$$V^E = V_m - x_1V_{m,1} - x_2V_{m,2} = x_1x_2[(-b_2 - \tfrac{3}{2}b_3) - (b_3/2)(x_1 - x_2)] \quad (3)$$

where b_2 and b_3 are the parameters listed in Table II. The obtained excess volumes as a function of composition are plotted in Figures 1-4. The values of $V^E/(x_1x_2)$ at $x_1 = x_2 = 0.5$ together with the volume ratio, V_1/V_2, and the molecular masses of the individual components are listed in Table III.

The 2,2,2-trifluoroethanol and 2,2,2-trichloroethanol systems exhibit roughly equal positive V^E values and the ethanol system exhibits negative V^E values. From the two systems containing the acids, the trifluoroacetic acid system shows negative V^E values and the trichloroacetic acid system exhibits small positive V^E values. From the two anhydride systems, the trifluoroacetic anhydride exhibits large negative V^E values and the trichloroacetic anhydride shows small negative V^E values only. The data on the substituted-toluene systems indicate (at least qualitatively) that the steric effect in combination with the electron charge-transfer interactions determines the V^E values of the systems. V^E is more negative for the *tert*-butylbenzene system than it is for the cumene system and V^E for the cumene system is more negative than it is for the toluene system.

An interpretation of the V^E values in terms of the molecular structure of the solution constituents will be presented in another publication.

Registry No. NB, 98-95-3; toluene, 108-88-3; α,α,α-trichlorotoluene, 98-07-7; α,α,α-trifluorotoluene, 98-08-8; cumene, 98-82-8; *tert*-butylbenzene, 98-06-6; ethanol, 64-17-5; 2,2,2-trichloroethanol, 115-20-8; 2,2,2-trifluoroethanol, 75-89-8; acetic acid, 64-19-7; trifluoroacetic acid, 76-05-1; acetic anhydride, 108-24-7; trifluoroacetic anhydride, 407-25-0.

Literature Cited

(1) Fredenslund, Aa.; Gmehling, J.; Rasmussen, P. "Vapor-Liquid Equilibrium Using UNIFAC"; Elsevier: Amsterdam, 1977.
(2) Sørensen, J. M.; Magnussen, T.; Rasmussen, P.; Fredenslund, Aa. *Fluid Phase Equilib.* **1979**, *2*, 297.
(3) Sørensen, J. M.; Magnussen, T.; Rasmussen, P.; Fredenslund, Aa. *Fluid Phase Equilib.* **1979**, *3*, 47.
(4) Sørensen, J. M.; Magnussen, T.; Rasmussen, P.; Fredenslund, Aa. *Fluid Phase Equilib.* **1980**, *4*, 151.
(5) Miller, L. P.; Wachter, H. N.; Fried, V. *J. Chem. Eng. Data* **1975**, *20*, 417.
(6) Fried, V.; Miller, L. P.; Wachter, H. N. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 497.
(7) Timmermans, J. "Physicochemical Constants of Pure Organic Compounds"; Elsevier: New York, 1950.

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Isobaric Vapor-Liquid Equilibria for the Ternary System Acetone-Ethyl Acetate-Ethanol

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VLE data at 760 mmHg for the ternary system acetone-ethyl acetate-ethanol have been experimentally obtained. The measurements were conducted in a modified Gillespie-type, two-phase recirculation still. The VLE data for the binary system acetone-ethanol were also measured and compared with some literature values to check the modified still. The activity coefficients of the binary systems were correlated according to the Wilson, NRTL, and UNIQUAC equations and the binary parameters obtained were employed to predict the ternary VLE. These results, together with the values predicted by the UNIFAC method, are compared with experimental points, showing a good agreement.

Introduction

Vapor-liquid equilibria data provide useful information both theoretical and of interest in process design. While numerous experimental data are readily available for VLE of binary system, this is not so for multicomponent systems. This paper aims at increasing the number of existing experimental data and at verifying the possibility of predicting the behavior of ternary mixtures from the binary data. To this end the Wilson (*1*), NRTL (*2*), and UNIQUAC (*3*) equations were utilized, due to their great flexibility in the representation of VLE. Furthermore, the reliability of the UNIFAC method (*4*) in the quantitative estimation of ternary system phase equilibria was also tested.

The system examined is interesting since the binary ethyl acetate-ethanol system shows a minimum boiling point azeotrope. Hence, it is useful to establish whether the ternary system also presents an azeotrope or not.

