$E_{T,\max}$ maximum absolute deviation for T, °C
$E_{y_{i,\max}}$ maximum absolute deviation for y_i

Registry No. Acetone, 67-64-1; ethyl acetate, 141-78-6; ethanol, 64-17-5.

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Received for review August 8, 1983. Accepted May 25, 1984.

New Property Tables of Chlorine in SI Units

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Selected values of the vapor pressure, specific volume, enthalpy, entropy, and fugacity for the saturated liquid and vapor of chlorine, from the triple point (172.17 K) to the critical point (416.90 K), are presented. A vapor pressure equation and a saturated-liquid density equation were used to correlate experimental values from the literature. The Martin–Stanford equation of state was used to predict the properties of chlorine for densities less than 2 times the critical density. For densities greater than 2 times the critical density, an equation of state developed by Wagenbreth to correlate his compressed-liquid data for chlorine was used. The ideal-gas heat capacity was calculated by using statistical thermodynamics. The datum plane for the thermodynamic properties was chosen to be the perfect solid crystal at 0 K. The enthalpy, entropy, fugacity, velocity of sound, Joule–Thomson coefficient, and second virial coefficient were calculated by using classical thermodynamic relationships.

Introduction

Chlorine is one of the most widely used chemicals, and yet, because it is highly corrosive and if released very dangerous, there is not much experimental data available. Table I and Figure 1 give an overview of the experimental data in the literature.

In 1950, Ziegler (*1*) compiled and correlated the meager experimental data and produced a limited saturation table. In 1957, Kapoor and Martin (*2*) extrapolated the experimental data to the high temperature–pressure superheat region and then used a computer to produce detailed saturation and superheat tables. In 1981, the Chlorine Institute (*3*) expanded and updated Kapoor and Martin's work and also added properties in the subcooled region. Unfortunately, the Institute's development work had been completed before the vapor pressure and critical point data of Ambrose et al. (*4*) were available, and so they were not used. This work, sponsored by the Chlorine Institute, incorporates the results of Ambrose. The differences between the updated properties and those of the 1981 study are small except for conditions close to the critical point.

Table I. Experimental Data on Chlorine from the Literature

year	investigator	type of measurement
1900	Knietsch (*8*)	saturated-liquid density and vapor pressure measurements
1900	Lange (*7*)	saturated-liquid density and vapor pressure measurements
1908	Pier(*11*)	low-pressure *PVT* measurements
1913	Jacquerod and Tourpaian (*12*)	low-pressure *PVT* measurements
1915	Pellaton (*5*)	vapor pressure, saturated-vapor and liquid density measurements
1939	Giauque and Powell (*6*)	the triple point, vapor pressure, heat capacities of solid and liquid, and normal heats of fusion and vaporization
1940	Ross and Maass (*10*)	low-pressure *PVT* measurements
1968	Wagenbreth (*13*)	compressed-liq *PVT* measurements
1979	Ambrose et al. (*4*)	vapor pressure measurements

Table II. Physical Constants and Conversion Factors

	physical constants				
ref	T_c, K	P_c, kPa	ρ_c, kg/m^3	bp, K	triple point, K
this work	416.90	7977	573	239.18	172.17
5	417.15	7710.83	573	238.65	
4	416.90	7977		239.184	
8	419.15	9474		239.55	
6				239.10	172.17

conversion factors

1 atm = 101.325 kPa (exact value)
1 cal = 4.1840 J (exact value)
1 kPa m^3/kg = 1 kJ/kg (exact value)
1 cal/(g-mol·K) = 5.900770034 × 10^{-2} kJ/(kg·K) (for chlorine)
molecular weight of Cl_2 = 70.906 (based on carbon-12 with atomic weight = 12)
R = 8.3144 J/(g-mol·K)
R = 8.3144 Pa m^3/(g-mol·K)
R = 0.11725947 kJ/(kg·K)
R = 82.057 atm cm^3/(g-mol·K)
R = 1.98719 cal/(g-mol·K) (thermo calorie)

Complete tables and plots may be purchased from the Chlorine Institute when published.

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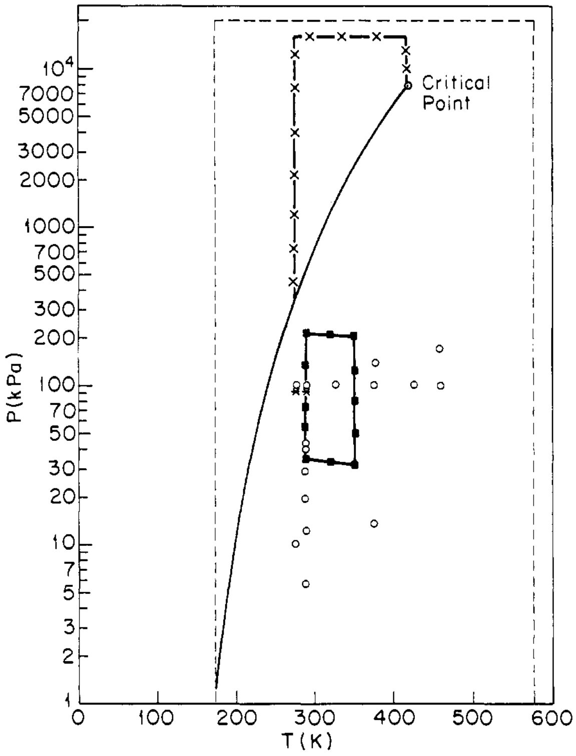

Figure 1. Scope of the literature data for chlorine: (- - -) region encompassed by this work; (-X-) region encompassed by Wagenbreth (*13*); (-■-) region encompassed by Ross and Maass (*10*); (—) vapor pressure data: Pellaton (*5*), Giauque and Powell (*6*), Ambrose et al. (*4*); (—) saturated-liquid density data: Knietsch (*8*), Lange (*7*), Pellaton (*5*); (O) Pier (*11*); (*) Jacquerod and Tourpaian (*12*).

Physical Constants and Conversion Factors

The physical constants and conversion factors used in this paper are listed in Table II. The critical temperature and pressure of Ambrose et al. (*4*) were used directly. The critical volume and density were taken from Pellaton's (*5*) work.

