

the lithium chloride solutions, showing a specific effect due to the hydrogen ion. Much further information on the properties of these solutions will be necessary before any quantitative analysis of these effects can be attempted.

In connection with the present data an attempt was made to test the applicability in the case of a weak electrolyte of Åkerlöf's equation¹³ for the solubility of strong electrolytes. Åkerlöf¹⁴ has derived equations to fit the data of Herz and Paul⁹ on the solubility of mercuric chloride in solutions of lithium and calcium chlorides. Since the data of these latter authors exhibit internal inconsistencies of several per cent., the agreement of the equations with the data in these two cases cannot be considered as very significant. It has been found impossible to fit similar equations to the data of this paper. The Åkerlöf equation is of the form

$$\log P = f(m)$$

where P is the thermodynamic solubility product and $f(m)$ contains terms in $\log m$ and hence cannot be solved explicitly for m . Writing

$$\delta_i = \log P - f(m_i)$$

it is possible to calculate and minimize $\sum \delta_i^2$ and thus develop a least square procedure for treating

(13) Åkerlöf and Thomas, *THIS JOURNAL*, **56**, 593 (1934).

(14) Åkerlöf, *J. Phys. Chem.*, **41**, 1053 (1937).

the data. The necessary equations have been derived and applied to the present data in the cases of hydrochloric acid and lithium chloride solutions. The equations so obtained do not reproduce the experimental data, and the constants of the equations are so widely discrepant that they lose all physical significance. That the least square procedure is adequate has been tested by applying it to the case of potassium ferri-cyanide in potassium chloride solutions.¹⁴ An entirely satisfactory equation was thus obtained. The least square calculations were done using the smoothed data, hence the ill effects of one or two somewhat erroneous determinations have been largely avoided. It appears, then, that while the Åkerlöf equation gives excellent results with strong electrolytes it cannot be applied to the case of a weak electrolyte which forms complex ions in solution.

Summary

1. The solubility at 25° of mercuric chloride in water and in solutions of various chlorides has been determined.

2. In the concentration range corresponding to the solid phase HgCl_2 the results suggest that the $\text{HgCl}_2\text{-Cl}^-$ complex is similar in all cases studied.

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The Critical Constants of Ethane

BY JAMES A. BEATTIE, GOUQ-JEN SU AND GERALD L. SIMARD

The critical constants of propane,¹ *n*-butane,² and *n*-heptane³ have all been determined in the same apparatus by the compressibility method.⁴ The compressibility of ethane from 25 to 250° and from 0.5 to 5.0 moles per liter has been studied⁵; and in the course of the extension of these measurements to a density of 10 moles per liter, we determined the compressibility of ethane for several isotherms in the critical region and located the critical point. Several determinations

of the critical data for ethane are reported in the literature and they will be considered later.

The method of operation has been described elsewhere⁴; for ethane the all-steel bomb was used. The ethane was from the same stock used in the earlier measurements⁵ and was supplied by the Buffalo Laboratory of The Linde Air Products Company through the courtesy of Dr. L. I. Dana. It was distilled several times to re-

TABLE I

THE EFFECT OF VARYING THE VAPOR VOLUME ON THE VAPOR PRESSURE OF ETHANE AT 25.00° (INT.)

Vapor volume, cc.	40	25	14	6
V. p., normal atm.	41.377	41.378	41.378	41.379
Vapor volume, cc.	3	0.7	0.4	0.2
V. p., normal atm.	41.379	41.378	41.378	41.378

(1) J. A. Beattie, N. Poffenberger and C. Hadlock, *J. Chem. Phys.*, **3**, 96 (1935).

(2) J. A. Beattie, G. L. Simard and G.-J. Su, *THIS JOURNAL*, **61**, 24 (1939).

(3) J. A. Beattie and W. C. Kay, *ibid.*, **59**, 1586 (1937).

(4) J. A. Beattie, *Proc. Am. Acad. Arts Sci.*, **69**, 389 (1934).

(5) J. A. Beattie, C. Hadlock and H. Poffenberger, *J. Chem. Phys.*, **3**, 93 (1935).

TABLE II
ISOTHERMS OF ETHANE (C₂H₆) IN THE CRITICAL REGION
Molecular Weight, 30.0462

Critical point from Fig. 1: $t_c = 32.27 \pm 0.01^\circ$ (Int.), $p_c = 48.20 \pm 0.02$ normal atm., $v_c = 0.148$ liter per mol (4.93 cc. per gram), $d_c = 6.76$ moles per liter (0.203 gram per cc.). The uncertainty in the critical volume and density is 1%.

