One equation only was used for barium nitrate and for sodium sulfate. It was found more convenient in the case of sulfuric acid to divide the concentration range into two approximately equal and overlapping parts and employ two equations. The actual working equations were based on 1000 times the reciprocal of the measured resistance.

Summary

1. Conductance measurements as a means of determining the concentration of an unknown solution are reliable if the proper precautions are taken. The procedure must be carefully standardized and the same cell must be used in measuring the known and unknown solutions.
2. It is probable that relatively large errors of an indeterminate amount exist in published conductance values. It does not seem possible so to define the procedure and to describe the cell that the exact conductance of a solution can be given.
3. The uncertainties exist within the cell.
4. The behavior of sulfuric acid and sodium sulfate indicates that by a systematic study of cell constant ratios in quartz cells with these and other salts a standard more suitable than potassium chloride can be obtained. Sodium sulfate is provisionally suggested for such a standard.
5. Measurements of the molal conductance of barium nitrate, sodium sulfate and sulfuric acid solutions at 0° are given.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE FREEZING POINT AND ACTIVITY COEFFICIENT OF AQUEOUS BARIUM NITRATE, SODIUM SULFATE AND SULFURIC ACID

BY MERLE RANDALL AND GORDON N. SCOTT

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The proof of the inter-ionic attraction theory[1] depends largely upon the accurate determination of the properties of solutions in the concentration range where modern experimental methods, however refined, seem inadequate to yield dependable results. We have studied the freezing-point lowerings by the method suggested by Randall[2] and find values of the function $j/m^{1/2}$ which, in general, agree with the theoretical value at $m = 0$ within the experimental error. But the measurements in the most dilute ranges are unsatisfactory. The relatively accurate data of Randall and Vanselow[3] for hydrochloric acid, and the data of the other

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

[2] Randall, THIS JOURNAL, **48**, 2512 (1926); $j = 1 - (\theta/\nu\lambda m)$, where θ is the freezing-point lowering, ν the number of ions formed from one molecule, $\lambda = 1.858$, the freezing-point constant, and m the molality.

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

investigators for acids, do not agree with the theoretical value in the most dilute solutions.

Experimental errors may not be the only cause of the non-agreement. Weak electrolytes[4] and readily hydrolyzable ions will show deviations unaccounted for by the simple Debye and Hückel formulas. However, in the case of hydrochloric acid there does not appear to be any such reason for the existence of an anomalous behavior. The deviation of the results commences at a point where, from the precision of the instruments, good measurements are to be expected. It seemed worth while, therefore, to study systematically the errors involved in the experimental methods of Randall and Vanselow and to redesign and improve their apparatus and technique wherever possible.

Experimental Part

Materials and Concentration of the Solutions.—The preparation of the materials, and the detailed study of the determination of the concentration of the equilibrium solutions have been described in the previous paper.[5]

Freezing-Point Apparatus.—The apparatus was the same as that of Randall and Vanselow with the following changes.

The position of the electrodes was raised to 7 cm. above the bottom of the glass-stirrer tubes, and the bottoms of the tubes were flared slightly to facilitate the attachment of the gauze. Because it was difficult to introduce known solutions at a definite temperature into the Dewar vessels, and for reasons discussed in the previous paper, the cells were used only in following the concentration changes during an experiment.

The stirrers fitted into the cylindrical conductance cells with a small clearance. Conductivity-time curves showed that complete mixing was easily obtained for solutions, added at room temperatures, within a few minutes even at the slowest rate. The attainment and maintenance of a steady temperature state is, however, the critical factor involved in the accurate determination of freezing-point lowerings at great dilutions. Without such a condition no amount of refinement in the temperature measurement, or in the analysis of the solution could possibly add to the certainty of the value of the temperature decrement for a given molality.

