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Saturation Properties of Chlorine by the Principle of Corresponding States

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Vapor pressures, saturation densities, and enthalpies of evaporation of chlorine have been estimated from the triple point to the critical point and correlated by appropriate equations. The only reliable experimental data are vapor-pressure measurements below the normal boiling point. The work described here shows that with this limited information a modified corresponding-states technique, where the critical-point parameters and the acentric factor are determined from the reliable vapor-pressure measurements using a nonlinear fitting procedure, gives accurate values.

Table I. Experimental Vapor-Pressure Data

ref	T_R range	date
3	0.41–0.58	1939
4 (series I)	0.49–0.65	1979
4 (series II)	0.8–1.0	1979
5	0.47–1.0	1915

ref	critical-point values
5	417.15 K, 7.7011 MPa
4	416.76 K, 7.991 MPa
	416.87 K, 7.974 MPa
	416.90 K, 7.977 MPa

Table II. Experimental Saturation Density Data

ref	T_R range	date
	Gas	
5	0.66–0.97	1915
	Liquid	
5	0.47–0.97	1915
7	0.47–0.58	1909
8	0.46–0.84	1890
9	0.50–0.58	1937

Introduction

The thermodynamic properties of a fluid at saturation, as well as being of use in themselves, are important in defining an equation of state for use over a wide range in the liquid and gas regions. As part of a study of the properties of the industrially important fluid chlorine, a survey of the experimental data on the saturation curve showed that the only measurements in which the modern correlator can have confidence are restricted to vapor pressures over a limited temperature range. The most comprehensive correlation based on experimental results, by Kapoor and Martin (*1*), predates some of the better data and does not achieve the accuracy that is now attainable. Stein (*2*) has calculated properties based on generalized corresponding states which are useful for some purposes but again do not achieve high accuracy.

Available Data

After a critical evaluation of all of the vapor-pressure data for chlorine available in the literature, the experimental data sets listed in Table I were considered to be the only ones approaching the precision required for accurate correlation.

The results of Giauque and Powell (*3*) and the series-*I* results of Ambrose et al. (*4*) are in close agreement where they overlap and show little scatter, but the series-II results of Ambrose et al. and those of Pellaton (*5*) are scattered and differ by between 1 and 5%. From the experimental details reported in these references the results of Giauque and Powell and the series-I results of Ambrose et al. were judged to be the most reliable, and a requirement for any new correlation is that these data should be adequately reproduced. The value of the critical point reported throughout the literature is that found by Pellaton. The recent values reported by Ambrose et al. are of at least equal precision. In view of the differences, the critical point must be regarded as uncertain.

The only correlations of vapor pressure based on experimental data are that by Ambrose et al. (*4*), which was fitted only to results from their laboratory, and that by Kapoor and Martin (*1*), which predates the results of Ambrose et al. Tables of properties based on predictive generalized corresponding-states methods have been calculated by Stein (*2*) using the constants of Lee and Kesler (*6*). These are useful for some purposes but can be in error by several percent. This may be due either to the fact that the properties of the reference fluids are based on data for several real fluids which are of low accuracy near the saturation curve or to the fact that the extended BWR equations used by Lee and Kesler have incorrect behavior near saturation.

All of the measurements of saturation densities, which are listed in Table II, are of dubious quality. The results of Pellaton, which were previously thought to be accurate, were carried out at the same time as his vapor-pressure measurements, the reliability of which is now in question. The work of the other experimenters can be criticized on several counts, e.g., purity of samples and accuracy of temperature scale. The usual

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recourse of the correlator in such cases is to extrapolate single-phase *PVT* measurements to an accurately determined vapor-pressure curve, but this is not possible in this case since *PVT* measurements for chlorine are only available over very limited ranges.

The only correlation of saturation densities based on experimental results is by Kapoor and Martin (*1*), which gives great weight to the results of Pellaton. The remarks about the vapor-pressure tables of Stein also apply to his tables of saturation densities.

There is only one measurement of the enthalpy of evaporation, by Giauque and Powell (*3*), at 1 atm.

As a result of the data evaluation, it seemed that a reliable table of saturation properties could only be obtained by a careful application of the principle of corresponding states. The technique used is described in the following section.

