The Elimination of Liquid Junction Potentials. IV. The Conditions of Extrapolation[1a]

BY BENTON BROOKS OWEN AND STUART R. BRINKLEY, JR.[1b]

In the preceding communications[2,3,4] of this series it is shown experimentally that accurate thermodynamic information can be derived from cells with heterionic liquid junctions by suitable extrapolations. In each of these investigations the following conditions were fulfilled.

$$\text{Ag, AgCl (s)} \left| \begin{array}{c} \text{AgCl [satd.]} \\ \text{KNO}_3 \ [(1-x)m] \\ \text{KCl } [xm] \end{array} \right.$$

I. The composition of the liquid systems in contact are so chosen that, in a series of measurements, these systems can be made to approach by extrapolation either absolute identity, or some condition which may be treated by present thermodynamic methods.

II. The ionic strengths of the liquid systems in contact are the same, and the extrapolation is performed at constant ionic strength.

These conditions are the subject of the present communication.

Condition I

The necessity of Condition I scarcely requires comment, but it will be useful to distinguish between and to classify several types of junctions which can fulfill this condition. The classification of junctions will be based upon their characteristics in limiting states attained by extrapolation, because it is ordinarily these characteristics which justify their use in thermodynamic calculations. The concentration of one or more solutes at every junction will be expressed in terms of a variable, x ($1 \geqslant x \geqslant 0$), which will always be reduced to zero by the extrapolation. Therefore when the properties, or types of any junctions are referred to, it is implied that the condition, $x \rightarrow 0$, has been imposed.

$$\text{Ag, AgCl(s)} \left| \begin{array}{c} \text{AgCl [satd.]} \\ \text{KCl } [xm] \\ \text{KNO}_3 \ [(1-x)m] \end{array} \right.$$

Limiting Liquid Junctions, Type A.—The two liquid systems comprising Type A junctions become absolutely identical in the limit when $x \rightarrow 0$, and their junction potentials are zero. The

following cells illustrate this type of junction.

$$\text{H}_2 \left| \begin{array}{c} \text{H}_2 \text{ [satd.]} \\ \text{HCl } [m] \end{array} \right| \left| \begin{array}{c} \text{H}_2 \text{ [satd.]} \\ \text{HCl } [(1+x)m] \end{array} \right| \text{H}_2 \qquad \text{I}$$

$$\left| \begin{array}{c} \text{AgCl [satd.]} \\ \text{KNO}_3 \ [m] \end{array} \right| \left| \begin{array}{c} \text{AgCl [satd.]} \\ \text{KNO}_3 \ [(1-x)m] \\ \text{AgNO}_3 \ [xm] \end{array} \right| \text{AgCl (s), Ag} \quad \text{II}$$

It is characteristic of such cells that each constituent of the limiting junction solutions, *including soluble components of the electrodes*, is present in both solutions at the same concentration. The electromotive forces of these cells are therefore independent of standard electrode potentials. In other respects such cells may be widely dissimilar. Thus, Cell I is homo-ionic, and its liquid junction potential is thermodynamically defined at *all* values of x. The e. m. f. of this cell is a simple function of transference numbers and activities at all values of x, and is independent of the geometry of the junction. Cell II is heterionic for values of x different from zero, and its junction potential is thermodynamically defined only in the limit.

Limiting Liquid Junctions, Type B. The two liquid systems comprising Type B junctions do not become identical in the limit when $x \rightarrow 0$, but differ only with respect to the soluble components of the two electrodes. The following cells will serve as illustrations.

$$\text{Hg, HgCl (s)} \left| \begin{array}{c} \text{HgCl [satd.]} \\ \text{KCl } [m] \end{array} \right| \left| \begin{array}{c} \text{H}_2 \text{ [satd.]} \\ \text{KCl } [(1-x)m] \\ \text{HCl } [xm] \end{array} \right| \text{H}_2 \qquad \text{III}$$

$$\text{Ag, AgCl(s)} \left| \begin{array}{c} \text{AgCl [satd.]} \\ \text{KCl } [xm] \\ \text{KNO}_3 \ [(1-x)m] \end{array} \right| \text{KNO}_3 \ [m] \left| \begin{array}{c} \text{AgNO}_3 \ [xm] \\ \text{KNO}_3 \ [(1, x)m] \end{array} \right| \text{Ag} \quad \text{IV}$$

Although the limiting liquid junction potentials of these cells are not zero, they are of the type which is always present when the so-called "cells without liquid junctions" are used to compare standard electrode potentials. Such junction potentials are neglected in thermodynamic practice, and are therefore integral parts of all measured standard electrode potentials. For example, the replacement of potassium chloride by hydrogen chloride throughout Cell III would lead to the familiar cell

$$\text{Hg, HgCl(s)} \left| \begin{array}{c} \text{HgCl [satd.]} \\ \text{HCl } [m] \end{array} \right| \left| \begin{array}{c} \text{H}_2 \text{ [satd.]} \\ \text{HCl } [m] \end{array} \right| \text{H}_2 \qquad \text{V}$$

(1a) Presented April, 1941, at the Saint Louis meeting of the American Chemical Society.

