good, and the activity coefficients of the ions of hydrochloric acid can be considered to be determined within a few tenths of a per cent. It seems clear that the freezing-point measurements cannot determine the activity coefficient more closely than the difference between the results required by Equations 1 and 2. The values computed from electromotive-force measurements lie within this range and determine the most probable values still more accurately.

In conclusion I wish to express my gratitude to the National Research Council for its financial assistance, and to Professor F. G. Keyes and the other members of the staff of this Laboratory, especially to Professor D. A. MacInnes, for the suggestions and help they have given.

Summary

1. The electromotive force at 25° of the cell, $Pt,H_2 | HCl,AgCl | Ag$, has been measured at several concentrations in the range 0.01–1.5 *M*, using a rocking hydrogen-electrode vessel designed for use in a water thermostat.

2. The mean activity coefficients of the ions have been calculated from these measurements and earlier ones on the same type of cells.

3. The coefficients are in very good agreement with those calculated from the freezing-point measurements of Randall and Vanselow.

4. The resulting activity coefficients at low concentrations are consistent within the experimental error with the limiting equation of Debye and Hückel, retaining the theoretical value of the constant of that equation.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 165]

THE ACTIVITIES OF STRONG ELECTROLYTES. II. A REVISION OF THE ACTIVITY COEFFICIENTS OF POTASSIUM, SODIUM, AND LITHIUM CHLORIDES, AND POTASSIUM HYDROXIDE[1]

BY GEORGE SCATCHARD[1a]

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I. Introduction

For a study of liquid-junction potentials, to be published later, values for the mean activity coefficient of the ions of potassium chloride more accurate than those available in the literature were necessary. In an attempt at accurate revision the activity coefficients of the salts named in the title were calculated from all available measurements of electromotive force, freezing point and vapor pressure.

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[1] Revised manuscript received December 11, 1924.

[1a] National Research Fellow.

The methods of computation are essentially those of Lewis and Randall[2] except for the extrapolation to zero concentration, which was in accordance with the theory of Debye and Hückel.[3] This theory expresses the variation from the laws of an ideal solution due to the electrical charges on the ions. If Raoult's law be taken as the ideal, the equation may be written

$$-\log \frac{a_{\pm}}{55.5\ N} = \frac{Aw\sqrt{c}}{1 + \alpha\sqrt{c}} \qquad (1)^{4}$$

where $a_{\pm}$ is the mean activity of the ions so expressed as to approach the molality (m) at zero concentrations, N is the mole fraction, A is a constant depending on the medium and temperature, w is another constant depending on the valence type of the salt (for uni-univalent electrolytes it is unity), α is a constant for each salt depending on the mean diameter of the ions, and c is the concentration in moles per liter.

For dilute aqueous solutions this equation may be simplified by expanding to a power series in c and neglecting powers higher than the first, by giving A the value 0.5 at all temperatures, and by ignoring the small differences between 55.5 N, c and m. The equation may be written

$$-\log \frac{a_{\pm}}{c} = 0.5w\sqrt{c} - Bc \qquad (2).$$

or

$$-\log \gamma = -\log \frac{a_{\pm}}{m} = 0.5w\sqrt{m} - Bm \qquad (3)^{5}$$

Equation 3 has been used in this paper: at zero concentration it approaches

$$-\log \gamma = 0.5w\sqrt{m} \qquad (4)$$

For freezing-point measurements it is convenient to use the quantity $j = 1 - \frac{\theta}{1.858\ \nu m}$, where θ is the freezing-point depression and ν is the number of ions formed from one molecule of salt. The equation corresponding to (3) is

$$j = 0.38w\sqrt{m} - bm \qquad (5)$$

which gives,

$$-\log \gamma = 0.495w\sqrt{m} - 0.868bm \qquad (6)$$

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[2] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., **1923**, Chapters 26–28.

[3] (a) Debye and Hückel, *Physik. Z.*, **24**, 185 (1923). (b) Debye, *ibid.*, **24**, 334 (1923). (c) Hückel, *Ergebnisse exact. Naturwiss.*, **3**, 199 (1924).

[4] An equivalent form of the equation is given in Ref. 3 c; the original statement in 3 a gave the less accurate form using $a_{\pm}/c$.

[5] $B = \alpha A w$. The value of B determined experimentally also includes deviations from the simple Equation 1. Two possible causes for deviations approximately proportional to the concentration are ionic hydration [Bjerrum, *Z. anorg. Chem.*, **109**, 275 (1920)], and changing dielectric constant with changing concentration (Hückel, not yet published).