Corresponding-States Principle

A simple approach to corresponding states is provided by defining a factor, Ω, in terms of the reduced pressure at a given reduced temperature, as

$$\Omega = [\log P_R^{(0)} - \log P_R]_{T_R} \tag{1}$$

where superscript (0) refers to a reference fluid, the properties of which are accurately known. For any fluid conforming to the corresponding-states principle, the vapor pressure and the compressibility factor can be expressed in a power series in terms of Ω

$$\log P_R = \log P_R^{(0)} + \Omega\ [\delta \log P_R/(\delta\Omega)] + \cdots \tag{2}$$

at a specificied value of T_R, and

$$Z_R = Z_R^{(0)} + \Omega[\delta Z_R/(\delta\Omega)] + \cdots \tag{3}$$

at specified values of P_R and T_R.

The theoretical principles and practical applications of this approach were first developed by Pitzer (*10*, *11*), who defined the reference fluid as a "simple fluid", with the approximate properties of the heavier rare gases (A, Kr, Xe) and methane. For these gases the reduced vapor pressure is almost precisely 0.1 at a reduced temperature of 0.7, and Pitzer consequently defined Ω at this temperature as

$$\omega = -(\log P_R)_{T_R=0.7} - 1.0 \tag{4}$$

where Ω is given the symbol ω and is the "acentric factor" commonly found in the literature. Pitzer showed that, for fluids which have small values of ω (e.g., <0.2), the first two terms in eq 2 and 3 are sufficient. He tabulated the properties of the simple reference fluid and the auxiliary terms in square brackets in eq 2 and 3 using the experimental data that existed at the time.

In order to improve the accuracy and the consistency of the method, and also to make it more convenient for computer use, Lee and Kesler (*6*) replaced the auxiliary terms by a numerical difference expression

$$\log P_R = \log P_R^{(0)} + (\omega/\omega^{(1)})[\log P_R^{(1)} - \log P_R^{(0)}] \tag{5}$$

$$Z_R = Z_R^{(0)} + (\omega/\omega^{(1)})[Z_R^{(1)} - Z_R^{(0)}] \tag{6}$$

thus introducing a second reference fluid, superscript (1). The properties of the reference fluids were represented by extended BWR equations and the range of the equations was extended to low temperatures by using data of light hydrocarbons in addition to the rare gases for the simple fluid and of *n*-octane for the second reference fluid. The constants of the equations were adjusted to give a good overall representation of many hydrocarbons.

Vapor Pressures and Critical Point

It was decided to retain the Lee-Kesler model but to choose different reference fluids more suitable to the problem. The criteria for choosing these fluids were (a) that both experimental measurements and correlations of vapor pressure and saturation densities to the highest accuracy attainable exist, (b) that the reduced temperature range covered by such measurements and correlations extend down to the triple point of chlorine ($T_R \approx 0.4$), and (c) that the reference fluids and the fluid under study have acentric factors of similar value ($\omega < 0.2$).

Recent correlations of vapor pressures and saturation densities by Wagner et al. (*12*) for oxygen and by Goodwin (*13*) for ethylene fulfill these criteria. Oxygen was arbitrarily chosen as fluid (0) and ethylene as fluid (1).

As the vapor-pressure measurements for chlorine above $T_R = 0.65$ are in doubt, for convenience the factor Ω was defined by eq 1 at a reduced temperature of 0.6.

As was stated earlier, the critical point of chlorine is not established, and so the factor Ω of eq 1, which is defined in terms of the reduced temperature and vapor pressure, cannot be calculated accurately. Therefore these parameters were determined from the experimental vapor pressures by using a weighted nonlinear least-squares (NLLS) procedure in the following manner.

The NLLS minimized the sum of squares

$$\sum_{i=1}^{N} [\log P_{R_{\mathrm{data}}} - \log P_R(\Omega, T_c, P_c)]^2$$

over *N* data points. The function $\log P_R(\Omega, T_c, P_c)$ is provided by eq 5 written as

$$\log (P/P_c) = [\log P_R^{(0)}]_{T/T_c} + (\Omega/\Omega^{(1)})[\log P_R^{(1)} - \log P_R^{(0)}]_{T/T_c} \tag{7}$$

where Ω, T_c, and P_c are adjustable variables.

The shape of the chlorine vapor-pressure curve is defined by the oxygen and ethylene vapor-pressure equations, and the NLLS adjusts the position of the curve in Ω, T_c, P_c space so as to coincide as closely as possible with the data within a specified limit of convergence of the sum of squares. The NLLS procedure was applied to various combinations of the data sets. Reasonable first estimates of the unknown variables were required, and the procedure was sensitive to the consistency of the input data. Use of either the results of Pellaton or the series-II results of Ambrose et al. caused systematic deviations between values calculated from eq 7 and the more reliable data in the low-temperature range. Thus the final results were obtained by using only the results of Giauque and Powell and the series-I results of Ambrose et al., restricting the range of data used to below $T_R = 0.65$.