Experimental Section

The isobaric measurements of VLE were carried out in a modified Gillespie-type still (*5*). The still was further modified, as shown in Figure 1, in order to improve the recirculation of condensate and liquid. The modified still was tested by measuring VLE data for the binary system acetone-ethanol, extensively reported in the literature (*6-8*). Figure 2 illustrates the good agreement between experimental points and data retrieved from the literature and confirms the reliability of the still.

The analyses were performed with a Perkin-Elmer gas chromatograph (3M column packed with Carbowax 20 M, +2%

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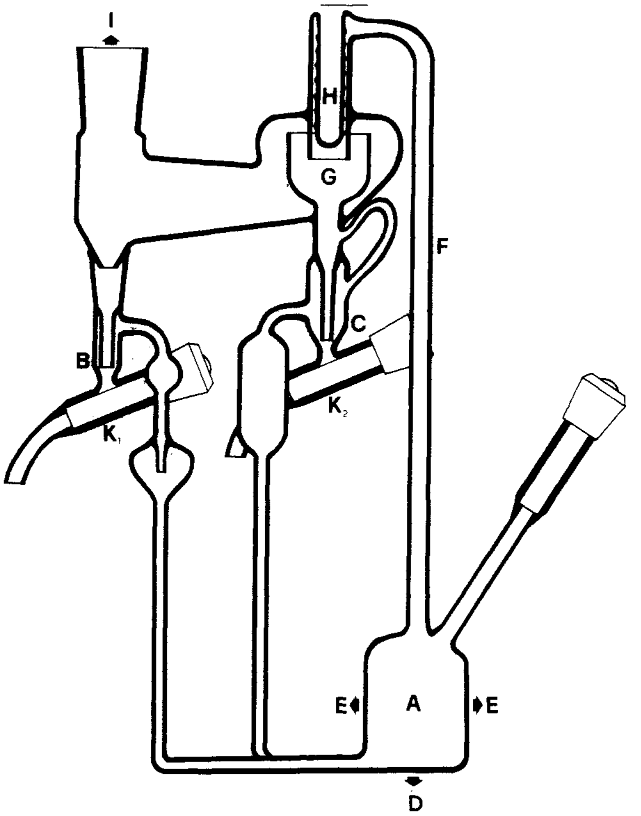

Figure 1. Vapor-liquid equilibrium still: (A) boiling flask; (B, C) collectors for condensate and liquid; (D) magnetic stirrer and heater; (E) electric mantle; (F) Cottrell pump; (G) equilibrium chamber; (H) thermometer well; (I) to condenser; (K_1, K_2) sampling cocks.

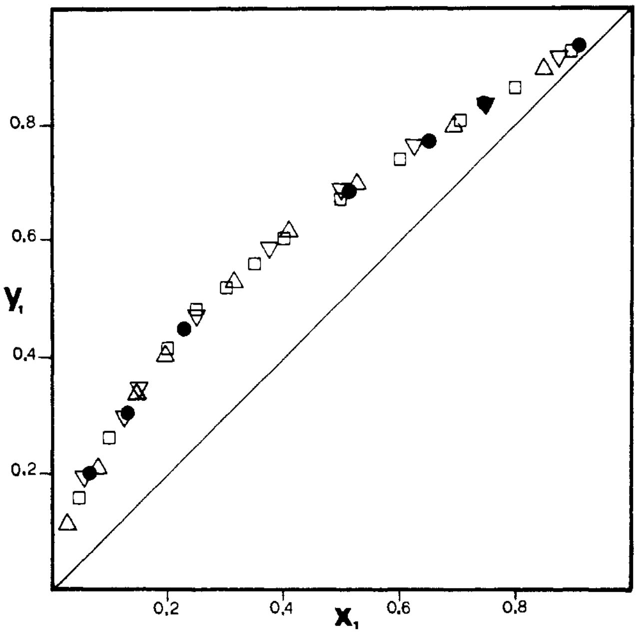

Figure 2. Vapor-liquid equilibrium data at 760 mmHg for the system acetone (1)–ethanol (2): (●) this work, (□) from ref *6*, (△) from ref *7*, (▽) from ref *8*.

H_3PO_4, on Chromosorb W. AW. 80–100 mesh).

Purities of the components (Carlo Erba) were as follows (wt%): acetone, 99.7; ethanol, 99.9; ethyl acetate, 99.5.

The accuracy in determining pressure and temperature was $\Delta P = \pm 1$ mmHg and $\Delta T = \pm 0.1$ °C, while mole fractions in both phases were measured to within ±0.005.