Lewis and Linhart[6] and Lewis and Randall use the equation

$$j = \beta m^{\alpha} \tag{7}$$

which gives

$$-\log \gamma = \beta' m^{\alpha} \tag{8}$$

Equations 5 and 7 may be compared by taking the logarithms:

$$\log j = 0.5 \log m + \log (0.38\, w - b\sqrt{m}) \tag{5'}$$

and

$$\log j = \alpha \log m + \log \beta \tag{7'}$$

Equation 7 is claimed to be valid only up to 0.01 M, and the error in determining j is very large below 0.003 M. Through the range 0.003–0.01 M, Equations 5 and 7 may both fit the experimental data. If b is small $0.38w - b\sqrt{m}$ will be nearly constant, α will equal 0.5 but β will be less than 0.38 w. This is the case with all uni-univalent electrolytes studied and with lead nitrate. For the complex salts used in the solubility measurements of Brönsted and La Mer,[7] b is so small that the difference between β and 0.38 w is not measurable up to 0.01 M.

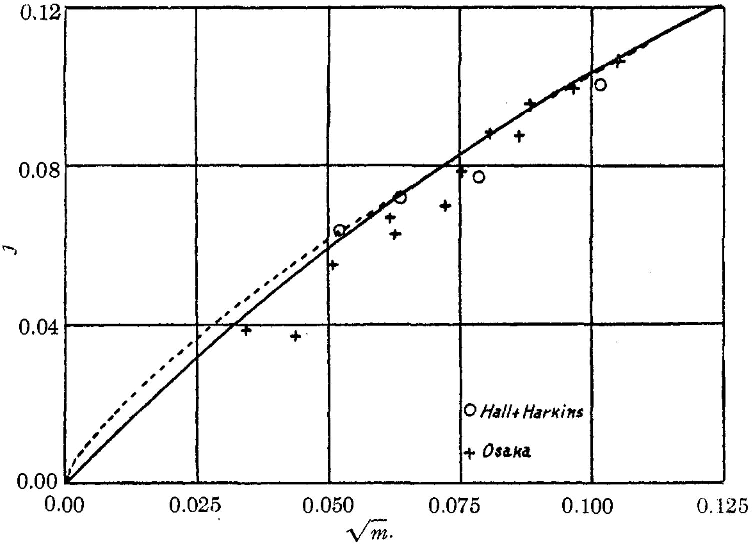

Fig. 1.—Potassium sulfate freezing points.

If b is large the variation in $0.38w - b\sqrt{m}$ will appear in Equation 7 as a value for α less than 0.5. This happens with most salts of higher valence types where w and b are both large. Fig. 1 shows the values of j for potassium sulfate, upon which the most accurate measurements have been made. The circles are the experimental points of Hall and Harkins,[8]

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[6] Lewis and Linhart, This Journal, **41**, 1952 (1919).

[7] Brönsted and La Mer, *ibid.*, **46**, 555 (1924).

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

the crosses those of Osaka.[9] The full line represents the equation $j = 1.316\sqrt{m} - 2.8m$, the dotted line $j = 0.572m^{0.374}$. Through the range of experimental test the two equations are almost identical, although they deviate considerably at both lower and higher concentrations.

Similarly the freezing-point data for all the salts discussed by Lewis and Randall may be represented within their apparent experimental error by Equation 5. The data for potassium and sodium chlorides are discussed later in this paper. The measurements of Randall and Vanselow[10] on hydrochloric acid have already been discussed.[11] Their measurements on thallous chloride and lead nitrate fit Equation 5 with $b = 1.0$ and 1.034, respectively, almost exactly as well as they do Equation 7 with the constants given by the authors.

Noyes[12] concludes that by giving to the constant in Equation 4 a value about five-sixths of that demanded by the theory of Debye and Hückel, values of the activity coefficients are obtained which are in better agreement with the experimentally derived values. This conclusion, however, is based on the use of the simple equation even up to 0.1 or 0.2 M, and by comparison with values many of which are derived through extrapolations by means of Equation 8. The Debye-Hückel theory demands that, if the ions have molecular dimensions, the deviations from Equation 4 shall be evident at approximately 0.001 M.