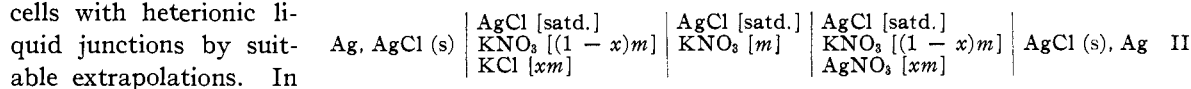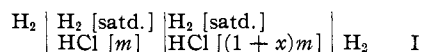(1b) Present address, Mallinckrodt Chemistry Laboratory, Harvard University.

(2) B. B. Owen, THIS JOURNAL, **60**, 2229 (1938).

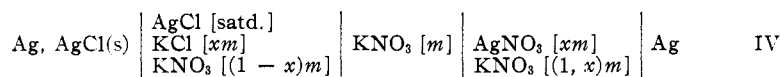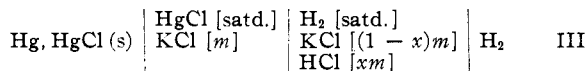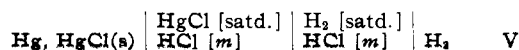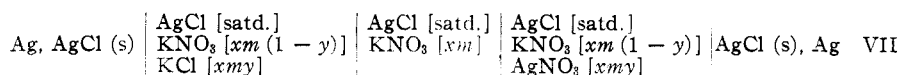(3) B. B. Owen and S. R. Brinkley, Jr., *ibid.*, **60**, 2233 (1938).

(4) B. B. Owen and E. J. King, *ibid.*, **63**, 1711 (1941).

without changing the nature[5] of the liquid junction. Note that the Type A junction of Cell II changed to Type B in Cell IV by elimination of the silver chloride from the right-hand electrode and solution.

Limiting Liquid Junctions, Type C.—The following cells give rise to Type C junctions

$$\text{Ag, AgCl(s)} \begin{vmatrix} \text{AgCl [satd.]} \\ \text{KCl } [xm] \end{vmatrix} \begin{vmatrix} \text{AgCl [satd.]} \\ \text{HCl } [xm] \end{vmatrix} \text{AgCl (s), Ag} \quad \text{VI}$$

$$\text{Ag, AgCl (s)} \begin{vmatrix} \text{AgCl [satd.]} \\ \text{KNO}_3 \ [xm \ (1 - y)] \\ \text{KCl } [xmy] \end{vmatrix} \begin{vmatrix} \text{AgCl [satd.]} \\ \text{KNO}_3 \ [xm] \end{vmatrix} \begin{vmatrix} \text{AgCl [satd.]} \\ \text{KNO}_3 \ [xm \ (1 - y)] \\ \text{AgNO}_3 \ [xmy] \end{vmatrix} \text{AgCl (s), Ag} \quad \text{VII}$$

The variable y $(1 \geqslant y \geqslant 0)$ in the last cell is used to express changes in the ratio of the solute concentrations. In this respect, y plays the same rôle in Cell VII that x plays in Cell II, but the conditions of extrapolation in these otherwise similar cells are quite different. In the operation of Cell II, m is kept constant during a given extrapolation to $x \to 0$, and the limiting junction becomes two identical solutions of potassium nitrate of concentration, m. In the operation of Cell VII, y and m are kept constant during a given extrapolation to $x \to 0$, and the junction consists of two solutions which do not become identical in the limit so long as y is different from zero.