Vapor Pressure

The vapor pressure data of Ambrose et al. (*4*), from 205.945 to 416.90 K, and Giauque and Powell (*6*), from 172.17 to 240.10 K, were used to determine the constants in the Martin-Shin-Kapoor vapor pressure equation (eq 1)

$$\ln P = A + \frac{B}{T} + C \ln T + DT + \frac{E(F - T)\ln(F - T)}{FT} \tag{1}$$

where P is in kilopascals and T is in kelvin. The values of the constants are listed in Table III. The equation had three constraints placed on it. The normal boiling point was set at $T_{\mathrm{nbp}} = 239.18$ K, the critical point was set as $P_c = 7977$ kPa at $T_c = 416.90$ K, and $M = 6.30$ where $M = dP_r/dT_r$ at the critical point. The average deviation between the predicted vapor pressure and the experimental values is 0.20% with a standard deviation of 0.29%. The vapor pressure work of Pellaton (*5*) was not used in determining the equation constants. His vapor pressures averaged 2.7% lower than those predicted by using eq 1.

Saturated-Liquid Density Equation

The saturated-liquid data of Lange (*7*) and Pellaton (*5*) were fitted to the following equation:

$$\rho^l = a_0 + a_1(1 - T_r)^{1/3} + a_2(1 - T_r)^{2/3} + a_3(1 - T_r) + a_4(1 - T_r)^{4/3} \tag{2}$$

where ρ^l is in g/cm³. The constants for eq 2 are listed in Table III. The average deviation between the predicted and experimental values was 0.098%. The standard deviation was found to be 0.13%. The data of Knietsch (*8*) was inconsistent with those of Lange and Pellaton and was not used.

Table III. Equation Constants and Units

Vapor Pressure Equation Constants (Eq 1)	
P = pressure, kPa; T = temperature, K	
$A = 62.402508$	$D = 1.0666308 \times 10^{-2}$
$B = -4343.5240$	$E = 95.248723$
$C = -7.8661534$	$F = 424.90$
Saturated-Liquid Density Equation Constants (Eq 2)	
ρ^l = density, g/cm³	T = temperature, K
$a_0 = \rho_c = 0.573$ g/cm³	
$a_1 = 1.0606083$	$a_3 = 0.83708192$
$a_2 = -0.16041800$	$a_4 = -0.24720716$
PVT Relation Parameters and Constants (Eq 3)	
R = gas constant = 8.3144 J/(g-mol·K) or Pa·m³/(g-mol·K)	
Parameters	
$T_B = 1042.25$ K	$S_{1.5V_c} = 0.55$ M
$M = 6.55$	$S_{1.4\rho_c} = 1.83$ M
$B_{0.8} = -0.655$	$S_{3.4\rho_c} = 3.4$ M
$k = 5.0$	$Z_c = 0.284777$
Constants	
$A_2 = -0.531700767$	$B_2 = 0.177907999$
$A_3 = 6.33375300 \times 10^{-2}$	$B_3 = -8.75699822 \times 10^{-3}$
$A_4 = -4.28235260 \times 10^{-3}$	$B_4 = 1.03051770 \times 10^{-3}$
$A_5 = -5.02954607 \times 10^{4}$	$B_5 = 6.91027428 \times 10^{4}$
$A_6 = 1.77703549 \times 10^{6}$	$B_6 = -1.66349849 \times 10^{6}$
$C_2 = -3.14743220$	$tP_c/(RT_cZ_c) = 0.122120115$
$C_3 = 1.17535330$	$c = 2.9280357 \times 10^{-6}$
$C_4 = -9.71238126 \times 10^{-2}$	$m = 1.39393939$
$a = 16.5$	$n = 8.53946931 \times 10^{-2}$
Wagenbreth *PVT* Relation Constants (Eq 4)	
$W_1 = 2.44499$	$W_4 = 0.10051$
$W_2 = -3.32748$	$W_5 = 2.28208$
$W_3 = -0.39755$	$W_6 = 0.60677$
Ideal-Gas Heat Capacity Equation Constants (Eq 5)	
T = temperature, K	C_p^* = ideal-gas heat capacity, cal/(g-mol·K)
$\alpha = 10.265952$	$\gamma = -709.60655$
$\beta = -7.8085907 \times 10^{-4}$	$\delta = 40821.249$

PVT Behavior of the Gas and Liquid Phases

The *PVT* behavior of the gas for densities less than 2 times the critical density were predicted by the Martin-Stanford equation (eq 3). The constants in eq 3 were determined by

$$P_r = \frac{T_r}{Z_c\left(V_r - \frac{tP_c}{RT_cZ_c}\right)} + \frac{A_2 + B_2T_r + C_2e^{-kT_r}}{z_c^2\left(V_r - \frac{tP_c}{RT_cZ_c}\right)^2} + \frac{A_3 + B_3T_r + C_3e^{-kT_r}}{Z_c^3\left(V_r - \frac{tP_c}{RT_cZ_c}\right)^3} + \frac{A_4 + B_4T_r + C_4e^{-kT_r}}{Z_c^4\left(V_r - \frac{tP_c}{RT_cZ_c}\right)^4} + \frac{A_5 + B_5T_r}{e^{aV_r}(1 + ce^{aV_r})} + \frac{A_6 + B_6T_r}{e^{maV_r}(1 + nce^{maV_r})} \tag{3}$$

the method described in ref *9*. The values of the required parameters used in the development, and the constants that resulted, are listed in Table III. The densities predicted by using eq 3 were compared with three low-pressure data sets. Ross amd Maass (*10*) made 40 density measurements from 288.15 to 348.15 K. The average deviation between the predicted and experimental densities was found to be 0.074% with

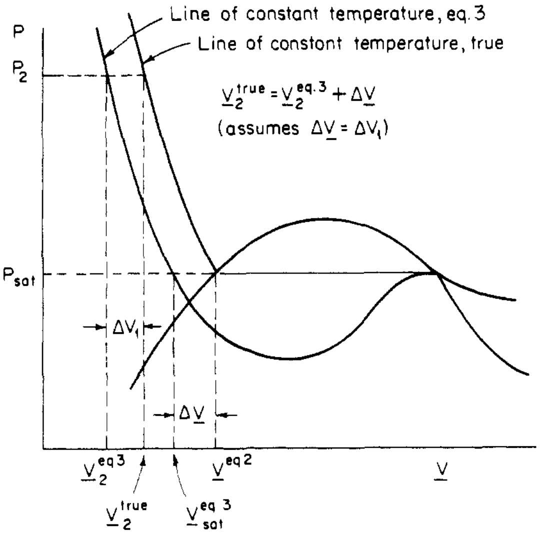

Figure 2. Technique used to calculate the compressed-liquid properties from the critical to twice the critical density.

a standard deviation of 0.093% (one inconsistent data point was excluded). Pier (*11*) made 16 density measurements between 273.15 and 457.65 K. These had an average deviation from the predicted values of 0.096% and a standard deviation of 0.12%. Lastly, Jacquerod and Tourpaian (*12*) made measurements at 273.15 and 288.15 K which differed from the predicted density by −0.0090% and 0.062%, respectively.

