De Forcrand,[9] in his determinations of the heat of solution of zinc oxide in acid, used samples of oxide from different sources and thus obtained the following results for the heat of formation:

ZnO prepared from $Zn(OH)_2$ at 125°	82,970 cal.
from $Zn(NO_3)_2$ at 350°	83,000 cal.
from "rouge blanc"	84,300 cal.
by combustion of zinc	84,700 cal.

He considered that his data showed a progressive "polymerization" or transformation of the zinc oxide at high temperatures but, as Maier and Ralston have pointed out, his determinations were not made upon the same samples prepared at high and low temperatures. Certainly our present results obtained with samples of zinc oxide which have been subjected to varying heat treatment fail to confirm this polymerization theory.

Summary

1. ΔH, the heat absorbed in the reaction, $ZnO(s) + 2HCl(2.63\ N) = H_2O + ZnCl_2$ (the resulting solution being about 2.39 N in hydrochloric acid and 0.24 N with respect to zinc chloride), has been found to be —15,263 15° cal. at 20°.

2. By combination of this value with the result of Richards and Burgess for the heat of solution of zinc in acid of the same concentration, the heat of formation of zinc oxide from its elements has been calculated to be 83,240 (±200) cal.

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THE FREEZING POINTS OF AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID[1]

BY HARRIS MARSHALL CHADWELL

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The technique of determining the depression of the freezing point of a solvent by a second chemical substance has improved in two directions since the days of the pioneers in this field. More accurate methods of measuring temperature have been substituted for the mercury thermometer. Thermocouples have been used by Hausrath,[2] Osaka,[3] Jahn,[4]

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[9] De Forcrand, *Ann. chim. phys.*, [7] **27**, 38 (1902).

[1] Determinations similar to those reported in this paper were made in 1922 at the Wolcott Gibbs Memorial Laboratory at Harvard University with the collaboration of Professor T. W. Richards. The platinum thermometer used in the earlier experiments was subsequently ruined during standardization. The technique is practically the same as that developed in 1922.

[2] Hausrath, *Ann. Physik*, [4] **9**, 522 (1902).

[3] Osaka, *Z. physik. Chem.*, **41**, 560 (1902).

[4] Jahn, *ibid.*, **59**, 31 (1907).

Dixon,[5] Flügel,[6] Adams,[7] Harkins[8] with students, Randall and Vanselow[9] and Hovorka and Rodebush.[10] Bedford,[11] and Barnes, Archibald and McIntosh[12] used a differential platinum thermometer and Griffiths,[13] as long ago as 1891, employed the platinum thermometer for boiling- and freezing-point determinations.

The second development is that of improving the determination of concentration. Roloff[14] was the first to analyze his solution after a large amount of solid solvent had separated. Some method of analyzing the solution in equilibrium with the solid solvent has been used in all of the modern determinations. The same end was accomplished by Walker and Robertson[15] and by Richards[16] when they mixed the solution with pieces of ice. This method has distinct advantages, as enumerated in the latter paper.

The most careful determinations of the freezing point of dilute solutions of hydrochloric acid by Randall and Vanselow[9] include these improvements and constitute, with those of Hovorka and Rodebush,[10] the most refined experiments reported.

The purpose of the present experiments was to extend the results to more concentrated solutions. The activity coefficients as calculated by the methods of Lewis and Randall[17] are also reported.

Experimental Procedure

Temperature intervals were measured with a platinum thermometer and Wheatstone bridge manufactured by the Leeds and Northrup Company. The thermometer and bridge were standardized by the Bureau of Standards, the thermometer having a resistance in melting ice, (R_0), of 25.246 international ohms, a fundamental interval (F. I.) of 9.8059 ohms, a value of δ (in the Callendar formula) of 1.509 and an accuracy of 0.01% in the measurement of temperature intervals. The bridge was certified to be reliable to 0.00005 ohms under specified conditions. The bridge was maintained at a constant temperature within 0.1° by a suitable thermostat. A current of approximately 3 milli-amperes was used through the thermometer. As a consequence of the precautions taken, none of the connections being changed during the experiments and the

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[5] Dixon, *Sci. Proc. Roy. Dublin Soc.*, **13**, 49 (1911).

[6] Flügel, *Z. physik. Chem.*, **79**, 577 (1912).

[7] Adams, THIS JOURNAL, **37**, 481 (1915).

[8] Harkins *et al.*, *ibid.*, **38** (8 papers), 2643–2717 (1916).

[9] Randall and Vanselow, *ibid.*, **46**, 2418 (1924).

[10] Hovorka and Rodebush, *ibid.*, **47**, 1614 (1925).