The results of the NLLS are as follows: $T_c = 416.952$ K, $P_c = 7.97187$ MPa, and $\Omega = 0.111475$.

A comparison of all of the experimental data listed in Table I is shown in Figure 1, as well as comparisons with values taken from the tables of Stein and values calculated by the vapor-pressure equation of Ambrose et al. Note that the equation of Ambrose et al. deviates systematically from the results of Giauque and Powell at low temperatures.

Saturation Densities and Enthalpies of Evaporation

Using the values of Ω, T_c, and P_c found in the preceding section and the correlations of Wagner et al. and of Goodwin for the reference fluids, we calculated the reduced compressibility factors of chlorine at saturation (and hence the reduced saturation densities, since $\rho_R = P_R/(Z_R T_R)$) from eq 8. The

$$Z_R = Z_R^{(0)} + (\Omega/\Omega^{(1)})[Z_R^{(1)} - Z_R^{(0)}] \tag{8}$$

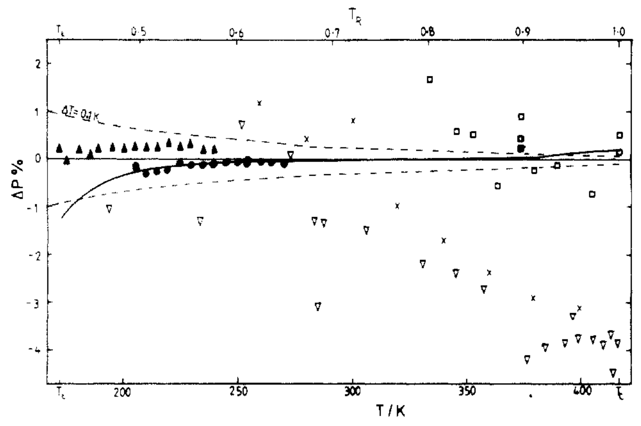

Figure 1. Comparison of vapor-pressure data for chlorine with values calculated from eq 7. Data used in correlation: (●) Ambrose et al. (series I); (▲) Giauque and Powell. Other data: (▽) Pellaton; (□) Ambrose et al. (series II); (X) Stein; (—) eq of Ambrose et al. $\Delta P\%$ is defined as $100(P_{\text{data}} - P_{\text{calcd}})/P_{\text{data}}$.

Table III. Properties of Chlorine on the Saturation Curve

T, K	P, MPa	ρ_l, mol dm^{-3}	ρ_g, mol dm^{-3}	ΔH, J mol^{-1}
172.170 (triple pt)	0.001 39	24.2252	0.000 98	22 613
180.0	0.002 77	23.9943	0.001 86	22 460
190.0	0.006 09	23.6870	0.003 87	22 199
200.0	0.012 26	23.3688	0.007 41	21 844
210.0	0.022 90	23.0415	0.013 22	21 487
220.0	0.040 10	22.7061	0.022 18	21 127
230.0	0.066 48	22.3630	0.035 36	20 759
239.160 (bp)	0.101 325	22.0417	0.052 16	20 414
240.0	0.105 13	22.0119	0.053 96	20 382
250.0	0.159 58	21.6524	0.079 32	19 990
260.0	0.233 78	21.2838	0.112 92	19 580
270.0	0.332 01	20.9050	0.156 41	19 148
280.0	0.458 84	20.5147	0.211 61	18 692
290.0	0.619 08	20.1112	0.280 56	18 206
300.0	0.817 75	19.6926	0.365 61	17 686
310.0	1.060 04	19.2564	0.469 49	17 128
320.0	1.351 28	18.7997	0.595 45	16 525
330.0	1.696 98	18.3187	0.747 48	15 872
340.0	2.102 77	17.8085	0.930 62	15 158
350.0	2.574 48	17.2627	1.151 53	14 372
360.0	3.118 17	16.6722	1.419 36	13 499
370.0	3.740 27	16.0238	1.747 61	12 516
380.0	4.447 73	15.2964	2.157 82	11 384
390.0	5.248 50	14.4526	2.688 73	10 039
400.0	6.152 41	13.4113	3.424 06	8 346
410.0	7.174 05	11.9109	4.629 65	5 888
416.952 (crit pt)	7.971 87	8.1345	8.134 5	0

reduced densities can be converted to actual densities if the critical density is known. In the low-pressure limit, $Z \rightarrow 1$ for all gases and eq 8 becomes eq 9, from which the critical

$$1/Z_c = 1/Z_c^{(0)} + (\Omega/\Omega^{(1)})[1/Z_c^{(1)} - 1/Z_c^{(0)}] \qquad (9)$$

compressibility factor was calculated and gives for chlorine $Z_c = 0.2827$ and $\rho_c = 8.1345$ mol dm^{-3}.