Along the saturated-liquid curve, eq 3 may not give the true volume as predicted by the saturated-liquid density equation (eq 2). However, the behavior of eq 3 in this subcooled region near the saturation dome is still considered to be correct. So, to predict the *PVT* properties in the compressed-liquid region where $T < T_c$ and $\rho \leq 2.0\rho_c$, the following technique was used. For a specific P_{sat} and T_{sat}, the quantity ΔV was calculated from

$$\Delta V = V^{eq\ 2} - V_{sat}^{eq\ 3}$$

(see Figure 2). Then, the true specific volume at a higher pressure, P_2, along the isotherm is

$$V_2^{true} = V_2^{eq\ 3} + \Delta V$$

This method was also used in the calculations of enthalpy and entropy.

Wagenbreth (*13*) used his own compressed-liquid data to develop an equation of state for the region from 273.15 to 417.15 K between the vapor pressure and 16 000 kPa. His equation was used, in reduced form with the critical constants selected in this paper, for densities from 2.0 to 2.7 times the critical density.

$$P_r = W_1 + W_2\rho_r^3 + W_3\rho_r^4 + W_4\rho_r^6 + \rho_r^3T_r(W_5 + W_6\rho_r) \tag{4}$$

The constants in this equation are listed in Table III.

As was true for eq 3, Wagenbreth's equation may not predict the same saturated-liquid density as eq 2. Therefore, the following technique, which is similar to that used with eq 3, was employed. For a specific P_{sat} and T_{sat}, $V^{eq\ 2}$ and $V_{sat}^{eq\ 4}$ were calculated. Then, for another pressure, P_2, along the isotherm, the quantity ΔV was calculated where

$$\Delta V = V_2^{eq\ 4} - V_{sat}^{eq\ 4}$$

(see Figure 3). Then, the true specific volume is

$$V_2^{true} = V^{eq\ 2} + \Delta V$$

This assumes that $\Delta V = V_2^{eq\ 4} - V_{sat}^{eq\ 4} = V_2^{true} - V^{eq\ 2}$ along the isotherms.

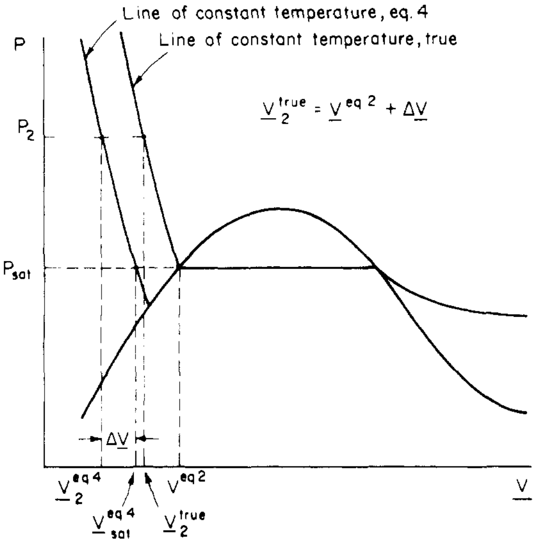

Figure 3. Technique used to calculate the compressed-liquid properties from 2.0 to 2.7 times the critical density.

Although both eq 3 and 4 accurately predict the compressed-liquid *PVT* behavior in the region of 2.0 times the critical density, they do not agree exactly. For temperatures greater than 403 K, eq 3 is used to predict the compressed-liquid properties. For temperatures less than 373 K, the properties are predicted by using eq 4. For isotherms in the transition region (373–403 K), both equations were used in predicting the properties. The maximum difference between the densities predicted by the two equations in the transition region was found to be less than 1%.

Ideal-Gas Heat Capacity

The molecular vibrational assignments of Douglas, Møller, and Stoicheff (*14*), based on a general internal model for diatomic gases, were used for a statistical thermodynamic calculation of the heat capacity of the ideal gas. The following empirical equation was then developed to represent the calculated data from 180 to 600 K:

$$C_p^* = \alpha + \beta T + \gamma/T + \delta/T^2 \tag{5}$$

where C_p^* is in cal/(g-mol·K) and T is in kelvin. The heat capacities calculated from this equation were compared to those calculated by Glushko et al. (*15*) and showed a maximum deviation of 0.022%. The constants used in this equation are listed in Table III.

Datum Plane for Thermodynamic Properties

The datum plane for the thermodynamic properties of enthalpy and entropy was the crystalline solid at absolute zero. Thus, at 0 K, **H** = 0 and **S** = 0.

The enthalpy of the saturated vapor at atmospheric pressure (525.7212 kJ/kg) was determined by using the heat capacity data of Giauque and Powell (*6*) for the solid and liquid with the latent heat of vaporization as determined from the Clapeyron equation. This enthalpy, H_{ref}, was used as the reference for all other calculations. To facilitate comparison with other tables, the enthalpy of the ideal gas at 298.15 K was calculated as 555.4796 kJ/kg.

Using the fundamental vibrational properties of the molecule, Glushko et al. (*15*) calculated the entropy of the ideal gas at 298.15 K and 1 atm to be 222.965 J/(g-mol·K) (3.144515 kJ/(kg·K)). The entropy of the real saturated vapor at 239.18 K and 1 atm was then calculated by using the ideal-gas heat capacity (eq 5) with the *PVT* relation (eq 3) and found to be 3.035173 kJ/(kg·K). This value was used as the reference for all other calculations.

