ied[33] in nine alcohols; the mean value of $k_{47\cdot 8}/k_{37\cdot 8} = 2.80$, average deviation 2.9%, maximum deviation 4.7%.

It is doubtful, therefore, whether the observed variations within each of these classes of reactions are greater than the experimental errors; we must conclude from the experimental evidence available that a variation of solvent has but little effect on the temperature coefficient.

Summary

1. The temperature coefficient of a reaction depends on the nature of the catalyst and is comparatively independent of the nature of the substrate.

2. Double compound formation of the substrate with one of the constituents of the solution may affect the temperature coefficient; since a small heat change is usually associated with double compound formation, this effect can only be small compared to the effect of a catalyst, whose combinations are usually associated with large energy changes.

3. We suggest that unsolvated ions be called "protions;" acid catalysis is attributed to the "hydrogen protion" and catalysis by alkalies to the "hydroxyl protion."

4. The temperature coefficient of a reaction is fixed by certain molecules which we call "residual molecules;" these are present in very small concentration and are connected with an equilibrium constant in such a way that their concentrations vary rapidly with temperature.

5. For a reaction to proceed with measurable speed, at least one of the reactants must be a residual molecule; on this basis the existence of slow unimolecular reactions is denied.

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[Contribution from the Chemical Laboratory of the University of California]

THE ACTIVITY COEFFICIENTS OF DILUTE AQUEOUS SOLUTIONS OF HYDROGEN CHLORIDE, THALLOUS CHLORIDE AND LEAD NITRATE

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Three quite independent experimental methods have been used for the accurate determination of the activity coefficients of dilute aqueous salt solutions. As examples of the precise application of these three methods we may mention hydrochloric acid by the electromotive force method, thallous chloride by the solubility method and potassium chloride by the freezing-point method.[1]

[1] For a detailed discussion of these methods and a summary of the results see (a) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, New York, **1923**, Chapters XXVI, XXVII and XXVIII,

The data available do not permit a direct comparison of the values of the activity coefficient, calculated from accurate measurements for any one salt, by two or more methods. However, for strong electrolytes of the same valence type the values of the activity coefficient become more nearly identical as the dilution is increased, and it has been assumed that the several methods would give identical results for a single substance.

The freezing-point method is the more general in its application. This investigation was undertaken to improve the technique of the method, and to obtain measurements of the freezing-point of hydrogen and thallous chloride solutions, from which a direct comparison with the activity coefficient calculated from the electromotive force and solubility measurements could be made. The freezing-points of solutions of lead nitrate were also obtained.

Theoretical

We shall follow the theoretical treatment and notation of Lewis and Randall,[2] but to avoid confusion we shall briefly summarize the definition and equations used in this paper.

The activity coefficient, γ, of a strong electrolyte is defined by the equation

$$\gamma = a_{\pm}/m_{\pm} \qquad (1)$$

where γ is the mean activity coefficient, $m_{\pm}$ is the mean molality of the ions, moles per 1000 g. of water, and $a_{\pm}$ is the mean activity of the ions. The mean molality is defined by the relation

$$m_{\pm} = m\,(\nu_{+}^{\nu_{+}} \times \nu_{-}^{\nu_{-}})^{1/\nu} \qquad (2)$$

where ν $(= \nu_{+} + \nu_{-})$is the number of ions into which the electrolyte dissociates according to the equation, $X = \nu_{+}X^{+} + \nu_{-}X^{-}$. The mean activity is likewise defined as

$$a_{\pm} = (a_2)^{1/\nu} = (a_{+}^{\nu_{+}} \times a_{-}^{\nu_{-}})^{1/\nu} \qquad (3)$$

where a_{+} and a_{-} are the activities of the positive and negative ions, respectively, and a_2 is the activity of the solute.

The activity of a solute is given by the equation

$$\mathrm{d}\,ln\,a_2 = \frac{\mathrm{d}\vartheta}{\lambda m} + 0.00057\,\frac{\vartheta\,\mathrm{d}\vartheta}{m} \qquad (4)$$

where λ is the molal lowering of the freezing-point at infinite dilution and has the value 1.858, ϑ is the freezing-point lowering when the molality is m. The last term of the equation is of no appreciable magnitude until the molality is nearly unity.

For an electrolyte, which on complete dissociation yields ν ions from each molecule, we may transform Equation 4 into

$$\frac{1}{\nu}\,\mathrm{d}\,ln\,a_2 = \mathrm{d}\,ln\,a_2^{1/\nu} = \mathrm{d}\,ln\,a_{\pm} = \frac{\mathrm{d}\vartheta}{\nu\lambda m} \qquad (5)$$

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[2] Lewis and Randall, (a) THIS JOURNAL, **43**, 1112 (1921). (b) Ref. 1. In Equation 3, p. 343, note that $\mathrm{d}\,ln\,(a_{\pm}/m) = \mathrm{d}\,ln\,(a_{\pm}/m_{\pm})$.

if we neglect the last term of Equation 4. The quantity j is defined by the equation

$$j = 1 - \vartheta/(\nu\,\lambda\, m) \tag{6}$$

and it is obvious that in so defining j it approaches a limiting value of zero as the molality approaches zero. Differentiating Equation 6, combining with Equations 2 and 5, and subtracting d $ln\ m$ from both sides we arrive at the relation,

$$\mathrm{d}\ ln\,\frac{a_{\pm}}{m} = \mathrm{d}\ ln\,\frac{a_{\pm}}{m_{\pm}} = \mathrm{d}\ ln\ \gamma = -\mathrm{d}\,j - j\,\mathrm{d}\ ln\ m \tag{7}$$

Lewis and Linhart[3] showed that for concentrations up to 0.01 M the relation of j to m can be expressed by the equation

$$j = \beta m^{\alpha}. \tag{8}$$

On substituting this value into Equation 7 and integrating we get, d $ln\ \gamma$ $= -\beta\ \mathrm{d}\ m^{\alpha} - \beta\, m^{\alpha-1}\ \mathrm{d}\, m$, and

$$\log\gamma = -\frac{\beta(\alpha+1)m^{\alpha}}{2.303\alpha} \tag{9}$$

Lewis and Randall pointed out that for electrolytes of the uni-univalent type the value of α is approximately one-half; and on giving α a value of one-half, Equation 9 becomes

$$\log\gamma = -\frac{1.5\beta}{2.303\times 0.5}m^{1/2} \tag{10}$$

which is essentially the equation later proposed by Brönsted,[4] in the form $\log\gamma = -\alpha m^{1/2}$, where his α obviously has the value $-1.5\beta/(2.303\times 0.5)$.

Thus for concentrations up to about 0.01 M we can calculate γ after determining the value of the constants α and β. On plotting as in Fig. 4 the values of log j against log m for the accurate freezing-point data available, Lewis and Linhart found that below $m = 0.01$, the points for any one substance fell within the experimental error on a straight line whose equation is

$$\log j = \log\beta + \alpha\log m \tag{11}$$

where α is the slope of the line and log β is the intercept on the axis of log j ($\log m = 0$).

