[CONTRIBUTION FROM THE NORTHERN REGIONAL RESEARCH LABORATORY[1]]

The Solubility of Propane and the Butanes in Ethanol[2]

BY CARL B. KRETSCHMER AND RICHARD WIEBE

The solubility of propane, *n*-butane and isobutane in ethanol was measured at temperatures between 0 and 50° and at pressures up to one atmosphere. The second virial coefficients of these gases were measured at 30°. A semi-empirical equation was fitted to the solubilities, which are reported as mole fraction of hydrocarbon at a given total pressure. The partial molal excess free energy and entropy and the partial molal heat of mixing of the hydrocarbons at infinite dilution were calculated from the data. The solutions exhibit large positive deviations from Raoult's law, and the excess partial molal entropies are negative.

This is a continuation of previous work on the solubility of selected substances in alcohols and alcohol–hydrocarbon mixtures.[3,4] The most extensive data on the solubility of the lower hydrocarbons were obtained in the I. G. Laboratories, and the work was summarized recently.[5] These measurements, however, were not of very great accuracy and were made at one temperature only. A review article on gas solubility,[6] published in 1941, lists no accurate measurements of the solubility in the lower alcohols of any gaseous hydrocarbons except methane.

In order to obtain a more accurate and complete picture of the solubility relationships of the lower hydrocarbons in alcohols, the present work was undertaken.

Experimental

Apparatus.—Figure 1 shows the apparatus. The manometer A of 15 mm. inside diameter was read with a cathetometer, and all necessary corrections were applied to ensure that the uncertainty in pressure measurements was less than 0.05 mm. The gas buret B consisted of eight 35-ml. bulbs joined by 3-mm. capillary tubing. (Only five bulbs are shown in Fig. 1.) It was kept at 30° by circulating water from a constant-temperature bath through the jacket. For each bulb the volume between lines etched on the connecting tubes was determined from the weight of mercury contained, with an uncertainty of a few thousandths of a milliliter.

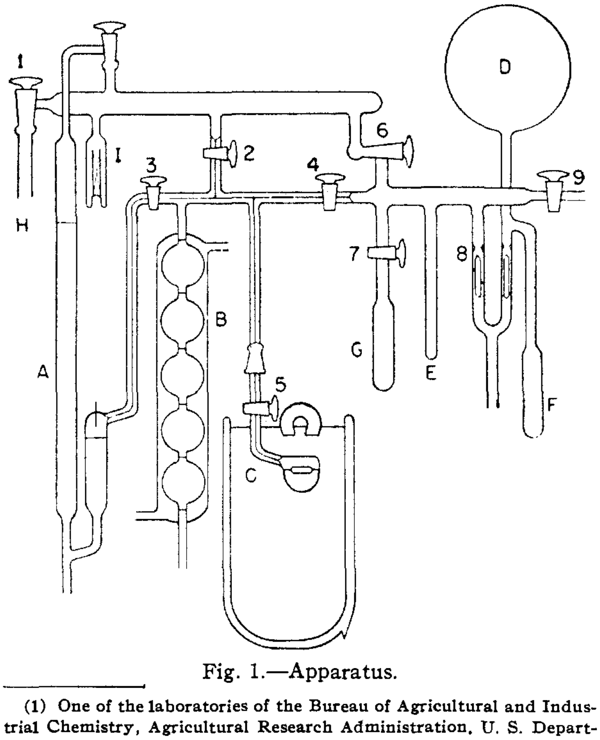

Fig. 1.—Apparatus.

The solubility bulb C having a volume of 23 ml. was connected to the apparatus through a ground joint so that it could be removed and weighed. It contained a stirrer consisting of iron wire sealed into a light glass capsule which floated on the surface of the solution in the bulb and was actuated by a rotating permanent magnet above the bulb. Bulb C was immersed in a constant-temperature bath contained in a one-gallon dewar vessel. The bath was controlled by a platinum resistance thermometer in a bridge circuit operating a galvanometer and photoelectric-cell relay. A second platinum resistance thermometer and a Mueller bridge served to measure the temperature of the bath. The reported temperatures are believed to have an uncertainty of the order of 0.005°. For measurements below room temperature the water in the bath was replaced by a mixture of carbon tetrachloride and chloroform which was circulated through a coil immersed in a cooling mixture.