The following factors contribute to the alteration of the conditions within each Dewar vessel. (1) The hydrostatic pressure of the solution itself causes a slight difference in the equilibrium temperatures at the top and bottom of each vessel. (2) Energy is dissipated by the stirrers as heat. (3) The dissolution of the ice and the consequent liberation of occluded gas bubbles and soluble substances may change the concentration of the solution. (4) The concentration of the solution may change owing to the solubility of the glass in the liquid. The effect of acids on soda glass is

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[4] See Bjerrum, *Kgl. Danske Videnskab. Selskab, Math.-fys. Medd.*, **7**, No. 9 (1926).

[5] Randall and Scott, THIS JOURNAL, **49**, 636 (1927).

marked. (5) The solubility of air will be greater in the solution because it is at a lower temperature than the pure water. Added electrolyte will decrease the solubility in the solution to a small extent. (6) Electrolyte is absorbed on the glass surfaces, and perhaps on the ice surface.

It was desired to balance these effects so that in the initial measurements, over a considerable length of time, constant conditions could be maintained. The two stirrers were not identical in their characteristics, and the same speed, therefore, would not produce the same effects within the vessels. To overcome this difficulty the stirrers were supplied with separate motors. Once a balance had been attained it was necessary to keep these speeds constant. Automobile speedometers, stripped of their mileage recording devices, were connected by suitable reducing gears to the stirrers, thus enabling us to maintain constant stirring. Our only proof that our procedure was justifiable lies in the reproducibility of the results obtained under varying sets of conditions.

Procedure.—The procedure was the same as that of Randall and Vanselow, except that the speed of the stirrers was maintained constant at the optimum speed of the preliminary run. It is not necessary to describe all the precautions taken.

The Freezing Points

The freezing points obtained are given in Tables I, II and III. Col. 1 gives the molality, the second the observed depression of the freezing point, and the last the value of the function $j/m^{1/2}$.

TABLE I

FREEZING-POINT LOWERING OF BARIUM NITRATE

m	θ	$j/m^{1/2}$	m	θ	$j/m^{1/2}$
	Series A			Series B	
0.0016688	0.008794	1.3368	0.0008335	0.004348	2.2158
.0052205	.026671	1.1551	.0015922	.008372	1.4200
.0073814	.037146	1.1311	.0034676	.017897	1.2577
.0086670	.043362	1.1003	.0058070	.029416	1.2250
.011667	.057431	1.0823	.010820	.053392	1.1027
.018114	.086920	1.0338	.020125	.095854	1.0257
.026490	.12392	0.9878	.035050	.16064	1.0531
.038505	.17493	.9427	.048651	.21736	0.8998
.059745	.26223	.8717	.072790	.31374	.8404
.084219	.35747	.8219	.092957	.39074	.8065
.11406	.46769	.7827	.12562	.51087	.7630

TABLE II

FREEZING-POINT LOWERING OF SODIUM SULFATE

m	θ	$j/m^{1/2}$	m	θ	$j/m^{1/2}$
0.0008753	0.004798	0.5569	0.016155	0.079371	0.9328
.0017966	.009551	1.0930	.032064	.15160	.8476
.0035272	.018382	1.0953	.060975	.27700	.7491
.0057657	.029610	1.0358	.10338	.45099	.6702
.0086030	.043557	0.9884			

TABLE III

FREEZING-POINT LOWERING OF SULFURIC ACID

m	θ	$j/m^{1/2}$
	Series A	
0.004140	0.020888	1.4687
.006020	.029714	1.4757
	Series B	
0.000976	0.005232	1.2292
.003124	.015978	1.4748
.005126	.025620	1.4451
.006332	.031211	1.4578
.007649	.036973	1.5191
	Series C	
0.0007826	0.004208	1.2580
.0011087	.005936	1.1827
.0023097	.011934	1.5206
	Series D	
0.004520	0.022578	1.5457
.007488	.036349	1.4926
.011116	.052222	1.4911
.016612	.076345	1.3618
.022014	.098742	1.3164
.035778	.15408	1.2023
.054160	.22483	1.0966
	Series D (cont.)	
0.10559	0.42096	0.8764
.12820	.50749	.8095
	Series E	
0.10516	0.41927	0.8778
	Series F	
0.0009783	0.005308	0.8505
.0013135	.006993	1.2400
.0017968	.009374	1.5117
.0028863	.014831	1.4547
.006808	.27652	1.0400
.012291	.48756	0.8225
	Series G	
0.0009289	0.004990	1.1891
.0011841	.006293	1.3528
.0019566	.010187	1.4919
.031223	.13588	1.2410
.039092	.16686	1.1849
.069494	.28259	1.0261
.10126	.40368	0.8949