In view of the discrepancy between the equation of Milner and that of Debye and Hückel, I should base the justification of Equations 3 and 5 upon the electromotive-force measurements of Linhart with hydrochloric acid, and especially upon the solubility measurements of Brönsted and La Mer.[7] Both indicate clearly a value for A not greatly different from 0.5. Greater experimental accuracy in the future may justify the use of a more accurate form of the equation even in dilute solutions. At present there are no experimental data which are not fitted within their experimental error by Equation 3 up to 0.01 M, and none on uni-univalent electrolytes other than hydrochloric acid for which the equation does not hold up to 0.1 M.

II. Potassium Chloride

A. Calculation from Electromotive-Force Measurements.—The electromotive force of the cell, Ag | AgCl,KCl(c') | K,Hg | KCl(c''),AgCl | Ag, has been measured at 25° by MacInnes and Parker[13] with the solution pairs 0.005–0.05, 0.01–0.1 and 0.05–0.5 M, and by Beattie[14] with 0.1–

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

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

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

[12] Noyes, *ibid.*, **46**, 1080, 1098 (1924).

[13] MacInnes and Parker, THIS JOURNAL, **37**, 1445 (1915).

[14] Beattie, *ibid.*, **42**, 1130 (1920).

1.0 M. Because of difficulties in exactly duplicating the amalgam concentration, no attempt was made to measure the half-cells alone. So E_0' ($E_0' = E + 118.3 \log m = E_0 - 118.3 \log \gamma$, where E is the measured electromotive force, E_0 is the value of E_0' at zero concentration and γ is the mean activity coefficient of the ions) cannot be calculated directly, but only differences between its values in different solutions. Moreover, the second cell of MacInnes and Parker is not correlated with the other two, so we have the problem of fitting together two overlapping series of three points each.

The procedure was to give an arbitrary value to E_0' for one solution, to calculate from this its value in the other solutions of that series, to plot these E_0' values against $\sqrt{m}$, to draw through them a curve approaching the slope 59.15 asymptotically with decreasing concentration, to fit the points of the second series to this curve, and to draw a smooth curve through all the points. This curve was then tested to see if the deviation from the linear asymptote was proportional to the molality in accordance with Equation 3. If it was not, a new value of E_0 was tried, shifting the relative position of the two series if necessary. The final curve fits the two cells with the more concentrated solutions exactly. For the other two the deviations are 0.5 and 0.8 mv. in the direction which would indicate a steeper slope than that of Equation 3. At least part of this discrepancy is probably due to the fact that the measurements of MacInnes and Parker antedate some of the improvements in technique both with silver chloride and with the amalgam electrodes.

Since the transference numbers of potassium chloride in dilute solutions are accurately known, it is possible to utilize the measurements of MacInnes and Parker[13] at 25° and of Jahn[15] at 18° on cells with transference, Ag | AgCl,KCl(c') | KCl(c''),AgCl | Ag. The ratio of the electromotive force of the cell with transference to that without is 0.496 at 25° and $0.496 \times 291/298$ at 18° (making in the latter case the very reasonable assumption that in such dilute solutions the activity coefficient does not change appreciably with this small temperature change). For the measurements of MacInnes and Parker the deviations are in the same direction and of about the same magnitude as for the cell without transference. Jahn's measurements deviate in the same direction, about 0.3 mv. on the average. This is not much greater than the difference between his two series and is probably within his experimental error. The values of the activity coefficients calculated from these measurements are given in the last column of Table I.

B. Calculation from Freezing-Point Measurements (KCl).—The values of j calculated from the measurements of Jahn,[16] Flügel[17] and

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[15] Jahn, *Z. physik. Chem.*, **33**, 545 (1900).

[16] Jahn, *ibid.* **50**, 144 (1904); **59**, 35 (1907).

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

Adams[18] were plotted against $\sqrt{m}$ and a smooth curve was drawn through them approaching the line $0.38\sqrt{m}$ asymptotically at zero concentration, but without further restrictions. The position of the curve is determined very largely by the points in the more concentrated solutions, but those at lower concentrations agree with the curve within their experimental error. Those of Adams fall a little below the curve, those of Flügel a little above and those of Jahn are evenly distributed about it. Fig. 2 is a small-scale reproduction of the plot.

