56	67.55	60.41
PS, atm =	1.531	0.796	0.358	0.133	0.039	0.008
Temp., K	Pressure, atm					
62.00						57.072
64.00						126.932
66.00						195.835
68.00						263.793
70.00						330.814
72.00						396.909
74.00						
76.00				42.206		
78.00				98.360		
80.00				153.806	381.456	
82.00			17.183	208.552		
84.00			67.713	262.606		
86.00			117.641	315.979		
88.00			166.978	368.680		
90.00		47.007	215.731	420.717		
92.00		91.884	263.910			
94.00		136.270	311.524			
96.00	34.780	180.173	358.581			
98.00	75.049	223.602	405.091			
100.00	114.921	266.566	451.062			
102.00	154.404	309.073				
104.00	193.506	351.132				
106.00	232.237	392.753				
108.00	270.604	433.943				
110.00	308.616					
112.00	346.281					
114.00	383.607					

TABLE 2-a. Internal energies

<i>D</i> , mol/l =	18.00	19.00	20.00	21.00	22.00	23.00	24.00	25.00	26.00
TSAT, K =	153.55	152.71	151.59	150.18	148.45	146.40	144.00	141.25	138.14
ES, J/mol =	6247.0	6101.7	5944.8	5776.2	5595.9	5403.6	5199.2	4982.4	4753.4
Temp., K	Energy, J/mol								
140.00									-1387.4
145.00									-1256.9
150.00									-1127.3
155.00	109.2	-15.0	-144.3	-278.1	-551.2	-689.5	-963.9	-1108.7	-978.4
160.00	264.6	132.1	-3.7	-142.2	-415.9	-557.4	-832.2	-849.2	-998.4
165.00	407.6	271.4	132.1	-9.4	-283.4	-427.0	-702.0	-720.9	-870.3
170.00	544.5	406.1	264.5	121.0	-152.9	-298.1	-573.0	-593.3	-742.6
175.00	677.6	537.6	394.6	249.7	-24.0	-170.3	-444.9	-466.3	-615.6
180.00	807.7	666.8	522.7	376.9	103.6	-317.8	-191.4	-214.1	-488.9
185.00	935.7	794.1	649.3	502.9	230.0	82.5	-65.6	-88.7	-236.8
190.00	1061.9	919.9	774.7	627.8	355.5	207.7	59.6	36.3	-111.2
195.00	1186.7	1044.5	899.0	752.0	480.2	332.3	184.3		
200.00	1310.2	1168.0	1022.4	875.3	604.2	456.4	308.5	161.0	
205.00	1432.8	1290.6	1145.1	998.1	727.7	579.9	432.4		
210.00	1554.4	1412.4	1267.1	1120.3	850.6	703.1	555.9		
215.00	1675.3	1533.6	1388.5	1242.0	973.0	825.8			
220.00	1795.6	1654.2	1509.5	1363.3	1095.0				
225.00	1915.2	1774.3	1629.9	1484.1	1216.7				
230.00	2034.4	1893.9	1750.0	1604.7					
235.00	2153.1	2013.1	1869.8						
240.00	2271.5	2132.0							
245.00	2389.5	2250.6							
250.00	2507.1								
255.00	2624.5								