Table IV. Saturation Properties of Chlorine

		V, m^3/kg		H, kJ/kg			S, kJ/(kg·K)			
temp, °C	*P*, kPa	liquid	vapor	liquid	latent	vapor	liquid	latent	vapor	*f*, kPa
−100.98	1.3945	0.000 581 91	14.465	176.58	320.98	497.56	1.5314	1.864 3	3.3957	1.3933
−90.00	3.5935	0.000 590 48	5.965 3	186.68	315.62	502.30	1.5883	1.723 3	3.3116	3.5869
−80.00	7.6625	0.000 598 65	2.945 9	195.79	310.82	506.61	1.6367	1.609 2	3.2459	7.6370
−70.00	15.028	0.000 607 22	1.576 2	204.86	306.04	510.90	1.6824	1.506 5	3.1889	14.944
−60.00	27.456	0.000 616 21	0.902 26	213.91	301.22	515.14	1.7259	1.413 2	3.1391	27.215
−50.00	47.217	0.000 625 66	0.546 83	222.99	296.31	519.29	1.7675	1.327 8	3.0953	46.598
−40.00	77.084	0.000 635 62	0.347 93	232.11	291.24	523.34	1.8073	1.249 1	3.0565	75.645
−33.97	101.325	0.000 641 90	0.270 38	237.64	288.08	525.72	1.8307	1.204 5	3.0352	99.028
−30.00	120.31	0.000 646 15	0.230 76	241.30	285.96	527.26	1.8458	1.176 1	3.0219	117.23
−20.00	180.60	0.000 657 30	0.158 61	250.57	280.45	531.02	1.8830	1.107 8	2.9909	174.47
−10.00	262.00	0.000 669 16	0.112 40	259.95	274.64	534.59	1.9192	1.043 7	2.9628	250.56
0.00	368.92	0.000 681 80	0.081 793	269.43	268.52	537.95	1.9543	0.983 04	2.9373	348.67
10.00	505.98	0.000 695 34	0.060 888	279.05	262.03	541.08	1.9885	0.925 40	2.9139	471.86
20.00	678.04	0.000 709 90	0.046 224	288.81	255.13	543.94	2.0219	0.870 32	2.8923	622.90
30.00	890.12	0.000 725 65	0.035 686	298.72	247.78	546.50	2.0547	0.817 36	2.8721	804.27
40.00	1147.4	0.000 742 79	0.027 949	308.83	239.91	548.74	2.0869	0.766 13	2.8530	1018.0
50.00	1455.1	0.000 761 57	0.022 154	319.15	231.45	550.60	2.1186	0.716 23	2.8348	1265.8
60.00	1818.8	0.000 782 34	0.017 735	329.75	222.29	552.03	2.1500	0.667 22	2.8173	1548.9
70.00	2244.2	0.000 805 56	0.014 309	340.68	212.29	552.97	2.1814	0.618 64	2.8000	1867.9
80.00	2737.2	0.000 831 90	0.011 608	352.04	201.27	553.30	2.2128	0.569 92	2.7828	2223.3
90.00	3304.1	0.000 862 30	0.009 445 9	363.95	188.95	552.91	2.2448	0.520 32	2.7651	2614.7
100.00	3952.0	0.000 898 32	0.007 685 3	376.62	174.95	551.57	2.2776	0.468 84	2.7465	3041.6
110.00	4688.5	0.000 942 59	0.006 223 9	390.34	158.60	548.94	2.3121	0.413 94	2.7260	3502.9
120.00	5522.9	0.001 000 4	0.004 978 5	405.69	138.71	544.40	2.3495	0.352 81	2.7024	3996.9
130.00	6466.7	0.001 085 0	0.003 866 4	423.92	112.53	536.45	2.3929	0.279 12	2.6720	4521.1
135.00	6984.6	0.001 150 1	0.003 320 8	435.20	94.720	529.92	2.4192	0.232 07	2.6513	4793.3
140.00	7537.1	0.001 259 9	0.002 719 2	450.15	68.871	519.02	2.4540	0.166 70	2.6207	5071.2
141.00	7652.1	0.001 296 2	0.002 575 9	454.19	61.388	515.58	2.4634	0.148 23	2.6117	5127.3
141.50	7710.2	0.001 318 6	0.002 497 3	456.50	57.012	513.51	2.4688	0.137 49	2.6063	5155.4
142.00	7768.8	0.001 345 4	0.002 411 5	459.10	51.994	511.09	2.4749	0.125 24	2.6001	5183.5
142.40	7815.9	0.001 371 8	0.002 335 1	461.48	47.303	508.79	2.4805	0.113 83	2.5943	5206.0
142.80	7863.3	0.001 405 2	0.002 247 7	464.30	41.650	505.95	2.4871	0.100 13	2.5872	5228.5
143.00	7887.1	0.001 426 4	0.002 197 5	465.98	38.250	504.23	2.4910	0.091 913	2.5830	5239.8
143.20	7911.0	0.001 452 5	0.002 140 0	467.93	34.220	502.15	2.4957	0.082 190	2.5779	5251.1
143.40	7934.9	0.001 487 4	0.002 070 2	470.38	29.112	499.49	2.5015	0.069 888	2.5713	5262.3
143.60	7958.9	0.001 543 4	0.001 972 4	473.97	21.504	495.48	2.5100	0.051 598	2.5616	5273.5
143.75	7977.0	0.001 745 2	0.001 745 2	484.70	0.000	484.70	2.5357	0.000 000	2.5357	5281.9

Latent Heat of Vaporization

The latent heat of vaporization was calculated from the Clapeyron equation by utilizing the vapor pressure, liquid density, and *PVT* relations. The heat of vaporization is

$$\Delta \mathbf{H}_{\mathrm{vap}} = T(\mathbf{V}^{\mathrm{g}} - \mathbf{V}^{\mathrm{l}})(\mathrm{d}P/\mathrm{d}T)_{\mathrm{sat}} \tag{6}$$

where $(\mathrm{d}P/\mathrm{d}T)_{\mathrm{sat}}$ is the slope of the vapor pressure curve. The calculated heat of vaporization at the new boiling point (288.084 kJ/kg at 239.18 K) compares favorably with Giauque and Powell's experimental value (*6*) of 287.752 kJ/kg measured at their normal boiling point of 239.10 K.

