1.8% of sulfur. At the end of four months one sample gave no indication of coagulation; it was affected little or not at all by the electrolytes and organic substances which were tried as coagulants. When the benzene was removed by evaporation, a sticky, yellow residue of amorphous sulfur remained, which could not be redispersed in benzene. It dialyzed more slowly than dissolved sulfur through membranes of beef bladder and of cellulose acetate. It seems doubtful whether either water or acids are responsible for the stability of these sols.

2. Needle-like crystals of sulfur were obtained in ethyl alcohol at room temperature. These crystals were shown to be monoclinic by microscopic examination, and by melting-point and density determinations. Some of these crystals were stable for several weeks.

NEW BRUNSWICK, NEW JERSEY

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

THE VARIATION OF THE CELL CONSTANT WITH CONCENTRATION AND THE MOLAL CONDUCTANCE OF AQUEOUS BARIUM NITRATE, SODIUM SULFATE AND SULFURIC ACID AT 0°

BY MERLE RANDALL AND GORDON N. SCOTT

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Several recent investigations[1] have shown that relatively large errors probably exist in the values of the specific and equivalent conductances reported. As the precision of conductivity measurements is great, we wished to find the procedure which would best enable us to use this method as a means of determining the concentration of dilute aqueous solutions in freezing-point measurements. Our apparatus was capable of high precision, and we shall report several observations which confirm and extend some of the conclusions reached by the above authors. The investigation, however, is confined to Pyrex cells with platinized electrodes.

We also give the values of the molal conductance of barium nitrate, sodium sulfate and sulfuric acid at 0°.

Experimental Methods

Electrical Circuit.—The conductance set was the same as that used by Randall and Vanselow,[2] except that the oscillator was entirely rebuilt on a new design and a two-stage audio amplifier was added to the bridge circuit.

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[1] (a) Schlesinger and Reed, THIS JOURNAL, **41**, 1727 (1919). (b) Kraus and Parker, *ibid.*, **44**, 2422, 2429 (1922). (c) Parker, *ibid.*, **45**, 1366, (d) 2020 (1923). (e) Morgan and Lammert, *ibid.*, **45**, 1692 (1923); (f) **48**, 1220 (1926). (g) Haworth, *Trans. Faraday Soc.*, **16**, 365 (1921). (h) Parker and Parker, THIS JOURNAL, **46**, 312 (1924).

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

The design of the oscillator[3] was furnished us by the Bell Telephone Laboratories, Inc. It consisted of an oscillating tube (101 D, Western Electric) coupled to a 5-watt output tube (UV 302 A Radio Corporation). The unique feature of this oscillator is a series resistance in the oscillator plate circuit, of such magnitude as to restrict the grid potential variations to the linear portion of the "characteristic" curve, thus insuring a pure sinusoidal wave form. All parts of the electrical circuit were thoroughly shielded. The set was tuned to resonance at 1000 cycles per second, by means of a microphone hummer. Its operation was quite independent of impedance variations in the measuring circuit.

The bridge circuit was enclosed in a sound-proof booth. The usual intercomparisons of the slide wire, and coils and resistances, which were Curtis coils over 10 years old, were made.

The advantages of a two-stage audio amplifier in the telephone circuit have been pointed out by Hall and Adams.[4] The position of the region of silence was independent of any change in the amplifier circuit.

A potentiometer was inserted ahead of the output tube of the oscillator set to control the voltage delivered to the bridge. Parker[1c] used 0.2 and 12 v. at the terminals and found a change in the position of the point of silence at high electrolytic resistances. We used from 0.06 to 0.4 v. and found no change. The only effect which we noticed was a small change in the character of the minimum which required a slight shift of the capacities in the arms of the bridge.

At moderately high resistances the capacity settings were sometimes extremely critical. It was frequently found that the small change caused by a slight displacement of the leads to the condensers was sufficient to destroy or make a perfect minimum.

Within a certain resistance range the null setting was also critical, and the region of silence was so small that the hands were scarcely capable of setting the slide wire.

No heating effects were noted, and satisfactory minima have been obtained with resistances as low as 13 ohms, using sulfuric acid.

Before measurements were made, the oscillator was allowed to operate for over 30 minutes to allow the circuits to become stabilized.