In solutions of greater molality than 0.01 the plot of log j against log m is no longer a straight line, the values of j being less than those given by the straight-line relation. The last term of Equation 4 must also be considered in the solutions of higher molalities. Starting again with the Equations 4 and 6, changing to common logarithms and integrating, the constant of integration being zero, we obtain

$$\log\gamma = \int_0^m -j\ \mathrm{d}\log m - \frac{j}{2.303} + \frac{0.00025}{\nu}\int_0^m \frac{\vartheta}{m}\,\mathrm{d}\,\vartheta \tag{12}$$

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[3] Lewis and Linhart, THIS JOURNAL, 41, 1952 (1919).

[4] Brönsted, *ibid.*, **44**, 938 (1922).

The last definite integral, the value of which is negligible below 0.1 M, is obtained by taking the area under the curve of ϑ/m plotted against ϑ and multiplying by the numerical factor. The first definite integral is the total area under the curve of j plotted against log m. From $m=0$ to $m=0.01$ this area can be evaluated by using the equation of Lewis and Linhart, namely,

$$\int_0^{0.01} -j \, d \log m = -\frac{\beta}{2.303\alpha}(0.01)^{\alpha} \tag{13}$$

and we need plot only the values from $m=0.01$ to arrive at the area of this first definite integral in Equation 12.

Experimental Part

For accurate freezing-point measurements the original supercooling method of Raoult is, of course, useless. It was Roloff[5] who first analyzed the solution in equilibrium with a large amount of ice frozen out of the solution. Jahn[6] and Flügel[7] used the same method; Walker and Robertson[8] used pure ice mixed with salt solutions instead of freezing the ice out of the salt solution. Instead of mercury thermometers, compound thermo-elements were used by Hausrath,[9] Jahn, Flügel and Osaka.[10] Bedford[11] used a differential platinum resistance thermometer.

Of the work mentioned thus far only portions of Jahn's, Flügel's, Hausrath's and Bedford's measurements are of any real value. Adams[12] attacked the freezing-point problem in a manner which gave accurate values. He used greater refinement in the temperature measurement and followed a rapid, reliable method for the determination of the composition. Later Hall and Harkins[13] used the method of Adams in some accurate freezing-point measurements. Adams, and likewise Hall and Harkins, used an interferometric method of analysis for determining the composition of the solution in equilibrium with the ice.

The apparatus used in this investigation is a modification of that used by Adams. One of the uncontrolled sources of error in Adams' experiments was the presence of dissolved air in the solutions and in the pure water. Hall and Harkins mentioned in their paper the necessity of having the same amount of air dissolved in both the solution and the pure water, but they failed to note the possibility of the solute salt having an effect

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

[6] Jahn, *ibid.*, **59**, 31 (1907); **50**, 129 (1905).

[7] Flügel, *ibid.*, **79**, 577 (1912).

[8] Walker and Robertson, *Proc. Roy. Soc. Edinburgh*, **24**, 363 (1902).

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

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

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

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

[13] Hall and Harkins, *ibid.*, **38**, 2658 (1916).

on the solubility of air. The apparatus used by the authors was designed to obviate this difficulty, by permitting of prolonged evacuation to remove all appreciable amounts of dissolved air and other gases. Determinations of the concentrations at equilibrium were made by means of conductivity measurements. The conductivity method yields accurate results which are practically independent of the concentration. Adams used the interferometric method in which the accuracy is directly proportional to the concentration and is none too great at even moderately low concentrations. Moreover, since the sensitivity is proportional to the actual weight composition of the solution, the interferometric method is particularly unsuitable for analysis of solutions of substances of low molecular weight, such as hydrochloric acid.

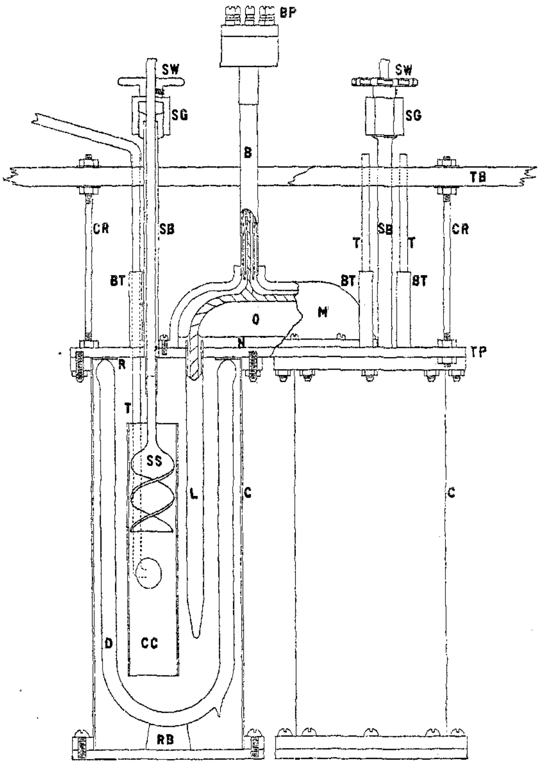

Fig. 1.

The Apparatus.—The arrangement and construction of our freezing-point apparatus are shown in the accompanying figures, 1, 2 and 3.

Fig. 1 is an elevation of the apparatus with the left-hand half drawn in section; Fig. 2 is a plan with the right-hand half of the supporting board more or less broken away; while Fig. 3 is an elevation showing the stand, the apparatus in the thermostat (in dotted lines), and the arrangement for raising and lowering the freezing-point apparatus. Two 1-liter Dewar[14] vessels D were contained in the two metal cylinders C and C′, and were firmly held against thin rubber rings R by the soft rubber blocks RB. The metal cylinders were bolted against the brass top-plate TP, gaskets of blotting paper soaked in molten beeswax and vaseline making the joints vacuum-tight. The top-plate TP had the left-hand portion of its lower surface gold-plated and the right-hand portion silver-plated. This top-plate was supported at the four corners by brass rods CR from the supporting top-board TB, which was thoroughly dried and impregnated with molten beeswax. The top-board TB had two cross pieces X fastened across its ends, and in the ends of these cross pieces were four eye-bolts E to which 0.7 cm. diameter rope was fastened. The two ropes on each cross piece were fastened together a short distance above the center of the cross piece; and the two ropes thus remaining (one for each of the cross pieces) brought up, passed over the pulleys P and fastened to the counterpoise weight W. Four metal tubes GT were fastened in the cross pieces X, and served as guides on the four guide rods GR, the lower ends of the rods GR being firmly fastened in the top of the thermostat Q, and their upper ends in the top of the stand S. This arrangement permitted lowering and raising of the freezing-point apparatus with no appreciable sideward motion. The thermo-element, terminating at an equal depth in the two Dewar vessels, had its junctions enclosed in two Pyrex glass tubes L, which projected a few millimeters through the brass top-plate TP. A brass manifold M enclosed the remainder of the thermo-element and was screwed against the top-plate TP. The lower portion N of the manifold was filled to a depth of about 1 cm. with molten de Khotinsky cement, and the remaining portion O then filled with molten paraffin. The leads from the thermo-element were brought up through a glass tube inside of the brass manifold tube B and were soldered to the copper binding posts BP on the Bakelite cap. Inside the Dewar vessels were two exactly similar conductivity cells CC with glass screw-shaped stirrers SS. The conductivity cells CC consisted of glass tubes open

