Pt, I_2 sat., I^- ($\alpha = 1.0$), 1 N KCl, HgCl, Hg $E = -0.2544$
Hg, HgCl, 1 N KCl, 0.1 N KCl, H^+ ($\alpha = 1.0$) H_2 (g), Pt $E = -0.2822$
Liquid junction correction 1 N KCl, 0.1 N KCl $E = +0.0004$
Pt, I_2 sat., I^-($\alpha = 1.0$), H^+(α=1.0) H_2 (g) $E = -0.5362$

No attempt will be made at this time to compute the normal potential of the iodine–iodide electrode referred to the hydrogen electrode at 0°, owing to inadequate data on the difference between hydrogen and calomel electrodes at this temperature.

Summary

The normal potential of the iodine–iodide electrode has been redetermined, using solutions containing so little free iodine that the effect of formation of tri-iodide is minimized and can be accurately allowed for. The activity of the iodine has been determined by a new device. The activity coefficient of the iodide ion in solutions of potassium iodide has been determined by measurements of the potential of iodide concentration cells with transference containing silver–silver iodide electrodes. The results can be expressed by the formula of the form suggested by Brönsted: $\log f = -373 \sqrt{c} + 0.125\, c$. The normal potential of the iodine–iodide electrode against the normal calomel electrode at 25° is found to be −0.2544 volt; and at 0° is found to be −0.2522 volt.

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THE EXTRAPOLATION OF ELECTROMOTIVE FORCE MEASUREMENTS TO UNIT IONIC ACTIVITY

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The relation between the electromotive force, E, of a cell such as Ag, AgCl, HCl, H_2 and the mean activity coefficient, γ, of the ions of the electrolyte is given by the equation

$$E = E_0 - 2k \log m - 2k \log \gamma \qquad (1)$$

Here m is the molality of the acid, k is 2.3026 RT/NF, and E_0 is the electromotive force which the cell would have if the mean activity of the ions, or the product $m\gamma$, were equal to unity. In order to calculate activity coefficients from electromotive force data alone, it is necessary to determine the value of E_0 by extrapolation. This has usually been done, following Lewis and Randall,[1] by plotting the quantity E_0', which is defined as $E + 2k \log m$, against $\sqrt{m}$. Since $\gamma = 1$ when $m = 0$, it follows from equation (1) that $E_0' = E_0$ when $m = 0$. Curves which have

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[1] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 335.

been obtained in this way for aqueous hydrochloric acid[1,2] are straight lines only for the region of extreme dilution (well below 0.01 M), where the scattering of the points makes the position of the line, and hence the extrapolated value, somewhat uncertain.

If the Debye-Hückel equation, in its simplest approximate form

$$-\log \gamma = 0.5\sqrt{m} \tag{2}$$

applies to the data, it follows from Equations (1) and (2) that a plot of E_0' against $\sqrt{m}$ should be a straight line of slope equal to k over the range where the approximate equation holds. Scatchard[2a] found it possible to draw a curve whose slope approached this value asymptotically at $m = 0$, using data obtained by himself, by Linhart,[3] and by Noyes and Ellis.[4] Nonhebel[2b] found that his data when plotted in this way gave points falling around a line having a slope equal to $0.78k$. He concluded, therefore, that his data were not in agreement with the Debye theory.

The method of extrapolation just described lays great weight on the determinations in very dilute solutions, where the measurements are reproducible only with difficulty and where, as Randall and Young[5] have pointed out, all existing data are probably erroneous on account of the solubility of glass. It would therefore be desirable to find a method of extrapolation from the more reliable determinations at somewhat higher concentrations.

If the Debye-Hückel theory holds, any experimental data should agree with the second approximate equation over a wider range than with the first. For the case in question this equation is

$$-\log \gamma = 0.5\sqrt{m} - Bm \tag{3}$$

where B is an additional constant whose value is not known independently. This form of equation has been shown by Brönsted,[6] Scatchard,[7] and others to apply to a number of electrolytes, in some cases up to 0.1 M. The combination of Equations (1) and (3) gives

$$E + 2k \log m - k\sqrt{m} = E_0 - 2kBm \tag{4}$$

or

$$E_0' - k\sqrt{m} = E_0 - 2kBm. \tag{4a}$$

Over the range where Equation (3) holds, it follows that the left member of Equation (4) or (4a), which may be called E_0'', should be a linear function of m.[8] Moreover, if Equation (4) holds, it follows that $E_0'' = E_0$ when $m = 0$.

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[2] (a) Scatchard, This Journal, **47**, 641 (1925); (b) Nonhebel, *Phil. Mag.*, [7] **2**, 1085 (1926).

[3] Linhart, This Journal, **41**, 1175 (1919).

[4] Noyes and Ellis, *ibid.*, **39**, 2532 (1917).

[5] Randall and Young, *ibid.*, **50**, 989 (1928).

[6] Brönsted, *ibid.*, **45**, 2898 (1923).

[7] Scatchard, *ibid.*, **47**, 648 (1925).

[8] The quantity E_0'' was used by Nonhebel and Hartley, *Phil. Mag.* [6] **50**, 729 (1925), who called it E_0 Debye, and found, in the case of hydrogen chloride in methyl alcohol, that it was a linear function not of m but of $\sqrt{m}$.

Hence this furnishes a method of extrapolation for the determination of E_0. If the experimental points fall on a straight line over a range of concentration where the data are reliable, a linear extrapolation to $m = 0$ may be made with considerable confidence.