TABLE 2-b. *Internal energies*

<i>D</i> , mol/l =	27.00	28.00	29.00	30.00	31.00	32.00	33.00	34.00
TSAT, K =	134.67	130.84	126.65	122.11	117.22	112.00	106.45	100.60
ES, J/mol =	4512.0	4258.5	3992.9	3715.2	3425.5	3123.8	2810.3	2485.1
Temp., K	Energy, J/mol							
102.00								-3664.4
104.00								-3607.2
106.00								-3550.1
108.00								-3493.0
110.00								-3436.1
112.00							-3065.7	-3223.8
114.00							-3010.6	-3167.9
116.00							-2955.5	-3112.1
118.00						-2742.9	-2900.5	-3056.3
120.00						-2688.6	-2845.6	-3000.6
122.00						-2634.4	-2790.7	-2945.0
124.00					-2423.6	-2580.2	-2736.0	-2889.5
126.00					-2370.0	-2526.2	-2681.3	-2834.0
128.00			-2160.8		-2316.5	-2472.2	-2626.6	-2778.6
130.00			-2107.7		-2263.1	-2418.3	-2572.1	-2723.3
132.00		-1900.4	-2054.7		-2209.8	-2364.4	-2517.6	-2668.0
134.00		-1847.7	-2001.8		-2156.5	-2310.7	-2463.1	-2612.8
136.00	-1642.6	-1795.1	-1949.0		-2103.4	-2257.0	-2408.8	
138.00	-1590.1	-1742.6	-1896.3		-2050.3	-2203.3	-2354.5	
140.00	-1537.8	-1690.3	-1843.7		-1997.2	-2149.7	-2300.2	
142.00	-1485.6	-1638.0	-1791.2		-1944.3	-2096.2	-2246.0	
144.00	-1433.6	-1585.8	-1738.7		-1891.4	-2042.8		
146.00	-1381.6	-1533.7	-1686.3		-1838.5	-1989.3		
148.00	-1329.8	-1481.7	-1634.0		-1785.7	-1936.0		
150.00	-1278.0	-1429.8	-1581.7		-1733.0	-1882.7		
152.00	-1226.4	-1377.9	-1529.5		-1680.4			
154.00	-1174.8	-1326.1	-1477.4		-1627.7			
156.00	-1123.3	-1274.4	-1425.3		-1575.2			
158.00	-1071.9	-1222.8	-1373.3		-1522.7			
160.00	-1020.6	-1171.2	-1321.3					
162.00	-969.3	-1119.7	-1269.4					
164.00	-918.2	-1068.2	-1217.6					
166.00	-867.1	-1016.8	-1165.7					
168.00	-816.0	-965.4						
170.00	-765.0	-914.1						
172.00	-714.1	-862.9						
174.00	-663.2	-811.7						
176.00	-612.4							

TABLE 2-c. Internal energies

<i>D</i> , mol/l =	35.00	36.00	37.00	38.00	39.00	40.00
TSAT, K =	94.46	88.05	81.41	74.56	67.55	60.41
ES, J/mol =	2148.5	1801.1	1443.6	1077.2	703.1	323.0
Temp., K	Energy, J/mol					
62.00						-5812.0
64.00						-5743.4
66.00						-5675.1
68.00						-5606.9
70.00						-5539.0
72.00						-5471.2
74.00						-5273.7
76.00				-5066.4	-5208.2	
78.00				-5002.6	-5142.7	
80.00				-4939.0	-5077.5	
82.00			-4727.6	-4875.6	-5012.3	
84.00			-4665.8	-4812.2		
86.00			-4604.1	-4749.0		
88.00			-4542.5	-4686.0		
90.00		-4329.9	-4481.0			
92.00		-4269.9	-4419.7			
94.00		-4210.0	-4358.4			
96.00	-3995.9	-4150.2	-4297.3			
98.00	-3937.4	-4090.5	-4236.2			
100.00	-3879.0	-4030.8	-4175.3			
102.00	-3820.6	-3971.3				
104.00	-3762.4	-3911.9				
106.00	-3704.2	-3852.6				
108.00	-3646.1	-3793.3				
110.00	-3588.1					
112.00	-3530.2					
114.00	-3472.4					