Zero-Degree Thermostat.—As a zero-degree thermostat we used a 4.5-liter glass vacuum vessel (Icy-Hot Bottle Company, Cincinnati, Ohio), equipped with a tightly-fitting cover, 7 cm. in thickness, of Balsa wood. The conductivity cells and an efficient stirrer were attached to the cover. The stirrer consisted of a thin copper tube, 4 cm. in diameter by 20 cm. in length. It contained a close-fitting copper Archimedes spiral, which was mounted upon a heavy glass shaft. The lower end of the cylinder was covered with a metal screen, and the upper end was placed about 3 cm. below the surface of the ice and water mixture. Distilled water and ice which had been washed with distilled water were used. Several tests showed that readings could be maintained constant and reproducible to within a few thousandths of a per cent. over a period of 48 hours if the thermostat were filled to capacity with ice. Additional ice was required every eight to ten hours. Parker and Parker[1h] used drained ice, but found some difficulty in maintaining a constant temperature. The use of a stirred ice-water mixture in a well insulated vessel is to be preferred.

The Cells.—Two cells of the Washburn[5] type were used. Cell I had electrodes about 2 cm. square spaced about 1 cm. apart, and was suitable for measurements at

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[3] We wish to thank Mr. H. G. Tasker of the Physics Department for his help in perfecting the design of the oscillator, and Dr. John Chipman for his assistance in construction and testing.

[4] Hall and Adams, THIS JOURNAL, **41,** 1515 (1919).

[5] Washburn, *ibid.*, **38,** 2431 (1916).

extreme dilution. Cell II had electrodes about 1 cm. square spaced about 3.5 cm. apart and could be used at somewhat higher concentrations. The volumes were 20 and 8 cc., respectively. The platinum leads to the electrodes were glass-enclosed to prevent easy mechanical displacement. All electrodes were well platinized.

The glass tubes leading to the electrodes of the cell were filled with mercury. Heavy copper leads, enclosed in rubber tubing, dipped into the mercury; there was a separate set of leads for each cell. Heavy copper terminal lugs were soldered to the free ends of the leads, and these were clamped to similar lugs on the leads to the bridge. No measurable change of resistance was noted when the connections were made and remade.

The lead resistances were measured with the cells filled with mercury while the cells were in the thermostat, and the terminal lugs connected in the usual way. All measurements have been corrected for lead resistance.

The inlet and outlet tubes of the cells were connected through two-way stopcocks to soda lime tubes. All glass parts were of Pyrex.

Materials.—Conductivity water was kept in large Jena glass bottles. So much water was used, however, that it was rarely stored for more than a few days. The conductivity varied somewhat, but was always below 0.6×10^{-6} mhos per cc.

The potassium chloride was repeatedly recrystallized from conductivity water. It was dried to constant weight.

The barium nitrate was thrice recrystallized. It was dried in an electric oven at 120° to constant weight.

The sodium sulfate was obtained from a large quantity of the hydrated salt which had been repeatedly recrystallized and used for thermel calibrations. It was twice recrystallized, dehydrated at 100°, and finally heated to constant weight.

The salt solutions were made up by weight, vacuum corrections being used in all cases. Concentrations are in moles per 1000 g. of water.

The sulfuric acid was Bakers' Analyzed. It was purified by a method similar to that of Grollman and Frazer.[6] An all-glass still was employed and the distillate was absorbed in conductivity water. It showed no reducing action, after distillation, with a 0.0005 *M* potassium permanganate solution, proving the absence of sulfite. Only a sufficient quantity of the central portion of the distillate, to make about 2 liters of a 1.5 *M* solution, was absorbed. This acid was roughly analyzed and a portion diluted to about 0.1 *M*. This solution was then accurately standardized by the sodium carbonate method.[7]

Preparation of Solutions.—Standard mother solutions were made up by weight to an accuracy of 0.01% or better, and stored in Jena glass bottles. For any one particular electrolyte at least two mother solutions were independently prepared, from which secondary standard solutions, whose conductivities were measured, were prepared by weight.

Not less than three separate conductance series were made with a given salt. The secondary standards for a series were all prepared at the same time, in Pyrex flasks which had been thoroughly cleaned and allowed to stand, for more than one week, filled with conductivity water.

