LIQUID JUNCTION POTENTIALS
AT
MIXED ELECTROLYTE SALT BRIDGES.

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BY

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CONTENTS.

1. GLOSSARY OF ABBREVIATIONS AND SYMBOLS.

Listed below are the abbreviations used throughout the the text. Others which are used only in one place, are defined as they are introduced.

a_i = activity of ionic species i.

$a_\pm$ = mean ionic activity.

c = molar-concentration
= concentration in gram-molecules per litre of solution.

e = base of Napierian logarithms
= 2.7183.

E = total electromotive force of a cell in absolute volts.

E_{Bj} = liquid junction potential estimated by means of the Bjerrum extrapolation method.

E_{el} = total electrode potential of a cell.

E^I_{el} = sum of the ideal single electrode potentials of a cell.

E^S_{el} = contribution to E_{el} of departures from ideal solution behaviour.

E_j = liquid junction potential
= diffusion potential.

E^I_j = ideal junction potential.

E^S_j = contribution to E_j of deviations from ideal solution behaviour.

$E_{3.5}$ = diffusion potential at a 3.5N salt bridge.

$E_{1.75}$ = diffusion potential at a 1.75N salt bridge.

f_i = molal activity coefficient of ionic species i.

$f_\pm$ = mean ionic activity coefficient.

F = Faraday.

G = free energy.

J = ional concentration of bridge solution.

m = molal concentration
= concentration in gram-molecules per 1000 gram solution.

$m_\pm$ = mean ionic molal concentration.

mV = millivolts.

nm/cm = nanomhos per centimeter
= 10^{-9} per ohm-cm.

N = normality,
= gram-equivalents per litre of solution.

^{o}C = degrees centigrade.

R = ideal gas constant per mole.

T = absolute temperature.

Temp. = temperature.

t_i = transport number of ionic species i.

t_i^{+} = transport number of cationic species i.

t_i^{-} = transport number of anionic species i.

u_i = mobility of cationic species i.

U_g = $\sum_{+} u_{i(g)} c_{i(g)}$
= value of U in solution g.

$\bar{U}_g$ = $\sum_{+} u_{i(g)} c_{i(g)} |z_i|$ = value of $\bar{U}$ in solution g.

v_i = mobility of anionic species i.

V_g = $\sum_{-} v_{i(g)} c_{i(g)}$
= value of V in solution g.

$\bar{V}_g$ = $\sum_{-} v_{i(g)} c_{i(g)} |z_i|$
= value of $\bar{V}$ in solution g.

z_i = valence of ionic species i.

$|z_i|$ = valence of ionic species i without regard to sign.

2. INTRODUCTION.

The potentiometric method is one of the most exact techniques of electrochemistry. Its use is widespread in both routine measurements, such as pH determination, and in applications which demand the highest accuracy. Perhaps its severest limitation is the error due to liquid junction potentials. Although this has been the subject of much study, and although various means of combating it havebeen proposed, it has defied all attempts at a satisfactory solution. Indeed, so serious is the position that it has become the accepted practice in the more accurate fields to abandon altogether the use of potentiometric techniques in favour of others, usually less convenient and otherwise less accurate, when the presence of liquid junctions cannot be avoided.

One of the most disturbing features of the question of the liquid junction potential error is the decided tendency which exists among many workers, to minimise its importance. This is particularly noticeable in the field of pH measurement. It is commonly accepted, although on no apparent basis, than an accuracy of 0.01 to 0.02 pH units is attainable by the methods in common use. In a recent investigation (1), however, D.A. Clur in conjunction with the present author showed that even a precision of this order is only possible by the use of special techniques, and that, in fact, the error normally encountered is at least 0.1 pH units. It can be seen, therefore, that not only are the errors involved considerable, in themselves, but that the position is aggravated by the failure of workers to recognise their magnitude.

For the sake of completeness it should be mentioned, at this point, that one aspect of the subject has proved to be less complex and less intractable. Liquid junctions can be classified into two broad types: homoionic junctions formed by juxtaposition of solutions differing only in ionic concentrations; and heteroionic junctions involving differences in ionic species, or in both ionic species and concentrations. The former are capable of exact thermodynamic definition. Furthermore, they present no difficulty in their practical preparation, as they are found to be completely independent of the manner in which junction is effected. It is with the second type which are more commonly met with, that this investigation is solely concerned.

It was considered that all possibilities of a satisfactory solution had not been fully exhausted. In particular, it was felt that one of the lesser known aspects - that of mixed electrolyte salt bridges - offered some promise; and it is from this angle that the problem has been attacked.

3. CRITICAL SURVEY OF PREVIOUS WORK ON LIQUID JUNCTION POTENTIALS.

3.1. THE THEORY OF LIQUID JUNCTION POTENTIALS.

By considering the changes in free energy which occur, as ions diffuse across the boundary between two solutions, 1 and 2, it can be shown thermodynamically that, if there is a transition layer in which the composition varies continuously from 1 to 2, then

$$E_j = - \frac{RT}{F} \sum_i \int_1^2 \frac{t_i}{z_i} \, d \ln a_i \qquad \ldots\ldots\ldots\ldots 3.1\ (i)$$

Equation 3.1 (i) is easily integrated, if it is assumed that t_i is independent of a_i :

$$E_j = -\sum_i (t_i^+ - t_i^-) \frac{RT}{F} \ln \frac{a_{i(2)}}{a_{i\,(1)}} \qquad \ldots\ldots\ldots 3.1\ (ii)$$

The assumption, however, is certainly not valid, and must be rejected. This complicates the problem, and it is now necessary to assign some structure to the boundary before 3.1(i) can be integrated. This has been done in several cases, and it is found that the calculated diffusion potential depends on the type of transition layer postulated.

M. Planck(2) in 1890 was able to integrate 3.1(i) by assuming that

(i) the solvent is the same throughout the junction;

(ii) the laws of ideal solution are obeyed;

(iii) the mobility of an ion is the same throughout the junction;

(iv) the boundary between the two solutions has the following form: ions may diffuse freely between two planes A and B, but to the left of A and to the right of B the concentration of the solutions remains unaltered. This is known as a "constrained diffusion" boundary.

The resulting transcendental equation was extended by Pleijel (3) to cover ions of different valencies.