Temp., °C. (Int.)	Density moles/liter	Volume liters/mole	32.200	32.250	32.260	32.270	32.280	32.300
			Pressure, normal atmospheres					
5.682	0.1760		48.0930	48.1345		48.1510		48.1800
5.938	.1684		48.1205	48.1650	48.1750	48.1830	48.1915	48.2140
6.028	.1659		48.1245					
6.124	.1633		48.1295	48.1755	48.1845	48.1950	48.2040	
6.219	.1608		48.1310	48.1775	48.1885			48.2285
6.321	.1582		48.1325	48.1805	48.1905	48.2010	48.2120	
6.423	.1557			48.1830	48.1935	48.2025	48.2135	48.2340
6.527	.1532	48.1325		48.1835	48.1945	48.2035	48.2140	48.2345
6.640	.1506			48.1850	48.1950	48.2045	48.2155	48.2350
6.752	.1481	48.1335		48.1840	48.1955	48.2055	48.2165	48.2370
6.873	.1455			48.1850	48.1955	48.2065	48.2175	48.2375
6.993	.1430	48.1335		48.1850	48.1965	48.2080	48.2185	48.2390
7.117	.1405	48.1330		48.1865	48.1975	48.2090	48.2210	48.2405
7.252	.1379	48.1345		48.1880	48.1995	48.2100	48.2225	
7.386	.1354	48.1345		48.1885	48.2015	48.2125		48.2445
7.530	.1328	48.1400		48.1930	48.2060	48.2170	48.2325	
7.675	.1303	48.1475		48.2010		48.2265		48.2590
7.981	.1253	48.1825		48.2370				48.3010

move permanent gases. The vapor pressures at 25° as a function of the vapor volume are given in Table I. The vapor pressure at 25°, 41.38 normal atm., is in good agreement with the value, 41.37 atm., previously found⁵ for this sample.

Results

In Table II are given the compressibility data in the critical region, and these values are plotted in Fig. 1. The pressures are given to 0.0005 atm. since relative values are consistent to about 0.001 atm. The critical data resulting from our measurements are given in Table II.

Germann and Pickering⁶ select $t_c = 32.1^\circ$, $p_c = 48.8$ atm., $d_c = 0.21$ g. per cc., giving most weight to the measurements of Cardoso and Bell⁷ for t_c and p_c . Our data are in better agreement with the measurements of Prins,⁸ who gives $t_c = 32.32^\circ$, $p_c = 48.13$, d_c not measured. Recently Sage, Webster, and Lacey⁹ have found $t_c =$

(6) "International Critical Tables," Vol. III, 1928, p. 248; see S. F. Pickering, Sci. Papers Bur. Standards, No. 541 (1926).

(7) E. Cardoso and R. Bell, *J. Chim. Phys.*, **10**, 497 (1912).

(8) Prins, *Proc. Acad. Sci., Amsterdam*, **17**, II, 1095 (1915). Data reported in reference 6.

(9) B. H. Sage, D. C. Webster and W. N. Lacey, *Ind. Eng. Chem.*, **29**, 658 (1937).

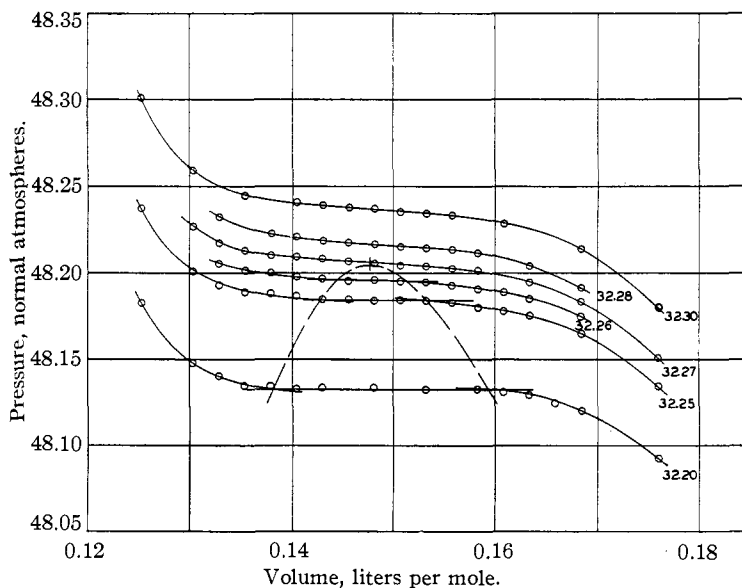


Fig. 1.—Isotherms of ethane in the critical region. The radius of each circle is 0.002 atm.

32.5° , $p_c = 48.9$ atm., $d_c = 0.212$ g. per cc.

Summary

The critical constants of ethane (C₂H₆, mol. wt. 30.0462) are: $t_c = 32.27 \pm 0.01^\circ$ C. (Int.), $p_c = 48.20 \pm 0.02$ normal atm., $v_c = 0.148$ liter per mole (4.93 cc. per gram), $d_c = 6.76$ moles per liter (0.203 gram per cc.). The uncertainty in the critical volume and density is 1%.

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