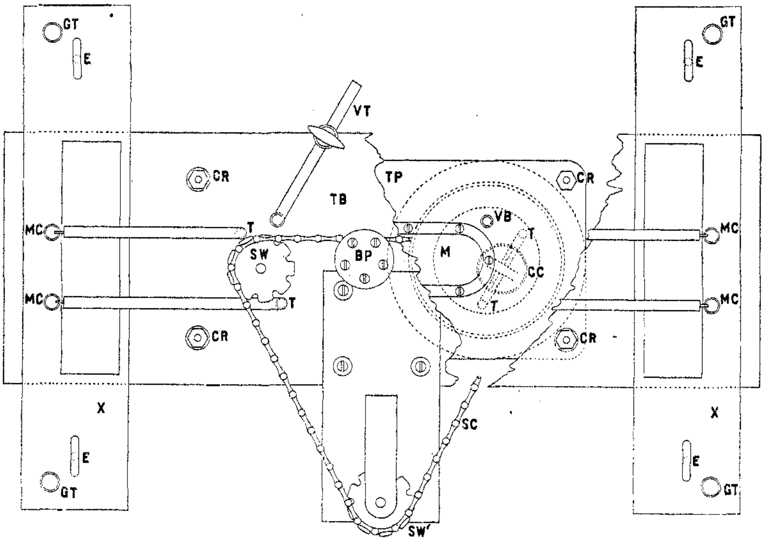

Fig. 2.

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[14] No. 521 F, one quart Jar Filler, Vacuum Specialty Co., Meriden, Conn. These vessels are manufactured in a uniform size.

on both ends, 3.2 cm. in diameter and 17 cm. long. These cells were held in place by the side tubes T which passed up through the brass tubes BT in the top-plate. The electrodes[15] were 2 cm. in diameter and 0.5 cm. apart; the leads from the electrodes passed up through the side tubes T, which were sealed in the brass tubes BT by means of litharge-glycerol cement capped at both ends of the brass tubes with a layer of soft de Khotinsky cement. Above the top-board TB the lead wires from the conductivity cells were enclosed in paraffined glass tubes and terminated in mercury cups mounted on the cross pieces X. The lower ends of the conductivity cells had a fine-mesh cotton netting tied over them, so that when the stirrers SS drew the solution or the water up through the cells the ice was prevented from entering. There was a clearance of 1.5 mm. between the stirrers and the cell tubes. The shafts of the glass stirrers were cemented into sleeves on brass shafts 0.63 cm. in diameter, which passed through the brass tubes SB, in which bearings were located at both ends. The brass bearing tubes SB were provided with stuffing glands SG. Absorbent cotton soaked in vaseline proved to be an excellent material for packing the glands. A sprocket chain SC connected the two sprocket wheels SW with a third SW′, which was belted to and driven by an electric motor. This motor was shunted by a rheostat so that it could be run at any speed to 300 r.p.m. The brass tubes VB (shown in Fig. 2) were sealed into glass T-tubes VT, which had the top ends open and fitted with small rubber stoppers. The side tubes were connected so that the two cylinders could be evacuated independently. The freezing-point apparatus was submerged (as shown by the dotted lines in Fig. 3), in a water-ice thermostat Q. This thermostat consisted of a Monel metal tank 28 cm. by 33 cm. and 43 cm. deep fitted with a propeller stirrer in a metal tube 7.5 cm. in diameter. The tank was lagged on the four sides and the bottom with a 7.5cm. layer of cork, the tank and cork lagging being contained in a wooden box.

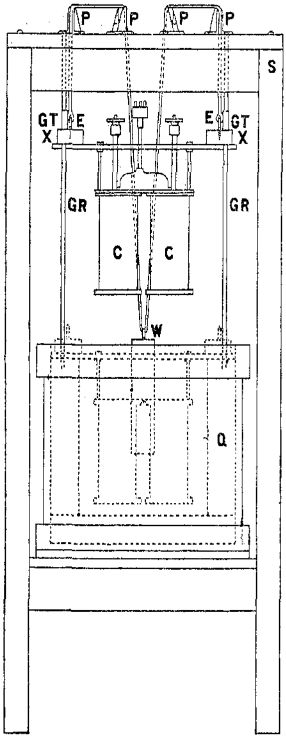

Fig. 3.

The Potentiometer.—A White double potentiometer, Leeds and Northrup Company, Type 7623 of 100,000 microvolt range was used for the electromotive-force measurements. The working batteries were Edison cells, Type B 6 H; two cells in series were used for each of the upper and lower potentiometer circuits. The voltage of these two cells in series was 2.8 volts, resistances of fine copper wire being used to reduce the voltage to 2 volts at the battery terminals of the instrument. The batteries, the potentiometer table, the galvanometer and the lead wires from the thermo-element were protected from electrical leakage by the double shielding system of White.[16] The lead wires from the thermo-element were No. 26 double silk covered copper wire and were supported on paraffined glass tubes between heavy outside shielding wires.

The Conductivity Set.—The source of 1000-cycle current for the conductivity measurements was a two-bulb audion oscillator. This oscillator is the Bell Telephone Co. 500-cycle circuit, brought to the attention of the authors by Mr. A. K. Astor of the

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[15] See Ref. 19, on p. 2429.

[16] White, This Journal, **36,** 2011 (1914).

Physics Department of the University of California, slightly modified to give a 1000-cycle current. Two bulbs are used because of the inability of any one-bulb circuit to give an unvarying frequency on a varying output load. The entire oscillator is enclosed in a metal box which is connected to the shielding system of the conductivity bridge outfit. The bridge used is a Leeds and Northrup Company, Kohlrausch bridge, Type 4258, equipped with the end coils. The resistance box is a five dial Curtis Coil Box, Type 4650, of the Leeds and Northrup Company. Variable air condensers are connected across the conductivity cell and the Curtis resistance box to balance out capacity effects, thereby giving perfect minima. The entire conductivity set, including the oscillator, is shielded by the method of Dr. E. W. Washburn described in detail in *Bulletin* **48,** of the Leeds and Northrup Company.