Temperature–composition data at constant pressure (P = 760 mmHg) for the ternary system acetone–ethyl acetate–ethanol are presented in Table I and Figure 3.

Table I. Experimental Data for the System Acetone (1)–Ethyl Acetate (2)–Ethanol (3) at 760 mmHg

	T, °C	x_1	x_2	y_1	y_2
1	57.4	0.96	0.043	0.933	0.029
2	59.9	0.078	0.187	0.769	0.135
3	60.3	0.669	0.144	0.750	0.103
4	60.9	0.582	0.168	0.685	0.123
5	61.1	0.596	0.171	0.702	0.126
6	61.5	0.587	0.260	0.684	0.190
7	61.8	0.569	0.229	0.666	0.171
8	62.3	0.545	0.041	0.673	0.033
9	63.1	0.452	0.233	0.578	0.181
10	63.5	0.491	0.389	0.589	0.294
11	63.9	0.428	0.300	0.514	0.248
12	64.1	0.420	0.024	0.603	0.025
13	64.5	0.390	0.162	0.511	0.150
14	64.9	0.329	0.358	0.470	0.285
15	65.1	0.345	0.264	0.446	0.233
16	65.8	0.377	0.513	0.496	0.381
17	65.9	0.289	0.426	0.412	0.337
18	66.1	0.295	0.277	0.408	0.255
19	66.2	0.355	0.054	0.504	0.057
20	66.3	0.346	0.090	0.474	0.098
21	66.4	0.267	0.327	0.381	0.290
22	67.6	0.197	0.439	0.282	0.380
23	67.6	0.242	0.564	0.356	0.447
24	67.6	0.303	0.612	0.418	0.479
25	67.9	0.223	0.172	0.336	0.183
26	68.2	0.164	0.417	0.239	0.383
27	68.4	0.185	0.631	0.276	0.518
28	68.4	0.239	0.037	0.393	0.046
29	68.5	0.152	0.351	0.238	0.336
30	69.1	0.199	0.186	0.292	0.209
31	69.2	0.115	0.513	0.183	0.462
32	69.6	0.171	0.679	0.248	0.566
33	69.6	0.183	0.120	0.293	0.138
34	69.7	0.111	0.626	0.167	0.550
35	69.9	0.157	0.136	0.253	0.161
36	69.9	0.187	0.050	0.313	0.073
37	70.1	0.228	0.762	0.341	0.632
38	70.2	0.069	0.467	0.107	0.464
39	70.2	0.074	0.409	0.118	0.406
40	70.2	0.133	0.733	0.204	0.626
41	70.3	0.075	0.349	0.121	0.385
42	70.3	0.091	0.265	0.149	0.295
43	70.3	0.095	0.271	0.146	0.303
44	70.7	0.171	0.082	0.283	0.101
45	70.9	0.126	0.117	0.211	0.150
46	71.0	0.074	0.225	0.129	0.266
47	71.1	0.066	0.720	0.106	0.628
48	71.8	0.055	0.182	0.103	0.238
49	72.2	0.116	0.080	0.204	0.111
50	72.3	0.060	0.140	0.120	0.187
51	72.4	0.083	0.828	0.135	0.746
52	72.7	0.012	0.291	0.026	0.344
53	73.1	0.034	0.207	0.038	0.265
54	73.5	0.057	0.886	0.094	0.816
55	73.6	0.096	0.051	0.184	0.074
56	74.8	0.021	0.124	0.032	0.186
57	75.4	0.051	0.029	0.114	0.051
58	76.0	0.004	0.074	0.016	0.119
59	76.8	0.020	0.011	0.056	0.022

Data Reduction and Discussion

The VLE data for the binary systems acetone–ethanol (*6*), acetone–ethyl acetate (*9*), and ethyl acetate–ethanol (*10*) were correlated by using the Wilson, NRTL, and UNIQUAC equations. Table II gives the results obtained, where A_{ij} has the following meaning: Wilson, $A_{ij} = \lambda_{ij} - \lambda_{ii}$ cal/mol; NRTL, $A_{ij} = g_{ij} - g_{ii}$ cal/mol; UNIQUAC, $A_{ij} = u_{ij} - u_{ii}$ cal/mol.