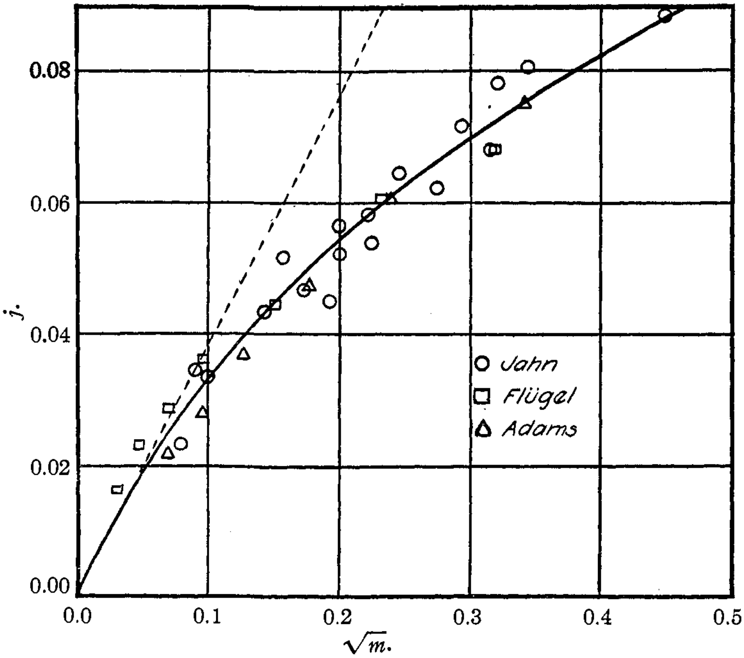

Fig. 2.—Potassium chloride freezing points.

After this curve was drawn it was found that up to 0.2 *M* it fitted, within the accuracy of drawing, the equation $j = 0.38\sqrt{m} - 0.57m + 0.8m^2$, which gives $-\log \gamma = 0.495\sqrt{m} - 0.495m + 0.52m^2$. For the more concentrated solutions $\log \gamma$ was determined by graphic integration by the method of Lewis and Randall.[2] The term in m^2 is regarded as simply an empirical device to fit the j curve as drawn, and without theoretical significance. Below 0.1 *M* it does not affect the value of γ as much as 0.1%; above 0.2 *M* it causes wide deviation from the experimental points. The values of γ_0 calculated from these measurements are given in the fourth column of Table I. By analogy to sodium chloride γ_{25} should be a few tenths of one per cent. higher than γ_0 at 0.2 and 0.3 *M*. So the activity val-

[18] Adams, This Journal, **37**, 494 (1915).

ues from freezing points are about 1% higher than those from electromotive force. The discrepancy is not greater than the possible experimental error of either method.

C. Calculations from Vapor-Pressure Measurements (KCl).—Lovelace, Frazer and Sease[19] have measured the vapor pressure at 20° of aqueous potassium chloride solutions through the concentration range 0.05–4.0 *M*. The calculation of the activity coefficients from these measurements was made by the equations

$$\log \frac{a_2}{N_2} = -\int^{N_1} \frac{N_1}{N_2}\, d \log \frac{a_1}{N_1} + C \qquad (9)^{20}$$

and

$$\log \gamma = \frac{1}{2} \log \frac{a_2}{N_2} + \frac{1}{2} \log N_2 - \log m \qquad (10)$$

where a_1 and a_2 are the activities of the solvent and solute, respectively, and N_1 and N_2 are their mole fractions. The vapor pressure of water at 20° is taken as 17.539 mm.,[21] so that $a_1 = \dfrac{17.539 - \Delta p}{17.539}$. The value of the constant C cannot be determined from these measurements because they do not extend to low enough concentrations, and in the most dilute solutions a small error in the measurements or in the graphic integration affects the value of γ markedly. Therefore the value of γ in the 1.0 *M*

Table I

Mean Activity Coefficients of the Ions of Potassium Chloride

Molality	γ_{25} Lewis and Randall	γ_{25} Noyes and MacInnes	γ_0 Freezing points	γ_{20} Vapor pressures	γ_{25} E.m.f.
0.001	0.977	0.979	0.966		0.965
.002	.967		.952		.951
.005	.946	.923	.928		.926
.01	.922	.890	.902		.899
.02	.892		.870		.865
.05	.841	.790	.818	0.849	.809
.1	.796	.745	.772	.789	.762
.2	.749	.700	.719	.728	.715
.3		.673	.686	.692	.688
.4				.667	.669
.5	.682	.638		.652	.654
.6				.640	.642
.75				.627	.627
1.0	.634	.593		(.605)	.605
2.0				.574	
3.0				.569	
4.0				.580	

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[19] Lovelace, Frazer and Sease, This Journal, **43,** 102 (1921).

[20] Ref. 2, Chapter 22, p. 269. Eq. 22–23 with subscripts changed.