Entropy of Vaporization

The entropy of vaporization was found from the relation

$$\Delta \mathbf{S}_{\mathrm{vap}} = \Delta \mathbf{H}_{\mathrm{vap}}/T$$

Heat Capacity of the Saturated Liquid

Giauque and Powell (*6*) measured the saturated-liquid heat capacity, $C_s^{\,\mathrm{l}}$, at 11 temperatures, from 173.17 to 239.10 K. These were used to check the thermodynamic consistency of the various equations used in this report. The procedure consisted of calculating $C_s^{\,\mathrm{l}}$ by using classical thermodynamic relationships along with the vapor pressure, *PVT* (eq 3), saturated-liquid density, and ideal-gas heat capacity equations and then comparing the calculated value with the experimental values. The calculated saturated-liquid heat capacities averaged 3.16% less than the experimental values with the differences ranging from 1.39% to 3.90%. The agreement is considered acceptable since the values depend on the second derivatives of some of the relations.

Enthalpy of the Vapor

The property relation for enthalpy is

$$\mathrm{d}\mathbf{H} = C_p\,\mathrm{d}T + [\mathbf{V} - T(\partial V/\partial T)_p]\,\mathrm{d}P$$

Then, after some manipulation and utilization of the ideal-gas heat capacity and *PVT* relations (eq 5 and 3), the enthalpy is given by

$$\begin{aligned}\mathbf{H} = \mathbf{H}_{\mathrm{ref}} + \Bigg|(\alpha - R)T + \frac{\beta T^2}{2} + \gamma \ln T - \frac{\delta}{T} + P\mathbf{V} + {} \\ P_c\mathbf{V}_c\Bigg[\frac{A_2 + (1 + kT_r)C_2 e^{-kT_r}}{Z_c^{\,2}\left(V_r - \dfrac{tP_c}{RT_cZ_c}\right)} + {} \\ \frac{A_3 + (1 + kT_r)C_3 e^{-kT_r}}{2Z_c^{\,3}\left(V_r - \dfrac{tP_c}{RT_cZ_c}\right)^2} + {} \\ \frac{A_4 + (1 + kT_r)C_4 e^{-kT_r})}{3Z_c^{\,4}\left(V_r - \dfrac{tP_c}{RT_cZ_c}\right)^3} + {} \\ A_5\left[cV_r + \frac{1}{ae^{aV_r}} - \frac{c}{a}\ln\,(1 + ce^{aV_r})\right] + {} \\ A_6\left[ncV_r + \frac{1}{mae^{maV_r}} - \frac{nc}{ma}\ln\,(1 + nce^{maV_r})\right]\Bigg]\Bigg|_{(T,P,\mathbf{V})_{\mathrm{ref}}}^{T,P,\mathbf{V}}\end{aligned}$$

where **H** is in kJ/kg.

The enthalpy of the saturated vapor is found by substituting T_{sat}, P_{sat}, and $\mathbf{V}_{\mathrm{sat}}$ into the above equation.

Enthalpy of the Saturated Liquid

The enthalpy of the saturated liquid, $\mathbf{H}^{l}_{\text{sat}}$, was found by subtracting the heat of vaporization from the enthalpy of the saturated vapor.

Enthalpy of the Compressed Liquid

Changes in the liquid enthalpy can be found from the following property relation:

$$d\mathbf{H}^{l} = [T(\partial P/\partial T)_{v} + \mathbf{V}(\partial P/\partial \mathbf{V})_{T}]\ d\mathbf{V}$$

Using the liquid PVT relation (eq 4) to evaluate the partial derivatives, then integrating between state 1 and state 2 at constant temperature where state 1 is the saturated liquid, one obtains the enthalpy:

$$\mathbf{H}^{l} = \mathbf{H}^{l}_{\text{sat}} + \mathbf{V}_{c}P_{c}\left|\left(\frac{W_{5}}{V_{r}^{2}} + \frac{W_{6}}{V_{r}^{3}}\right)T_{r} + \frac{4W_{3}}{3V_{r}^{3}} + \frac{6W_{4}}{5V_{r}^{6}} + \frac{3W_{2}}{2V_{r}^{2}}\right|_{(V_{r})_{\text{sat}}}^{V_{r}}$$

Entropy of the Vapor

Starting with the property relation

$$d\mathbf{S} = C_{v}\frac{dT}{T} - \left(\frac{\partial P}{\partial T}\right)_{v} d\mathbf{V}$$

and then manipulating it and utilizing the ideal-gas heat capacity and PVT relations (eq 5 and 3), one obtains the entropy:

$$\begin{aligned}\mathbf{S} = \mathbf{S}_{\text{ref}} + \Bigg|(\alpha - R)\ln T + \beta T - \frac{\gamma}{T} - \frac{\delta}{2T^{2}} + \\ \frac{P_{c}\mathbf{V}_{c}}{T_{c}}\Bigg[\frac{\ln\left(V_{r} - \frac{tP_{c}}{RT_{c}Z_{c}}\right)}{Z_{c}} - \frac{B_{2}}{Z_{c}^{2}\left(V_{r} - \frac{tP_{c}}{RT_{c}Z_{c}}\right)} - \\ \frac{B_{3}}{2Z_{c}^{3}\left(V_{r} - \frac{tP_{c}}{RT_{c}Z_{c}}\right)^{2}} - \frac{B_{4}}{3Z_{c}^{4}\left(V_{r} - \frac{tP_{c}}{RT_{c}Z_{c}}\right)^{3}} - \\ B_{5}\left[cV_{r} + \frac{1}{ae^{aV_{r}}} - \frac{c}{a}\ln(1 + ce^{aV_{r}})\right] - \\ B_{6}\left[ncV_{r} + \frac{1}{mae^{maV_{r}}} - \frac{nc}{ma}\ln(1 + nce^{maV_{r}})\right] + \\ \left[\frac{C_{2}}{Z_{c}^{2}\left(V_{r} - \frac{tP_{c}}{RT_{c}Z_{c}}\right)} + \frac{C_{3}}{2Z_{c}^{3}\left(V_{r} - \frac{tP_{c}}{RT_{c}Z_{c}}\right)^{2}} + \right. \\ \left.\frac{C_{4}}{3Z_{c}^{4}\left(V_{r} - \frac{tP_{c}}{RT_{c}Z_{c}}\right)^{3}}\right]ke^{-kT_{r}}\Bigg]\Bigg|_{T,P,\mathbf{V})_{\text{ref}}}^{T,P,\mathbf{V}}\end{aligned}$$

where $\mathbf{S}$ is in kJ/(kg·K).