The cells, when not in use, were also filled with conductivity water. The delivery tubes of the cells were dried with a clean linen cloth, after the tubes had been blown free of the residual liquor in the tubes, and then washed externally with a few drops of the solution to be introduced. Three rinsings were found sufficient to reduce the error by dilution to less than 0.01%. A guard solution of the same concentration as the one to

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[6] Grollman and Frazer, THIS JOURNAL, 47, 712 (1925).

[7] Richards and Hoover, *ibid.*, 37, 108 (1915). Randall and Scalione, *Met. Chem. Eng.*, 13, 787 (1915).

be studied was first introduced into the cell and allowed to stand for more than two hours. The solutions were not precooled.

The time to attain temperature equilibrium was not over 30 minutes. The technique was standardized, however, and 60 minutes per solution was allowed. Ordinarily the stirring device in the thermostat was not operated during readings, since in spite of good grounding the noise of the stirrer was audible in the phones.

Cell Constants.—All cell constants are referred to a single standard, the 0.01 Demal solution of Parker and Parker.[8] Between the series of measurements with sulfuric acid and those with barium nitrate and sodium sulfate the cells were filled with mercury. This caused a slight change in the cell constants. The constants were frequently redetermined, using fresh electrolyte for each determination. The average values are given in Table I.

TABLE I

CELL CONSTANTS

Cell	Const. with H_2SO_4	Const. with salts
I	0.20428	0.21693
II	3.3831	3.5865

Change of Cell Constant with Concentration

Preliminary Measurements with Lead Chloride.—A preliminary series of measurements with fifteen slightly acid lead chloride solutions, ranging in concentration from 0.0005 *M* to the limit of solubility, was made. A plot of the molal conductance[9] against the cube root of the molality gave approximately a straight line. Due to an accident, the electrodes suffered a slight displacement. After a redetermination of the cell constant a second series of solutions was measured and the results were plotted. The plots did not coincide, but crossed one another at the dilute end. In other words, the ratio of the cell constants before and after the accident varied with the concentration. The result of the accident was merely a small shift in the relative position of the electrodes, yet it was apparently enough to make the cell constant ratio vary.

Measurements with Four Salts.—Parker[1c] made an extended study, at 25°, of the change of the ratio of the constants for a number of cell pairs over an extensive resistance range, with potassium chloride, and found a minimum ratio in moderately concentrated solutions. Taylor and Acree[10] measured the cell constant with sodium chloride and found a constant ratio between 0.05 and 0.2 *N*, but Parker points out that their range of concentration was too small to show the effect if it exists. Schlesinger and Reed[1a] found a shift in the cell constant ratio with potassium chloride. Parker[1c] considered that the cell with the electrodes at the greatest distance gave the best results.

Parker[1d] also studied the effect with hydrochloric acid and found results similar to those obtained with potassium chloride. He chose to take his

[8] Ref. 1 h. (Moles per cu. dcm.)

[9] 1000 k/m, where k is the specific conductance and m is the molality. See Ref. 2.

[10] Taylor and Acree, THIS JOURNAL, **38**, 2403, 2415 (1916).

cell constant for hydrochloric acid at the minimum point in the curve, or in a solution as strong as possible, but with a resistance high enough to avoid "polarization" effects.

We have made a series of measurements at 0° similar to those of Parker, using, however, a single pair of cells but with several electrolytes.

The data are given in Table II. Cols. 1, 3, 5 and 7 give the resistance of Cell I, while Cols. 2, 4, 6 and 8 give the ratios of the measured resistances of Cells I and II when filled with solutions of barium nitrate, sodium sulfate, sulfuric acid and potassium chloride, respectively. The method of introducing the solutions into the cells was not as elaborate as that used by Parker; nevertheless, the reproducibility of the data was well within 0.01% and is quite comparable in accuracy with his results.