[21] Landolt-Börnstein "Tabellen," **1912,** p. 360. The 1923 edition gives 17.535 based on the same experimental work. The difference is unimportant.

solution was taken, the same as that from the electromotive force measurements. The values for γ_{20} so determined are given in the fifth column of Table I. Down to 0.3 M the results by the two methods agree within a few tenths of one per cent.; between 0.2 and 0.05 M the discrepancy increases to 4%, which is probably not beyond the errors in measurement and calculation of the vapor pressure method.

The values for the mean activity coefficients of the ions of potassium chloride given by Lewis and Randall and by Noyes and MacInnes[22] are also given in the second and third columns of Table I. My results lie between the two earlier ones but closer to those of Noyes and MacInnes. The differences all lie in the methods of extrapolation. Lewis and Randall assumed that in very dilute solutions the activity coefficients of potassium chloride are the same as the values they found for sodium chloride.

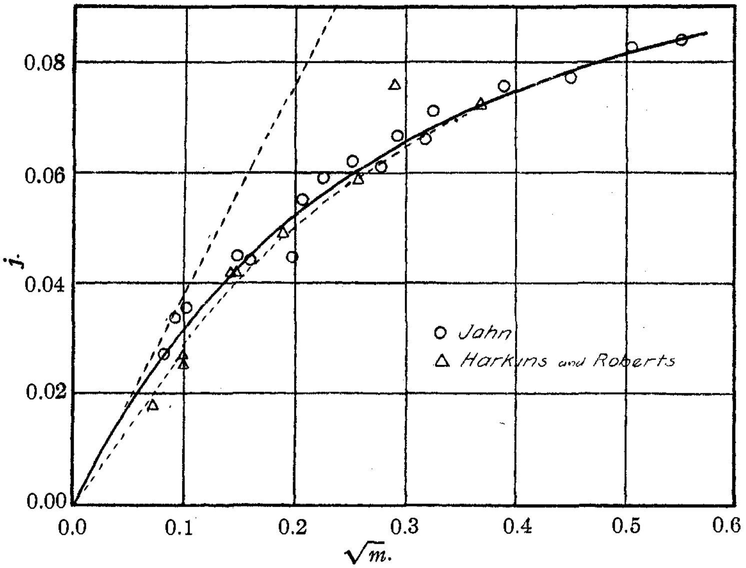

Fig. 3.—Sodium chloride freezing points.

III. Sodium Chloride

A. Calculation from Freezing-Point Measurements.—The method used was exactly the same as that employed for potassium chloride in Section IIB. Fig. 3 is a small-scale reproduction of the plot of the j values of Jahn[16] and of Harkins and Roberts.[23] The upper dotted line is the asymptote, $j = 0.38\sqrt{m}$, the full line is the smooth curve used. Up to 0.2 M it is fitted within the accuracy of drawing by the equation $j = 0.38\sqrt{m} - 0.6m + 0.7m^2$, which gives $-\log \gamma = 0.495\sqrt{m} - 0.521m +$

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[22] Noyes and MacInnes, This Journal, **42,** 239 (1920).

[23] Harkins and Roberts, *ibid.*, **38,** 2676 (1916).

$0.46m^2$. As in the case of potassium chloride the position of the curve is determined largely by the points at higher concentrations and the limiting law. It fits the results of Jahn for dilute solutions very well; the deviations of the measurements of Harkins and Roberts in the dilute solutions correspond to less than 0.0003°. It should be noted that Hall and Harkins,[8] and presumably Harkins and Roberts, correct "all measurements at low concentration" by 0.0001° because this was the average deviation of non-electrolytes from the ideal law, $\theta = 1.858\ m$. This correction is in the direction to decrease j.

The lower dotted line represents the j values used by Lewis and Randall.[24] They have apparently given full weight to the measurements of Harkins and Roberts in dilute solutions. To obtain a smooth curve they have given little weight to the measurements at 0.02 M ($\sqrt{m} = 0.14$), whose deviation from their curve is again nearly 0.0003°. Their curve also fits the measurements of Adams on potassium chloride better than mine does, but the deviation of his results from my curve in dilute solutions is less than 0.0002°. I believe that, taken as a whole, the experimental results for sodium chloride, like those for potassium chloride, are fitted better by my curve than by that of Lewis and Randall. Certainly, neither offers important evidence for preference of Equation 7 to Equation 5 for extrapolation, or for a change in the value of the constant A.