[11] Bedford, *Proc. Roy. Soc. (London)*, **83A**, 454 (1910).

[12] Barnes, Archibald and McIntosh, THIS JOURNAL, **27**, 47 (1905).

[13] Griffiths, *ibid.*, **48**, 220 (1891) [through *Jour. Chem. Soc.*, **60**, ii, 251 (1891)]; also Elliott, *J. Phys. Chem.*, **28**, 611 (1924).

[14] Roloff, *Z. physik. Chem.*, **18**, 572 (1895).

[15] Walker and Robertson, *Proc. Roy. Soc. Edinburgh*, **24**, 363 (1903).

[16] Richards, *Z. physik. Chem.*, **44**, 563 (1903); THIS JOURNAL, **25**, 291 (1903).

[17] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, Chapter 27.

battery and galvanometer circuits including mercury-cup switches, the recorded temperature intervals should be accurate to 0.0005°, making certain the third decimal figure.

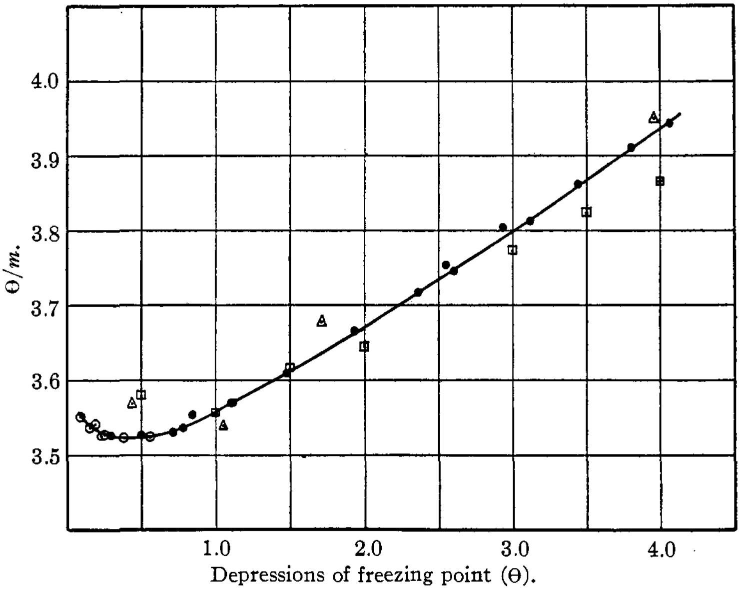
The temperatures were calculated by the Callendar formula

$$pt = \frac{R_t - R_0}{FI} \times 100$$

$$t - pt = \delta \left(\frac{t}{100} - 1\right)\left(\frac{t}{100}\right)$$

where t is the temperature in Centigrade degrees and pt the "platinum temperature."

The apparatus in which the freezing mixture was maintained consisted of an unsilvered Dewar cylinder of Pyrex glass approximately 24 cm. deep with an inside diameter of 5 cm. It was fitted with a rubber stopper holding the thermometer, a stirrer, a tube for the withdrawal of a sample of solution and a tube by which the system could be evacuated or pressure applied. The tube for the removal of the sample extended to a depth about three-quarters down the coil of platinum wire in the thermometer and terminated in a small bulb filled with glass wool to prevent the passage of any small pieces of ice.[18] The sample of solution was removed by applying a pressure of clean air, thus avoiding the possibility of losing material in the form of a vapor. This precaution is not so important in the case of solutions of hydrochloric acid as if the solute had an appreciable vapor pressure, when an indeterminate amount of material would be lost if suction was applied.



The data of Richards and Jackson are represented by squares; those given in Landolt and Börnstein's "Tabellen" by triangles, and those of Randall and Vanselow by circles.

Fig. 1.—The change of the ratio Θ/m plotted against Θ; the depressions of the freezing point are plotted as abscissas, the ratios as ordinates.

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[18] For a similar device, see Richards and Fraprie, *Proc. Amer. Acad. Arts Sci.*, **36**, 507 (1901).

The Dewar cylinder was immersed in an agitated bath of ice and salt solution whose concentration was regulated so that the temperature was maintained slightly below that inside the Dewar cylinder.

The water used had been thrice distilled (freed from organic matter, ammonia and carbon dioxide). A sample prepared on the day previous to the experiment was boiled for about two hours to free it from dissolved air, then stoppered in a Pyrex flask and chilled to 0°, cooling under its own vapor. Precautions to prevent the solution of air are necessary, for its solubility may be different in water than in the hydrochloric acid. Randall and Vanselow seem to be the first to report precautions of this nature.