Table II

Cell Constant Ratios at Various Concentrations at 0°

R of Cell I, ohms	Ratio $Ba(NO_3)_2$	*R* of Cell I, ohms	Ratio Na_2SO_4	*R* of Cell I, ohms	Ratio H_2SO_4	*R* of Cell I, ohms	Ratio KCl
3054.1	0.060651	1872.1	0.060553	308.27	0.060404	3884.4	0.060841
1836.6	.060584	1305.8	.060497	156.71	.060402	2171.2	.060639
1189.7	.060553	962.31	.060497	69.042	.060395	1771.2	.060589
525.11	.060506	410.38	.060488	63.846	.060393	723.13	.060503
413.24	.060514	375.91	.060493	58.003	.060403	392.08	.060482
343.65	.060490	232.12	.060498	39.996	.060396	280.70	.060486
284.03	.060499	194.60	.060512	30.590	.060402	203.15	.060493
217.55	.060500	149.60	.060501	12.624	.060403	149.62	.060499
189.57	.060492	71.324	.060502			106.68	.060504
155.49	.060495	60.242	.060494			56.473	.060500
134.48	.060489	28.907	.060501			44.125	.060518
98.188	.060497					30.497	.060531
59.736	.060493						
39.141	.060493						
21.687	.060484						

In Fig. 1 the cell constant ratios from Table II are plotted as ordinates and the resistances of Cell I as abscissas. The data for sulfuric acid are not included in the figure since the measurements were not made with the same cell pair, and because the ratios are constant to within 0.01%. One of Parker's curves for potassium chloride at 25° has been recalculated and replotted to our scale as the upper curve.

Parker, of course, used different cells and we can only compare the form of the curves. We find the same sharp rise in the cell-constant ratio at low resistances in the case of potassium chloride. With barium nitrate however, while the ratio increases in the dilute solutions, there is no tendency to increase in the more concentrated. Sodium sulfate and sulfuric acid solutions give constant ratios, except that sodium sulfate shows a single "high" point.

Variation of Cell Constant with Separation of Electrodes.—We also redetermined the cell constants, using 0.1 Demal solution, and found a 0.23% increase in the case of Cell I and a 0.16% increase in the case of Cell II. Cell II has the greater spacing between the electrodes, and shows the smallest variation in the apparent cell constant. This result is in agreement with the theory of Parker that the variation may be accounted for by a layer of the electrolyte absorbed upon the electrodes. He assumed[1d] negative absorption for potassium chloride and positive for hydrogen chloride. In either case the result is a small layer of high-resistance solution and a smaller percentage effect, the greater the separation of the electrodes.

Although the resistance of Cell I with the more concentrated standard was only 30 ohms, and such cells are not recommended, it is quite possible that the measured difference in the apparent cell constants is a real effect and not due to experimental error. The percentage increase is in the same direction for both cells, hence the changes in the cell-constant ratios are smaller than they would be if the constant of Cell II remained fixed. Since the relative change is appreciable, the absolute variation must be larger. Just to what extent any one series of measurements would be affected by this absorption effect, if it is absorption, would depend upon the type of cell used to determine the standard and the cell used to make the measurements. The lead chloride measurements indicate that these effects are large. The cell-constant change was only a few per cent., but the curves could not be made to coincide within 0.1%, except by a rotation of one of the curves. The greatest deviation occurred in the concentrated end, where uncertainties as to a water correction are negligible.

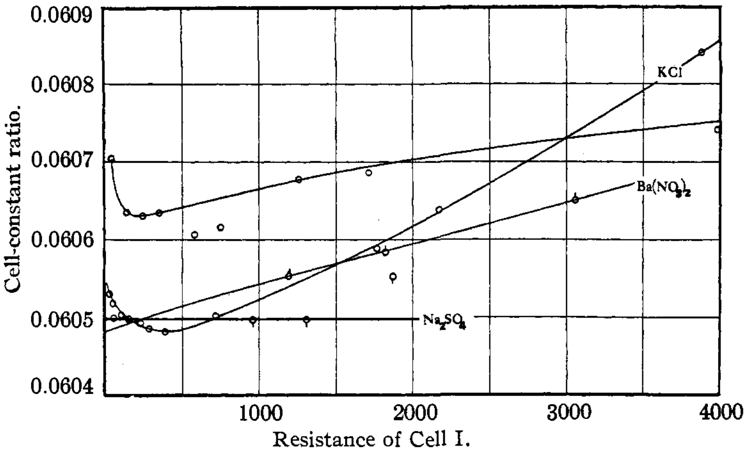

Fig. 1.—Variation in cell-constant ratio.