Thus, in general, the solutions composing Type C junctions contain constituents which are not shared by both in common, and this asymmetry is not eliminated by extrapolation. The liquid junction potential produced by this asymmetry when $x \to 0$ is not of the type inherent in "cells without liquid junctions," and cannot logically be neglected. Fortunately there are both experimental and theoretical grounds for believing that it is possible to estimate the magnitudes of such residual junction potentials within reasonable limits. This possibility argues the practical utility of cells which lead to this "calculable" type of junction potential, but does not permit the use of such junctions with the same confidence with which Types A and B are employed in thermodynamic calculations. This category can be made to include cells whose limiting junction potentials are partly calculable and partly neglected. For example, if the silver chloride is eliminated from the

right hand solution and electrode of Cell VII, extrapolation to $x \to 0$ results in a junction with characteristics of both Types C and B. This composite junction might be termed Type CB, but since the asymmetry of the B variety is absorbed in the standard electrode potentials, it will not be necessary to distinguish between Types C and CB in the following discussion.

The estimation of a liquid junction potential, E_j, is based upon the expression[6]

$$-\mathrm{d}\, E_j = \frac{RT}{F} \sum \frac{T_i}{z_i} \, \mathrm{d} \ln m_i \gamma_i \qquad (1)$$

in which T_i, m_i, and γ_i are the transference number, molality and activity coefficient of any ionic constituent, i. The valence, z_i, carries the sign of the charge. The activity coefficients may be disregarded, as the equation will be employed only in the limit, $\mu \to 0$. The summation extends over all the ion constituents present, except those produced by dissociation of the solvent.[7]

Ordinarily, the exact values of T_i and m_i are not known at all points throughout the region of the junction, and some assumptions are required before equation (1) can be integrated. For this purpose Planck[8] assumed "constrained diffusion" across the junction, and Henderson[9] assumed a "continuous mixture boundary" which leads to linear concentration gradients. Both of these assumptions, as well as those employed in more elaborate treatments[10,11,12] of the problem, yield values of E_j which are in reasonable agreement (plus or minus a few tenths of a millivolt) with each other and with experiment, if the solutions are dilute and differences in ionic mobilities are not extreme. So long as the objectives do not demand more than this reasonable agreement, it is not necessary to decide which, if any, of these assumptions is strictly valid.

With this in mind, and purely as a matter of

(5) The magnitude of the junction potential would vary to some extent depending upon the properties of the electrolyte at the concentration m, but this variation is also neglected. Thus, in determining the activity coefficient of HCl in salt solutions, the same value of E^0 is used regardless of the nature of the salt. Since E^0 contains the junction potential of Cell V at $m = 0$, the calculated activity coefficient contains the variation of this junction potential with the composition of the solutions at finite concentrations.

(6) D. A. MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, N. Y., 1939, pp. 220–245.

(7) F. O. Koenig [*J. Phys. Chem.*, **44**, 101 (1940)] has shown that the quantities T_i in equation (1) are properly the Hittorf transference numbers, corrected for the conductivity of the solvent.

(8) M. Planck, *Wied. Ann.*, **40**, 561 (1890); H. Pleijel, *Z. physik. Chem.*, **72**, 1 (1910).

(9) P. Henderson, *Z. physik. Chem.*, **59**, 118 (1907); **63**, 325 (1908); M. Gouy, *J. chim. phys.*, **14**, 185 (1916).

(10) P. B. Taylor, *J. Phys. Chem.*, **31**, 1478 (1927); K. Sitte, *Z. Physik*, **91**, 622 (1934).

(11) J. J. Hermans, Dissertation, Leiden, 1937.

(12) F. O. Koenig, *J. Phys. Chem.*, **44**, 101 (1940).

convenience, the Henderson assumption will be used in the present discussion because it leads to the relatively simple expression

$$-E_j^0 = \text{Lim} \frac{RT}{F} \frac{\Sigma(\lambda_i^0/z_i)(m_i'' - m_i')}{\Sigma\lambda_i^0(m_i'' - m_i')} \quad (2)$$

at infinite dilution. This choice does not imply that the authors can dispose of the theoretical objections[11] to the general application of this assumption to heterionic junctions. The primes and double primes in equation (2) refer to concentrations in the immediate neighborhood of the left and right hand electrodes, respectively, and λ_i^0 is the limiting conductance of the i-ions.

In order to evaluate the limit appearing in this equation, the ionic concentrations m_i', m_i'', etc., may be expressed as fractions

$$\rho_i' \equiv m_i'/m', \quad \rho_i'' \equiv m_i''/m'', \text{ etc.} \quad (3)$$

of the total ionic concentrations, m' and m''. In the limit, as $x \to 0$

$$\frac{m'' - m'}{m'' + m'} = 0 \quad (4)$$

for the Type A and C junctions. The application of this equation to Type B and CB junctions can only be considered permissible in view of the *convention* of disregarding the soluble constituents of the electrodes in cells containing these junctions.