Henderson (4) performed the integration by assuming, in addition to Planck's first three assumptions, a "continuous mixturè" boundary. The composition at any point of a transition layer of this type is a linear combination of the concentrations of the extreme liquids. His equation is

$$E_j = \frac{RT}{F} \frac{(U_1 - V_1) - (U_2 - V_2)}{(\overline{U}_1 + \overline{V}_1) - (\overline{U}_2 + \overline{V}_2)} \ln \frac{(\overline{U}_1 + \overline{V}_1)}{(\overline{U}_2 + \overline{V}_2)} \quad \ldots.3.1(iii).$$

where
$$\overline{U}_1 = \sum_{+} u_{i(1)} |z_i| c_{i(1)} \qquad \overline{V}_1 = \sum_{-} v_{i(1)} |z_i| c_{i(1)}$$
$$\overline{U}_2 = \sum_{+} u_{i(2)} |z_i| c_{i(2)} \qquad \overline{V}_2 = \sum_{-} v_{i(2)} |z_i| c_{i(2)}$$
$$U_1 = \sum_{+} u_{i(1)} c_{i(1)} \qquad V_1 = \sum_{-} v_{i(1)} c_{i(1)}$$
$$U_2 = \sum_{+} u_{i(2)} c_{i(2)} \qquad V_2 = \sum_{-} v_{i(2)} c_{i(2)}$$

and where $\sum_{+}$ and $\sum_{-}$ signify summation of positive and negative ions respectively. It is more widely used than the Planck equation, and is indeed the most common means of calculating diffusion potentials. This is probably due more to its greater simplicity than, as Dole (5) implies, to the fact that "continuous mixture" boundaries are more easily realised experimentally than the "constrained diffusion" type.

It is surprising to find that, despite its wide application, little has been done to verify the Henderson equation experimentally. Certainly no attempt has been made to compare potentials measured by the accurate experimental techniques introduced by Guggenheim (6) (see section 3.3) with those calculated from it in the important case where one of the solutions is very concentrated. When, in justifying improved expressions, other workers have criticised the equation, it has always been on theoretical grounds.

The next important equation is that published by P.B.Taylor (7) in 1927.

$$E_j = \frac{R\ T}{F}\,\frac{\eta_1(U_1 - V_1) - \eta_2(U_2 - V_2\ )}{\eta_1(\bar{U}_1 + \bar{V}_1) - \eta_2(\bar{U}_2 + \bar{V}_2\ )}\ \ln\frac{\eta_1(\bar{U}_1 + \bar{V}_1)}{\eta_2(\bar{U}_2 + \bar{V}_2)}$$

$$+ \quad (\frac{1}{W_H} - \frac{1}{W})dY \ \ldots\ldots\ldots\ldots 3.1(iv)$$

The quantities $U,V,\bar{\bar{U}},\bar{\bar{V}}$, are similar to those appearing in the Henderson equation, except that the ion mobilities, u_i, are replaced by their specific ionic conductances, λ_i; $W = \sum_i \lambda_i m_i$, where the λ_i and m_i used are those occurring in a transition layer of structure rigidly defined by relations determined by Taylor in the same paper. W_H differs from W in that the λ_i and m_i used are those occurring in a continuous mixture boundary. $dY = \sum_i \lambda_i\ z_i m_i dG_i$.

The equation applies to what have been called "free diffusion" junctions, i.e. where the boundary is made initially sharp, and the two solutions are then allowed to diffuse freely. It takes into account, by means of the functions η_1 and η_2, the variation of mobilities and activity coefficients across the boundary. The first term is, essentially, an extension of the Henderson expression, while the second is a correction which allows for the difference between the continuous mixture concentration distribution, and the free diffusion distribution deduced mathematically. Taylor applied the equation only to the junction

$$HCl(0.1N)\ \Big|\ KCl(0.1N) \ldots\ldots\ldots\ldots\ldots 3.1(v)$$

and claimed a closer agreement with experiment than that given by the Henderson equation. Guggenheim (6), however, has criticised some of the assumptions underlying the equation. In addition, the equation involves long, tedious calculations, and data which has not been fully determined, and is never used in practice.

In 1940, F.O.Koenig (8) criticised the treatment of certain fundamentals, such as spontaneous diffusion, in previous theories of cells with liquid junctions, and went on to develop a new equation based on what he called "the condition of quasi-reversible conduction." This expression takes into account the effect of gravitational, electric and magnetic fields, and yet is of no direct practical use; for it is a differential equation of similar form to equation 3.1(i), and thus presents the same mathematical difficulties.

In a series of papers published between 1929 and 1936 (6,9,10,11,12), Guggenheim threw into sharp relief the principles involved in the concept of diffusion potentials, and placed the whole subject on a much more secure footing. He stressed the importance of recognising the difference between thermodynamically and physically real quantities, and those which merely arise from convention. He stated (10) the following general principle, which previously (7) had only been hinted at:

"The electric potential difference between two points in different media can never be measured, and has not yet been defined in terms of physical realities; it is, therefore, a conception which has no physical significance." If, for example, we consider a cell with liquid junction,

Cu(1) | Solution X ¦ diffusion layer ¦ Solution Y | Cu(2) ....3.1(vi)

we can actually measure the potential difference, E, between the copper electrodes, and thus know it to be physically real. When, on the other hand, we regard E as being composed of a nett electrode potential, E_{el}, and a diffusion potential, E_j, so that

$$E = E_{el} + E_j, \quad \ldots\ldots\ldots\ldots\ldots\ldots 3.1(vii).$$

we must consider the split to be quite arbitrary; for neither single electrode potentials nor diffusion potentials can be measured, except in terms of single ion activities, which thenselves are arbitrary quantities.

The diffusion potential is, therefore, no more than a mathematical device. As such, however, it is undoubtedly of great use, and Guggenheim himself suggested that E could best be divided as follows:

$$E = E^I_{el} + E^I_j + E^S \ldots\ldots\ldots\ldots\ldots\ldots 3.1(viii).$$

and further

$$E = E^I_{el} + E^I_j + E^S_{el} + E^S_j \ldots\ldots\ldots 3.1(ix).$$

where E^I_{el} = the ideal electrode potential;

E^I_j = the ideal junction potential;

E^S = the potential due to the departures from ideal solution behaviour

$= E^S_{el} + E^S_j$.

Equation 3.1(viii) has come to be called Guggenheim's Rule.

This indefiniteness in the meaning of the liquid junction potential does not, of course, mean that no exact equation is possible for the potential across a cell containing a liquid junction; nor does it mean that any error is necessarily incurred in splitting such a relation. It merely places the liquid junction potential in its true perspective, and shows that the already considerable mathematical difficulties inherent in the problem may be increased by the fact conventional qualities have been introduced.