The connecting tubing between the manometer, the buret and the solubility bulb as far as stopcocks 2 and 4 was all capillary tubing of 2-mm. or smaller bore. The portion of the apparatus to the right of 4 was used for purification and storage of the gas. The apparatus was joined at H to a high vacuum system.

The dead volume of 7.3 ml., bounded by a plane through the tungsten reference point in the short arm of the manometer, the uppermost graduation mark on the buret and stopcocks 2, 4 and 5, was determined by a gas expansion method. A quantity of dry air was isolated in the gas measuring system and pressures were read at three different buret settings. In making readings the mercury was set to the reference point and the height of the meniscus was measured so that the gas volume could be corrected for the covolume of the meniscus. The second virial coefficient of air was taken into account in calculating the dead volume. The three observations yielded two independent evaluations of the dead volume, and the agreement between these demonstrated that the number of moles of gas in the system could be determined with a precision of one part in ten thousand.

The volume of the solubility bulb C was determined by the same method. It was also determined from the weight of alcohol required to fill the bulb. The two results agreed very closely.

Materials.—Purification and storage of the ethanol were as previously described.[7] Several density determinations during the course of the work gave $d^{25}{}_4$ 0.78505. The gases were Research Grade hydrocarbons from the Phillips Petroleum Company, reported to have the following purities in mole per cent.: propane 99.99$^+$, *n*-butane 99.78 ± 0.08, isobutane 99.88 ± 0.06. They were not further purified, except for the removal of air and traces of moisture introduced during transfer of the gas into the apparatus. Sufficient gas was introduced through stopcock 9 to fill flask D to atmospheric pressure. The gas was distilled from bulb F at −78° to bulb G at −196°. With stopcock 7 closed, F was warmed and the water and permanent gases were

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

[2] This paper was presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Cleveland, Ohio, April 8–12, 1951.

[3] C. B. Kretschmer and R. Wiebe, *Ind. Eng. Chem.*, **37**, 1130 (1945).

[4] C. B. Kretschmer, J. Nowakowska and R. Wiebe, *ibid.*, **38**, 506 (1946).

[5] P. Feiler, "Solubility of Gaseous Hydrocarbons in Organic Solvents," Charles A. Meyer and Co., New York, N. Y., 1947.

[6] A. E. Markham and K. A. Kobe, *Chem. Revs.*, **28**, 519 (1941).

[7] C. B. Kretschmer, J. Nowakowska and R. Wiebe, THIS JOURNAL, **70**, 1785 (1948).

pumped out. Stopcock 7 was opened and the residual gas was pumped from G. The distillation was repeated until the residual pressure after condensation of the hydrocarbon at −196° was less than one micron as measured on Pirani gage I. In the case of propane it was necessary to pump off about one-third of the sample from the liquid phase at −78° to remove all permanent gas. The gas was stored in flask D closed by mercury float valve 8.

Procedure.—Bulb C was evacuated and weighed, and about 15 ml. of ethanol was condensed in it from the ethanol storage flask. It was attached to the system and, with the stirrer operating, a small amount of ethanol was distilled through stopcocks 5, 4 and 7 into bulb G at −78°. The dissolved gas liberated in this step was expanded through 6 into the vacuum manifold where its pressure was measured with the Pirani gage. The system as far as stopcock 5 was pumped out and the process was repeated. At each repetition the Pirani gage reading became less until it finally reached a constant value dependent on the vapor pressure of the alcohol, showing that all dissolved gas had been removed from the alcohol. The bulb was removed, weighed and replaced.

A quantity of hydrocarbon was condensed in calibrated tube E sufficient to fill the gas-measuring system to a convenient pressure. It was vaporized into the gas-measuring system through stopcock 4, which was then closed. The initial amount of gas in the system was measured. The stirrer was started and stopcock 5 was opened to allow gas to enter bulb C. The mercury level in the short arm of the manometer was kept below the reference point by raising the mercury in the buret. During the final stages of the approach to equilibrium, the mercury level in the buret was left unchanged and stopcock 5 was opened only occasionally. Equilibrium was considered to be reached when the pressure remained unchanged upon opening 5 after ten minutes stirring of the solution. This pressure was measured, the mercury in the buret was adjusted to one of the marks, and the amount of gas remaining in the system was measured. The gas was compressed to a higher pressure and equilibrium was again established. In this manner as many as four measurements were made with each sample of ethanol at different pressures up to 760 mm.