TABLE 3-a. Enthalpies

<i>D</i> , mol/l =	18.00	19.00	20.00	21.00	22.00	23.00	24.00	25.00	26.00
TSAT, K =	153.55	152.71	151.59	150.18	148.45	146.40	144.00	141.25	138.14
HS, J/mol =	6516.3	6348.6	6169.3	5978.6	5776.2	5562.4	5336.9	5100.1	4852.1
Temp., K	Enthalpy, J/mol								
140.00									-1235.1
145.00								-890.7	-959.4
150.00					-338.2	-448.1	-545.2	-625.3	-684.1
155.00	402.3	271.8	143.8	20.7	-94.6	-198.8	-288.7	-360.3	-409.7
160.00	642.4	508.9	380.5	259.5	148.6	50.3	-32.1	-95.2	-135.2
165.00	873.0	740.9	614.6	497.2	391.1	298.9	223.7	168.9	138.1
170.00	1099.2	969.7	846.9	733.6	632.8	546.9	479.0	432.3	410.3
175.00	1322.4	1196.4	1077.5	969.0	873.6	794.1	733.5	694.9	681.8
180.00	1543.4	1421.3	1306.8	1203.2	1113.5	1040.6	987.2	956.5	950.9
185.00	1762.6	1644.7	1534.9	1436.7	1352.9	1286.4	1240.1	1217.3	1221.8
190.00	1980.4	1866.9	1762.0	1669.2	1591.3	1531.3	1492.2	1477.6	1492.1
195.00	2197.0	2088.1	1988.3	1900.8	1828.9	1775.4	1743.9	1738.9	
200.00	2412.4	2308.3	2213.6	2131.8	2065.8	2018.4	1992.5		
205.00	2626.8	2527.5	2438.0	2361.7	2301.4	2259.5	2238.6		
210.00	2840.4	2746.0	2661.8	2591.1	2536.5	2500.3			
215.00	3053.1	2963.5	2884.8	2821.9	2780.5				
220.00	3265.1	3180.3	3107.3	3052.3	3024.0				
225.00	3476.5	3396.5	3327.9	3276.6					
230.00	3687.4	3612.2	3548.2	3500.6					
235.00	3897.5	3825.4	3760.7						
240.00	4107.1	4038.3							
245.00	4320.7	4265.8							
250.00	4533.9								
255.00	4742.7								

TABLE 3-b. *Enthalpies*

<i>D</i> , mol/l =	27.00	28.00	29.00	30.00	31.00	32.00	33.00	34.00
TSAT, K =	134.67	130.84	126.65	122.11	117.22	112.00	106.45	100.60
HS, J/mol =	4593.1	4323.6	4043.7	3753.6	3453.4	3143.3	2823.1	2493.0
Temp., K	Enthalpy, J/mol							
102.00								-3576.0
104.00								-3411.3
106.00								-3247.5
108.00								-3084.7
110.00								-2922.9
112.00							-3044.3	-2762.1
114.00							-2897.1	-2602.1
116.00							-2750.5	-2443.0
118.00						-2681.1	-2604.5	-2284.8
120.00						-2541.9	-2459.0	-2127.4
122.00						-2403.2	-2314.1	-1970.8
124.00					-2310.8	-2264.8	-2169.7	-1815.0
126.00					-2178.9	-2126.7	-2025.7	-1659.9
128.00			-2061.0		-2047.2	-1989.0	-1882.2	-1722.3
130.00				-1934.3	-1914.9	-1852.1	-1739.8	-1572.6
132.00		-1795.7	-1808.6	-1784.0	-1715.7	-1597.8	-1424.6	
134.00		-1675.8	-1683.3	-1653.3	-1579.7	-1453.8	-1265.7	
136.00	-1519.9	-1555.6	-1558.3	-1523.0	-1443.5	-1312.6		
138.00	-1404.9	-1435.8	-1433.6	-1393.0	-1308.0	-1171.8		
140.00	-1290.0	-1316.2	-1308.9	-1263.0	-1172.7	-1031.7		
142.00	-1175.2	-1196.8	-1184.7	-1133.5	-1037.1	-888.7		
144.00	-1060.5	-1077.6	-1060.9	-1005.3	-905.3			
146.00	-946.1	-958.2	-936.3	-876.1	-773.4			
148.00	-831.6	-839.4	-812.8	-747.1	-637.4			
150.00	-717.4	-720.7	-689.3	-618.7	-503.9			
152.00	-603.5	-602.4	-566.5	-491.1				
154.00	-489.2	-483.6	-443.0	-362.7				
156.00	-375.7	-365.1	-321.1	-246.7				
158.00	-261.8	-247.7	-197.3	-103.3				
160.00	-148.1	-130.7	-80.6					
162.00	-34.9	-13.6	39.9					
164.00	78.2	103.5	160.3					
166.00	191.2	220.5	282.0					
168.00	303.9	337.5						
170.00	416.5	454.5						
172.00	529.0	570.8						
174.00	641.4	687.1						
176.00	752.4							