3.2. THE ELIMINATION OF THE LIQUID JUNCTION POTENTIAL ERROR.

From the above outline of developments in the theoretical treatment of diffusion potentials, it would appear to be unlikely that there will be devised an exact general equation which will allow diffusion potentials to be calculated. At the best only approximations can be expected. Although approximate equations are at present widely used in estimating diffusion potentials, the accuracy of the computed potentials rarely justifies the labour involved. It seems, therefore, that the error due to liquid junction potentials which is, after all, a practical problem, will best be approached from an experimental point of view; and it is here, as an aid in devising experimental methods of countering the error, that the approximate equations can, perhaps, be of greatest value. This has long been realised, and many semi-empirical methods have been devised.

The earliest and most often used of these, involves the interposition between the two solutions of a "salt bridg consisting of a concentrated solution of some salt - usually potassium chloride, potassium nitrate, or ammonium nitrate - whose cation transport number is almost equal to 0.5. Kline, Meacham and Acree (13) have reviewed the method, and estimate its accuracy to be of the order of ± 1.0mV. The method is based on the fact that any expression for the liquid junction potential can be reduced to a form in which the quantity $\sum_i (t_i^+ - t_i^-)$ is a factor of the largest term. When a bridge solution is used in which cation and anion have equal transference numbers - Grove-Rasmussen (14) has applied the name "equitransferent" to such solutions -, and which is so concentrated that the conductance due to the ions of the adjacent solution can be neglected, this factor, and with it the diffusion potential is reduced to zero. This device is extremely simple to use, but, as the condition $t^+ = t^- = 0.5$ is never completely satisfied, it does not fully eliminate the diffusion potential. In addition, when it is applied with unsatisfactory junction-forming techniques, as is usually the case large, indefinite, and irreproducible errors are introduced. This has been clearly demonstrated in the case of electrometric pH measurements (1).

The same principle is sometimes applied in a slightly different manner, when the concentrated solution also acts as the electrolyte of one of the electrodes. This variant is usually employed in conjunction with saturated calomel electrodes. In such cases, of course, there is strictly speaking no "bridge", in the sense of a link between two solutions, as there is only one liquid junction.

The two cases usually behave similarly, and can be treated together. There are, however, occasions when they must be distinguished. The following nomenclature will be used in this work, for this purpose:

The term "bridge" will be used to refer to the general case, as well as to true salt bridges.

The terms"full bridge" and "half bridge" will be used to distinguish between the two types.

The term "swamped" will be used to denote the fact that one of the solutions at a junction is so concentrated that its ions can be considered responsible for all the conductance at the boundary, and, therefore, for the diffusion potential.

Niels Bjerrum (15,16) introduced an extrapolation method for eliminating the residual potential at a salt bridge, or estimating its value. This depends on the assumption, suggested by Planck and Henderson equations, that the diffusion potential at a 3.5N bridge is half that at one of normality 1.75. If, therefore, measurements are taken using first a 1.75 and then a 3.5N bridge, the residual junction potential at the latter is given by the difference between the two potentials. The method as usually used, is not very accurate, and can only be said to give an orientation about the order of magnitude of the true potential, if the magnitude of the difference is small. .

A second group of practical methods makes use of the fact that the diffusion potential decreases, as the two solutions become more alike. Thus, the junction potential is reduced by adding to both the solutions large, equal amounts of an indifferent electrolyte. Many modifications and extensions of this method have been suggested. In the most accurate of these, which is due to Owen and Brinkley (17,18), the errors due to the diffusion potential still remaining, and to the salt effects caused by the presence of the indifferent electrolyte are eliminated by extrapolations. This procedure has been applied with success in solubility product and dissociation constan determinations, but is too long and exacting for all but the most accurate work. The methods in this class are not of very general application, for the addition of large quantities of electrolyte is in many cases not permissible.

3.3. THE MEASUREMENT OF LIQUID JUNCTION POTENTIALS.

From an experimental point of view liquid junction potentials have presented no less of a problem. The conflicting methods and techniques used by the early workers (e.g. Bjerrum(16),Cummings and Gilchrist (19),Takegami (20) Lewis, Brighton and Sebastian (21))may be taken as an indication of the complexity of the difficulties facing them.

It was again Guggenheim (6)who placed the subject on a sound footing, and who was able to separate from the mass of contradictory evidence the essentials governing the behaviour of diffusion potentials. He rejected the widely held idea that junction potentials vary with time, and pointed out that, just as the magnitude of the calculated potentials depends on the type of transition layer assumed, so must the measured potentials at heteroionic junctions depend on the way in which the junction is made. He went on to classify the various types of liquid junctions used in practice, and to discuss them both theoretically and experimentally. Throughout he stressed the need for careful experimental techniques and precise satisfaction of the conditions essential to the various types of boundary. This analysis is now accepted as the basis of all work on cells with liquid junctions, and is worth summarising here: -

(a) Continuous Mixture. This is the type to which the Henderson equation applies, and which was defined above during the discussion of the equation. According to theory it should not give rise to constant potentials, as diffusion produces no steady state. Guggenheim, however, using an ingenious siphoning method to make a long transition layer which satisfied the continuous mixture condition, was able to obtain very satisfactory stability, and reproducibility.

(b) Constrained Diffusion. This type is described theoretically by the Planck equation, and is best made experimentally at a porous plug or membrane kept washed on either side with the two solutions. Guggenheim found these junctions to be sensitive to the rates of flow of the solutions, and generally not very stable.

(c) Free Diffusion. This junction is defined by the following conditions: the transition layer should be as short as possible, initially, after which unconstrained diffusion should be allowed to take place. Guggenheim emphasised that the essential requisite for the stability of these junctions is that diffusion should indeed be unconstrained, and that this can only be satisfied if the junction has "cylindrical symmetry", that is, if "the gradients of the concentrations and the electrical potential are throughout parallel to a fixed straight line." Practically, this means that the junction must be contained within a tube of regular bore. He found that free diffusion junctions were more simple to produce, and, if set up with due regard to the condition of cylindrical symmetry, more stable and more reproducible than any of the other types. Unfortunately, they have proved to be exceedingly intractable, mathematically, and there exists no adequate, explicit formula for their potentials.

(d) Sharp Indefinite. These very simple junctions are widely used, and are made by dipping a tube containing the one solution into a vessel of the other. Guggenheim found them to be unstable, and irreproducible to the extent of several millivolts.

(e) Flowing. In this type of junction the two solutions stream towards each other, and, after meeting flow away in parallel streams. These junctions give good reproducibility, but are rather inconvenient to use. In addition, their theory is so complicated that little serious discussion has been attempted.