TABLE II

MEAN ACTIVITY COEFFICIENTS OF THE IONS OF SODIUM CHLORIDE

Molality	γ' Lewis and Randall	γ' Scatchard	Ratio γ'_S/γ'_{L+R}	γ_{25} Lewis and Randall	γ_{25} Scatchard
0.001	0.977	0.966	0.989	0.977	0.966
.002	.967	.953	.985	.967	.953
.005	.946	.928	.981	.946	.928
.01	.922	.903	.979	.922	.903
.02	.892	.871	.977	.892	.871
.05	.842	.821	.975	.842	.821
.1	.798	.778	.975	.798	.778
.2	.750	.732	.976	.752	.734
.3		.703			
.5	.682			.689	.671
1.0	.630			.650	.634
2.0	.613			.661	.645
3.0	.627			.704	.686
4.0	.657			.765	.746
5.0	.713			.852	.831
5.2	.729			.874	.852

Between 0.05 and 0.2 M, the ratio of γ' calculated by Lewis and Randall and by me is constant within 0.1%. For the more concentrated solutions I have taken their values of γ' multiplied by the factor 0.975. Through-

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[24] Ref. 2, p. 348.

out I have used their values for the ratio γ_{25}/γ'. Table II contains the values of γ' calculated by Lewis and Randall and by me, the ratio of these two, and the values of γ_{25} calculated from the two values of γ'.

B. The Electromotive Force Measurements (NaCl).—Allmand and Polack[25] have measured the electromotive force at 25° of the cell, Hg,Na | NaCl,HgCl | Hg, with various concentrations of sodium chloride. They tell of no precautions to eliminate oxygen, which has a very serious effect on the amalgam electrodes, and it appears from the description of their procedure that oxygen must have been present. It is probably a consequence of this that their measurements on dilute solutions give results far different from any other determinations of activity, and indicating a curve much steeper than that for Equation 5. Between 0.1 and 3.2 *M* the average value of the deviation from the curve for γ determined from freezing points is 1.2% (of γ), but there is a trend of 3.5% in these values. Since the results in dilute solutions show a deviation so much greater, it is probable that this deviation may be attributed to experimental error and that these measurements are not sufficiently accurate for the calculation of activity coefficients.

IV. Lithium Chloride

A. Calculation from Electromotive-Force Measurements.—MacInnes and Beattie[26] have measured the electromotive force at 25° of the cell, Ag | AgCl,LiCl(c') | Li,Hg | LiCl(c''),AgCl | Ag, over a wide range of concentration. The treatment of their data in this paper is the same as that of the similar potassium chloride cells in Section IIA, except that a larger number of points are more accurately determined and so linked together that it is only necessary to select arbitrarily one value of E_0', which cancels out in the calculation of γ. The deviations of the experimental points from the curve are much smaller than for potassium chloride. Down to 0.1 *M* they do not exceed 0.03 mv.; from 0.003 to 0.1 *M* they average 0.2 mv. For the cell 0.001–0.01 *M* the deviation is 0.8 mv., probably due to the formation of lithium hydroxide from the lithium of the amalgam. Their measurements on cells with transference cannot be utilized because there are no independent measurements of the transference numbers of sufficient accuracy. The values of γ_{25} calculated from these measurements are given in the last column of Table III.

B. Calculation from Freezing-Point Measurements (LiCl).—The freezing points of lithium chloride solutions have been measured by Loomis[27] and by Jahn.[16] The measurements are not very accurate and do not agree well among themselves, with Equation 5, or with the electromotive force measurements, all of which can probably be attributed to

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[25] Allmand and Polack, *J. Chem. Soc.*, **115**, 1020 (1919).

[26] MacInnes and Beattie, THIS JOURNAL, **42**, 1123 (1920).

[27] Loomis, *Ann. Physik*, **60**, 523 (1897).

errors in the freezing-point measurements. The mean activity coefficients calculated from their measurements by the method used for potassium and sodium chlorides are given in the second column of Table III.

C. Calculation from Vapor-Pressure Measurements (LiCl).—The vapor pressure of aqueous lithium chloride solutions at 20° has been measured by Lovelace, Bahlke and Frazer[28] in the concentration range 0.1–1.0 *M*. The calculation of the activity coefficients from their data is the same as the corresponding calculation for potassium chloride in Section IIC; the results are given in the third column of Table III. In dilute solutions the agreement with the results for electromotive force is better than for potassium chloride. The differences of less than 1% in the more concentrated solutions may very possibly be due to the temperature variation of γ.