Change of Cell-Constant Ratio with Temperature.—Over the same resistance range Parker's curve for potassium chloride in Fig. 1 shows a variation of 0.2%, while our curve at 0° shows 0.6%. This might indicate a greater absorption in our case, for Parker's measurements were at 25° and ours at 0°; or the difference may be in the different characteristics of the cell.

The cell-constant ratio was found to be 0.060497 at 0° with a solution of barium nitrate which had remained in the cells for 24 hours. The cells were then transferred to a thermostat at 25° and the cell-constant ratio was found to be 0.060503. To make sure that no evaporation had occurred the cells were returned to the 0° bath and the ratio was found to be again 0.060497. The increase was only 0.01%.

From equations given by Washburn[11] we should predict a decrease in the cell constant ratio of 0.01% due to mechanical effects alone, whereas the measured effect was of opposite sign. The effects are too small, however, to draw any conclusions from this single measurement.

Absorption and Polarization Effects.—For the dilute solutions the rate at which a given solution comes to a constant reading is apparently a function of the resistance of the cell, the character of the electrodes, the material of the cells and the nature of the electrolyte. At moderate resistances 30 minutes is ample for a constant reading, the time being dependent upon the rate of cooling of the solution in the cell. At high resistances the time increases, and at extremely high dilutions the time required may be several days. It is for this reason that a standard procedure was adopted to be used when the conductivity method is to be used for the determination of unknown solutions.

Parker continually agitated his solutions, and so the effect here mentioned may have escaped his attention. He mentions that his readings remained constant, but he does not specify for how long. It is possible that agitation prevents the attainment of an absorption and diffusion equilibrium. The "bending back" of his cell constant-ratio curves at high dilutions might possibly be accounted for by incomplete absorption.

Unfortunately, there was not sufficient time to investigate further the incidental effects; neither did we study the most dilute solutions. Our time-conductivity curves, however, would seem to indicate that if absorption is the cause of the effects, then the quantity of electrolyte absorbed does not vary greatly with concentration.

It is interesting that with one of Parker's pairs of cells with hydrochloric acid the cell-constant ratio did not rise in the dilute end. In this case, however, the sharp rise in the concentrated end was present. Parker has explained this sharp rise on the basis of polarization but it is hard to understand, on the basis of this explanation, why solutions of barium nitrate, sodium sulfate and sulfuric acid are not similarly affected.

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[11] See (a) Kohlrausch and Holborn, "Das Leitvermögen der Elektrolyte," Teubner, Leipzig, **1916**, p. 123; (b) Ref. 1 h. (c) Washburn, THIS JOURNAL, **38**, 2452 (1916).

We must note, however, that the rise in the concentrated end is observed only with chloride solutions. There is a possibility that the chlorine reacts with the platinum black. It may also be significant that the rise obtained by Parker, who used a higher voltage and hence a higher current density, is steeper than the rise obtained by us. If platinic chloride were formed, then it would form the complex ion in the vicinity of the electrode and cause a rise in resistance. This explanation is at most only a tentative suggestion.

That considerable absorption occurs is shown by the fact that the conductance of the initial solution of a series was always low. It was the custom, therefore, to use a "guard solution" of the same concentration which was allowed to stand in the cells for two or more hours before starting a series. There is no *a priori* reason why absorption should be limited to the electrodes, and we have evidence to show that the absorption must occur on the glass walls as well. A liter of potassium chloride solution, whose conductivity was accurately known, had been left standing for several months undisturbed. When its conductivity was again determined several months later with two cells, it was found that its conductivity had diminished considerably, although the cell-constant ratio remained constant. The quantity of the solution to be measured was pipetted from the vessel containing the solution, which was not shaken. Had the conductivity increased, the observation would have been attributed to evaporation.