Combination of equations (2), (3) and (4) leads to the following result at infinite dilution.

$$-E_j^0 = \frac{RT}{F} \frac{\Sigma(\lambda^0/z_i)(\rho_i'' - \rho_i')}{\Sigma\gamma_i^0(\rho_i'' - \lambda_i')} \ln \frac{\Sigma\lambda_i^0\rho_i''}{\Sigma\lambda_i^0\rho_i'} \quad (5)$$

For Type A junctions, $\rho_i' = \rho_i''$, etc., and the logarithmic factor is zero. According to the convention referred to above, this factor is also zero for Types B and CB junctions. For the simplest Type C junctions (Cell VI), equation (2) reduces to the familiar equation of Lewis and Sargent.[13]

MacInnes and Yeh[14] investigated cells of Type VI which contained pairwise combinations of the chlorides of hydrogen, ammonium and the alkali metals. Unfortunately, only two concentrations (0.1 and 0.01) were used, but the values of E_j^0 obtained by linear extrapolation for all combinations (except those involving potassium chloride) are in reasonable agreement with equation (5) the average deviation being 0.11 mv. For the potassium salts the disagreement is of the order of 1.2 mv. Data are available which can be used

(13) G. N. Lewis and L. W. Sargent, THIS JOURNAL, **31**, 363 (1909).

(14) D. A. MacInnes and Y. L. Yeh, *ibid.*, **43**, 2563 (1921).

for a similar "two point" ($m = 0.05$ and 0.03) extrapolation for the system KCl (m) | KBr (m), and this also is not in accord with equation (5). The disagreement in this case amounts to 0.25 mv.

In order to determine whether the discrepancies obtained with potassium salts represent a failure of the equation or of the "two point" extrapolation, the family of straight lines shown in Fig. 2 of the first paper of this series[2] has been used to obtain interpolated values of $E - 2 k \log (xmy) + 2 k \alpha \sqrt{\mu}$ which would be applicable to Cell VII. The constants $k = 0.05915$ and $\alpha = 0.506$ at 25°. The addition of $k \log K$ ($= -0.5768$) to these values yields the values of $k \log \gamma_{Cl}\gamma_{Ag} + 2 k \alpha \sqrt{\mu} + E_j$ which are plotted as ordinates in Fig. 1.
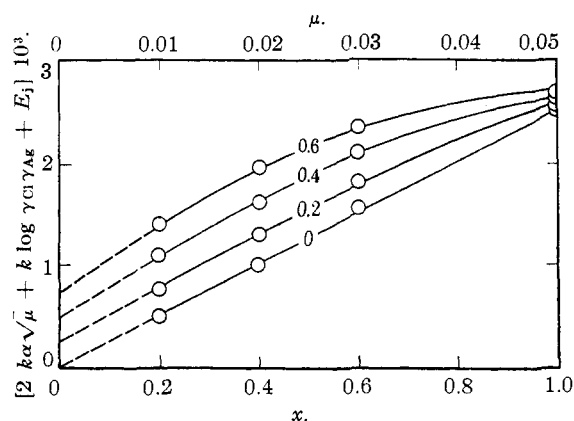

Fig. 1.—Extrapolation of the results for Cell VII. Values of y are indicated on the curves; m is constant and equal to 0.05 mole per kg. of water. The intercepts, E_j^0, were calculated by equation (5).

The abscissa is expressed in terms of x at the bottom, and μ at the top of the figure. Two important conclusions may be drawn from this plot. First, for all values of y greater than zero the plots are not linear, and as the system KCl|AgNO$_3$ is approached ($y = 1$), a very pronounced curvature appears in the neighborhood of $\mu = 0.025$. Second, the extrapolated portions of the curves have been drawn to intercepts, E_j^0, calculated by equation (5) without producing any apparent discontinuity with the experimental curves. These results supply a reasonable explanation of the discrepancies referred to above, and appear to justify the use of equation (5) in estimating E_j^0 for practical purposes. The rigorous validity of this equation is, of course, a question which cannot be decided by such curved extrapolations from so few data.

The classification of liquid junctions according to their limiting characteristics ($x \rightarrow 0$) is helpful in determining the propriety of using a given cell for thermodynamic purposes.