TABLE 3-c. Enthalpies

<i>D</i> , mol/l =	35.00	36.00	37.00	38.00	39.00	40.00
TSAT, K =	94.46	88.05	81.41	74.56	67.55	60.41
HS, J/mol =	2153.0	1803.4	1444.6	1077.5	703.2	323.1
Temp., K	Enthalpy, J/mol					
62.00						-5667.4
64.00						-5421.9
66.00						-5179.0
68.00						-5432.2
70.00						-4938.7
72.00						-5202.1
74.00						-4701.0
76.00				-4953.9		-4465.8
78.00				-4740.4		
80.00				-4528.9		
82.00			-4680.6	-4319.5		
84.00			-4480.3	-4112.0		
86.00			-4281.9	-3906.5		
88.00			-4085.2	-3702.9		
90.00		-4197.6	-3890.2	-3501.2		
92.00		-4011.3	-3696.9			
94.00		-3826.4	-3505.3			
96.00	-3895.2	-3643.1	-3315.3			
98.00	-3720.1	-3461.1	-3126.9			
100.00	-3546.3	-3280.6	-2940.1			
102.00	-3373.6	-3101.4				
104.00	-3202.2	-2923.6				
106.00	-3031.9	-2747.1				
108.00	-2862.7	-2571.9				
110.00	-2694.7					
112.00	-2527.7					
114.00	-2361.8					

TABLE 4-a. Entropies

<i>D</i> , mol/l =	18.00	19.00	20.00	21.00	22.00	23.00	24.00	25.00	26.00
TSAT, K =	153.55	152.71	151.59	150.18	148.45	146.40	144.00	141.25	138.14
SS, J/mol K =	62.81	61.77	60.66	59.47	58.21	56.85	55.40	53.84	52.17
Temp., K	Entropy, J/(mol deg)								
140.00									119.52
145.00								121.53	120.44
150.00					125.49	124.50	123.48	122.42	121.32
155.00	130.15	129.24	128.32	127.36	126.38	125.37	124.33	123.26	122.16
160.00	131.13	130.18	129.21	128.22	127.22	126.20	125.15	124.08	122.98
165.00	132.01	131.04	130.04	129.04	128.02	126.99	125.94	124.86	123.76
170.00	132.83	131.84	130.83	129.82	128.79	127.75	126.70	125.62	124.52
175.00	133.60	132.60	131.59	130.57	129.53	128.49	127.43	126.35	125.26
180.00	134.34	133.33	132.31	131.28	130.24	129.20	128.14	127.06	125.97
185.00	135.04	134.03	133.00	131.97	130.93	129.88	128.82	127.75	126.66
190.00	135.71	134.70	133.67	132.64	131.60	130.55	129.49	128.42	127.33
195.00	136.36	135.35	134.32	133.28	132.24	131.19	130.13	129.06	
200.00	136.98	135.97	134.94	133.91	132.87	131.82	130.76		
205.00	137.59	136.58	135.55	134.51	133.47	132.43	131.37		
210.00	138.18	137.16	136.14	135.10	134.06	133.02			
215.00	138.74	137.73	136.71	135.68	134.64				
220.00	139.30	138.29	137.27	136.23	135.20				
225.00	139.84	138.83	137.81	136.78					
230.00	140.36	139.35	138.33	137.31					
235.00	140.87	139.87	138.85						
240.00	141.37	140.37							
245.00	141.85	140.86							
250.00	142.33								
255.00	142.79								

TABLE 4-b. *Entropies*

<i>D</i> , mol/l =	27.00	28.00	29.00	30.00	31.00	32.00	33.00	34.00
TSAT, K =	134.67	130.84	126.65	122.11	117.22	112.00	106.45	100.60
SS, J/mol K =	50.38	48.45	46.37	44.13	41.70	39.06	36.18	33.04
Temp., K	Entropy, J/(mol deg)							
102.00								100.43
104.00								100.99
106.00								101.53
108.00								103.59
110.00								102.07
112.00							104.10	102.59
114.00							104.61	103.10
116.00							105.10	103.60
118.00						107.03	105.59	104.10
120.00						108.88	107.50	106.06
122.00						109.33	107.96	106.53
124.00						109.78	108.41	105.99
126.00						111.54	110.22	106.99
128.00						111.97	110.65	109.29
130.00						113.65	112.39	109.72
132.00						114.07	112.80	110.15
134.00						115.68	114.47	111.50
136.00						116.08	114.87	110.17
138.00						117.64	116.47	110.56
140.00						118.02	116.85	110.97
142.00						118.40	117.23	110.59
144.00						118.77	117.60	105.52
146.00						119.13	117.96	105.98
148.00						119.49	118.32	107.44
150.00						119.84	118.68	107.89
152.00						120.19	119.03	108.32
154.00						120.53	119.37	108.75
156.00						120.87	119.71	111.77
158.00						121.20	120.04	112.16
160.00						121.53	120.37	112.55
162.00						121.85	120.70	
164.00						122.17	121.02	
166.00						122.48	121.33	
168.00						122.79	121.64	
170.00						123.10	121.95	
172.00						123.40	122.25	
174.00						123.70	122.55	
176.00						123.99	122.85	
						124.28		