As other examples of the absorption of the electrolyte upon the electrode surfaces the following may be mentioned. One of our cells had been standing filled with conductivity water and the other filled with an acid cleaning mixture. These cells after thorough washing, were filled with a standard potassium chloride solution, and after several hours a constant reading was found. Upon repeating the measurements the following day, however, it was found that the conductivity of the solution in one cell had risen a small amount, whereas the other had fallen, corresponding to an absorption of the potassium chloride and a salting out of the sulfuric acid. If, after a relatively concentrated solution had been measured, the cell was filled with water, the conductivity rapidly dropped with the cooling, reached a minimum and then slowly rose for many hours. The interesting fact in such an experiment, however, is the considerable change found necessary in the bridge capacity to balance that in the cell. The capacity setting required becomes constant only when the conductivity of the water becomes reproducibly constant. Many similar illustrations of the manifestations of absorption could be given. Enough has been said, however, to show that in accord with Parker's conclusions, these effects must arise within the cell itself.

Change of Conductivity of Acids with Time.—An extremely disturbing effect of a different nature, already pointed out by Kraus and Parker,[12]

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[12] Ref. 1 b, p. 2429.

occurs in dilute solutions of strong acids. They studied the influence of impurities on the conductance of dilute solutions of iodic acid and found that the curve they obtained depended upon the initial conductance of the water and the material of the cell. They used quartz, Pyrex and soda lime glass cells. The true conductance curve was obtained with the quartz cell and with water of a high degree of purity. The effect is attributed to the reaction of the acid upon the impurities in the water and upon the cell walls. The deviation found between the best and poorest values of the equivalent conductances at 0.001 *M* was about 0.5%. The various curves coincided at a concentration of about 0.005 *M*. That Randall and Vanselow experienced this difficulty in the case of hydrochloric acid can easily be shown by plotting their molal conductances against the logarithm of the molality. The curves corresponding to the two runs start to deviate at 0.01 *M*, and at 0.001 *M* the interpolated difference in the two curves is 0.1%. At the low concentrations at which our conductance measurements were made our procedure was standardized, which would in part eliminate this effect. One very dilute sulfuric acid solution was studied over a period of three or four days, but a final minimum conductance was never obtained. Dr. John Chipman[13] of this Department observed, in studying the Soret effect of hydrochloric acid, that even after three or four weeks, the conductance of the acid in both halves of his Soret tubes was still dropping. The change from the initial conductance was 3 or 4%.

Long before our measurements on the cell constant ratios were completed, it was predicted, on the basis of Parker's positive and negative absorption theory, that if absorption did occur positively and negatively, an electrolyte might be found where the absorption would be such as to cause no change in the cell constant ratio, in which event this substance would serve better for the standardization of conductance cells. That such substances apparently do exist has been partially demonstrated in the case of sulfuric acid and sodium sulfate. Sulfuric acid could not be used in very dilute solutions except in quartz cells.

Molal Conductance of Barium Nitrate, Sodium Sulfate, and Sulfuric Acid Solutions at 0°

From the foregoing it is evident that the results of conductance measurements are very reproducible if precautions, such as those suggested, are taken to standardize the technique, but the values may be a few per cent. different if other technique or other cells are used. We believe our values will be of some general interest, and give in Table III the results of our measurements interpolated to round molalities. Col. 1 gives the molality, and the other columns the molal conductances of the several salts. The molal conductance is the specific conductivity divided by the moles per g.

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[13] Chipman, THIS JOURNAL, 48, 2577 (1926).

of water. The water correction has not been subtracted from the conductivity of the sulfuric acid solutions.

TABLE III

MOLAL CONDUCTANCE OF BARIUM NITRATE, SODIUM SULFATE AND SULFURIC ACID SOLUTIONS AT 0°

	1000 k/m		
m	$Ba(NO_3)_2$	Na_2SO_4	H_2SO_4
0.001	137.60	127.08	471.7
.002	133.57	123.49	456.3
.005	126.34	117.39	426.4
.01	119.29	111.50	399.0
.02	110.67	104.51	369.3
.05	97.18	93.99	333.3
.1	85.47	85.24	310.9
.2	72.08	75.62	...

Extrapolation and Interpolation of Results.—Since, if the technique is properly standardized, the measurements of the specific conductance of an unknown solution are reliable, it is convenient to have a simple, accurate method of obtaining the molality.

The method here used for interpolation is partly analytical and partly graphical, and is dependent upon the fact that over the comparatively small range of concentration in which we were interested a plot of the logarithms of molality against the logarithms of the specific conductivity yields a curve which does not depart to any great extent from linearity.