Calculations.—The volumetric behavior of the hydrocarbons and the alcohol vapor may be expressed with sufficient accuracy for the present purpose by the equation of state

$$pV = nRT(1 + \beta p) \qquad (1)$$

which involves only the second virial coefficient β. If p is expressed in atm., β is in atm.$^{-1}$. The number of moles of gas in the gas-measuring system was calculated from equation (1). A suitable correction for the dead space was applied, and the value of R was taken to be 0.0820544 ± 0.0000034 liter atm. deg.$^{-1}$.[8] The difference between initial and final values gave the number of moles of hydrocarbon which had entered bulb C. The number of moles of ethanol in C was obtained from the weights of the bulb empty and with the ethanol. The bore of stopcock 5 and two-thirds of the capillary below it—a total volume of 0.090 ml.—were assumed to be filled with pure hydrocarbon at a temperature half-way between that of the bath and the room. This assumption was justified by the observation that no alcohol condensed in the capillary above the bath level when the bath was at 50°—*i.e.*, the alcohol could not diffuse very far into the one-mm. capillary joining stopcock 5 to bulb C.

The remaining hydrocarbon and the alcohol were distributed between liquid and vapor phases in the remaining volume of the bulb. The number of moles n_i of either component in the vapor phase was calculated from the equation

$$n_i = p_i V_g / RT(1 + \beta_1 p_1 + \beta_2 p_2) \qquad (2)$$

In equation 2 and the remainder of this paper, subscripts 1 and 2 refer to ethanol and hydrocarbon, respectively, and subscript i refers to either component. V_g is the volume occupied by the vapor, and p is the total pressure; p_i is the partial pressure of component i, $p_i°$ its vapor pressure in the pure state, x_i its mole fraction in the solution, β_i its second virial coefficient, and v_i its liquid molal volume. Equation 2 is based on the assumption that the second virial coefficient of the vapor mixture is equal to $(p_1\beta_1 + p_2\beta_2)/p$. The partial pressure of ethanol p_1 was calculated from the equation

$$\log(p/{}_1p_1{}^\circ x_1) = 1.6x_2^2 - (p - p_1^\circ)(\beta_1 - v_1/RT)/2.3 \qquad (3)$$

based on the consideration that the logarithm of the activity coefficient of ethanol at small values of x_2 must be proportional to x_2^2. The factor 1.6 was taken from results for the system ethanol–methylcyclohexane.[9] It is somewhat too high for the present systems, but the resulting error is negligible. The partial pressure of hydrocarbon p_2 is equal to $p - p_1$. V_g was obtained by subtracting from the total volume the sum of the volumes of liquid ethanol and dissolved hydrocarbon.

The calculation was carried out by successive approximations. Initial values of V_g and x_2 were calculated assuming that the total contents of the bulb were in the liquid phase, and these values were used in equations (2) and (3) to calculate the amounts in the vapor. These were subtracted from the total amounts of ethanol and hydrocarbon to give values of V_g and x_2 which were used in the next step. The process converged in about three steps.

The molal volumes of the dissolved hydrocarbons were estimated by extrapolating recorded values of liquid density at higher pressures[10–17] to zero pressure. It was assumed that the hypothetical liquid hydrocarbon at zero pressure would mix with ethanol with no volume change. Since the allowable error in molal volume of hydrocarbon is 3%, this assumption should be adequate. Molal volumes of ethanol were taken from previous work.[7]

The recorded information on low-pressure volumetric behavior of the butanes is rather fragmentary and discordant. Therefore, the second virial coefficients at 30° were measured in the apparatus of Fig. 1. The pressure exerted by a sample of gas in the buret was measured at three different volumes. A plot of pV *vs.* p was linear within experimental error: $pV = k + lp$. By comparison with equation (1), $\beta = l/k$.

With the present apparatus, β could be measured with an uncertainty of about 5 × 10^{-4} atm.$^{-1}$. The following values of $-\beta$ in atm.$^{-1}$ at 30° were obtained and were used in the calculations: for propane, 0.0159; for *n*-butane, 0.0306; for isobutane, 0.0259. They may be compared with the values 0.0155 for propane obtained by Deschner and Brown,[18] and 0.03174 for *n*-butane and 0.02814 for isobutane obtained by Jesson and Lightfoot.[19]

Values of β at other temperatures were estimated from the values at 30°. For propane the temperature dependence

TABLE I

ESTIMATED LIQUID MOLAL VOLUMES AND SECOND VIRIAL COEFFICIENTS OF HYDROCARBONS

Temp., °C.	Propane	*n*-Butane	Isobutane
0°, v, ml.	83.2		
$-\beta$, atm.$^{-1}$	0.0217		
10°, v			102.1
$-\beta$			0.0316
25°, v	89.6	101.4	105.7
$-\beta$	0.0168	0.0326	0.0273
35°, v		103.6	108.2
$-\beta$		0.0288	0.0242
50°, v	100.4	106.8	112.6
$-\beta$	0.0129	0.0240	0.0204

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[8] D. D. Wagman, *et al.*, *J. Res. Natl. Bur. Standards*, **34**, 143 (1945).