It is surprising how little development has followed Guggenheim's lucid exposition of the fundamentals of the making of liquid junctions. In fact, only three papers have appeared in which any significent additions have been made to the experimental side of the field.

During their study of diffusion potentials at free diffusion junctions, Ferguson, van Lente, and Hitchins (22)used a cell in which the junctions were made at 9 mm three-way T-taps. This was a development of Guggenheim's apparatus, and had the advantage of greater simplicity. The potentials resulting took from six to twenty-six hours to become constant, but were then stable to ± 0.04mV mean deviation, and reproducible to within 0.1 mV. Large fluctuations of potential occurred during the first few hours after the junctions were made. In a second paper (23) these authors compared their static free diffusion junctions with flowing junctions of similar form. As was to be expected, they found that the diffusion potentials at the two types were almost identical, when the solutions used were homoionic. In the heteroionic case, however, marked differences arose. They showed, in addition, that the potentials at heteroionic boundaries of the flowing type depended on the rate of flow of the solutions, and, more serious, that their response to certain treatments differed from junction to junction. These observations lead one to the conclusion that free diffusion junctions are in every way more precise than flowing junctions, although they have the disadvantage of taking a long time to reach a steady state.

The third paper of importance is due to Brown and MacInnes (24) who devised a new method of making free diffusion boundaries in the course of their work on concentration cells with transference. In their apparatus the two solutions are contained in identical tubes, each of which is attached to a plate glass disc. Junctions are made by rotating the upper disc, until the tubes are in juxtaposition. This device has the advantage over those involving taps that the technical difficulties in ensuring exact cylindrical symmetry are greatly reduced. Amongst its less desirable features must be counted the fact that one of the electrodes is attached to the moving disc, which is a distinct drawback in the case of calomel electrodes, and the lack of data on its performance with heteroionic junctions.

Another surprising feature of the experimental work in the field of liquid junction potentials during the last 25 years is the fact that many investigators disregard the work of Guggenheim (6), and Ferguson and his co-workers (22,23).Bonnemay and Fairbank (25) and K.V. Grove-Rasmussen (33,26) may be cited as examples. The latter, it must be admitted, did use a simple form of cylindrically symmetrical junction; but he measured potentials during the period of extreme instability which follows the establishment of a free diffusion junction, and neglected, on quite inadequate grounds, the effect of a second junction of the indefinite-sharp type. He gave no indication of the accuracy of the resultant readings, but quotes them correct to 0.1mV. This seems to be a rather optimistic estimate of the reliability of the measurements.

4. THE USE OF MIXED ELECTROLYTE SALT BRIDGES.

4.1. THE PRINCIPLE OF THE METHOD.

The use of salt bridges in the suppression and estimation of junction potentials is based on the assumption that the anionic and cationic transport numbers in the bridge solution are equal. (See section 3.2). When this solution is so concentrated relative to the adjacent solution that it can be considered responsible for all the conduction at the boundary, the quantity $\sum_i t_i^+ - \sum_i t_i^-$ becomes a factor of the expression for the diffusion potential, E_j; thus, if now the condition

$$\sum_i t_i^+ = \sum_i t_i^-$$

is fulfilled, E_j, is reduced to zero.

The commonly used bridges which consist of a concentrated solution of a single salt are assumed to be equitransferent, and, are nearly so. For example, the cationic transport number of potassium chloride is 0.486, of potassium nitrate, 0.507, and of ammonium chloride, 0.490. Despite this seemingly close approximation, their behaviour differs widely from that of an equitransferent solution. In the first place, the residual diffusion potentials are usually appreciably different from zero. Secondly, they suffer from the serious drawback, as Grove-Rasmussen (26) pointed out, that the numerical value of the potential increases exponentially with decreasing concentration of the adjacent solution. On the other hand, the potential at the boundary between a dilute and a truly equitransferent solution is much closer to zero, and approaches even more closely as the