We may express this approximate linearity by the equation

$$\log m = a \log k + \log b \quad (1)$$

where m is the molality and k the specific conductivity. The slope of the line is given by the constant a. The intercept on the axis of $\log m$ is the constant, $\log b$. For any fixed line which is determined by the slope a, which cuts the experimental $\log m$ against $\log k$ curve, the values of $\log b$ will vary with the simultaneous experimental values of m and k. We assume, therefore, that $\log b = f(\log k)$, and plot the calculated values of $\log b$ against any

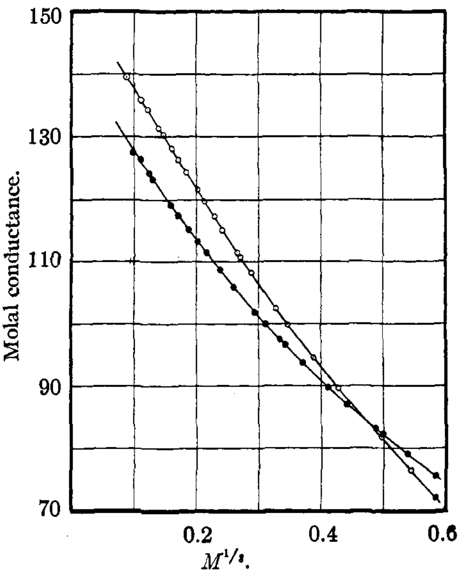

Fig. 2.—Molal conductance of barium nitrate and sodium sulfate at 0°. ●, Na_2SO_4; ○, $Ba(NO_3)_2$.

function of the logarithm of the corresponding value of *k*. The method of interpolation is clear. Having determined the value of *k*, the algebraic sum of the product of log *k* and *a*, and the value of log *b*, obtained from the graph of log *b* and the function of log *k* employed, gives directly the logarithm of the molality corresponding to *k*. It can readily be seen that the accuracy can be carried to any degree desired, depending only upon the number of points available over any given concentration range and how greatly log *b* varies with the function of log *k*. For the three cases with which we were concerned, log *b* changed by only a few per cent. for large changes in log *k*. For example, in the case of sodium sulfate when log *k* changed from —1.6 to +0.7, log *b* changed from —0.7220 to —0.7320. With about the same distribution of points as that which was used by Randall and Vanselow we were able to obtain at least ten times their accuracy of interpolation.

It is interesting to note that the relationship in the "molal conductance" plots which they have pointed out is borne out with the electrolytes which we have studied, including lead chloride. Our molal conductances are plotted against the cube root of the molality in Figs. 2 and 3 and yield curves approximating straight lines in the dilute end. The molal conductances are plotted as ordinates and the cube roots of the molalities as abscissas. We have found these plots of value in aiding us to select fixed points for the calculation of *a*, since the sensitivity is greater than that in the logarithmic plots.

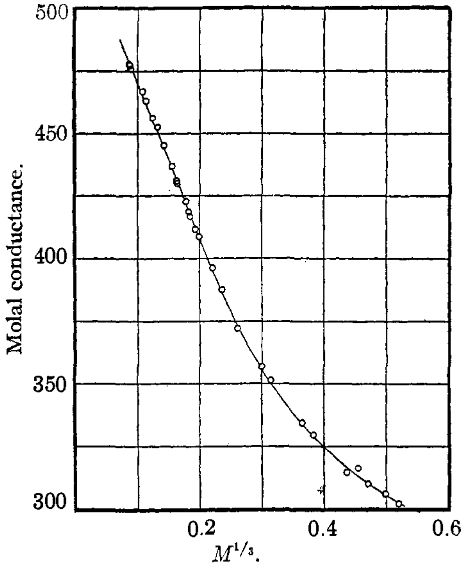

Fig. 3.—Molal conductance of sulfuric acid at 0°.

In the cases of the salts another expedient was used in order to reduce the variation in log *b* to a minimum. The specific resistances were corrected by a small ohmic number before the constant *a* of the straight-line equation was calculated. This small quantity largely affects the specific conductivities in the concentrated range where the maximum departure from linearity of the logarithmic curves occurred, and hardly affects at all the section of the curve in the dilute end. The general equation is, therefore

$$\log m = a \log (1/(1/k) - \Delta) + \log b \qquad (2)$$

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).