The ice was prepared from a commercial product by shaving—thereby producing a finely divided solid that would make a mush with water—washed three times, finally with the best water. Clear pieces of ice were selected for the preparation of the sample. When this ice was mixed with the water, air was held mechanically in the interstices. This was immediately removed by suction. Precaution was taken to prevent the melting of the ice during the whole manipulation. The temperature of this freezing mixture corresponded well within 0.001° with a mixture of water and ice prepared by supercooling a sample of the best water and then shaking.[19]

The hydrochloric acid was prepared from c. p. acid by fractionally distilling three times, the middle portion being used each time. A final distillation, to remove any dissolved glass, was made just before the experiment. The all-Pyrex distilling apparatus had been used with hydrochloric acid many times. This acid was chilled before introduction into the freezing mixture.

The procedure during a determination was as follows. The washed ice was mixed with the water and evacuated several times to remove air held in the ice and then evacuated again for twenty minutes after the thermometer had been introduced and the apparatus assembled. The pressure was then released and the mixture stirred. The resistance of the thermometer in this ice-bath was determined each day and taken as R_0. A sufficient amount of acid was then added, the system evacuated for about fifteen minutes after a brief preliminary stirring and the resistance of the thermometer measured again (at atmospheric pressure). With a suitable regulation of the temperature in the outside bath, this equilibrium temperature would remain constant within the accuracy of the thermometer for some time. After about five minutes of constant temperature, a final reading was made and the sample withdrawn by applying pressure.

This sample, of approximately 40 cc., was divided into two portions, weighed and analyzed gravimetrically by precipitating and weighing as silver chloride. All weights were reduced to vacuum. The concentrations, expressed in gram equivalents per 1000 g. of solution (6.9764 wt. AgCl/wt. solution) and thence the molality (*m*, the gram equivalents per 1000 g. of solvent), were calculated using the molecular weight of hydrochloric acid as 36.466.

A second point was obtained by adding more chilled water and acid and repeating the technique. Not more than three points were obtained on the same day. The concentrations were so chosen that the determinations

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[19] Ref. 10, p. 2426.

of one day would overlap those of another day, thus producing verifications of previous experiments.

The results are given in Table I. The first column gives the number of the experiment; the second the molality, (m); the third the temperature lowering, (Θ), or the freezing point in degrees below Centigrade zero; and the fourth the ratio of temperature to molality, (Θ/m).

TABLE I

THE FREEZING POINTS OF AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID

No.	m	Θ	Θ/m
1	0.08321	0.2934	3.526
2	.1427	.5033	3.527
3	.2024	.7145	3.530
4	.2198	.7771	3.538
5	.2374	.8440	3.554
6	.3080	1.1000	3.571
7	.3137	1.1202	3.571
8	.4082	1.4738	3.610
9	.5275	1.9344	3.666
10	.6363	2.3664	3.719
11	.6785	2.5465	3.753
12	.6969	2.6114	3.747
13	.7736	2.9420	3.803
14	.8187	3.1219	3.813
15	.8945	3.4545	3.862
16	.9765	3.8192	3.911
17	1.0324	4.0721	3.944

Of these determinations, three are inconsistent with the rest, namely, numbers 5, 11 and 13. They have not been considered in subsequent calculations.

The ratio Θ/m is plotted as ordinate against Θ as abscissa in Figure 1. Data as enumerated in Landolt-Börnstein's "Tabellen,"[20] as well as those of Richards and Jackson[21] and a few of Randall and Vanselow's are plotted for comparison.

Theoretical Calculations

From these data can be calculated by the graphical methods of Lewis and Randall[22] the mean activities of the ions and the activity coefficients. The latter can be compared with those calculated by Lewis and Randall[23] from the e.m.f. measurements of Linhart[24] and those of Scatchard.[25]

The graphical method of calculating the "preliminary activity co-

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[20] Landolt-Börnstein-Roth-Scheel, "Tabellen," 5th ed., **1923**, Vol. II, p. 1441.

[21] Richards and Jackson, *Proc. Am. Acad. Arts Sci.*, **41**, 451 (1906).

[22] Ref. 17, Chapters 23 and 27.

[23] Lewis and Randall, THIS JOURNAL, **43**, 1112 (1921).

[24] Linhart, *ibid.*, **39**, 2601 (1917); **41**, 1175 (1919).

[25] Scatchard, *ibid.*, **47**, 641 (1925).

efficient" (γ'), that applying to the temperature of the freezing mixture and uncorrected for the heat of solution, necessitates the evaluation of areas under curves from infinite dilution to the concentration in question. The value of $\gamma_{25°} = 0.819$ for $m = 0.070$, as interpolated from Scatchard's data, was accepted in order to evaluate the area for more dilute solutions. If the value of $\gamma_{25°} = 0.824$ (interpolated from Randall and Vanselow's data) is used, the results are correspondingly higher.