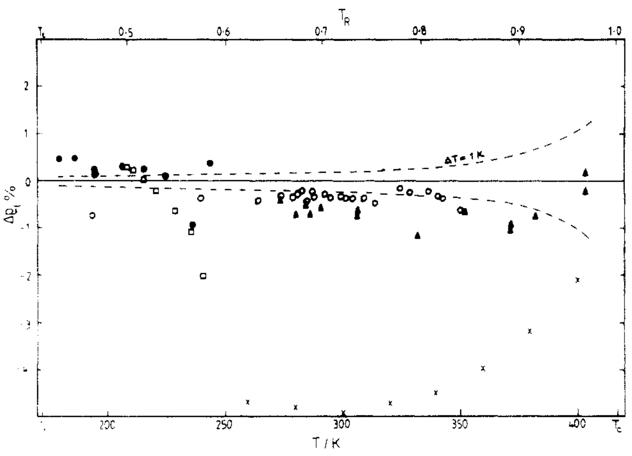

Figure 2. Comparison of saturated liquid density data for chlorine with values calculated from eq 8: (●) Johnson and McIntosh; (□) Kanda; (O) Knietsch; (▲) Pellaton; (X) Stein. $\Delta\rho_l\%$ is defined as $100(\rho_{l_{\text{data}}} - \rho_{l_{\text{calcd}}})/\rho_{l_{\text{data}}}$.

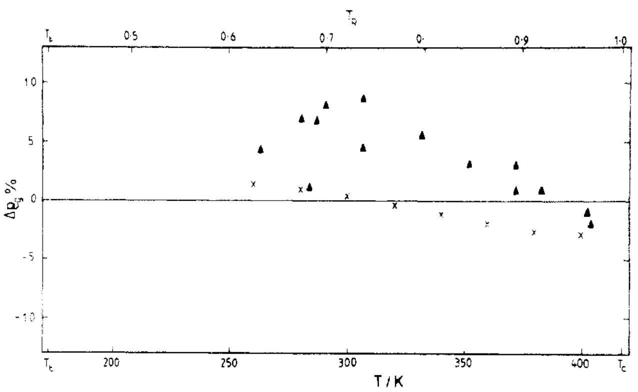

Figure 3. Comparison of saturated vapor density data for chlorine with values calculated from eq 8: (▲) Pellaton; (X) Stein. $\Delta\rho_g\%$ is defined as $100(\rho_{g_{\text{data}}} - \rho_{g_{\text{calcd}}})/\rho_{g_{\text{data}}}$.

The calculated density values were compared with the experimental measurements, and the deviations are shown in Figures 2 and 3. Also shown are comparisons with values taken from the tables of Stein.

Enthalpies of evaporation were calculated from the Clausius-Clapeyron equation which can be written as eq 10, where

$$\Delta H = (-\mathrm{d} \ln P_R/\mathrm{d}T_R^{-1})RT_c\Delta Z \qquad (10)$$

ΔZ is calculated from eq 8 and the differential is found numerically from eq 7. The difference between the single experimental point of Giauque and Powell at the boiling point is -121.1 J mol^{-1} (0.6%). The average difference between values calculated from eq 10 and those listed by Stein between 260 and 400 K is -254.25 J mol^{-1} with a maximum difference of -357 J mol^{-1} at 360 K.

Equations

Vapors pressures, saturation densities, and enthalpies of evaporation at 10 K intervals from the triple point to the critical point, calculated by the method described, are given in Table

Table IV. Values of the Coefficients of Eq 11-14

coeff	eq 11, a_i	eq 12, b_i	eq 13, c_i	eq 14, d_i
k_1	−6.300 003 2	1.620 139 4	−1.516 949 2	$0.206\,242\,5 \times 10^5$
k_2	0.984 134 45	−0.528 257 64	−2.487 500 0	$0.632\,927\,71 \times 10^5$
k_3	−6.006 296 8	−0.269 496 50	−2.307 696 0	$-0.131\,227\,19 \times 10^6$
k_4	−0.609 815 73	0.483 103 09	−0.429 366 52	$0.862\,944\,09 \times 10^5$
k_5	0.045 291 36	−0.262 119 04	0.234 862 59	$-0.173\,389\,97 \times 10^5$
k_6				$-0.927\,482\,01 \times 10^2$