The values of $j/m^{1/2}$ are plotted against $m^{1/2}$ in Figs. 1, 2 and 3. The values taken from all existing measurements are also shown in the plots. In drawing the curves which we believe represent the most probable values, we have taken into consideration not only the points for each salt, but also the curves for all other strong electrolytes. It is not practical, however, to present these curves here. Notwithstanding the scattering of the points on such a sensitive plot as the one used here, both the purely empirical extrapolation[2] of the curves to $m^{1/2} = 0$ and theoretical considerations point to a value of $j/m^{1/2} = 1.30$ at $m^{1/2} = 0$ for strong uni-bivalent electrolytes.

From a study of these curves several observations as to the reliability of the several measurements may be made. In making the plots we have attempted to reduce all the data to moles per 1000 g. of water and have made corrections in the case of the older measurements, such as for changes in the accepted molecular weights. Notwithstanding the application of the corrections to the published data it is obvious that there are certain unknown errors in the methods and in the calibration of the various instruments used, which cause systematic and other errors. Only those measurements in which the solutions were analyzed, after equilibrium with the ice was attained, can be given much weight, but we have included the measurements made by the supercooling method used extensively by Arrhenius, Loomis, Jones and others because these comparisons will aid in determining the best values of other salts when more reliable data are lacking. In general, in those series in which the analysis of the solution was made after the attainment of equilibrium, we find that if the values of $j/m^{1/2}$ in the dilute solutions are high, or low, then all the measurements will be slightly higher, or lower, than the average curve by progressively smaller amounts as the concentration is increased. It is impossible to say, however, that the apparatus used by any one investigator always gives high or low results as the case may be. In the case of any single electrolyte, usually the data of some investigators tend to be high in the dilute end while those of others are low.

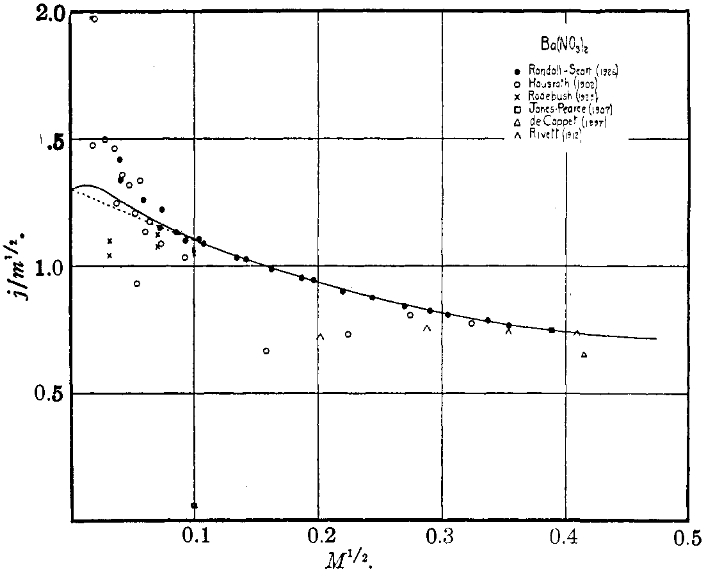

Fig. 1.—Freezing-point function for barium nitrate.