TABLE III

MEAN ACTIVITY COEFFICIENTS OF THE IONS OF LITHIUM CHLORIDE

Molality	γ_0 Freezing point	γ_{20} Vapor pressure	γ_{25} E.m.f.
0.001	0.96		0.965
.002	.95		.952
.005	.93		.927
.01	.91		.901
.02	.89		.869
.05	.85		.819
.1	.81	0.791	.779
.2	.78	.756	.750
.3	.77	.739	.739
.4		.732	.735
.5		.731	.736
.6		.734	.738
.75		.740	.743
1.0		(.754)	.753
3.0			1.165

V. Potassium Hydroxide

The cell, $\text{Pt,H}_2 \mid \text{KOH}(c') \mid \text{K,Hg} \mid \text{KOH}(c'') \mid \text{H}_2\text{,Pt}$, has been measured at 25° by Knobel,[29] who interpreted it as measuring directly the activity of the potassium hydroxide. However, the cell reaction must be $\frac{1}{2}\ H_2 + KOH = H_2O + K$, so that the net effect of passing a faraday of electricity through the cell is to transfer one mole of potassium hydroxide from the first cell to the second and one mole of water in the reverse direction. The electromotive-force equations are, $E = \frac{RT}{F}\ ln\ \frac{a'_2}{a''_2} - \frac{RT}{F}\ ln\ \frac{a'_1}{a''_1} = 59.15$

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[28] Lovelace, Bahlke and Frazer, THIS JOURNAL, **45**, 2930 (1923).

[29] Knobel, *ibid.*, **45**, 70 (1923).

$\log \frac{a_2'}{a_2''} - 59.15 \log \frac{a_1'}{a_1''}$, and $E_0' - E_0'' = 118.3 \log \frac{\gamma'}{\gamma''} - 59.15 \log \frac{a_1'}{a_1''}$, where the superscripts refer to the first (′) and second (″) solutions, the subscripts to the solvent ($_1$) and solute ($_2$), and the millivolt is the unit of electromotive force. The quantity $E_0' - E_0$ was calculated by the same method as that used for potassium and lithium chloride cells. In dilute solutions the effect of the activity of the water is so small that it does not alter the extrapolation to zero concentration. The curve fits the measurements within the difference between duplicate experiments.

Although there are no independent measurements of the activity of water in potassium hydroxide solutions, it may be calculated from these electromotive-force measurements by a series of approximations. For the first approximation the activity of the water was made the same as that in potassium chloride solutions at 20°. The corresponding electromotive force was added to the quantity $E_0' - E_0$ (both are negative for this type of cell), and the activity of the water was calculated from Equation 9, with subscripts changed and Equation 10. In the calculation of the activity of the solvent by this method the extrapolation to zero concentration is unambiguous. The operation was repeated using the new values of the activity of the water until the fourth repetition gave results identical to 0.01 mv. with those of the third.

TABLE IV

ACTIVITY OF WATER AND POTASSIUM HYDROXIDE FROM CONCENTRATION CELLS

Molality	$E_0' - E_0$	Activity of water	E.m.f. due to water	γ_{25} uncorr.	γ_{25} corr.
0.001	−1.82	0.99996	0.00	0.965	0.965
.003	3.08	.99989	.00	.942	.942
.01	5.37	.99963	− .01	.901	.901
.03	8.70	.99897	.03	.844	.844
.1	13.20	.99668	.09	.773	.772
.3	16.14	.98988	.26	.730	.727
1.0	14.36	.96439	.94	.756	.743
3.0	+5.64	.87482	3.42	1.116	1.044

In Table IV the second column gives the quantity $E_0' - E_0$ in millivolts; the third gives the activity of the water and the fourth the resulting electromotive force; the fifth column gives the values of γ calculated without correcting for the activity of the water, the sixth column the corresponding corrected values. The correction is negligible in dilute solutions, but amounts to 7% in the 3 *M* solution. The values of γ_{25}, at rounded concentrations, are tabulated in the sixth column of Table V.

Chow[30] has measured at 25° the electromotive force of the cell, Hg | HgO,KOH(c') | K,Hg | KOH(c''),HgO | Hg, which he also erroneously in-

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[30] Chow, THIS JOURNAL, **42**, 488 (1920).

terpreted as giving directly the activity of potassium hydroxide. The equations for the cell reaction and for the electromotive force are $\frac{1}{2}$ Hg + KOH = $\frac{1}{2}$ HgO + $\frac{1}{2}$ H_2O + K, and $E_0' - E_0'' = 118.3 \log \frac{\gamma'}{\gamma''} - 29.58 \log \frac{a_1'}{a_1''}$.