Construction and Calibration of the Thermo-element.—The 50-junction thermo-element was made of No. 30 double silk covered constantan wire (Electrical Alloy Company, "Ideal") and No. 36 double silk covered copper wire. The constantan wire was tested for homogeneity by the method of White;[17] the copper wire was assumed to be sufficiently uniform. The junctions were arc-welded and insulated by a double coating of Bakelite varnish. The couples were bundled together and wrapped with a layer of silk binding tape. No. 26 double silk covered copper wire was used for the lead wires, four of the leads dividing the element into two separate sets of 25 junctions, and a fifth lead dividing one of the 25-junction elements into 10- and 15-junction elements. After being bound into a single bundle the element was submerged in a dish of molten paraffin at 190° for five hours to remove all moisture. It was then inserted into the glass tubes one-third full of molten anthracene heated about 30° above its melting point. The remaining space in the tubes was filled with molten paraffin and the element was mounted in the freezing-point apparatus. The lead wires were then soldered to the copper binding posts on the Bakelite cap. An accurate check was made on the resistance of the thermo-element at every stage of its construction and mounting.

The thermo-element was calibrated against melting mercury, melting ice and the sodium sulfate transition point. The ice-against-ice readings were less than 0.05 microvolt for the 50 junctions. Several different samples of mercury were used against ice, the various samples of mercury giving electromotive-force readings agreeing to better than one part in 72,000 on the 50 junctions. The sodium sulfate had been recrystallized about 20 times until it gave a constant transition temperature. The electromotive force per junction is given in Table I.

TABLE I

E.M.F. PER JUNCTION OF COPPER-CONSTANTAN THERMO-ELEMENT

	Ice-ice	Mercury-ice	Na_2SO_4-ice
Temp., °K.	273.1	234.2	305.5
E.m.f.	0.00	1449.30	—1317.20

From these values those of the constant in the Eastman-Rodebush equation,[18] $\mathbf{E} = \mathbf{E}_0 + aT^n$ were calculated. The values obtained per junction are $\mathbf{E}_0 = 6414.3$, $a = 0.55847$ and $n = 1.6665$. From these the values $d\mathbf{E}/dT_{273.1} = 1956.95$ and $d^2\mathbf{E}/dT^2_{273.1} = 4.75$ microvolts were calculated. The practice, in converting an electromotive-force reading for a freezing-point measurement into degrees centigrade, was to divide the e.m.f. by 1956.95 and to add to this quotient a small correction (taken from a plot) due to the $d^2\mathbf{E}/dT^2$ term.

The Calibration of the Potentiometer.—The potentiometer was calibrated by the

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[17] White, THIS JOURNAL, **36**, 2292 (1914).

[18] Rodebush, *ibid.*, **40**, 1204 (1918).

auto-calibration method described in the Leeds and Northrup *Bulletin*, **726**. But after a dozen calibrations of this type on consecutive days it was found that no check results could be obtained. This method does, however, give a very accurate relationship of the nine coils in any one dial; but the ratio of one dial to a coil in the next higher dial was not the same for any two auto-calibrations. A method was devised for the calibration of the potentiometer by measuring externally set up electromotive forces on the potentiometer. External electromotive forces of the desired magnitudes were measured on as many coils as the scale of the galvanometer permitted. From these readings the relations of the various coils and dials were calculated. Three separate calibrations of this type made on different days gave results agreeing as well as was desired, while three auto-calibrations made during the same three days gave widely differing results. From the results of the external calibration a table of corrections for the four dials was prepared. Using these corrections the sum of the electromotive forces of the two 25-junction elements was within 0.05 microvolt of the value given by the combined 50-junction element. Various temperature differences between the element junctions were tried and satisfactory agreement between the sum of the two 25-junction readings and the 50-junction reading was always obtained.

Preparation of the Materials.—Conductivity water was used for making up all solutions as well as for all the freezing-point measurements. It was distilled from alkaline permanganate solution and about one-third of the distillate condensed in a block tin condenser, the remainder escaping as steam to prevent the entrance of air into the condenser and the receiver. Its conductance ranged from 0.3 to 0.8 $\times$ 10^{-6} mhos; it contained, however, a small quantity of dissolved air which, on freezing the water, formed fine bubbles throughout the ice. In the first freezing-point measurements it was the practice to freeze conductivity water for the source of ice; but on investigation it was found that clear pieces of commercial artificial ice on melting gave water with as low a conductance as the average conductivity water. Furthermore, these clear pieces of commercial ice were absolutely free from air bubbles, which was not the case with the ice made by the freezing of conductivity water. Clear portions of commercial ice were washed with distilled water and were crushed in well washed linen bags with a mallet, so that no pieces larger than 1 cm. remained. These were then sifted through a 0.6cm.-mesh sieve and all the finely cracked ice passing through the sieve was discarded. The cracked ice was finally washed thrice with ice-cold conductivity water.

The hydrochloric acid used was prepared from some C.P. acid. A large amount of 20.2% acid was made up and submitted to distillation, the middle third portion being collected and again distilled. The middle third portion of this second distillation was collected and its composition calculated from the barometric pressure. This constant-boiling solution of hydrochloric acid was used for making up the solutions of known concentrations and also for the freezing-point measurements.

The thallous chloride was prepared from C.P. thallous nitrate by precipitation. It was then repeatedly recrystallized from conductivity water until its solution saturated at 0° gave a constant conductivity value on recrystallization. A large amount of the solution saturated at 0° was prepared and submitted to analysis. The known solutions used for the conductivity data were made up from this saturated solution by adding weighed amounts of water to weighed amounts of the solution. Vacuum corrections were made in all cases.

The lead nitrate had already been recrystallized several times in this Laboratory by Mr. W. V. Vietti. It was recrystallized. however, from conductivity water, but the solution saturated at 0° gave the same conductance after one recrystallization as it did after three recrystallizations. The crystallized lead nitrate was filtered off and dried in an air-bath at 130° to a constant weight. The known solutions used for the conductivity measurements were made up by weight from this dried salt.

The Measurement of the Conductivity of the Known Solutions.—Known solutions of hydrochloric acid from about 0.0005 to 0.2 *M* were made up by weight from the constant-boiling acid. Their conductivities were measured at 0° in a suitable conductivity cell surrounded by cracked ice and water. Corrections for the conductance of the water used in preparing the solutions were made in the usual manner. The conductance of a solution prepared by dissolving 7.4555 g. of potassium chloride (weighed in air) in conductivity water and diluting to 1 liter at 18° was taken as 0.00715 mhos at 0°.

Since in all thermodynamic work we express concentrations as molalities or moles per 1000 g. of water, and since we are using the conductivity merely as a means of determining the molalities, it is convenient to use a quantity which we call the "molal conductance." It is 1000 times the specific conductance of the solution, as defined in the usual manner, divided by the molality of the solution.