Considering barium nitrate[6] in detail, five of our points in the most dilute solutions are high while with sulfuric acid and sodium sulfate and, with the same apparatus, with hydrochloric acid, thallous chloride and lead nitrate, Randall and Vanselow found low points in the dilute end. Hausrath had high points with hydrochloric acid and some salts, but low points with sulfuric acid and a few salts. The points of Hovorka and Rodebush are low, but in all other cases they are high. We might, therefore, feel fairly confident that the empirical extrapolation to 1.30 as shown

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[6] (a) de Coppet, *Z. physik. Chem.*, **22,** 239 (1897); (b) *J. Phys. Chem.*, **8,** 531 (1904). (c) Hausrath, *Ann. Physik*, [4] **9,** 522 (1902). (d) Hovorka and Rodebush, THIS JOURNAL, **47,** 1614 (1925). (e) Jones and Pearce, *Am. Chem. J.*, **38,** 683 (1907). (f) Rivett, *Z. physik. Chem.*, **80,** 537 (1912).

by the dotted line of Fig. 1 is justified. But if we consider the chemical nature of barium nitrate, and give some weight to the more dilute points, we must draw the curve somewhat as shown in the solid curve. We shall later draw a similar curve for sulfuric acid, but the "hump" is much more marked in that case (see Fig. 3). The solid curve gives a value of the activity coefficient at 0.01 M and higher concentrations which is 0.8% lower than that given by the dotted curve. The values in Table IV are taken from the dotted curve.

Only one series of measurements was made with sodium sulfate.[7] These tend to be low in the dilute end while the values of Harkins and Roberts are high. We have drawn the curve extrapolated to 1.30. Without the acceptance of this limit we probably would have extrapolated the curve to 1.25 and this would have given γ' equal to 0.723 at 0.01 instead of γ' equal to 0.719, which is a small difference.

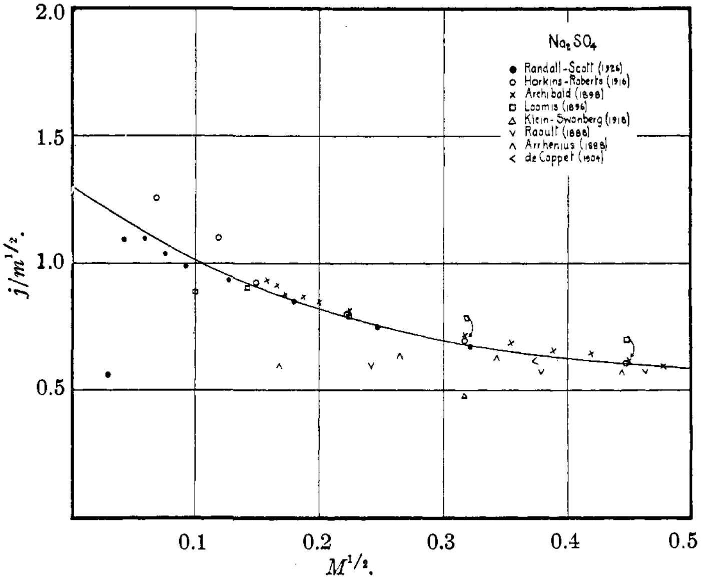

Fig. 2.—Freezing-point function for sodium sulfate.

In the case of sulfuric acid[8] the extrapolation is not so easy. Both our

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[7] (a) Archibald, *Trans. Nova Scotia Inst. Sci.*, **10,** 44 (1898–1902). (b) Arrhenius, *Z. physik. Chem.*, **2,** 488 (1888). (c) Ref. 6 b. (d) Harkins and Roberts, THIS JOURNAL, **38,** 2676 (1916). (e) Jones and Getman, *Z. physik. Chem.*, **46,** 244 (1903). (f) Klein and Swanberg, *Meddel. Vetenskapsakad. Nobelinst.*, **4,** No. 1 (1918). (g) Loomis, *Wied. Ann.*, [3] **57,** 503 (1896). (h) Raoult, *Z. physik. Chem.*, **2,** 488 (1888). (i) Tezner, *Z. physiol. Chem.*, **54,** 95 (1907).