The entropy of the saturated vapor is found by substituting T_{sat}, P_{sat}, and $\mathbf{V}_{\text{sat}}$ into the above equation.

Entropy of the Saturated Liquid

The entropy of the saturated liquid, $\mathbf{S}^{l}_{\text{sat}}$, is found by subtracting the entropy of vaporization from the entropy of the saturated vapor.

Entropy of the Compressed Liquid

Changes in the entropy can be found from the property relation

$$d\mathbf{S} = C_{v}\frac{dT}{T} + \left(\frac{\partial P}{\partial T}\right)_{v} d\mathbf{V}$$

Using the liquid PVT relation (eq 4) to evaluate the partial derivatives, and then integrating between state 1 and state 2 at constant temperature where state 1 is the saturated liquid, one obtains the entropy:

$$\mathbf{S}^{l} = \mathbf{S}^{l}_{\text{sat}} - \frac{\mathbf{V}_{c}P_{c}}{T_{c}}\left|\frac{W_{5}}{2V_{r}^{2}} + \frac{W_{6}}{3V_{r}^{3}}\right|_{(V_{r})_{\text{sat}}}^{V_{r}}$$

Fugacity

Fugacity, f, is defined by the equation

$$d\mathbf{G} = RT\ d(\ln f)$$

At constant temperature, for a fixed mass of a single substance

$$\mathbf{V}\ dP = RT\ d(\ln f)$$

After some manipulation

$$f = \exp\left[\ln\left(\frac{RT}{\mathbf{V}}\right) + \int_{\mathbf{V}^{*}}^{\mathbf{V}}\left[\frac{1}{\mathbf{V}} + \frac{\mathbf{V}}{RT}\left(\frac{\partial P}{\partial \mathbf{V}}\right)_{T}\right] d\mathbf{V}\right]$$

Substituting in the PVT relation for $\mathbf{V} \geq \mathbf{V}_{c}$ (eq 3 with the fifth and sixth terms truncated), one gets

$$\begin{aligned}f = \frac{RT}{\mathbf{V}_{c}\left(V_{r} - \frac{tP_{c}}{RT_{c}Z_{c}}\right)}\exp\Bigg[\left(\frac{\frac{tP_{c}}{RT_{c}Z_{c}}}{\left(V_{r} - \frac{tP_{c}}{RT_{c}Z_{c}}\right)}\right) + \\ \frac{2(A_{2} + B_{2}T_{r} + C_{2}e^{-kT_{r}})}{Z_{c}T_{r}}\left[\frac{1}{\left(V_{r} - \frac{tP_{c}}{RT_{c}Z_{c}}\right)} + \frac{\frac{tP_{c}}{RT_{c}Z_{c}}}{2\left(V_{r} - \frac{tPc}{RT_{c}Z_{c}}\right)^{2}}\right] + \\ \frac{3(A_{3} + B_{3}T_{r} + C_{3}e^{-kT_{r}})}{Z_{c}^{2}T_{r}}\left[\frac{1}{2\left(V_{r} - \frac{tP_{c}}{RT_{c}Z_{c}}\right)^{2}} + \frac{\frac{tP_{c}}{RT_{c}Z_{c}}}{3\left(V_{r} - \frac{tP_{c}}{RT_{c}Z_{c}}\right)^{3}}\right] + \\ \frac{4(A_{4} + B_{4}T_{r} + C_{4}e^{-kT_{r}})}{Z_{c}^{3}T_{r}}\left[\frac{1}{3\left(V_{r} - \frac{tP_{c}}{RT_{c}Z_{c}}\right)^{3}} + \frac{\frac{tP_{c}}{RT_{c}Z_{c}}}{4\left(V_{r} - \frac{tP_{c}}{RT_{c}Z_{c}}\right)^{4}}\right]\Bigg]\end{aligned}$$

where f is in kilopascals.

Velocity of Sound

The velocity of sound is given by

$$U_a = [(\partial P/\partial \rho)_S]^{1/2} = [-(C_p/C_v)\mathbf{V}^2(\partial P/\partial \mathbf{V})_T]^{1/2}$$

To evaluate this quantity, the constant-volume heat capacity is needed, which is given by

$$dC_v = T(\partial^2 P/\partial T^2)_v \, d\mathbf{V}$$

Integrating from $\mathbf{V} = \infty$, where the gas behaves ideally and $C_v = C_v^{\bullet}$, to a finite volume, $\mathbf{V}$

$$C_v = C_v^{\bullet} + \int_{\infty}^{\mathbf{V}} T(\partial^2 P/\partial T^2)_v \, d\mathbf{V}$$

The second derivative of the PVT relation (eq 3) was used in evaluating this equation to give

$$C_v = C_v^{\bullet} - \frac{T_r P_c \mathbf{V}_c k^2}{T_c} e^{-kT_r} \left[\frac{C_2}{Z_c^2\left(V_r - \frac{tP_c}{RT_cZ_c}\right)} + \frac{C_3}{2Z_c^3\left(V_r - \frac{tP_c}{RT_cZ_c}\right)^2} + \frac{C_4}{3Z_c^4\left(V_r - \frac{tP_c}{RT_cZ_c}\right)^3} \right]$$

where C_v is in kJ/(kg·K).

The constant-pressure heat capacity was then found from

$$C_p = C_v - T(\partial P/\partial T)_v^2/(\partial P/\partial \mathbf{V})_T$$

The temperature and volume derivatives of eq 3 were used to evaluate this, which gives

$$C_p = C_v + \frac{T_r P_c \mathbf{V}_c}{T_c} \left[\left[\frac{1}{Z_c\left(V_r - \frac{tP_c}{RT_cZ_c}\right)} + \frac{B_2 - C_2 k e^{-kT_r}}{Z_c^3\left(V_r - \frac{tP_c}{RT_cZ_c}\right)^2} + \ldots + \frac{B_6}{e^{maV_r}(1 + nce^{maV_r})} \right]^2 \middle/ \left[\frac{T_r}{Z_c\left(V_r - \frac{tP_c}{RT_cZ_c}\right)^2} + \frac{2(A_2 + B_2T_r + C_2e^{-kT_r})}{Z_c^2\left(V_r - \frac{tP_c}{RT_cZ_c}\right)^3} + \ldots + \frac{ma(A_6 + B_6T_r)(1 + 2nce^{maV_r})}{e^{maV_r}(1 + nce^{maV_r})^2} \right] \right]$$

where C_p is in kJ/(kg·K).