The values of the "molal conductance" were plotted against the square root of the molality and a smooth curve was drawn through the points. From this curve, points at round concentrations were read off and the corresponding values of the specific conductance calculated from the molalities and the molal conductances. These values of the molal conductances, designated by the symbol 1000 κ/m, were plotted against the specific-conductance values, designated by the symbol κ, and a smooth curve was drawn through the points. In a freezing-point measurement the specific conductance κ was determined at 0°; from the curve of 1000 κ/m against κ we find the value of 1000 κ/m. Then dividing the value of κ by this value of 1000 κ/m we obtain the molality m of the solution. The value of 1000 κ/m varies only by a few per cent. in the range of molalities used. A plot of molality against κ, which would be a more direct way of getting the value of m from the value of κ, would yield results not at all comparable with the accuracy obtained by using the "molal conductance" plots.

The known solutions of thallous chloride were made up by weight from the analyzed solution saturated at 0°. The method of treating their conductance data is entirely similar to that used for the hydrochloric acid data. The values of the "molal conductance" of the thallous chloride when plotted against the square root of the molality, gave points falling within the experimental error on a straight line. The composition of the solution, saturated at 0°, is 0.006779 mole per 1000 g. of water.

The known solutions of lead nitrate were made up from the dried salt, this being the more convenient way of handling this salt. In this case, however, the values of the molal conductance were plotted not against the square root of the molality but against the cube root, the points for concentrations of 0.01 to 0.0006 *M* falling within the experimental error on a straight line.

The measured conductivity data for hydrochloric acid, thallous chloride and lead nitrate are given in Table II, the first, third and fifth columns being the molalities, the second, fourth and sixth columns being the molal conductances for hydrochloric acid, thallous chloride and lead nitrate, respectively.

TABLE II

"MOLAL CONDUCTANCE" AT 0° OF KNOWN SOLUTIONS

Hydrochloric acid		Thallous chloride		Lead nitrate	
Molality	1000 κ/m	Molality	1000 κ/m	Molality	1000 κ/m
1st series					
0.22644	238.11	0.0067793	77.522	0.11922	77.877
.11589	244.61	.0053781	78.175	.089307	83.507
.05641	249.52	.0042877	78.595	.059240	91.604
.02766	253.33	.0033921	79.269	.041665	97.730
.009914	257.35	.0026071	79.833	.029716	103.681
.004848	259.49	.0017708	80.429	.011870	118.48
.002459	260.48	.0014505	80.704	.017700	112.24
.001004	261.52	.0011574	81.060	.0097281	121.11
2nd series		.0008749	81.408	.0072992	124.92
.10707	245.05	.0006733	81.950	.0048677	129.66
.04761	250.52			.0033993	133.32
.027454	253.40			.0024265	136.39
.015864	255.70			.0014453	140.47
.004875	259.65			.0009621	142.90
.002368	260.92			.0007367	144.69
.0013591	261.63				
.0007463	263.30				

The Procedure in Making Freezing-Point Measurements.—About 400 g. of cracked ice was put into each of the two Dewar vessels and enough ice-cold conductivity water added to bring the water level exactly 0.5 cm. above the upper end of the conductivity cells CC when the apparatus was closed. The Dewar vessels containing the ice and water are placed inside the metal cylinders and the cylinders in turn placed in the proper position on a board put across the top of the thermostat. The apparatus was then lowered into position and the cylinders screwed on tightly. The apparatus was lowered into the thermostat, the stirrers were set in motion and the vacuum leads connected to the vacuum pump. Evacuation was continued for three to four hours, after which time the conductance of the water inside the Dewar vessels dropped to a minimum value. The cylinders were then opened to the atmosphere through soda-lime tubes, and after a period of half an hour the thermo-element gave no appreciable electromotive force. The stirrers inside the Dewar vessels were rotated at about 100 r. p. m. The conductance of the water was then determined, and enough of a stock solution of the electrolyte to be studied was added to give a concentration of about 0.001 M in the left-hand Dewar vessel. The right-hand vessel remained untouched throughout a series of measurements and served as a fixed temperature for the ice-junction of the thermo-element.

After the addition of the electrolyte the stirrers were run at 300 r. p. m. until the conductivity reading indicated complete mixing of the electrolyte. This usually required from 10 to 15 minutes, after which time the speed of the stirrers was reduced to about 60 r. p. m. and potentiometer readings were taken every five minutes until they became constant over a period of at least 20 minutes. After temperature equilibrium was reached, a sample of the electrolyte was drawn out into a pipet and its conductivity measured in an external cell.[19] An equal volume of water, containing enough electrolyte to bring the concentration to the value desired for the next freezing-point measurement, was then added, and the above process repeated to obtain equilibrium conditions at the second point.

Incidental Observations.—Inasmuch as the solubility of air in water is nearly 0.001 *M* it is of the utmost importance that all air be removed before making any freezing-point measurements. The effect of dissolved air is particularly disturbing in the case of hydrochloric acid, where the solubility of air is appreciably less than in pure water. Measurements on the freezing points of this electrolyte were never very concordant when the initial evacuation was omitted.

The rate of stirring has an appreciable effect on the temperature recorded by the thermo-element. Some heat is developed by the dissipation of the mechanical energy of stirring. The temperature of the equilibrium mixture in the bottom of the Dewar vessel is lower than at the top, because of the greater hydrostatic pressure. When the stirrers are stopped, after establishment of equilibrium, the electromotive force drops slowly, particularly when the electrolyte is more concentrated. The proper speed, about 60 r. p. m., which gave a maximum electromotive force, was found by trial.

The conductivity readings made with the internal cell indicate complete mixing of the electrolyte after stirring for 10 to 15 minutes at full speed. The electromotive force of the thermo-element, however, had not reached either a steady state or its maximum value at the end of this time. In the first measurements made the finer portion of the cracked ice was not discarded, and in these measurements equilibrium was reached only after several hours.

The Freezing-Point Data and the Activity Coefficients

The data and the calculations made from them are given in Tables III, IV and V. The first columns give the measured specific conductance

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[19] In the apparatus as used in this investigation the electrodes of the conductivity cells (CC, Fig. 1) were within 1 cm. of the bottom of the stirrer tubes. It was found that the cell constant varied a small amount, owing to varying amounts of ice particles resting against the netting on the bottom of the stirrer tubes. Cells with electrodes placed as shown in Fig. 1 are being substituted. The constants of these cells will be independent of the amount of ice resting against the netting and will enable us to measure the conductivity without withdrawing a portion of the solution.