[9] C. B. Kretschmer and R. Wiebe, THIS JOURNAL, **71**, 3176 (1949).

[10] B. H. Sage, J. G. Schaafsma and W. N. Lacey, *Ind. Eng. Chem.*, **26**, 1218 (1934).

[11] H. H. Reamer, B. H. Sage and W. N. Lacey, *ibid.*, **41**, 482 (1949).

[12] B. H. Sage, D. C. Webster and W. N. Lacey, *ibid.*, **29**, 1188 (1937).

[13] W. B. Kay, *ibid.*, **32**, 358 (1940).

[14] C. C. Coffin and O. Maass, THIS JOURNAL, **50**, 1427 (1928).

[15] J. A. Beattie, D. G. Edwards and S. Marple, *J. Chem. Phys.*, **17**, 576 (1949).

[16] R. C. Wackher, C. B. Linn and A. V. Grosse, *Ind. Eng. Chem.*, **37**, 464 (1945).

[17] B. H. Sage and W. N. Lacey, *ibid.*, **30**, 673 (1938).

[18] W. W. Deschner and G. G. Brown, *ibid.*, **32**, 386 (1940).

[19] F. W. Jesson and J. H. Lightfoot, *ibid.*, **28**, 870 (1936); **30**, 312 (1938).

found by Casado, Massie and Whytlaw-Gray[20] was used, and for the butanes Roper's values for the butenes[21] were used to estimate the temperature dependence of β. Table I gives the molal volumes and second virial coefficients used in the calculations.

The equation of Keyes, Smith and Gerry[22] was used to estimate β for ethanol. This probably gives values of $-\beta$ which are too small. However, it can be shown that the calculated quantity of gas in the vapor phase is influenced only very slightly by the value of β used for the solvent vapor. It can also be shown that the existence of a quadratic term in the equation for the second virial coefficient of the vapor mixture

$$\beta = (p_1\beta_1 + p_2\beta_2)/p + p_1p_2\beta_{12}/p^2$$

would have a negligible effect on the result.

Results and Discussion

Table II gives the experimental values of vapor pressure and composition of the solutions. The vapor pressures for pure ethanol were calculated from the equation previously published.[23] By way of illustration, the results for *n*-butane at 25 and 50° are plotted in Fig. 2 together with the ideal vapor pressures calculated by means of Raoult's law. The solutions obey Henry's law only approximately, as is apparent from the curvature of the plots, and exhibit large positive deviations from Raoult's law.

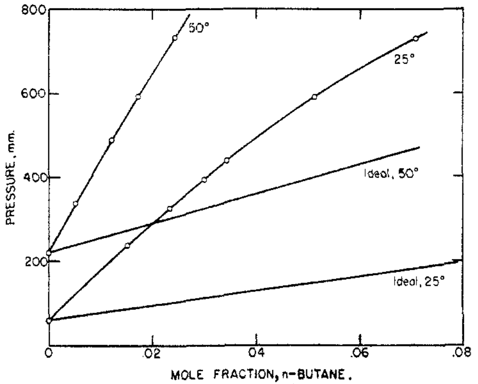

Fig. 2.—Vapor pressure of solutions of *n*-butane in ethanol.