Then, after eq 3 is used to evaluate $(\partial P/\partial \mathbf{V})_T$, the velocity of sound in the vapor is given by

$$U_a = \mathbf{V} \left[\frac{C_p}{C_v} \frac{P_c}{\mathbf{V}_c} \left[\frac{T_r}{Z_c\left(V_r - \frac{tP_c}{RT_cZ_c}\right)^2} + \frac{2(A_2 + B_2T_r + C_2e^{-kT_r})}{Z_c^2\left(V_r - \frac{tP_c}{RT_cZ_c}\right)^3} + \ldots + \frac{ma(A_6 + B_6T_r)(1 + 2nce^{maV_r})}{e^{maV_r}(1 + nce^{maV_r})^2} \right] (1000) \right]^{1/2}$$

where U_a is in m/s.

Joule–Thomson Coefficient

The Joule–Thomson coefficient is defined as

$$\mu = (\partial T/\partial P)_H$$

After manipulation, this becomes

$$\mu = [T[-(\partial P/\partial T)_v/(\partial P/\partial \mathbf{V})_T] - \mathbf{V}]/C_p$$

When one uses the PVT relation (eq 3) to evaluate $(\partial P/\partial T)_v$ and $(\partial P/\partial \mathbf{V})_T$, the Joule–Thomson coefficient is given as

$$\mu = \left| \left[-T_r\mathbf{V}_c \left[1 + \frac{B_2 - C_2ke^{-kT_r}}{Z_c\left(V_r - \frac{tP_c}{RT_cZ_c}\right)} + \ldots + \frac{B_6Z_c\left(V_r - \frac{tP_c}{RT_cZ_c}\right)}{e^{maV_r}(1 + nce^{maV_r})} \right] \middle/ \left[\frac{T_r}{\left(V_r - \frac{tP_c}{RT_cZ_c}\right)} + \frac{2(A_2 + B_2T_r + C_2e^{-kT_r})}{Z_c\left(V_r - \frac{tP_c}{RT_cZ_c}\right)^2} + \ldots + \frac{Z_c\left(V_r - \frac{tP_c}{RT_cZ_c}\right) ma(A_6 + B_6T_r)(1 + 2nce^{maV_r})}{e^{maV_r}(1 + nce^{maV_r})^2} \right] \right] - \mathbf{V} \right| \middle/ C_p$$

where μ is in K/kPa.

Second Virial Coefficient

At low pressure the PVT behavior can be described by a truncated version of eq 3

$$P_r = \frac{T_r}{Z_c\left(V_r - \frac{tP_c}{RT_cZ_c}\right)} + \frac{A_2 + B_2T_r + C_2e^{-kT_r}}{Z_c^2\left(V_r - \frac{tP_c}{RT_cZ_c}\right)^2}$$

Martin (*16*) showed that at low pressure the second virial coefficient, B, is given by

$$B = (RT/P_c)(\partial Z/\partial P_r)_T$$

Substituting in the truncated PVT relation, then letting $P_r \rightarrow 0$, one obtains

$$B = \frac{RT_c}{P_c} \left[\frac{tP_c}{RT_c} + \frac{A_2 + B_2T_r + C_2e^{-kT_r}}{T_r} \right]$$