Table III

Freezing-Point Data for Hydrochloric Acid

Specific conductance	Molality	E.m.f.	ϑ	$\frac{\vartheta}{\nu\lambda m}$	j
		Series A			
0.0001645	0.0006270	4.478	0.002287	0.98385	0.01615
.0003258	.0012448	8.901	.004548	.98318	.01682
.0004757	.0018208	13.066	.006676	.98671	.01329
.0009175	.0035261	25.177	.012865	.98184	.01816
.0013511	.005210	37.025	.018920	.97721	.02279
.0022109	.008573	60.620	.030971	.97213	.02787
.0033992	.013258	93.218	.047634	.96683	.03317
.012918	.051633	357.67	.18281	.95279	.04721
.012534	.050063	347.06	.17739	.95353	.04647
.017519	.070576	486.97	.24891	.94909	.05091
		Series B			
.0003086	.0011787	8.500	.004344	.99164	.00836
.0006268	.0024028	17.221	.008800	.98558	.01442
.0012513	.0048216	34.347	.017551	.97959	.02041
		Series C			
.0003856	.0014743	10.609	.005421	.98956	.01044
.0005816	.0022282	15.943	.008147	.98391	.01609
.0008926	.0034298	24.527	.012533	.98338	.01662
.0017785	.0068788	48.817	.024945	.97589	.02411
.0027471	.010633	75.303	.038480	.96931	.03069
.0044375	.017379	121.54	.062107	.96168	.03832
.0069527	.027439	190.71	.09746	.95586	.04414
.0110505	.044012	304.58	.15567	.95184	.04816
.0166723	.067072	462.51	.23641	.94853	.05147
.0256610	.104591	720.57	.36838	.94782	.05218
.0377458	.156044	1075.95	.55018	.94881	.05119
		Series D			
.0004930	.0018872	13.568	.006933	.98865	.01135
.0009672	.0037187	26.574	.013579	.98268	.01732
.0011737	.0045199	32.166	.016437	.97963	.02037
.0021486	.0083288	58.916	.030107	.97277	.02723

Table IV

Freezing-Point Data for Thallous Chloride

Specific conductance	Molality	E.m.f.	ϑ	$\frac{\vartheta}{\nu\lambda m}$	j
		Series A			
0.00003875	0.00047279	3.400	0.001737	0.98890	0.01110
.00007133	.00087657	6.294	.003216	.98738	.01262
.00010980	.0013490	9.749	.004982	.98697	.01303
.00015840	.0019733	14.159	.007235	.98669	.01331
.00023570	.0029640	21.193	.010830	.98324	.01676
.00029089	.0036794	26.263	.013421	.98156	.01844
.00034889	.0044380	31.583	.016139	.97862	.02138

TABLE IV (*Concluded*)

Specific conductance	Molality	E.m.f.	ϑ	$\frac{\vartheta}{\nu\lambda m}$	j
		SERIES B			
.00007015	.0008619	6.221	.003179	.99260	.00740
.00008579	.0010570	7.602	.003885	.98897	.01103
.00010555	.0013048	9.390	.004798	.98958	.01042
.00012943	.0016022	11.510	.005882	.98788	.01212
.00015972	.0019900	14.262	.007288	.98552	.01448
.00019641	.0024587	17.615	.009001	.98520	.01480
.00024169	.0030413	21.718	.011098	.98200	.01800
.00029747	.0037651	26.843	.013717	.98042	.01958
.00037290	.0047537	33.824	.017284	.97847	.02153
.00046265	.0059447	42.168	.021548	.97545	.02455

TABLE V

FREEZING-POINT DATA FOR LEAD NITRATE

Specific conductance	Molality	E.m.f.	ϑ	$\frac{\vartheta}{\nu\lambda m}$	j
		SERIES A			
0.00013775	0.0009625	10.001	0.005110	0.95255	0.04745
.00019687	.0014000	14.578	.007449	.95460	.04540
.00028695	.0020850	21.511	.010992	.94581	.05419
.00038885	.0028836	29.375	.015011	.93392	.06608
.00057412	.0043878	44.081	.022526	.92101	.07899
.00082171	.0065038	63.944	.032677	.90136	.09864
.00111523	.0091309	88.060	.045001	.88418	.11582
		SERIES B			
.0031632	.030795	268.19	.013707	.79853	.20147
.0065886	.076198	608.28	.31095	.73211	.26789
		SERIES C			
.00013460	.0009394	9.883	.005050	.96448	.03552
.00025490	.0018394	18.998	.009708	.94687	.05313
.00038786	.0028759	29.391	.015019	.93691	.06309
.00056223	.0042911	43.001	.021974	.91871	.08129
.00091616	.0073353	71.630	.036604	.89526	.10474
.0024529	.022666	203.73	.10412	.82411	.17589
		SERIES D			
.0022224	.020171	182.96	.093503	.83165	.16835
.0042868	.044349	375.95	.19215	.77732	.22268
.0074837	.089674	703.48	.35963	.71950	.28050

values, the second columns the calculated molalities, the third the electromotive-force readings in microvolts, the fourth the freezing-point lowerings in degrees, the fifth the values of $\vartheta/(\nu\lambda m)$, and the sixth the values of j.

In Fig. 4 the values of log m are plotted against the values of log j for all the freezing point measurements given in Tables III, IV and V. The best straight line was drawn through the points for any one electrolyte up to 0.01 M and from there on the line was curved to pass through the points

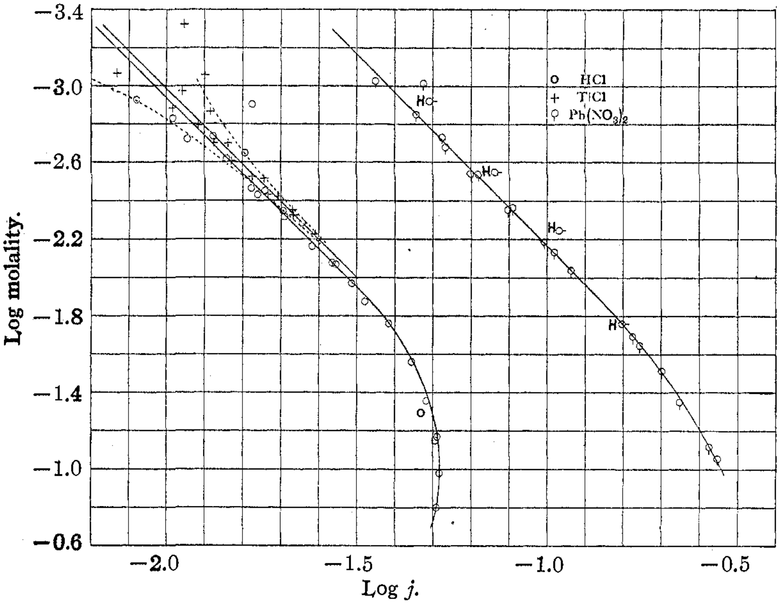

Fig. 4.

in the more concentrated solutions. The slopes, α, and the intercepts, $\log \beta$, on the axis, $\log m = 0$, were determined for the straight lines. The