TABLE II

VAPOR PRESSURE OF SOLUTIONS OF HYDROCARBONS IN ETHANOL

Propane		*n*-Butane	
x_2[a]	p[b]	x_2	p
0°		25°	
0	11.8	0	59.0
0.01497	309.8	0.01517	238.0
.02706	532.0	.02334	325.8
.04054	762.2	.02999	393.3
		.03440	436.8
25°		.05144	589.9
0	59.0	.07092	739.5
0.005089	248.3		
.01003	427.5	35°	
.01434	579.8	0	103.1
.01941	755.3	0.008298	233.0
		.01484	330.1
50°		.02198	430.5
0	221.0	.04476	719.3
0.003201	412.0		
.006342	596.4	50°	
.009245	764.4	0	221.0
		0.005210	337.8
		.01218	487.5
		.01716	590.6
		.02442	733.5
Isobutane			
10°		35°	
0	23.4	0	103.1
0.03528	389.7	0.009550	313.1
.05443	549.6	.01643	455.2
		.02391	602.4
25°		.03241	760.4
0	59.0		
0.009739	226.9	50°	
.01454	305.8	0	221.0
.02316	439.5	0.003121	317.3
.04368	725.4	.006801	429.2
		.01064	542.3
		.01828	758.7

[a] Mole fraction of hydrocarbon. [b] Total pressure in mm.

Since we plan to extend these measurements to other alcohols and possibly other light hydrocarbons, an effort was made to find a simple equation that would fit the results quite accurately, to minimize the number of experimental determinations required in further work. The excess partial molal free energy of the hydrocarbon $\overline{F}_2^{\mathrm{E}}$ is given by the equation

$$\overline{F}_2^{\mathrm{E}} = RT \ln (p_2/p_2^\circ x_2) + (p - p_2^\circ)(RT\beta_2 - v_2) \quad (4)$$

At small values of x_2, $\overline{F}_2^{\mathrm{E}}$ is linear in x_1^2, or approximately linear in x_2. If $p - p_1^\circ$ is inserted in place of p_2 in the right-hand side of equation 4, it can be shown that the resulting expression differs from $\overline{F}_2^{\mathrm{E}}$ by terms which are linear in x_2 for small values of x_2. Therefore, the equation

$$\log [(p - p_1^\circ)/x_2] + p(\beta_2 - v_2/RT)/2.3 = q - rx_2 \quad (5)$$

was tried and was found to reproduce the data accurately. It was found that for each hydrocarbon r has the same value at all temperatures. The dependence of q on temperature was fitted with an equation of the Antoine type

$$q = A - B/(t + C)$$

which is known[24] to provide a good representation for activity coefficients as well as for vapor pressures. The vapor pressures of the solutions are then given by the equation

$$\log [(p - p_1^\circ)/x_2] + p(\beta_2 - v_2/RT)/2.3 = A - B/(t + C) - rx_2 \quad (6)$$

with the values of the coefficients listed in Table III. Equation 6 can be solved for either p or x_2 in

TABLE III

COEFFICIENTS IN VAPOR PRESSURE EQUATION FOR SOLUTIONS OF HYDROCARBONS IN ETHANOL

Solute	A	B	C	r
Propane	6.39065	364.94	176	1.50
n-Butane	6.45405	474.61	176	1.78
Isobutane	6.37276	413.88	170	1.83

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(20) F. L. Casado, D. S. Massie and R. Whytlaw-Gray, *J. Chem. Soc.*, 1746 (1949).

(21) E. E. Roper, *J. Phys. Chem.*, **44**, 835 (1940).

(22) F. G. Keyes, L. B. Smith and H. T. Gerry, *Proc. Am. Acad. Arts Sci.*, **70**, 319 (1936).

(23) C. B. Kretschmer and R. Wiebe, THIS JOURNAL, **71**, 1793 (1949).

(24) G. W. Thomson, *Chem. Revs.*, **38**, 1 (1946).

terms of the other by a trial and error process. None of the observed vapor pressures differ from those calculated from equation 6 by more than 0.5 mm. The probable error of the determinations is considered to be somewhat less than 0.5 mm.

The excess partial molal free energy of the hydrocarbons at infinite dilution was calculated from equations 4 and 6. Vapor pressures of propane and *n*-butane required in this calculation were obtained from the equations published by Thodos[25] and that of isobutane was interpolated from the measurements of Aston[26] and Beattie.[15] The partial molal heats of mixing and excess entropies at infinite dilution were obtained from the free energies by standard thermodynamic formulas. The values are listed in Table IV. The excess entropy is seen to be negative, as it is for higher hydrocarbons in ethanol.[7,9,23] The excess partial molal free energy, which is a measure of the deviation from ideal behavior, increases on going from propane to the butanes, and for isoöctane in ethanol it amounts to 1470 cal./mole at 50°.[7]

TABLE IV

EXCESS PARTIAL MOLAL THERMODYNAMIC FUNCTIONS OF HYDROCARBONS AT INFINITE DILUTION, CAL./MOLE

Temp., °C.	$\overline{F}_2{}^E$	$\overline{H}_2{}^M$	$-T\overline{S}_2{}^E$
	Propane		
0	1020	147	873
25	1096	244	851
50	1164	315	848
	n-Butane		
25	1187	395	792
35	1213	439	774
50	1249	511	738
	Isobutane		
10	1158	227	931
25	1205	362	843
35	1231	456	775
50	1266	573	693

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[25] G. Thodos, *Ind. Eng. Chem.*, **42**, 1514 (1950).