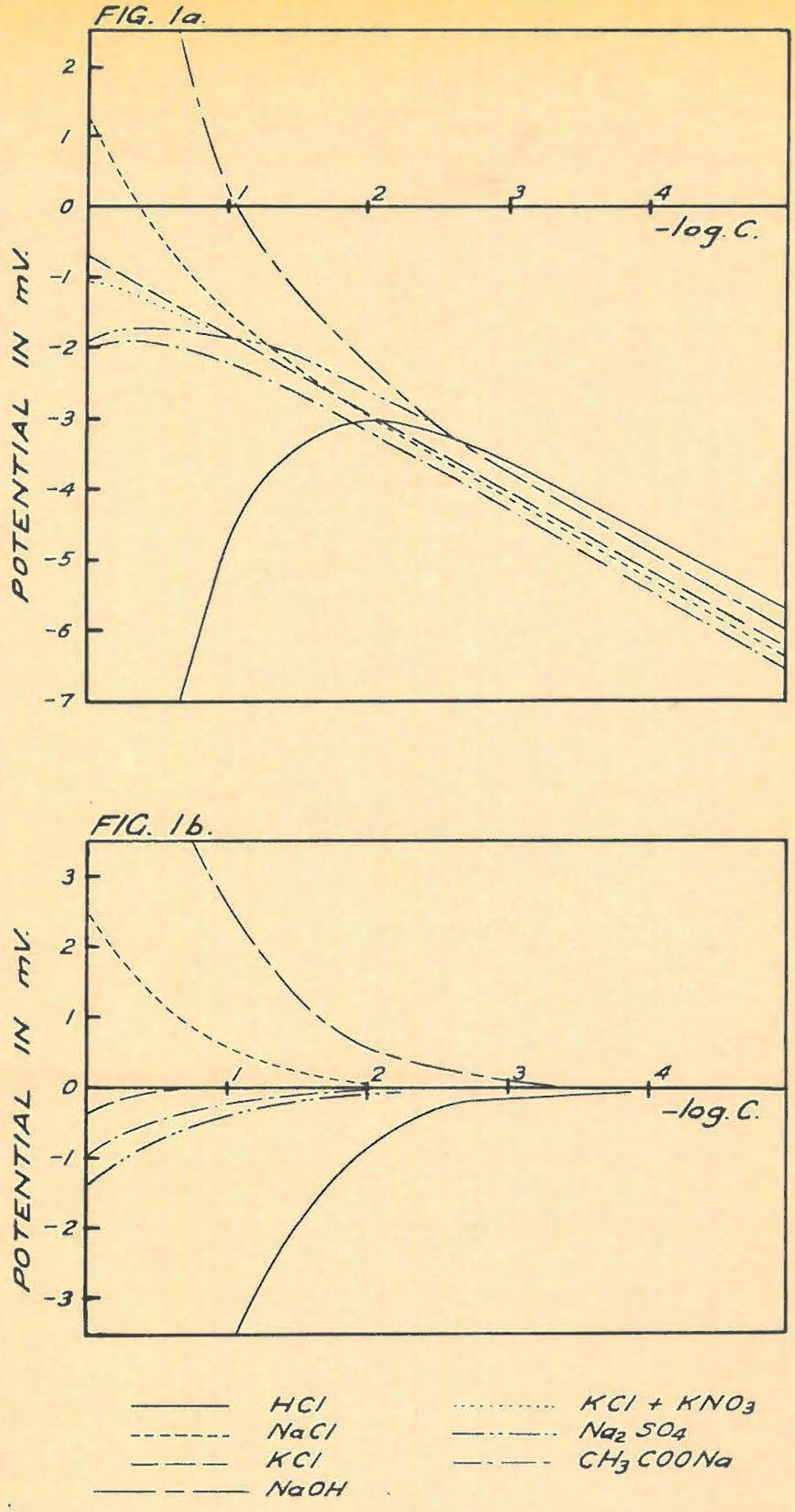


FIG. 1. GRAPHS OF DIFFUSION POTENTIAL AGAINST -LOG. C. (C = CONCENTRATION OF DILUTE SOLN.)

adjacent solution is diluted. Figures 1a and 1b show curves derived by Grove-Rasmussen (26) from the Henderson equation (equation 3.1(iii). These illustrate the variation with the concentration of the dilute solution of the potential across the junctions of various dilute solutions with 4.1N KCl and equitransferent 3.6N (KCl + KNO_3) solutions respectively. (See Note below.)

Thus, it is clear that the practice of using salt bridges in combating liquid junction potential errors without fully satisfying the condition of equitransference, reduces greatly the accuracy and reliability of the device. There can be no doubt of the need for developing some means of reducing the deviations from equitransference.

In considering the problem, it appeared to the present author that, if the solute were to consist of a pair of salts one of which has a cation transference number greater than, and the other less than 0.5, it should be possible to mix them in such a proportion that the resulting solution has a total cation transference number of exactly 0.5.

Suitable combination of salts are easily found, e.g. potassium chloride (t_K=0.486); and potassium nitrate (t_K=0.507); potassium nitrate and ammonium chloride (t_{NH_4}=0.490.) If, then, the equitransferent mixture could in some way be determined, the effectiveness of the salt bridge class of methods could be greatly increased with no loss of simplicity or convenience.

A search of the literature showed that this idea was by no means original. The use of mixed electrolyte salt bridges was first mooted over fifty years ago, and has since been studied by several workers. Nevertheless, no satisfactory determination of the equitransferent mixture has yet been made, nor has any practical method of applying mixed bridges been introduced. It therefore appeared that there was much to be gained from a detailed investigation of the subject.

Note:

The marked difference in the behaviour of completely equitransferent solutions and those commonly used, as demonstrated by Figures 1a and 1b, might at first sight appear strange. Particularly difficult to explain on general principles is the fact that, although a dilute adjacent solution is definitely an essential condition for the functioning of a salt bridge, increasing dilution results in an increase of the residual potential difference, when the bridge solution is not quite equitransferent.

A consideration of the Henderson equation makes clear the reason for this apparent anomaly:

Let us write the equation in the form

$$E_j = \frac{R\ T}{F\log e}\left[\frac{c_2(u_2 - v_2)}{c_2(u_2+v_2) - c_1(u_1+v_1)} - \frac{c_1(u_1 - v_1)}{c_2(u_2+v_2) - c_1(u_1+v_1)}\right] \cdot \log\frac{c_1(u_1 + v_1)}{c_2(u_2 + v_2)}$$

$$= \frac{R\ T}{F\log e}(A - B)C$$

where the subscripts 1 and 2 refer to adjacent and bridge solutions respectively.

If the bridge solution is equitransferent,

$u_2 = v_2$, and thus $A = 0$.

The variation of the diffusion potential with c_1 is thus determined by the quantities B and C. Now, as c_1 decreases, it is obvious that C will increase and B decrease, numerically. ($c_2(u_2+v_2)$ will be much greater than $c_1(u_1+v_1)$). As C is a logarithmic term, it will change more slowly than B, and thus the nett effect will be a decrease in the numerical value of E_j.

In the case where the bridge is not completely equitransferent, A changes very slightly with c_1, and is much greater than B, except for the greatest values of c_1.

Hence, the change in E_j with increasing c_1 is determined by the product AC, and is, therefore, an exponential numerical increase.

4.2. CRITICAL REVIEW OF PREVIOUS WORK ON MIXED ELECTROLYTE BRIDGES.

It is convenient at this stage to consider previous work on mixed electrolyte salt bridges. The literature contains some important contributions, but the subject is, in general, much neglected. In few books on electrochemistry is it mentioned, in none is it treated in any detail, and nowhere is there a complete review of the field. In these circumstances, it was felt to be desirable that the discussion presented here be both detailed and exhaustive.

The use of mixtures of electrolyte in attaining equitransference was initially suggested by Bjerrum in the first of his papers on salt bridges (15). He did not develop the idea which he credited to Professor Robert Luther of the Leipzig Physical Chemistry Institute, as he did not consider the transport data then available to be sufficiently accurate.

In 1924 Shirow Takegami (20) carried out an experimental test of the efficacy of mixed electrolyte salt bridges, and concluded that they had no advantage over the conventional type. His methods and techniques, however, were extremely unsound: he calculated the equitransferent mixture, and then measured the resulting diffusion potentials using a highly inaccurate and quite unjustifiable extrapolation to zero time. No reliance whatsoever can, therefore, be placed on his conclusions.

The next investigator, C.Drücker (27), came to the same conclusion as did Takegami, but his methods too are open to criticism. The electrolyte pair which he used as solute (potassium nitrate and potassium chloride) was most unsuitable owing to the low mobility of the sodium ion relative to the potassium and nitrate ion. Furthermore, the actual mixtures of these salts which he used, did not cover a sufficiently wide range to ensure that the equitransferent mixture was included.