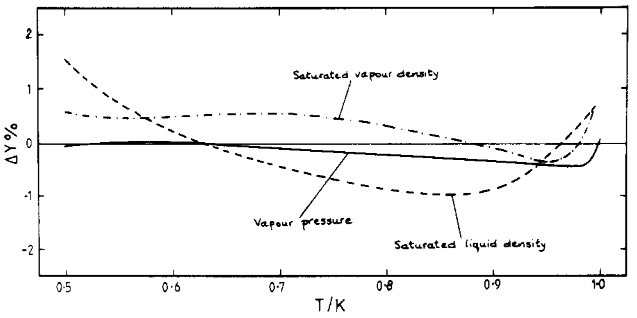

Figure 4. Comparison of saturation curve data for nitrogen from ref *15* with prediction. $\Delta Y\%$ is defined as $100(Y_{\mathrm{data}} - Y_{\mathrm{calcd}})/Y_{\mathrm{data}}$.

III. Equations which reproduce these values to within 0.1% and generally to within 0.05% were produced from data sets calculated at 1 K intervals, fitted by a weighted linear least-squares method due to de Reuck and Armstrong (*14*) which uses a search procedure to select significant terms in the equations. The equations are, for the vapor pressure

$$\ln \frac{P}{P_c} = \frac{T}{T_c}(a_1\theta + a_2\theta^{1.5} + a_3\theta^2 + a_4\theta^3 + a_5\theta^{4.5}) \qquad (11)$$

for the saturated liquid density

$$\ln(\rho_l/\rho_c) = b_1\theta^{1/3} + b_2\theta^{2/3} + b_3\theta^{6/3} + b_4\theta^{8/3} + b_5\theta^{9/3} \qquad (12)$$

for the saturated vapor density

$$\ln(\rho_g/\rho_c) = c_1\theta^{1/3} + c_2\theta^{2/3} + c_3\theta^{4/3} + c_4\theta^{11/3} + c_5\theta^{13/3} \qquad (13)$$

and the for enthalpy of evaporation

$$\Delta H = d_1\theta^{1/3} + d_2\theta^{3/3} + d_3\theta^{4/3} + d_4\theta^{5/3} + d_5\theta^{6/3} + d_6\theta^{19/3} \qquad (14)$$

where $\theta = T_c/T - 1$. Numerical values of the coefficients are listed in Table IV.

Accuracy of the Method

The same procedure was successfully followed through for several fluids for which accurate data were available, and the results obtained for nitrogen are representative. Figure 4 shows the deviations between the data of Angus, de Reuck, and Armstrong (*15*) and values estimated from the NLLS procedure. The difference between the enthalpies of evaporation given in ref *15* and the estimated values are of the order of −50 J mol^{-1}. It should be noted that only vapor pressures below $T_R = 0.65$ were used in the NLLS procedure so as to simulate the situation of the chlorine data. The accuracy of the predicted values of the properties of chlorine are expected to be of the same order as those of nitrogen. The predicted values of Ω, P_c, T_c, and ρ_c are 0.030 330 3, 3.399 97 MPa, 126.095 K, and 11.30 mol dm^{-3} compared with 0.026 87, 3.40 MPa, 126.20 K, and 11.21 mol dm^{-3} taken from ref *15*. On the basis of these results, the recommended values for chlorine are as follows: $T_c = 416.95 \pm 0.1$ K, $P_c = 7.792 \pm 0.005$ MPa, $\rho_c = 8.13 \pm 0.1$ mol dm^{-3}, $\Omega = 0.111 \pm 0.004$, and $\omega = 0.087 \pm 0.004$. The values of T_c and P_c, within the errors given, agree with those of Ambrose et al. given in Table I. The acentric factor, ω, agrees with the value 0.088 calculated from the vapor-pressure equation of Ambrose et al. and is preferred to the value 0.073 found throughout the literature.

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Glossary

a_i	constant coefficient
P	pressure
T	temperature, K
Z	compressibility factor, $P/(\rho RT)$
ΔZ	$Z_g - Z_l$ calculated at saturation
N	number of data points
ΔH	enthalpy of evaporation, J mol^{-1}
R	gas constant (8.314 34 J K^{-1} mol^{-1})
Y	property at saturation

Greek Letters

ω	acentric factor
Ω	corresponding states factor defined by eq 1
ρ	density
θ	a reduced temperature, $T_c/T - 1$

Subscripts

c	at the critical point
l	in the liquid phase at saturation
g	in the gas phase at saturation
R	reduced by the value at the critical point

Superscripts

(0), (1)	reference fluids

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