[8] (a) Barnes, *Trans. Roy. Soc. Canada*, [2] **6,** 37 (1900). (b) Bedford, *Proc. Roy. Soc.* (London), **83A,** 454 (1910). (c) Drucker, *Z. Elektrochem.*, **17,** 398 (1911); (d) *Z. physik. Chem.*, **96,** 381 (1920). (e) Ref. 6 c. (f) Hillmayr, *Sitzb. Akad. Wiss. Wien,* **106** [IIa], 5 (1897). (g) Jones, *Z. physik. Chem.*, **12,** 623 (1893). (h) Jones and Carroll,

values and those of Hausrath are low in the dilute end while, as it has been previously pointed out, Randall and Vanselow found low values with hydrochloric acid and Hausrath found very high values. The hydrochloric acid values, however, extrapolate to the value which corresponds to 1.30 for uni-bi electrolytes. A straight-line extrapolation, giving most weight to the points in the more concentrated solutions, would give $j/m^{1/2}$ equal to 1.685 at $m^{1/2} = 0$. Preliminary considerations show that if an electrolyte is not completely dissociated, then we should expect the $j/m^{1/2}$ curve to be higher than that for strong electrolytes. These considerations also point to the conclusion that in the most dilute solutions, where these weak electrolytes become fully dissociated, the values of $j/m^{1/2}$, at $m^{1/2} = 0$, should correspond to that for other electrolytes. We have accordingly drawn the curve arbitrarily to the limit $j/m^{1/2}$ equal to 1.30 at $m^{1/2} = 0$, and this curve represents the average of our values and Hausrath's values

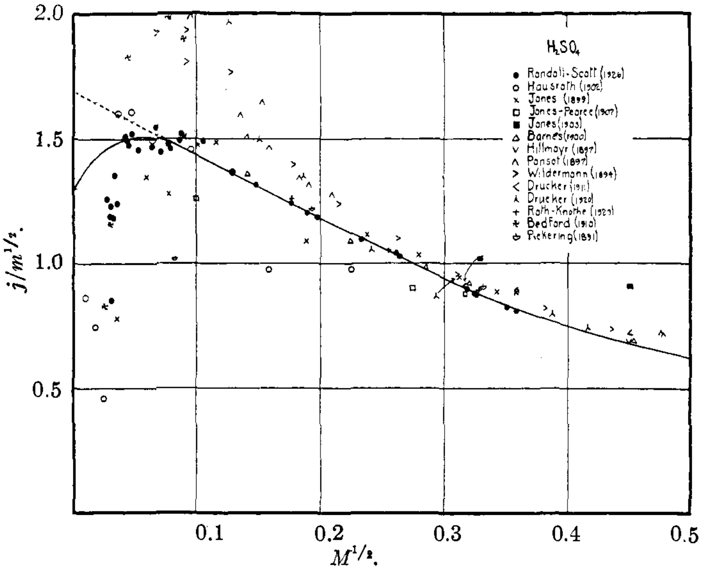

Fig. 3.—Freezing-point function for sulfuric acid.

Am. Chem. J., **28**, 284 (1902). (i) Jones and Getman, *ibid.*, **27**, 433 (1902); *Z. physik. Chem.*, **46**, 244 (1903); **49**, 446 (1904). (j) Jones and Murray, *Am. Chem. J.*, **30**, 207 (1903). (k) Ref. 6 e. (l) Loomis, *Phys. Rev.*, [1] **1**, 274 (1894); *Wied. Ann.*, [3] **51**, 500 (1894). (m) Ostwald, *Z. physik. Chem.*, **2**, 78 (1888). (n) Pfaundler and Schnegg, *Sitzb. Akad. Wiss. Wien*, **71** [II], 351 (1875). (o) Pickering, *Brit. Assoc. Advancement Sci. Repts.*, **60**, 311 (1890); *Z. physik. Chem.*, **7**, 378 (1891). (p) Pictet, *Compt. rend.*, **119**, 642 (1894). (q) Ponsot, *Ann. chim. phys.*, [7] **10**, 79 (1897). (r) Price, *J. Chem. Soc.*, **91**, 533 (1907). (s) Roth and Knothe, Landolt-Börnstein-Roth-Scheel, "Tabellen," Julius Springer, Berlin, **1923**, p. 1443. (t) Wildermann, *Z. physik. Chem.*, **15**, 337; **19**, 233 (1894).