Between 1932 and 1938, V.Čupr published a series of papers (28,29,30) dealing with diffusion potentials. As far as is known, this work has never been quoted or referred to by any subsequent author, and, indeed, only came to light towards the end of the present investigation. The majority of these papers are written in Czech and published in little known journals. When copies were finally obtained, it was not found possible to have them translated in this country, and considerations of time precluded any attempt to have this done overseas. Nevertheless, some detailed summaries appearing in Chemical Abstracts in conjunction with one of the papers (30) which was published in French gave an indication of the nature and standard of their contents. They deal, in general, with the more theoretical aspects of the subject, in an attempt to develop general methods of calculating diffusion potentials, and they seem to place great emphasis on outmoded mathematical treatments, such as Planck equation. The experimental techniques used were not very accurate and very few practical details are presented at all. Perhaps the most significant of the group is the first (29) in which the values of x and y are calculated for which the potential at the junction

$$KCl\ (0.1N)\ \Big|\ xHCl,\ yNaCl$$

is zero. These papers while undoubtedly of interest, do not appear to be of great importance in the present work, as they deal with dilute solutions rather than with concentrated bridges.

It was during this period, as well, that Acree and his co-workers at the National Bureau of Standards, Washington, carried outtheir investigations into the error in pH measurements due to junction potentials. In 1931, Murray and Acree (31) compared potassium chloride and ammonium chloride as eliminators of junction potentials, and concluded that the latter was the more satisfactory. They also showed, by means of potentials calculated from the Henderson equation, that the addition of potassium or ammonium nitrate to these chloride solutions results in a reductiom of the residual junction potential. They recommended that chloride-nitrate mixtures in the ratio 3 to 1 be used in annulling the diffusion potentials of solutions with pH values between 3 and 10. Later, Acree in conjunction with Kline and Meacham (13), urged that saturated potassium chloride salt bridges be adopted as a standard method of treating the liquid junction potential error. Again, Manov, de Lollis, and Acree (32) as a part of their determination of the relative activity coefficients of chloride ions in various mixtures of chlorides, calculated the diffusion potentials at the junctions of several mixtures of potassium chloride, potassium nitrate, and hydrochloric acid, and showed that these mixtures were more equitransferent than pure potassium chloride.

It is unfortunate that these workers who were so convinced of the need for more satisfactory methods of reducing liquid junction potential errors, and who were so insistent on the superiority of mixed chloride-nitrate solutions as bridges, did not attempt to prove their contention and to determine accurately the composition of the equitransferent mixture by experiment.

The most recent worker in the field is K.V. Grove-Rasmussen, whose approach to the problem is more sound than that of previous investigators. In particular, he seems to have appreciated its complexity, and the need for experimental verification.

In the first of his papers (14),Grove-Rasmussen suggested the use of the very apt term "equitransferent", and defined it as "having the same effective cation and anion transference."

His second paper (33), dealt with the determination of the composition of equitransferent mixtures. He showed that this cannot be calculated from transport number data, as had almost invariably been done in the past. In the first place the data does not exist. Very few measurements have been made of transference numbers in concentrated solutions of either pure or mixed electrolytes, nor are there any equations which might allow this deficiency to be circumvented. In the second place, as he points out, it is of no use to ensure the absolute equitransference in the bridge solution alone. What is needed is, rather, that"........the mixture of this solution is such that the boundary between it and a dilute solution on the average becomes equitransferent with regard to the ions originally present in the bridge solutions." This condition, of course, will prohibit any thought of calculation, until the detailed structure of the boundary layer is known. Thus it must be concluded that equitransferent mixtures can at present only be determined experimentally. The importance of this deduction cannot be over-emphasized; its significence is such, in the opinion of the present author, that it must be regarded as a general rule. In addition, it is a principle which invalidates much of the prior work on mixed electrolyte bridges.

Grove-Rasmussen's experimental determination of the equitransferent mixture of the ($KCl + KNO_3$) bridge was less successful. He used the cell

$$\text{Ag-AgCl}\Bigg|\,\text{HCl}\,\Bigg|\,\text{Glass}\,\Bigg|\begin{matrix}\text{HCl(0.01N)}\\ +\\ \text{KCl(yN)}\end{matrix}\Bigg|\begin{matrix}\text{KCl(xN)}\\ +\\ (5-x)\text{N KNO}_3\end{matrix}\Bigg|\,\text{KCl(satd)}\Bigg|\text{Hg}_2\text{Cl}_2\text{-Hg}$$

where both y and x could be varied . This cell suffers from several disadvantages: its accuracy is limited by the incorporation of a glass electrode with its high resistance and unknown asymmetry potential; liquid junction potentials are not read directly, and a complicated computation involving numerous approximations is necessary before the composition of the equitransferent mixture can be arrived at. Added to this, Grove-Rasmussen's experimental methods were not very precise. For example, he used free diffusion junctions, and measured their potentials directly after their formation which is when they are most unstable and irreproducible (22) (see section 4.6.2a). As a result, he could not fix the composition of the equitransferent mixture more precisely than between 40 and 60 moles KCl per cent.

Grove-Rasmussen's third paper on the subject was published in 1951 (26). It contained a demonstration by means of calculated diffusion potentials of the advantages of the use of equitransferent salt bridges. This has been discussed in section 4.1, and the curves shown in Figures 1a and 1b are taken from his paper. Grove-Rasmussen went on to consider the use of equitransferent salt bridges in conjunction with the Bjerrum extrapolation method. He measured the difference in potential at the junctions of dilute solutions with 3.6 and 1.8N solutions of potassium chloride and potassium nitrate in equimolar proportions, which he assumed to be equitransferent. He came to the conclusion that the extrapolation merely affords an indication of the magnitude of the true potential, and that only when an equitransferent bridge solution is used. Although the experimental techniques employed here were again not beyond criticism, the limiting factor was the accuracy of the potentials used as a standard of comparison. These were, of course, obtained from the Henderson equation,and hence cannot be relied upon to any great extent as a criterion of the practical value of the method. Thus Grove-Rasmussen's judgment of the Bjerrum extrapolation cannot be accepted without reservation.

An important point emerging from the above review is that too great a reliance has been placed on the predictions of the approximate equations by workers in the field of mixed electrolyte salt bridges. The factors involved are extremely complex, and one cannot extend to them, as has been done, relations which even under the most favourable conditions are approximate. It must be realised that, while these relations may possibly indicate general trends, clear experimental verification is necessary at every stage. Furthermore, any quantity required such as the composition of equitransferent solutions must be obtained experimentally.

4.3. OUTLINE OF THE PRESENT INVESTIGATION.

4.3 1. THE AIMS OF THE INVESTIGATION.

4.3 1a.The General Aim.

In the light of the review given above of previous work in the field of mixed electrolyte salt bridges, it is evident that present knowledge of the subject is very limited, and hardly extends further than an appreciation of the possible advantages of the use of equitransferent solutions. Certainly the fundamentals of the subject have not been established.