[26] J. G. Aston, R. M. Kennedy and S. C. Schumann, THIS JOURNAL, **62**, 2059 (1940).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Diffusion Coefficient of Zinc Sulfate in Dilute Aqueous Solution at 25°

BY HERBERT S. HARNED AND ROBERT M. HUDSON

The diffusion coefficient of zinc sulfate from 0.001 to 0.005 molar concentration has been determined by the conductometric method. The experimental results are considerably higher than those computed by the Onsager and Fuoss theory unless the influence of ion-pair formation is taken into consideration. A correction factor has been introduced for ion-pair formation which leads to a reasonable interpretation of the results.

Diffusion coefficients of lithium, sodium[1] and potassium chlorides[2] and potassium nitrate[3] in dilute aqueous solutions determined by the conductance method agree within very narrow limits with the theory of Onsager and Fuoss.[4] Conformity with theory is also found for lithium sulfate while the diffusion of sodium sulfate[5] appears to be somewhat higher than the theoretical value and the diffusion coefficient of calcium chloride[6] is considerably below the theoretical prediction.

To illustrate the behavior of another type of electrolyte, we have measured the diffusion coefficient of zinc sulfate from 0.001 to 0.005 molar. The behavior of this substance in relation to the theory should be interesting since its conductance indicates considerable ion-pair formation and recent work[7,8] has indicated dissociation constants of the order of 0.005 for 2–2 valence type electrolytes. The activity coefficient of zinc sulfate has been determined in dilute solutions from the electromotive forces of cells without liquid junctions by Cowperthwaite and LaMer[9] who found that the extended theory[10] was required to interpret the results. These activity coefficients prove useful in evaluating the thermodynamic factor required by the theory of diffusion.

Experimental Results

The apparatus and technique used in these conductometric measurements is the same as that previously employed in this Laboratory and described in detail.[2] As in the earlier investigations, it is assumed that the difference in conductance at the bottom and top electrodes in the cell is proportional to the difference in salt concentrations at these two positions. That no appreciable error is caused by this approximation is apparent from the data in Table I in which the specific conductances L_1 and L_2, at round concentrations, c_1 and c_2, taken from the measurements of Owen and Gurry are recorded. The last column contains the coefficient $(L_1 - L_2)/(c_1 - c_2)$ when $c_1 + c_2 = 0.011$. This quantity is fairly constant throughout the range considered.

TABLE I

SPECIFIC CONDUCTANCES OF ZINC SULFATE AT 25°

c_1	$L_1 \times 10^3$	c_2	$L_2 \times 10^3$	$[(L_1 - L_2)/(b_1 - c_2)]_{c_1+c_2=0.01}$
0.009	0.77822	0.002	0.21622	0.08029
.008	.70623	.003	.30841	.07956
.007	.63316	.004	.39452	.07955
.006	.55744	.005	.47746	.07998

Highest grade analytical zinc sulfate was purified by twice dissolving in conductivity water and pre-

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[1] Harned and Hildreth, THIS JOURNAL, **73**, 650 (1951).

[2] Harned and Nuttall, *ibid.*, **69**, 737 (1947); **71**, 1460 (1949); Harned and Blake, *ibid.*, **72**, 2265 (1950).

[3] Harned and Hudson, *ibid.*, **73**, 652 (1951).

[4] Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

[5] Harned and Blake, THIS JOURNAL, **73**, 2448 (1951).

[6] Harned and Levy, *ibid.*, **71**, 2781 (1949).

[7] Davies, *Trans. Faraday Soc.*, **23**, 351 (1927).

[8] Owen and Gurry, THIS JOURNAL, **60**, 3078 (1938).

[9] Cowperthwaite and LaMer, *ibid.*, **53**, 4333 (1931).

[10] Gronwall, LaMer and Sandved, *Physik Z.*, **29**, 358 (1928).