The use of Type A junctions assumes the possibility of a suitable extrapolation to $x \rightarrow 0$. If the accuracy of this extrapolation is not inferior to that of the data upon which it is based, the extrapolated quantity is subject to rigorous thermodynamic treatment. The accuracy of such extrapolations appears to fulfil this condition, but only one system with Type A junctions has been investigated.[2]

The extrapolation required for Type B junctions is similar to that for Type A, and appears equally accurate,[3,4] but the extrapolated quantity derived from a Type B junction contains an unknown residual junction potential. Although this unknown potential is disregarded in the use of all of the so-called "cells without liquid junctions," this convention does not always permit a rigorous thermodynamic interpretation of the data. For example, the values of E^0 and the activity coefficients calculated from the electromotive forces of Cell V are somewhat ambiguous for this rea-

son.[5] On the other hand, the modern electrometric determination of ionization constants of weak electrolytes is free from this defect, because the residual junction appears twice in the procedure (in the extrapolations for E^0 and for K) and cancels out.

The extrapolations which result in Types A and B are practically linear when performed at constant ionic strength.[2,3,4] Type C (CB) junctions are produced by extrapolation to zero ionic strength, and may depart widely from linearity, as in Fig. 1. In addition to the uncertainty caused by this curvature, the use of Type C (CB) junctions is under the disadvantage of requiring an estimate of E_j^0. Furthermore, all of the equations proposed for this purpose involve some extra-thermodynamic assumption that is difficult to justify *per se*, and attempts to verify the equations may have to contend with non-linear extrapolations such as those encountered in systems containing potassium salts. These considerations make it undesirable to employ Type C (CB) junctions for any purpose for which Types A and B, or cells "without liquid junctions" can be utilized, and leave room for doubt that condition I is rigorously fulfilled by Type C (CB) junctions.

Condition II

While the extrapolations ($x \rightarrow 0$) are not necessarily performed at constant total ionic strength, it appears that this condition must be fulfilled if a *linear* extrapolation is to be obtained, or even approximated. In the three systems investigated by the authors[2,3] and E. J. King,[4] the deviations of the experimental results from linearity are of the order of the reproducibility of the electromotive forces (0.05 mv.). The liquid junction potentials in these systems were small because of the choice of ions with nearly equal mobilities,[2,4] and the use of buffers[3] when acids were present. In cells containing high liquid junction potentials, there is evidence of only a slight departure from linearity. For example, the available data[1b] on Cell III ($m = 0.1$; $x = 0.1, 0.5$, and 1.0) show a maximum deviation of 0.25 mv. from a straight line drawn through the points corresponding to $x = 0$ and $x = 1$. This curvature is illustrated by curve III in Fig. 2, which was constructed as follows: (1) a large-scale plot of the function $E - k \log (mx)$ against mx was made from measurements on Cell III, (2) a smooth curve was drawn through these ex-
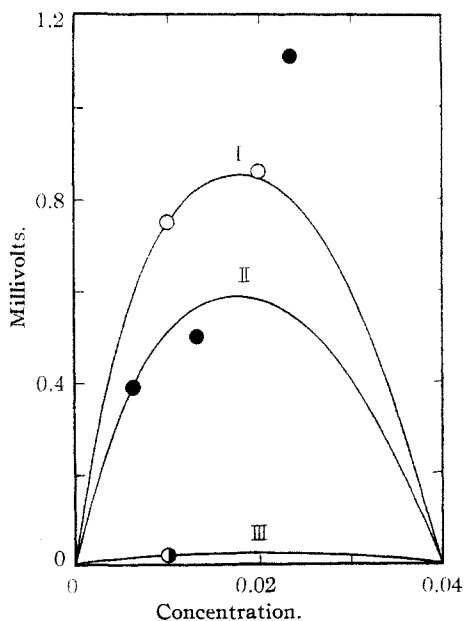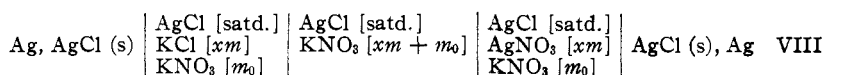

Fig. 2.—Departures of several extrapolations from linearity in dilute solutions. I. Cell VIII: abscissa, chloride (or silver) molality: potassium nitrate concentration constant, 0.01 molal. II. Cell IX: abscissa, total iron wt. normality: hydrochloric acid concentration constant, 0.05 wt. normal. III. Cell III: abscissa, hydrochloric acid normality: ionic strength constant, 0.1 normal.