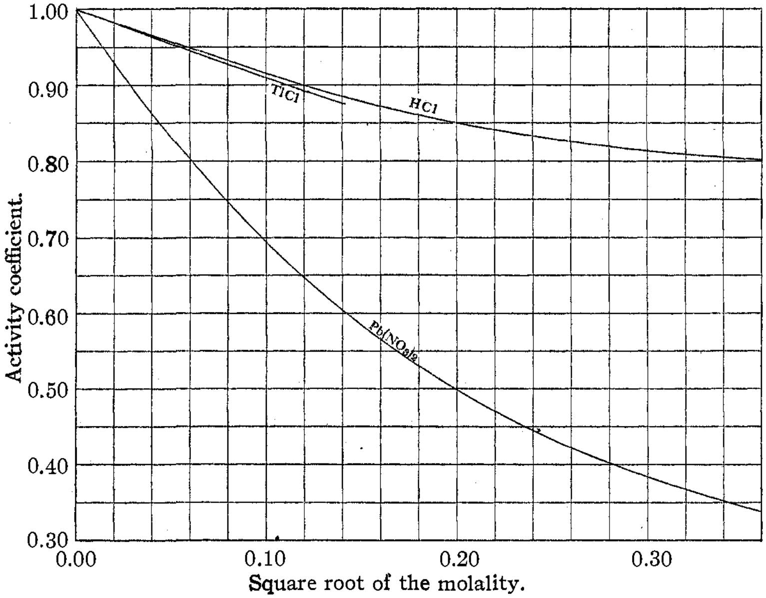

Fig. 5.

dotted lines in Fig. 4 represent the variation produced in the value of log j by an error of ± 0.00001° in the value of ϑ for thallous chloride. The four points, on or near the lead nitrate curve in Fig. 4, marked with an H to the left, are some measurements on lead nitrate made by Hausrath.[20]

The activity coefficients of the three electrolytes studied are shown in Fig. 5 and are given in the second columns of Tables VI, VII and VIII. The first column gives the molality, and the last the activity of the water as calculated by the equation[21]

$$\log a_1 = -0.004211\vartheta - 0.0000022\vartheta^2 \qquad (14)$$

The third column of Table VI gives the values of the activity coefficient of hydrochloric acid as calculated from the electromotive-force measurements, and the third column of Table VII gives the values for thallous chloride as calculated from the solubility measurements.

If we assume a value of exactly 0.5 for the slope α, then the values β = 0.302 for hydrochloric acid, β = 0.316 for thallous chloride and β = 1.231 for lead nitrate give approximate agreement with the experimental values.

Table VI

Activity Coefficient of Hydrochloric Acid

Value of α	0.513		0.500	
Value of β	0.316		0.302	
Molality	Activity coefficient by f. p.	Activity coefficient by e.m.f.	Activity coefficient by Eq. 10	Activity of the water, a_1
0.0001	0.992	...	0.991	......
.0005	.981	0.991	.980	......
.001	.973	.984	.972	0.999964
.002	.962	.971	.960	.999929
.005	.940	.947	.938	.999826
.01	.916	.924	.913	.999651
.02	.884	.894	.882	.999309
.05	.840	.850	.838	.99829
.1	.809	.814	.807	.99659
.2	.782	.783	.780	.99317

Table VII

Activity Coefficient of Thallous Chloride

Value of α	0.506		0.500	
Value of β	0.325		0.316	
Molality	Activity coefficient by f. p.	Activity coefficient by sol.	Activity coefficient by Eq. 10	Activity of the water, a_1
0.0001	0.991	...	0.990	......
.0005	.980	...	.979	......
.001	.971	0.970	.970	0.999964
.002	.959	.962	.958	.999929
.005	.936	.936	.935	.999824
.01	.910	.909	.910	.999651
.02	.875	.872	.874	......

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

[21] Ref. 1 a, p. 284, Equation 22.

The values of the activity coefficient calculated by Equation 10 from 0 to 0.01 *M*, assuming $\alpha = 0.5$, and the values at higher concentrations based on the value at 0.01 *M*, are given in Cols. 4 in Tables VI and VII and in Col. 3 of Table VIII.

TABLE VIII

ACTIVITY COEFFICIENT OF LEAD NITRATE

Value of α	0.502	0.500	
Value of β	1.233	1.231	
Molality	Activity coefficient by f. p.	Activity coefficient by Eq. 10	Activity of the water, a_1
0.0001	0.965	0.964	......
.0005	.922	.921	......
.001	.891	.890	0.999948
.002	.850	.848	.999898
.005	.773	.770	.999753
.01	.694	.692	.999526
.02	.600	.598	.999101
.05	.465	.463	.99794
.10	.369	.367	.99616

Discussion

Referring to the values of the activity coefficient of hydrochloric acid given in the second and third columns of Table VI, it will be noted that the values calculated from the electromotive force are uniformly about 1% higher below 0.05 *M*. The values of Col. 2, when substituted in the equation[22] $0.1183 \log \gamma = \mathbf{E}^\circ - (\mathbf{E} + 0.1183 \log m)$, give an average value of 0.2230 v. for $\mathbf{E}^\circ$, the electromotive force at unit activity of Linhart's hydrogen-silver chloride cell. We have reviewed the notes used in the original calculations of Lewis and Randall, and find that they chose $\mathbf{E}^\circ = 0.2232$ v., and considered a value as low as 0.2230 v. However, Linhart's published value 0.2234 v. was adopted, as this value seemed to be within the experimental error.

The values in Col. 2, Table VI, are for the activity coefficients at 0°, while those in Col. 3 are the values at 25°. Up to concentrations of 0.05 *M* the values should be the same,[23] but at molalities greater than about 0.05 the heat of dilution of the electrolyte must be considered in comparing activity coefficients at two different temperatures. No data are available to permit any accurate calculations of the activity coefficients of hydrochloric acid solutions at 25° from the freezing-point data. But if such calculations could be made they would give values of the activity coefficient at 0.1 and 0.2 *M* somewhat lower than those given in Col. 2, Table VI, and show, perhaps, a constant percentage difference between the values in Col. 2 and those in Col. 3.

[22] Ref. 1, Chap. XXVI.

[23] Ref. 1, pp. 288–290, 344–352.

The adoption of the new activity coefficients for hydrochloric acid given in Col. 2 of Table VI would necessitate several changes in the values of the standard calomel and numerous other single electrode potentials. Likewise, the use of these new values, and the present values of the single potentials will lead to inconsistencies. We hesitate at this time to suggest a change in the 1923 tables of Lewis and Randall until work now in progress is completed, and until we can consider the revision as a whole. The adoption of new values of this sort should be made only at relatively long intervals, and we recommend the continued use of their values.

The activity coefficients for aqueous solutions of thallous chloride obtained by the two independent methods are in excellent agreement.