fairly satisfactorily.[9] The shape of this curve is being further investigated. The difference in the value of log γ' at 0.01 or 0.1 M caused by assuming the dotted or solid curve is 0.0152. The continued decrease in the conductivity of a dilute solution with time as discussed in our previous paper will account for the rapid decrease in the value of $j/m^{1/2}$ below 0.005 M and for a similar decrease in the case of the measurements for hydrochloric acid by Randall and Vanselow.

The Activity Coefficients.—The activity coefficients calculated from the curves of Figs. 1, 2 and 3 are given in Tables IV, V and VI. Col. 1 gives the molality and Col. 2 the logarithm of the activity coefficient;

TABLE IV

ACTIVITY COEFFICIENT OF BARIUM NITRATE

m	$-\log \gamma'$	γ'	θ	$a_1(H_2O)$
0.0005	0.0382	0.915	0.00271	0.999975
.001	.0536	.884	.00535	.999950
.002	.0741	.843	.01053	.999898
.005	.1133	.770	.02556	.999750
.01	.1541	.701	.04955	.999520
.02	.2074	.620	.09532	.999078
.05	.3002	.501	.22274	.997840
.1	.3898	.408	.41702	.995965
.2	.5030	.314	.76449	.992615

TABLE V

ACTIVITY COEFFICIENT OF SODIUM SULFATE

m	$-\log \gamma'$	γ'	θ	$a_1(H_2O)$
0.0005	0.0365	0.920	0.00271	0.999975
.001	.0507	.890	.00536	.999950
.002	.0701	.851	.01057	.999895
.005	.1060	.783	.02574	.999748
.01	.1433	.719	.05013	.999515
.02	.1903	.645	.09706	.999060
.05	.2701	.537	.22978	.997775
.1	.3482	.449	.43551	.995787
.2	.4276	.374	.85767	.991715

TABLE VI

ACTIVITY COEFFICIENT OF SULFURIC ACID

m	$-\log \gamma'$	γ'	θ	$a_1(H_2O)$
0.0005	0.0400	0.912	0.00270	0.999975
.001	.0577	.876	.00532	.999950
.002	.0835	.825	.01040	.999899
.005	.1345	.734	.02491	.999759
.01	.1882	.648	.04774	.999538
.02	.2573	.553	.09052	.999127
.05	.3722	.424	.20865	.997977
.1	.4679	.341	.39844	.996150
.2	.5654	.272	.77445	.992520

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[9] Since this was written, Bjerrum (see Ref. 4) has reached a similar conclusion.

Col. 3 gives the activity coefficient at the freezing point uncorrected for heat of dilution. They are calculated according to the equation[2]

$$\log \gamma = -\frac{j}{2.303} - 2\int_0^m (j/m^{1/2})\mathrm{d}m^{1/2} + 0.000083\int_0^m \frac{\theta}{m}\,\mathrm{d}\theta \qquad (1)$$

The value of the first integral is found by evaluating the area under the curve. The second integral gives only a small correction.

Col. 4 gives the average values of the freezing-point lowering, and the last the activity of the water as calculated from the equation[10]

$$\log a_1 = -0.004211\,\theta - 0.0000022\theta^2 \qquad (2)$$

Relation of These Results to the Theory of Debye and Hückel.—The extended form of the Debye and Hückel equation for the activity coefficient can be expanded in the following form,

$$(\log \gamma_c)/c^{1/2} = A' + B'c^{1/2} + C'c + \ldots \qquad (3)$$

but if the composition of a solution is expressed in moles per 1000 g. of water (molality) instead of moles per liter (concentration), then there is no change in the composition as the temperature is changed. It is, therefore, imperative to use molality rather than concentration in thermodynamic work. But the molality may be expressed as a function of the concentration which has the same form as Equation 3, and we write

$$(\log \gamma)/m^{1/2} = A + Bm^{1/2} + Cm + \ldots \qquad (4)$$

The equation is similar to the empirical equation of Brönsted[11] divided through by $m^{1/2}$.