If the complete equation of Hückel[9] applies to the data, this method of plotting cannot give a truly straight line for more than a limited range. Scatchard[10] has calculated values of γ from this equation for aqueous hydrochloric acid at 25°, using electromotive force data only for the empirical determination of two constants in the equation. By substituting these values of γ in Equation (1), it is possible to calculate values for $E - E_0$ and hence, using the definition of E_0'', values of $E_0 - E_0''$. These calculated values, when plotted against m, appear to deviate slightly from a straight line above 0.02 M. A straight line through the points at 0.02 and 0.05 M makes the extrapolated value 0.2 millivolt too low. Hence the complete theory is not in agreement with an exactly linear plot. The theoretical points, however, deviate so little from a straight line, even up to 0.1 M, that it is possible to make an exact extrapolation from them by the use of a flexible spline which is held on the points at 0.01, 0.02, 0.05 and 0.1 M. Below 0.02 M the curvature is inappreciable. Hence this method of extrapolation, if a spline is used instead of a straight rule, gives a result in full agreement with the complete equation of Hückel.

The application of this method to the available experimental data[2a,b,3,4,5,11] for aqueous hydrochloric acid up to 0.1 M, at the temperatures 20, 25 and 30° is shown in Fig. 1. The curves were drawn with a spline from the points at 0.01 M and above, before the points for lower concentrations were plotted. The deviation of these curves from straight lines is so slight below 0.05 M that its effect on the extrapolated value is less than 0.1 millivolt. The position of the line for 25° is rather arbitrary on account of the multiplicity of discordant determinations. The values extrapolated from these curves are: for 20°, E_0 = 0.2253 volt; for 25°, 0.2223; and for 30°, 0.2193. Previous values are: for 20°, 0.2255 (Güntelberg), 0.2253 (Randall and Young, from Güntelberg's data); for 25°, 0.2234 (Linhart, Lewis and Randall), 0.2226, 0.2224, or 0.2223 (Scatchard, from compiled data), 0.2228 (Nonhebel), 0.2221 (Randall and Young, from compiled data adjusted to agree with freezing point determinations); at 30°, 0.2187 (Randall and Young, from two points of Harned and Brumbaugh, adjusted as above).

The ultimate test of such a method of extrapolation must lie in its application to points at low concentrations. Such determinations should

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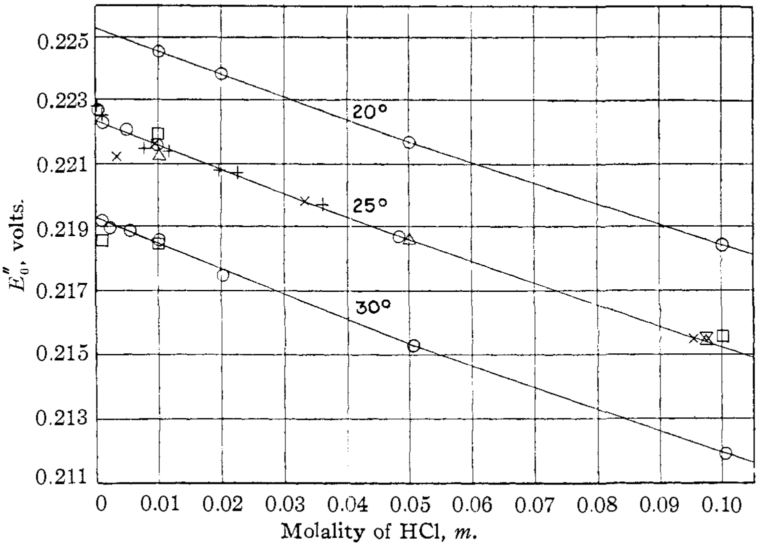
[9] Hückel, *Physik. Z.*, **26**, 93 (1925).

[10] Scatchard, THIS JOURNAL, **47**, 2098 (1925).

[11] (a) Harned and Brumbaugh, *ibid.*, **44**, 2729 (1922); (b) Harned and Swindells, *ibid.*, **48**, 126 (1926); (c) Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926); (d) Hitchcock, *J. Gen. Physiol.*, not yet published.

be made, as suggested by Randall and Young, in quartz vessels. At present the new method seems to apply reasonably well to all the data except those for 25° below 0.003 M. The large number of points obtained by Nonhebel in this range made it impossible to show them all in Fig. 1, but their trend is clearly toward a higher value of E_0. This agrees with the smaller slope found by him in using the older method of plotting. If this slope is correct, then neither the new method of extrapolation nor the Debye theory is applicable. The extrapolation as given here, then, must stand or fall with the constant 0.5 of the Debye equation.



○ Güntelberg at 20°; Linhart at 25°, Hitchcock at 30°; + Nonhebel;
× Noyes and Ellis; △ Scatchard; ▽ Randall and Young; □ Harned.

Fig. 1.—Extrapolation of e.m.f. data for Ag, AgCl, HCl(aq), H_2.

This method should be of use in the treatment of electrolytes of other valence types. In such cases Equations (1) to (4) will be of correspondingly different form.

Summary

A method is given, based on a partially expanded form of the Debye and Hückel equation, for an almost linear extrapolation of electromotive force data to unit ionic activity. The method is applied to compiled data for aqueous hydrochloric acid at 20, 25 and 30°. It is pointed out that the method is in agreement with the complete theoretical equation of Hückel, as well as with experimental data, up to 0.1 M.

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