The results of the lead nitrate freezing-point measurements are highly interesting in the light of some recent theoretical studies made by Debye and Hückel[24] and by Brönsted and La Mer.[25] Debye and Hückel developed an equation for the activity coefficients of electrolytes on a purely theoretical basis. The mathematical derivation is too complicated to be reproduced here; their equation, however, is given.

$$ln\ \gamma = \frac{e^2\ \kappa}{2\ \mathbf{D}\ kT} \times \frac{\Sigma\nu_i\ z^2_i}{\Sigma\nu_i}$$

In this equation e is the electronic charge, $1/\kappa$ is the "characteristic distance" of the ions, **D** is the dielectric constant for water, k is the Boltzmann gas constant per molecule, T is the absolute temperature, ν_i is the number of ions of the i^{th} type per unit volume, and z_i is the valence of this ion. On substituting numerical values Brönsted and La Mer[26] reduced the equation to $1 - ln\ \gamma = 1.14\ z_1z_2\sqrt{\mu}$, where γ is the activity coefficient, z_1z_2 is the product of the valences of the ions, and μ is the ionic strength as defined by Lewis and Randall. This equation can be written on changing to common logarithms,

$$\log \gamma = -0.495\ z_1z_2\sqrt{\mu} \qquad (15)$$

For uni-univalent electrolytes z_1z_2 is unity, and Equation 15 becomes

$$\log \gamma = -0.495\sqrt{m} \qquad (16)$$

since for salts of this type $m = \mu$. Giving α in Equation 9 the exact value of 0.5, the freezing-point measurements for hydrochloric acid lead to the equation

$$\text{HCl } (0.0\text{–}0.01\ M);\ \log \gamma = -0.393\sqrt{m} \qquad (17)$$

and for thallous chloride

$$\text{TlCl } (0.0\text{–}0.01\ M);\ \log \gamma = -0.412\sqrt{m} \qquad (18)$$

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[24] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

[25] Brönsted and La Mer, THIS JOURNAL, **46**, 555 (1924).

[26] Noyes [THIS JOURNAL, **46**, 1098 (1924)] in making the substitution of the numerical values, gives two equations, one for 0° and the other for 25°. He apparently overlooked the fact that the difference between the partial molal heat content of the salt at infinite dilution, where $a_{\pm} = m_{\pm}$, and in 0.01 to 0.03 M solution is zero or very small. Hence γ must be the same at 0° as at 25°. See Ref. 23.

The discrepancy between the values of these constants, 0.393 for hydrochloric acid, or 0.412 for thallous chloride, and the value 0.495 obtained by Brönsted and La Mer, might be attributed to the uncertainty in the numerical value of the dielectric constant of water appearing in the Debye and Hückel equation. On the other hand, we are not convinced that all salts of the same valence type have the same activity coefficients that the equation of Debye and Hückel calls for, and which Brönsted and La Mer claim is true up to concentrations of $m = 0.01$. Referring to Fig. 4, it seems unlikely that the experimental errors are large enough to give identical values of the constants in Equations 17 and 18. Granting that we are justified in choosing a line with a slope of exactly 0.5, then the values of the intercept, log β, are certainly quite different.

From Equation 10 we see that the values of the constants in Equations 17 and 18 are proportional to β. The values of the activity coefficient based upon the experimental values of α and β are preferred.

Turning now to electrolytes of the bi-univalent and uni-bivalent type, Equation 15 of Brönsted and La Mer reduces to

$$\log \gamma = -0.99\sqrt{\mu} = -0.99\sqrt{3m} \qquad (19)$$

From the measurements of the freezing points of lead nitrate solutions, assuming $\alpha = 0.5$, we have

$$\mathrm{Pb(NO_3)_2}\ (0.0\text{–}0.01\ M);\ \log \gamma = -0.925\sqrt{3m} \qquad (20)$$

Here again there is a wide discrepancy. It may be that lead nitrate is unique in having a value of α so nearly equal to 0.5; for in the case of other salts of this type the value of α is considerably less than 0.5, being more nearly equal to 0.33.[27] Probably the most important experimental problem in the field of dilute aqueous electrolytes is a sufficient determination of the answer to this question. Further investigation is being carried out on the freezing points of solutions of electrolytes of the various valence types.

Summary

1. An improved freezing-point apparatus has been developed, and is described in detail.

2. A method of accurately calibrating the White double combination potentiometer is given.

3. The freezing-point lowering and conductance of the same dilute solutions of hydrochloric acid, of thallous chloride and of lead nitrate have been obtained.

4. New conductance measurements of solutions of these salts of known molalities have been made.

5. The activity coefficients calculated from the measurements with hydrochloric acid show satisfactory agreement with those calculated from the electromotive-force measurements.

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[27] See Ref. 1, p. 344.

6. The activity coefficients calculated from the measurements with thallous chloride show satisfactory agreement with those calculated from solubility measurements.

7. The values of the activity coefficients calculated from measurements of the freezing-point lowering, electromotive force and solubility agree among themselves, but do not agree with the theoretical equation of Debye and Hückel and the modification of that equation by Brönsted and La Mer.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, UNIVERSITY OF MICHIGAN]

A REVISION OF THE ATOMIC WEIGHT OF ANTIMONY
THE ANALYSIS OF ANTIMONY TRICHLORIDE

BY PHILIP F. WEATHERILL

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Clarke, in the 4th edition of his "Recalculation of Atomic Weights"[1] gives a summary of the work on the atomic weight of antimony up to that time. Willard and McAlpine have since then published the results of their work on the analysis of antimony tribromide,[2] and have critically discussed previous work on this problem. The results obtained by Willard and McAlpine indicate that the value of 120.2, which has appeared in the tables for a number of years, is much too low, and that 121.77 is nearer the truth.

After the present research was completed, Professor O. Hönigschmid stated that in a recent investigation,[3] he had obtained the value 121.76 from the analysis of both the trichloride and the tribromide, confirming the results obtained by Willard and McAlpine.

In the present work antimony trichloride was prepared in a vacuum, purified by repeated distillation in a vacuum, and compared with pure silver. Since previous work indicated that the exclusion of all moisture is of greatest importance, all apparatus was dried with great care.

The fact that the ratio given by the trichloride is more favorable than in the case of the tribromide is about balanced by the fact that the end-point in the latter case can be determined more accurately. However, since the trichloride has a lower melting point, it is much easier to handle in the type of apparatus used here for its purification. By cooling the solution the sharpness of the end-point was increased so that the error here was probably no greater than that in other parts of the process.

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[1] Clarke, "Recalculation of Atomic Weights," Third Memoir, *Nat. Acad. Sci.*, **16**, 247 (1920).

[2] Willard and McAlpine, THIS JOURNAL, **43**, 797 (1921).

[3] Hönigschmid, personal communication. The work will appear in *Z. anorg. allgem. Chem.*