(15) A. Unmack and E. A. Guggenheim. *Kgl. Danske Videnskab. Selskab. Math.-fys. Medd.*, **X**, 8 (1930).

perimental results, and extrapolated to the limit, $mx = 0$, (3) a chord was drawn from $mx = 0$ to $mx = 0.04$, and (4) vertical distances between this chord and the curve were scaled off at several values of mx, and plotted as the ordinates of Curve III, in Fig. 2, against mx as abscissa. Curve III therefore represents the departure of the experimentally determined function, $E - k \log (mx)$, from linearity at acid concentrations (mx) between 0 and 0.04 mole per liter. In this particular case the ionic strength is constant (0.1 mole per liter at 18°), and the departure from linearity is very small.
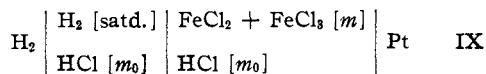
On the other hand, the upper curves[16] in Fig. 2 illustrate the relatively enormous curvatures encountered when the extrapolation is not performed at constant ionic strength. Curve I shows the departures of the function, $E - 2 k \log (xm) + 2k\alpha\sqrt{\mu}$, from linearity for the cell

$$\text{Ag, AgCl (s)} \begin{array}{|c|} \hline \text{AgCl [satd.]} \\ \text{KCl } [xm] \\ \text{KNO}_3 \ [m_0] \\ \hline \end{array} \begin{array}{|c|} \hline \text{AgCl [satd.]} \\ \text{KNO}_3 \ [xm + m_0] \\ \hline \end{array} \begin{array}{|c|} \hline \text{AgCl [satd.]} \\ \text{AgNO}_3 \ [xm] \\ \text{KNO}_3 \ [m_0] \\ \hline \end{array} \text{AgCl (s), Ag VIII}$$

at a constant concentration of potassium nitrate $(m_0 = 0.01)$. These results were obtained graphically from the family of straight lines given in Fig. 2 of the first paper in this series.[2] The temperature is 25°, and $m = 0.05$ molal. It is evident that this extrapolation at varying ionic strength is almost useless for practical purposes, although the ionic strength is uniform throughout the cell [equation (4)], and the mobilities of all of the ions are very nearly equal. In this case the departure from linearity is obviously due to variations in activity coefficients, rather than to large changes in E_j.

Curve II in Fig. 2 shows the departures of the function, $E + k \log (c_{Fe^{+++}}/c_{Fe^{++}})$, from linearity for the cell

(16) The construction of Curves I and II is analogous to that just described for Curve III, but differs in the nature of the plotted experimental functions.

$$\text{H}_2 \begin{array}{|c|} \hline \text{H}_2 \text{ [satd.]} \\ \text{HCl } [m_0] \\ \hline \end{array} \begin{array}{|c|} \hline \text{FeCl}_2 + \text{FeCl}_3 \ [m] \\ \text{HCl } [m_0] \\ \hline \end{array} \text{Pt IX}$$

used by Popoff and Kunz.[17] The constant acid concentration, m_0, is 0.05 mole per kilo of solution, and the total iron concentration, m, is here expressed in *equivalents* per kilo of solution to reduce the concentration range covered by the plot.[18] The temperature is 25°. The curvature in this case is probably due to considerable variations in E_j as well as in the activity coefficients.

Summary and Conclusions

In the elimination of liquid junction potentials by extrapolation, it is useful to classify junctions according to their characteristics in the limit obtained by extrapolation. This depends upon the fact that a given pair of junction solutions may lead to quite different limiting cell potentials depending upon the nature of the electrodes employed and the manner in which the limit is approached. Thus, the limiting potential of the liquid–liquid system KNO$_3$, KCl | KNO$_3$, AgNO$_3$ can be Type A $(E_j^0 = 0$, as in Cell II), Type B $(E_j^0$ neglected, as in Cell IV), or Types C and CB $(E_j^0$ calculable, as in Cell VII as written, or modified by elimination of silver chloride from the right-hand electrode).

New evidence (Fig. 1) is produced to show that the Henderson equation yields values of E_j^0 in reasonable agreement with experiment. An explanation is suggested for the previous failure of this equation in some systems involving the potassium salts.

The practical necessity of performing the extrapolations at constant ionic strength is illustrated by means of graphs (Fig. 2).

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(17) S. Popoff and A. H. Kunz, THIS JOURNAL, **51**, 382 (1929).

(18) If the *molar* concentration of iron had been used the maximum of Curve II would have been over twice as high. The experimental point at 0.025 normal was disregarded in drawing the curve because it was inconsistent with the data at higher concentrations.