The calculation of the factor by which the "preliminary activity coefficient" must be multiplied to give the corrected activity coefficient at 25° requires a knowledge of heat data, all of which are not available in the literature. The values for the partial molal heat capacities ($\overline{c_{p_1}}$) were taken from the paper of Randall and Ramage,[26] while those for the partial molal heat content of the solvent ($\overline{L}_1$) were very generously supplied by Professor Merle Randall.[27] The results of these calculations are given in Table **II**.

TABLE II

COMPARISON OF THE ACTIVITY COEFFICIENTS[a]

m	γ'	γ/γ'	$\gamma_{25°}$, F.P.	$\gamma_{25°}$, S.	$\gamma_{25°}$, L. and R.
0.1	0.803	0.996	0.800	0.801	0.804
.2	.780	.992	.774	.774	.783
.3	.773	.987	.763	.763	.768
.4	.774	.983	.761	.760	.763
.5	.781	.980	.765	.763	.762
.6	.789	.977	.771	.770	.770
.7	.800	.974	.779	.777	.782
.8	.812	.971	.788	.789	.794
.9	.830	.968	.804	.802	.808
1.0	.848	.965	.818	.817	.823

[a] If the value of Randall and Vanselow of $\gamma_{25°} = 0.824$ at $m = 0.070$ is used, the final values of $\gamma_{25°}$ become 0.779 at $m = 0.2$, 0.766 at $m = 0.4$, 0.776 at $m = 0.6$, 0.793 at $m = 0.8$ and 0.823 at $m = 1.0$.

The first column of Table **II** gives the molality; the second the "preliminary activity coefficient" (γ') at the temperature of the freezing point of the solutions and uncorrected for the change in heat content; the third column the factor by which the "preliminary" values are multiplied to give the activity at 25° and calculated from the thermal data. The fourth, fifth and sixth columns compare the final activity coefficients at 25° as calculated from the freezing points, from the e.m.f.'s by Scatchard and from e.m.f.'s as calculated by Lewis and Randall. The agree-

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[26] Randall and Ramage, THIS JOURNAL, **49**, 99 (1927).

[27] Unpublished data. The values were

$m =$	0.2	0.4	0.6	0.8	1.0
$\overline{c_{p_1}} - \overline{c}^{\,0}_{p_1}$	− .0075	− .021	− .039	− .062	−0.084
$\overline{L}_1$	− .33	−1.1	−2.0	−3.1	−4.6

ment is quite satisfactory. Similar data for solutions up to 0.1 *M* have been discussed by Scatchard.[28]

The writer wishes to express his indebtedness and gratitude to the Elizabeth Thompson Science Fund for providing mechanical aid in the calculations.

Summary

A report is made of the determination of the freezing points of aqueous solutions of hydrochloric acid up to a concentration of 1.0 molal, making use of a platinum thermometer as a temperature measuring device.

The activity coefficients are calculated and compared with those derived from electromotive force measurements.

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[CONTRIBUTION FROM THE LABORATORY OF THE LINDE AIR PRODUCTS COMPANY]

SOME PHYSICAL PROPERTIES OF VINYL CHLORIDE

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Although vinyl chloride (C_2H_3Cl) has been known as a chemical compound for a number of years, owing to the difficulties attending its preparation and purification, relatively little exact work has been done with it. Recent progress in chemical synthesis has made this material available in quantity commercially and therefore it has seemed worth while to review previous work on the subject in order to ascertain the present state of knowledge of the properties.

Beyond a few scattered values of the boiling point of vinyl chloride, very little has been published concerning its physical properties. Recently the desirability of utilizing vinyl chloride as a refrigerating fluid (boiling point —13.9°) has been suggested, and hence it has appeared desirable to conduct an experimental determination of its most important physical properties. In this investigation the measurements of the vapor-pressure curve, liquid densities and freezing point are reported; in addition a few of its other physical properties have been estimated from theory.

Description of Experiments

Vapor-Pressure Curve.—Commercial samples of vinyl chloride[1] were obtained in small steel cylinders. This liquid was purified by fractional distillation in a vacuum insulated, low-temperature Hempel column and was further subjected to a fractional distillation in a closed, low-

[28] Scatchard, THIS JOURNAL, **47**, 641 (1925). See also LaMer, *Trans. Amer. Electrochem. Soc.*, **51**, (1927), preprint No. 58; and Van Laar, *Z. anorg. allgem. Chem.*, **139**, 108 (1924).

[1] Material obtained from the Carbide and Carbon Chemicals Corporation, New York City.