Table V. Thermodynamic Properties of Chlorine

P, kPa	V, m^3/kg	H, kJ/kg	S, kJ/(kg·K)	f, kPa	u_a, m/s	J–T coeff, K/kPa	sec. virial coeff, m^3/kg
Temperature = 0 °C							
0	*c*	543.59	*c*	0	*d*	0	−0.004 782 1
101.325	0.311 26	542.10	3.0992	99.794	204.53	0.030 792	*e*
(368.92)[a]	0.081 793	537.95	2.9373	348.67	*d*	*d*	*e*
(368.92)[b]	0.000 682	269.43	1.9543	348.67	*d*	*d*	*e*
500	0.000 682	269.48	1.9541	*d*	*d*	*d*	*e*
1000	0.000 681	269.63	1.9534	*d*	*d*	*d*	*e*
10000	0.000 672	272.57	1.9419	*d*	*d*	*d*	*e*
20000	0.000 663	276.05	1.9303	*d*	*d*	*d*	*e*
Temperature = 50 °C							
0	*c*	567.52	*c*	0	*d*	0	−0.003 416 5
101.325	0.370 53	566.48	3.1812	100.40	222.34	0.020 965	*e*
500	0.072 236	562.24	2.9852	477.55	217.13	0.021 148	*e*
1000	0.034 184	556.46	2.8916	910.48	209.95	0.021 481	*e*
(1455.1)[a]	0.022 154	550.60	2.8348	1265.8	*d*	*d*	*e*
(1455.1)[b]	0.000 762	319.15	2.1186	1265.8	*d*	*d*	*e*
5000	0.000 753	319.54	2.1115	*d*	*d*	*d*	*e*
10000	0.000 743	320.32	2.1023	*d*	*d*	*d*	*e*
20000	0.000 726	322.46	2.0862	*d*	*d*	*d*	*e*
Temperature = 100 °C							
0	*c*	591.98	*c*	0	*d*	0	−0.002 582 5
101.325	0.429 24	591.21	3.2523	100.72	238.67	0.015 352	*e*
500	0.848 69	588.10	3.0596	485.30	235.11	0.015 460	*e*
1000	0.041 048	584.01	2.9709	941.39	230.42	0.015 618	*e*
(3952.0)[a]	0.007 6853	551.57	2.7465	3041.6	*d*	*d*	*e*
(3952.0)[b]	0.000 898	376.62	2.2776	3041.6	*d*	*d*	*e*
5000	0.000 889	375.91	2.2732	*d*	*d*	*d*	*e*
10000	0.000 857	373.85	2.2560	*d*	*d*	*d*	*e*
20000	0.000 816	372.86	2.2309	*d*	*d*	*d*	*e*
Temperature = 150 °C							
0	*c*	616.85	*c*	0	*d*	0	−0.002 025 7
101.325	0.487 66	616.24	3.3152	100.91	253.90	0.011 913	*e*
500	0.097 183	613.82	3.1243	489.83	251.38	0.011 976	*e*
1000	0.047 534	610.69	3.0380	959.44	248.13	0.012 061	*e*
5000	0.007 490	579.66	2.7971	4005.2	217.99	0.012 922	*e*
10000	0.001 219	453.84	2.4556	*d*	294.14	0.003 153	*e*
20000	0.000 964	430.17	2.3749	*d*	505.08	0.000 669	*e*
Temperature = 200 °C							
0	*c*	642.03	*c*	0	*d*	0	−0.001 626 0
101.325	0.545 93	641.53	3.3717	101.02	268.25	0.009 661	*e*
500	0.109 32	639.56	3.1818	492.70	266.43	0.009 696	*e*
1000	0.053 828	637.03	3.0969	970.88	264.13	0.009 740	*e*
5000	0.009 311	614.19	2.8744	4289.4	245.23	0.010 019	*e*
10000	0.003 543	574.47	2.7292	7234.0	227.27	0.009 226	*e*
20000	0.001 283	495.51	2.5208	*d*	339.38	0.002 286	*e*
Temperature = 250 °C							
0	*c*	667.45	*c*	0	*d*	0	−0.001 322 2
101.325	0.604 10	667.03	3.4230	101.10	281.87	0.008 094	*e*
500	0.121 36	665.37	3.2336	494.63	280.56	0.008 110	*e*
1000	0.060 010	663.26	3.1496	978.58	278.92	0.008 128	*e*
5000	0.010 887	645.03	2.9364	4478.3	266.47	0.008 174	*ϵ*
10000	0.004 709	618.27	2.8174	7986.4	256.16	0.007 672	*e*
20000	0.001 870	561.53	2.6536	12799.	295.03	0.003 884	*e*
Temperature = 300 °C							
0	*c*	693.06	*c*	0	*d*	0	−0.001 081 2
101.325	0.662 20	692.70	3.4698	101.16	294.87	0.006 943	*e*
500	0.133 33	691.27	3.2809	495.99	293.94	0.006 946	*e*
1000	0.066 123	689.45	3.1974	984.01	292.79	0.006 948	*e*
5000	0.012 348	674.27	2.9898	4611.1	284.59	0.006 876	*e*
10000	0.005 637	653.59	2.8819	8503.0	278.96	0.006 448	*e*
20000	0.002 442	611.52	2.7451	14610.	300.61	0.004 191	*e*

[a] Saturated vapor. [b] Saturated liquid. [c] Not applicable at these conditions. [d] Property not calculated at these conditions. [e] Same value as above. Independent of pressure.

where B is in m^3/kg.

Results

The above equations were evaluated by using a digital computer. Table IV contains the values of the thermodynamic properties along the liquid–vapor saturation curve for selected temperatures. Table V lists the properties of the compressed liquid and superheated vapor for selected temperatures and pressures. The pressures in parentheses in Table V are at saturated conditions.

Acknowledgment

The research for this work was done under the direction of Professor Joseph J. Martin. Without his guidance and autho-

ratative insight, this paper would not have been possible. Sadly, he lost his 3-year battle against cancer before the text of this paper was written. His courage and encouragement are greatly missed.

Glossary

A	vapor pressure equation constant
A_i	equation of state constants
a	equation of state constant
a_0	density at the critical point, g/cm^3
a_i	saturated-liquid density equation constants
B	vapor pressure equation constant, second virial coefficient, m^3/kg
$B_{0.8}$	equation of state parameter
B_i	equation of state constants
C	vapor pressure equation constant
°C	degrees Celsius
C_i	equation of state constants
C_p	heat capacity at constant pressure, kJ/(kg·K)
C_v	heat capacity at constant volume, kJ/(kg·K)
$C_p^{\bullet}$	ideal-gas heat capacity at constant pressure, cal/(g-mol·K)
C_s^l	saturated-liquid heat capacity, kJ/(kg·K)
c	equation of state constant
D	vapor pressure equation constant
E	vapor pressure equation constant
F	vapor pressure equation constant
f	fugacity, kPa
$\mathbf{G}$	specific Gibbs free energy, kJ/kg
$\mathbf{H}$	specific enthalpy, kJ/kg
K	kelvin
k	equation of state parameter
M	equation of state parameter
m	equation of state parameter
n	equation of state parameter
P	pressure, kPa
P_c	critical pressure, kPa
P_r	reduced pressure, P/P_c
R	gas constant, kJ/(kg·K) or J/(g-mol·K)
$\mathbf{S}$	specific entropy, kJ/(kg·K)
$S_{1.5V_c}$	equation of state parameter
$S_{1.4\rho_c}$	equation of state parameter
$S_{1.8\rho_c}$	equation of state parameter
T	temperature, K
T_B	Boyle temperature, K
T_c	critical temperature
T_r	reduced temperature (T/T_c)
t	equation of state constant
$tP_c/(RT_cZ_c)$	equation of state constant
U_a	velocity of sound, m/s
$\mathbf{V}$	specific volume, m^3/kg
$\mathbf{V}_c$	critical specific volume, m^3/kg
V_r	reduced volume ($\mathbf{V}/\mathbf{V}_c$)
W_i	compressed-liquid equation of state constants
Z	compressibility
Z_c	critical compressibility

Greek Letters

α	ideal-gas heat capacity equation constant
β	ideal-gas heat capacity equation constant
γ	ideal-gas heat capacity equation constant
δ	ideal-gas heat capacity equation constant
μ	Joule–Thomson coefficient, K/kPa
ρ^l	saturated-liquid density, g/cm^3

Subscripts

c	critical point
sat, s	saturated state
ref	vapor at 1 atm and 239.18 K

Superscripts

•	ideal state
g	vapor state
l	liquid state

Registry No. Chlorine, 7782-50-5.

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Received for review October 24, 1983. Accepted June 4, 1984.