Knobel[29] believes that Chow's results are in error for two reasons: (*a*) there was oxygen present in his cells, and (*b*) the solid mercuric oxide, due to its polymorphism, was not the same substance in the different solutions and therefore had different activities. Probably it had not always reached equilibrium. Certainly, the results of Chow differ widely from those of Knobel. The electromotive force of the cells was corrected for the activity of the water by subtracting 0.9 *m* mv., which is in accordance with Table IV up to 1.0 *M*. All the deviations are large, from 1.0 to 2.0 mv., and those in dilute solutions are in the opposite direction to those of other electromotive-force measurements.

VI. General Discussion

For purposes of comparison, there are collected in Table V the mean activity coefficients at 25° determined from electromotive-force measurements, except those for sodium chloride which are determined from freezing points and thermal measurements. The values for hydrochloric acid are included. In Fig. 4 the same data are represented by plotting $\log \gamma$ against $\sqrt{m}$. The only intersections of two curves are sodium chloride with lithium chloride and with potassium hydroxide. It is very probable that these are due to the difference in the methods of determination. It is interesting to note that the minima for hydrochloric acid,

TABLE V

MEAN ACTIVITY COEFFICIENTS OF THE IONS AT 25°

Molality	KCl	NaCl	LiCl	HCl	KOH
0.001	0.965	0.966	0.965	0.966	0.965
.002	.951	.953	.952	.954	.952
.005	.926	.928	.927	.932	.927
.01	.899	.903	.901	.910	.901
.02	.865	.871	.869	.881	.868
.05	.809	.821	.819	.836	.815
.1	.762	.778	.779	.801	.772
.2	.715	.734	.750	.774	.739
.3	.688		.739	.763	.727
.4	.669		.735	.760	.723
.5	.654	.671	.736	.763	.723
.6	.642		.738	.770	.725
.75	.627		.743	.783	.731
1.0	.605	.634	.753	.817	.743

lithium chloride and potassium hydroxide all occur at about the same concentration, very near 0.4 *M*. Sodium chloride also shows a minimum between 1 and 2 *M*, and potassium chloride (at 20°) one near 3 *M*.

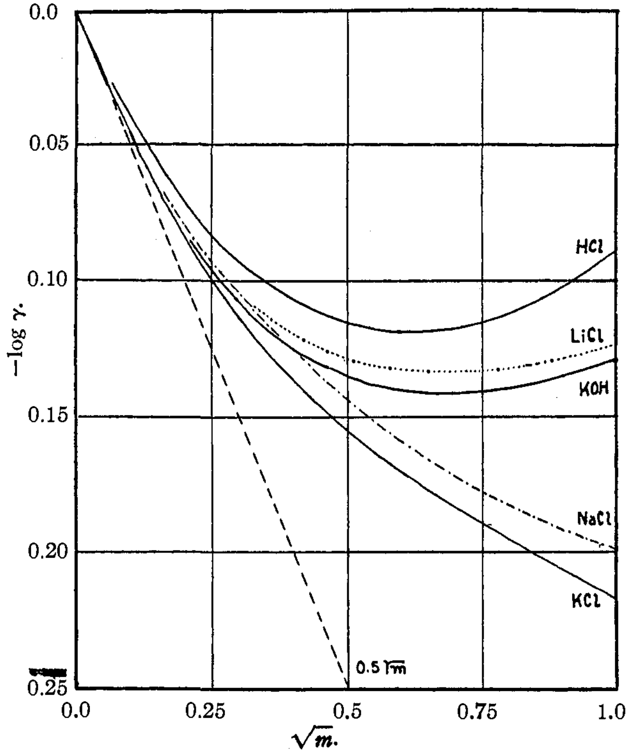

Fig. 4.—Mean activity coefficients of the ions.

VII. Summary

1. With the use of the formula, —log $\gamma = 0.5\sqrt{m} - Bm$, as a basis for extrapolation to zero concentration, the mean activity coefficient of the ions of the following electrolytes have been revised: potassium and lithium chlorides from electromotive force, from freezing point, and from vapor-pressure measurements; sodium chloride from freezing-point measurements; potassium hydroxide from electromotive-force measurements, taking into account the formation of water in the cell reaction.

2. The relation of the above equation to the Debye and Hückel theory of the effect of the ionic charges on the activity is discussed.

3. The equation is tested by a comparison with experimental measurements.

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