The purpose of this investigation was to establish these fundamentals, as far as possible, by a study of the variation of liquid junction potentials with the composition of the mixed electrolyte bridge solution.

4.3. 1b.<u>More Specific Aims.</u>

The following cell was used: -

$$\mathrm{Hg\text{-}Hg_2Cl_2}\Big|\mathrm{HCl}(m_1)\underset{(a)}{\Bigg|}\begin{matrix} J(1-x)\mathrm{KCl} \\ + \\ (Jx)\quad \mathrm{KNO_3}\end{matrix}\underset{(b)}{\Bigg|}\mathrm{KCl}(m_2)\Big|\mathrm{Hg_2Cl_2\text{-}Hg} \qquad \ldots\ldots\ldots\ 4.3(i)$$

in which the molalities m_1 and m_2 of the electrolyte solutions are much less than J, the concentration of the bridge solution, and are so chosen that the nett electrode potential of the cell is zero. (see section 4.3 2c.) The potential, E, of the cell will thus give the algebraic sum of the potentials at the junctions a and b directly.

Using the cell the general purpose of the investigation was pursued with the following more definite ends in view:

(i) To show how the cell potential, E_j, varies with the proportions of the two constituents of the bridge solution at constant ional concentration.

(ii) To provide a clear, practical proof that the residual potentials at salt bridges can be reduced to zero by the use of the correct mixture of two electrolytes whose predominantly conducting ions have different signs.

(iii) To ascertain whether this elimination of potential occurs in all cases, and, if not, what the factors are which govern it.

(iv) To obtain an estimate of the equitransferent ratio of the potassium chloride-potassium nitrate mixture.

(v) To show whether the use of equitransferent bridges does, indeed, improve the accuracy of the Bjerrum method of estimating residual diffusion potentials. (This topic is discussed in detail in section 4.3 3.)

In addition, it is considered that this would be an excellent opportunity of comparing the values of the experimental potentials with those calculated from the Henderson equation, as the experiments being carried out involve direct measurements of diffusion potentials. It will be recalled that the need for such a comparison in the case where concentrated solutions are involved, was stressed in section 3.1, above.

4.3.2. DETAILED DESCRIPTION OF THE CELL.

The cell will be discussed here with reference to the reasons which led to its choice, both in relation to its general form and to details such as the electrodes and solutions used. The practical aspects of the cell are described in the experimental sections 4.4 and 4.5.

4.3 2a General.

The essential characteristic demanded of the cell was that it allow liquid junction potentials to be read directly. In much of the previous work errors were introduced, and a good deal of the information contained in the measurements obscured, by the fact that the potentials given by the cells used were a combination of electrode and diffusion potentials which could only be resolved by introducing approximations. As the potentials of its electrodes are equal and opposite, the cell 4.3 (i) satisfies this requirement.

The potential of the cell is the sum of the diffusion potentials at the boundaries a and b. Hence, any variation of potential with change in the bridge solution must be regarded as being compounded of the individual variation at the two junctions. This is, in many ways, unfortunate. It means that an effect occurring at one of the boundaries may be obscured by the changes of potential at the other, and that the information which can be gained from the cell will be far less definite than if there were only one boundary. However, it is only in cells with two liquid junctions that diffusion potentials can be read directly without reference to electrode potentials. One has, therefore, to choose between two types of cell, each of which introduces some uncertainty. It was felt that the form of cell chosen was the better of the alternatives, because it does, at least, allow the value of the total diffusion potential across the salt bridge to be determined with certainty; and while, undoubtedly, it is difficult to interpret the information obtained from such a cell in terms of the potentials at the individual liquid junctions, it should be remembered that the investigation is concerned primarily with full bridges rather than with half bridges.

4.3 2b. Electrodes.

Several factors favoured the use of calomel electrodes: the work of Hills and Ives (34) has shown them to be capable of the highest accuracy: they are simpler to prepare and more convenient in use than, for example, hydrogen electrodes; and, in addition, are the most robust of the high-precision electrodes. Unlike, for instance silver-silver chloride electrodes, they can stand up to months of use with, as was proved during this investigation, very little loss of accuracy.

4.3 2c. Electrode Solutions.

As this research is concerned specifically with the effect on diffusion potentials of bridge solutions, it was considered essential that the same electrolyte solutions be retained throughout. Furthermore, in view of the fact that it was intended that this study be as general as possible, it was felt that the combination of bridge and adjacent solutions used should not be one which particularly favoured the elimination of the residual junction potential. The adjacent solutions chosen are, in fact, decidedly unfavourable. On account of their relatively high concentration (about 0.1m), and the high cationic transference of hydrochloric acid, they will tend to promote large junction potentials, and to resist the potential-eliminating effects of the salt bridges. It is, therefore, highly unlikely that any result revealed by this investigation was due to a fortuitous, favourable interaction of the bridge and adjacent electrolytes.

An added reason for the choice of the chain

$$\mathrm{HCl}\ (0.1\mathrm{m})\ \Big|\ (\mathrm{KCl} + \mathrm{KNO_3})\ \mathrm{J}\ \Big|\ \mathrm{KCl}(0.1\mathrm{m})$$

is that it is very similar to the only chain to have been studied at all widely,

$$\mathrm{HCl}\ (0.1\mathrm{N})\ \Big|\ \mathrm{KCl}\ (3.5\mathrm{N})\ \Big|\ \mathrm{KCl}(0.1\mathrm{N}) \ldots\ldots 4.3(\mathrm{ii})$$

This provides a basis for comparison with other work, (See section 4.6 4a).

In order that the potentials at the two opposed calomel half-cells should be equal (see cell 4.3(i)) it is necessary that the activities of the chloride ions in their respective solutions be equal. It is impossible to satisfy this requirement exactly in practice, as single ion activities are not physically real quantities. In his work on a cell of a similar form, Guggenheim (6) used electrode solutions of normality 0.1. He then considered that the electrode potentials cancelled, but that the measured potential was due to both E_J and E^S (see equations 3.1(viii) and 3.1(ix)), thereby neatly circumventing the difficulty. It was considered, however, that it would be highly undesirable, in the present case, for the measured "diffusion potentials" to include a contribution from E^S_{el}, which really is a part of the electrode potential. There was therefore no alternative but to approximate the condition on the basis of tabulated mean ionic activity coefficients. The following convention which has been adopted by several previous workers (eg. 6,35,32) was used:

In the HCl solution, $a_{Cl} = a_{\pm}\,(\mathrm{HCl})$.

and in the KCl solution $a_{Cl} = a_{\pm}\,(\mathrm{KCl})$ ....4.3(iii)

It is now necessary to calculate the molalities at which the hydrochloric acid and potassium chloride solutions have equal mean ionic activities. The mean ionic molal activity coefficients, $f_{\pm}$, have been determined for both these electrolytes at various molalities, m. From these the corresponding mean ionic activities, $a_{\pm}$, can be found from the formula

$$a_{\pm} = m \cdot f_{\pm} \quad \ldots\ldots\ldots\ldots\ldots 4.3(iv)$$

($m_{\pm} = m$ for uni-univalent salts.)