The required pure-component properties for the Wilson and UNIQUAC equations (v_i, r_i, q_i) are those given in the literature (*11*). The binary parameters obtained were used to estimate the ternary vapor-liquid equilibrium. The mean deviations $\bar{E}_T$,

Table II. Parameters of Wilson, NRTL, and UNIQUAC Equations and Mean Deviations for the Binary Systems

	A_{12}	A_{21}	α_{12}	$\bar{E}_{y_1}$	$E_{y_1,\max}$	$\bar{E}_T$	$E_{T,\max}$
		Acetone (1)–Ethyl Acetate (2)					
Wilson	−10.06	203.33		0.005	0.010	0.25	0.8
NRTL	−12.94	125.86	0.2	0.006	0.013	0.22	1.02
UNIQUAC	162.73	−93.31		0.005	0.011	0.24	0.8
		Acetone (1)–Ethanol (2)					
Wilson	118.67	272.64		0.016	0.026	0.54	0.87
NRTL	−421.56	933.40	0.2	0.013	0.015	0.65	1.15
UNIQUAC	−91.40	302.50		0.013	0.016	0.65	1.15
		Ethyl Acetate (1)–Ethanol (2)					
Wilson	149.12	570.21		0.011	0.026	0.24	0.5
NRTL	368.91	265.80	0.2	0.012	0.025	0.19	0.9
UNIQUAC	250.30	56.46		0.012	0.031	0.32	0.8

Table III. Mean Deviation of Vapor-Phase Compositions and Temperatures for the System Acetone (1)–Ethyl Acetate (2)–Ethanol (3)

	$\bar{E}_{y_1}$	$E_{y_1,\max}$	$\bar{E}_{y_2}$	$E_{y_2,\max}$	$\bar{E}_T$	$E_{T,\max}$
Wilson	0.040	0.106	0.031	0.071	3.99	6.60
NRTL	0.030	0.074	0.012	0.038	0.40	1.47
UNIQUAC	0.029	0.067	0.015	0.044	0.043	1.60

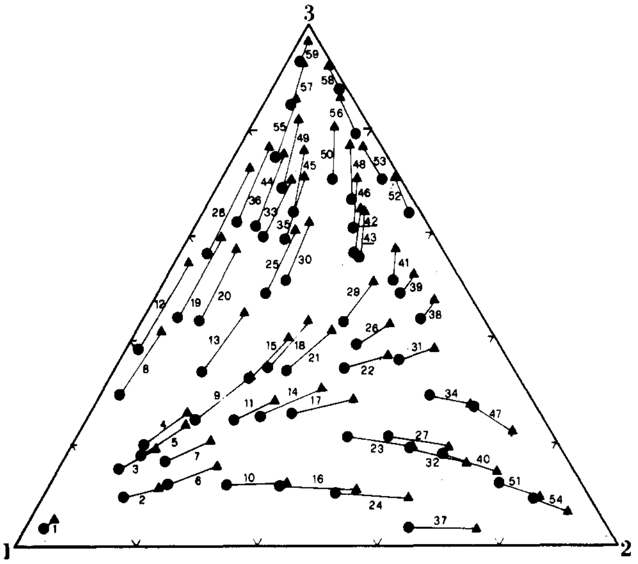

Figure 3. Vapor–liquid equilibrium data at 760 mmHg for the system acetone (1)–ethyl acetate (2)–ethanol (3): (▲) liquid, (●) vapor.

$\bar{E}_{y_1}$, and $\bar{E}_{y_2}$ obtained by employing the Wilson, NRTL, and UNIQUAC equations are reported in Table III.

These deviations are rather low, which proves that the prediction of VLE data is correct not only from a qualitative, but also from a quantitative, point of view. In particular, the NRTL and UNIQUAC equations yield better results than those obtained with Wilson's equation. The experimental data were also compared with those predicted by adopting the UNIFAC method, and the results are reported in Table IV. Once again, the comparison confirmed the ability of the UNIFAC method to predict VLE data for multicomponent systems; in fact, one can observe that the mean deviations relating to the values calculated by means of UNIFAC are of the same order of magnitude as those pertaining to the values obtained with the Wilson, NRTL, and UNIQUAC equations.

This behavior is illustrated in Figure 4, in which the isotherms of the liquid and vapor calculated with the NRTL equation and UNIFAC method are plotted along with some experimental points in the temperature range 69.7–70.3 °C.

Finally, so far as the ternary azeotrope is concerned, both the experimental data and the various equations employed exclude its existence.