TABLE 4-c. *Entropies*

<i>D</i> , mol/l =	35.00	36.00	37.00	38.00	39.00	40.00
TSAT, K =	94.46	88.05	81.41	74.56	67.55	60.41
SS, J/mol K =	29.58	25.77	21.55	16.85	11.58	5.64
Temp., K	Entropy, J/(mol deg)					
62.00						73.53
64.00						74.62
66.00						75.67
68.00					78.80	76.68
70.00					79.76	77.67
72.00					80.69	78.62
74.00						81.59
76.00				84.46	82.46	
78.00				85.29	83.31	
80.00				86.10	84.14	
82.00			88.78	86.88	84.94	
84.00			89.52	87.64		
86.00			90.25	88.39		
88.00			90.96	89.11		
90.00		93.43	91.65	89.82		
92.00		94.09	92.32			
94.00		94.74	92.98			
96.00	97.06	95.37	93.62			
98.00	97.66	95.98	94.25			
100.00	98.25	96.58	94.87			
102.00	98.83	97.17				
104.00	99.39	97.75				
106.00	99.95	98.32				
108.00	100.49	98.87				
110.00	101.02					
112.00	101.55					
114.00	102.06					

TABLE 5. *Comparisons of thermal properties* [6]

<i>PVT</i> state			100 · [ $G_s - G$ ]/ $G^a$		
$\rho$ , Mol/l	<i>T</i> , K	<i>P</i> , atm	<i>E</i>	<i>H</i>	<i>S</i>
18	180	131	+ 0.98	+ 0.58	+ 0.03
18	230	294	+ 0.47	+ 0.30	+ 0.04
26	145	76	+ 0.47	+ 0.87	+ 0.03
26	175	300	+ 2.33	+ 1.78	+ 0.05
34	104	66	+ 0.20	+ 0.26	+ 0.02
34	118	310	+ 0.18	+ 0.47	+ 0.01

<sup>a</sup> *G* represents *E*, *H*, or *S*. Values for *G<sub>s</sub>* are from [6].

TABLE 6. *Comparisons of thermal properties* [1]

<i>PVT</i> state			100 · [ $G_w - G$ ]/ $G^a$		
$\rho$ , mol/l	<i>T</i> , K	<i>P</i> , atm	<i>E</i>	<i>H</i>	<i>S</i>
18	180	131	+ 0.81	+ 0.44	+ 0.03
18	230	294	+ 0.37	+ 0.21	+ 0.04
26	140	39	+ 0.35	+ 0.40	+ 0.03
26	175	300	+ 2.00	+ 1.41	+ 0.05
34	104	66	- 0.09	- 0.05	- 0.03
34	118	310	- 0.05	- 0.09	- 0.02

<sup>a</sup> *G* represents *E*, *H* or *S*. Values for *G<sub>w</sub>* are from [1].

Table 6 gives analogous comparisons with properties interpolated from L. A. Weber's tabulations on isobars [1]. Weber also used Woolley's ideal gas functions. The recent *PVT* data were combined with some of the present specific heat data. His methods for describing portions of the *PVT* surface were quite different from the equation of state used by Stewart.

A discussion of the significance of deviations in tables 5 and 6 is not in the scope of this report. It requires a detailed analysis of uncertainties (in two independent variables) traced from experimental data

through the computational steps. It is a common experience to find disagreements of roughly 5 percent between experimental specific heats and those derived from good *PVT* data via the second derivative,  $(\partial^2 P / \partial T^2)_P$  [4]. For the values in tables 2, 3, and 4 we estimate a rough uncertainty of 1 percent, except for the small values near an inversion of sign, as follows. Our uncertainties for  $C_v$  and  $C_p$  range from 0.5 to over 1.0 percent [2, 3]. Relative errors in the integrals, i.e., the thermal functions, generally should be less than in these integrands.

## 5. References

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