When the function $(\log \gamma)/m^{1/2}$ is plotted against $m^{1/2}$, it is easy to see that the results for sodium sulfate agree with the form of Equation 4, but when we consider barium nitrate and sulfuric acid we find that the results are more nearly in accord with the interpretation of Bjerrum,[4] or we can say that a small part of the barium nitrate is undissociated, or that it is slightly weak, and that sulfuric acid is only a moderately strong electrolyte.

Our determination of the activity coefficients has been almost entirely empirical. The use of the limit $j/m^{1/2} = 1.30$ at $m^{1/2} = 0$, which is a consequence of the simple Debye and Hückel treatment, has served only as an aid and this limit might be obtained as the empirical average of all freezing-point measurements.

Lewis and Linhart, and later Lewis and Randall,[10] have used the plot of $\log j$ against $\log m$ to determine the extrapolation of freezing-point data. They found in every case that there was a curvature on the more concentrated solutions, but in the more dilute solutions the plot of $\log j$ against $\log m$ gave a straight line, the slope being about $^1/_2$ for uni-unielectrolytes and nearly $^1/_3$ for uni-bielectrolytes. Their values of the activity coeffi-

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[10] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, p. 284, Equation 22.

[11] Brönsted, This Journal, **44**, 938 (1922).

cient do not differ much from those calculated by the method used here. If their slope were exactly $^1/_2$ throughout the entire range, then the curves of our figures would have been horizontal lines; however, because the curves are not horizontal it is a curious coincidence, when the experimental points in certain concentration ranges were used, that the log j against log m curves were found to give approximately straight lines with slopes other than $^1/_2$, and that the values of the activity coefficients so calculated were not seriously in error.

Summary

1. The freezing-point apparatus of Randall and Vanselow has been improved. Measurements of the freezing points of dilute aqueous solutions of barium nitrate, sodium sulfate and sulfuric acid have been made.

2. The activity coefficients of these electrolytes have been calculated from the above measurements.

3. From the form of the $j/m^{1/2}$ plots we conclude that sodium sulfate is a typical strong electrolyte, that barium nitrate is very slightly weak, and that sulfuric acid must be considered as only a moderately strong electrolyte..

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE THERMAL DISSOCIATION OF IODINE AND BROMINE

BY THOMAS DEVRIES[1] WITH WORTH H. RODEBUSH

RECEIVED OCTOBER 13, 1926 PUBLISHED MARCH 9, 1927

Starck and Bodenstein[2] determined the constant for the reaction $I_2 \longrightarrow 2I$ by measuring the pressure produced by a known amount of iodine sealed in a quartz bulb of known capacity in the presence of an inert gas. They worked in the temperature range 800–1200° and summarized their results by an equation for log K_p. Braune and Ramstetter[3] repeated their work with somewhat different results.

The dissociation of bromine has been determined by the same method by Perman and Atkinson,[4] and Bodenstein and Cramer.[5]

Lewis and Randall[6] have commented on the fact that the results of Starck and Bodenstein are not in agreement with the values required by

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[1] This communication is an abstract of a thesis submitted by Thomas DeVries in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Starck and Bodenstein, *Z. Elektrochem.*, **16**, 961 (1910).

[3] Braune and Ramstetter, *Z. physik. Chem.*, **102**, 480 (1922).

[4] Perman and Atkinson, *ibid.*, **33**, 215 (1900).

[5] Bodenstein and Cramer, *Z. Elektrochem.*, **22**, 327 (1916).

[6] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, p.523.