Table IV. Mean Deviations between Experimental Data and Values Predicted by UNIFAC Method

	$\bar{E}_T$	$E_{T,\max}$	$\bar{E}_{y_1}$	$E_{y_1,\max}$	$\bar{E}_{y_2}$	$E_{y_2,\max}$
acetone (1)–ethyl acetate (2)	0.3	1.2	0.0085	0.020		
acetone (1)–ethanol (2)	1.1	1.4	0.038	0.061		
ethyl acetate (1)–ethanol (2)	0.34	0.6	0.012	0.026		
acetone (1)–ethyl acetate (2)–ethanol (3)	2.33	3.4	0.044	0.106	0.025	0.084

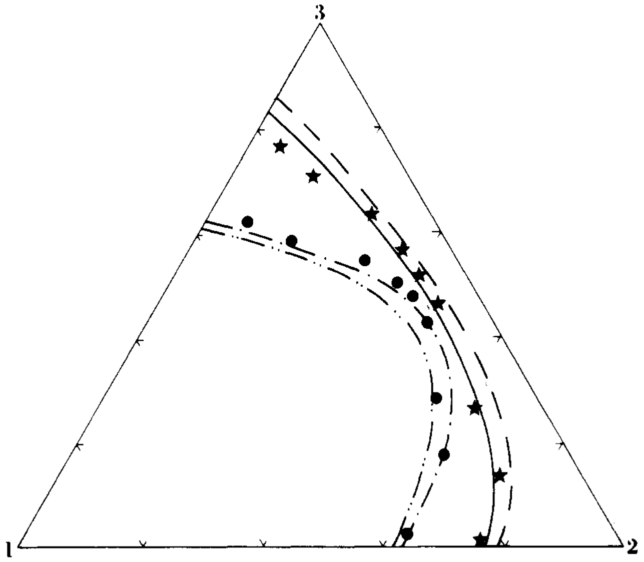

Figure 4. Vapor–liquid isotherms for the system acetone (1)–ethyl acetate (2)–ethanol (3) at 70.0 °C and 760 mmHg: (●) vapor, (★) liquid, (---) UNIFAC liquid isotherm, (-·-) UNIFAC vapor isotherm, (—) NRTL liquid isotherm, (-···-) NRTL vapor isotherm.

Glossary

A_{ij}	parameters used in the Wilson, NRTL, and UNIQUAC equations
g_{ij}	interaction parameter in the NRTL equation
α_{ij}	nonrandomness parameter in NRTL equation
λ_{ij}	interaction parameter in the Wilson equation
u_{ij}	interaction parameter in the UNIQUAC equation
q_i	relative van der Waals surface area of component i
r_i	relative van der Waals volume of component i
v_i	liquid molar volume of component i
x_i	mole fraction of component i in the liquid phase
y_i	mole fraction of component i in the vapor phase
n	number of data
$\bar{E}_T$	mean deviation for T, $\bar{E}_T = (1/n)\sum(T_{\text{exptl}} - T_{\text{calcd}})$
$\bar{E}_{yi}$	mean deviation for y_i, $\bar{E}_{yi} = (1/n)\sum(y_{i,\text{exptl}} - y_{i,\text{calcd}})$

$E_{T,\max}$ 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.

Literature Cited

(1) Wilson, J. M. *J. Am. Chem. Soc.* **1964**, *86*, 127–30.
(2) Renon, H.; Prausnitz, J. M. *AIChE J.* **1968**, *14*, 135–44.
(3) Abrams, D. S.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 116–28.
(4) Fredenslund, A.; Jones, R. L.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 1986–99.
(5) Şebastiani, E.; Carli, E.; Lacquaniti, C. *Ann. Chim.* (*Rome*) **1970**, *60*, 45–51.
(6) Duffey, H. R. Private communication to T. H. Chilton, 1935, reported in: "Chemical Engineer's Handbook", 3rd ed.; McGraw-Hill: New York, 1950; p 573.
(7) Amer, H. H.; Paxton, R. R.; Van Winkle, M. *Ind. Eng. Chem.* **1956**, *48*, 142–6.
(8) Vinichenko, I. G.; Susarev, M. P. *Zh. Prikl. Khim.* **1966**, *39*, 1583–9.
(9) Šubrahmanyam, V.; Murty, P. C. *J. Appl. Chem.* **1964**, *14*, 500–2.
(10) Murty, P. S.; Van Winkle, M. *Chem. Eng. Data Ser.* **1956**, *3*, 72–81.
(11) Gmehling, J.; Onken, V. "Vapor–Liquid Equilibrium Data Collection"; DECHEMA Chemistry Data Series: Frankfurt, 1977–78; V. 1/2a.

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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) = $5.900770034 \times 10^{-2}$ 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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