The problem of determining m at a given $a_{\pm}$ is, however, more complicated; for the data is only available at round molalities, and simple interpolations are not sufficiently accurate. The difficulty was overcome by using a method of successive approximations.

The detailed procedure was as follows: -

(i) The molality of the potassium chloride solution was fixed at 0.10000.

T. Shedlovsky (36) found $f_{\pm}$ for 0.10000m aqueous solutions of KCl at 25°C to be 0.7692 with an accuracy of ±0.05 per cent.

Therefore, by equation 4.3(iv), $a_{\pm} = 0.07692$ in a 0.10000m potassium chloride solution at 25°C.

(ii) The mean ionic activity of both solutions was taken to be 0.07692.

(iii) An approximate value of the molality of hydrochloric acid solution of mean ionic activity 0.07692 was found graphically from data given on page 92 of Conway's "Electrochemical Data." (37):-

At 25°C, m = 0.098, when $a_{\pm} = 0.07692$.

(iv) Harned and Ehler's (38) gave the following relation between f and m :

$$\log\ f = -\frac{A\sqrt{c}}{1+W'\sqrt{2c}} + Z - \log(1+0.036m) + Bc + Dc^2 \ldots\ldots\ldots\ldots\ldots\ldots 4.3(v)$$

where

B = 0.1390 - 0.00392θ ;

D = 0.0070 - 0.000033θ ;

θ = temperature on the centigrade scale;

$W' = K'\mathring{a}$;

K' = a constant ;

= 0.2324 at 25°C ;

$\mathring{a}$ = the apparent ionic diameter

= 4.3 Ångstrom units ;

A = constant in the Brønsted equation ($\log f = Am^{\frac{1}{2}}+Bm$)

= 0.506 ;

c = concentration in moles per litre, and was found from the following relation:

$$\frac{c}{m} = a_1 - b_1 m.$$

a_1 and b_1 are constants which at 25°C have the values 0.9972 and 0.01817, respectively.

Z = the contribution to log f of the Gronwall, La Mer, and Sandved (39) extension of the Debye - Hückel theory. The value of Z used was - 0.00080 throughout, for it was found that its variation was negligible over the concentration range 0.1m to 0.098m:

The values of all the quantities given above were taken from tables in Harned and Ehler's paper.

The value of f corresponding to m = 0.09800 was calculated from equation 4.3(v), and substituted in the equation.

$0.07692 = m.f.$ ....4.3(vi)

to give a closer approximation to the true molality. This was now substituted in 4.3(v), and the whole process repeated, until successive values of m were identical. In actual fact three stages of approximation were necessary.

The resultant value of m was 0.09917.

Hence, the electrode solutions used were hydrochloric acid and potassium chloride of molalities 0.09917 and 0.10000 respectively, and mean ionic activity 0.07692; and therefore, the complete cell used was

$$\mathrm{Hg{-}Hg_2Cl_2} \Bigg| \begin{matrix} \mathrm{HCl} \\ (0.09917\mathrm{m}) \end{matrix} \Bigg| \begin{matrix} J(1-x)\,\mathrm{KCl}, \\ Jx\quad \mathrm{KNO_3} \end{matrix} \Bigg| \begin{matrix} \mathrm{KCl} \\ (0.10000\mathrm{m}) \end{matrix} \Bigg| \mathrm{Hg_2Cl_2{-}Hg}$$

.................4.3(vii)

The error in these figures is equal to the inaccuracy of ± 0.05 per cent in Shedlovsky's determination of $f_{\pm(KCl)}$. This introduces an uncertainty of ± 0.05mV in the nett electrode potential of the cell.

4.3 2d. Bridge Solutions.

Various reasons led to the use of potassium chloride and potassium nitrate as the components of the solute of the bridge solutions: the combination has been used and studied previously (13, 24, 33); their cation transport numbers in the pure solutions at high concentrations, approximately 0.485 and 0.516, respectively, suggest that the equitransferent ratio will lie towards the centre of the range of mixtures, which is considered a desirable feature; and finally, the fact that they have a common ion would simplify any accurate calculations or determinations of transport numbers which might possibly have proved necessary..

Diffusion potentials depend on the concentration as well as the nature of the solute. Hence, it was essential that the total solute concentration be kept constant, as the relative proportions of KCl and KNO_3 were varied. As we are concerned here with transport phenomena, the concentration unit used for expressing the "total solute concentration" must be one involving volume rather than weight of solvent. It was, therefore, arranged that the mixtures used were at constant ional concentration, J. J is defined as follows

$$J = \frac{1}{2}\sum_{i} z_i^2 c_i \qquad \ldots\ldots\ldots\ldots\ldots\ldots 4.3(viii).$$

As the ions concerned here are all univalent, this means that the total solute normality was kept constant. For convenience bridge solutions will be referred to in terms of their normalities. The upper limit of these concentrations was set, in the case of mixed KCl-KNO_3 bridges by the solubility of KNO_3. The most concentrated mixed electrolyte bridge solution used was 3.5N, and it was possible to use mixtures at this concentration, containing up to 80 moles of KNO_3 per cent of the solute (40).

4.3 3 THE BJERRUM EXTRAPOLATION.

The Bjerrum method of estimating residual diffusion potentials has never been regarded as highly accurate. Bjerrum, himself, warned that it should be used only when the extrapolation is small in value. Once widely used, the method has now fallen into disuse.

The most serious criticism of the method was made by Kline, Meacham, and Acree (13) on the basis of potential measurements which they, themselves, as well as other workers had carried out. A previous investigation, presumably unpublished, led these authors to the conclusion that, when x=4.12, the potential across the junction

HCl (0.1N) | KCl (xN) | HCl (0.1N).....4.3(ix)

is "practically completely annulled." They therefore assumed that a 4.12N KCl bridge reduces to zero the potential between 0.1N HCl and 0.1N KCl solutions. Other measurements taken in this former investigation agree with the determinations by other workers that the difference in the potentials, when x=3.5 and when x=1.75 was about 4.3mV. According to the Bjerrum extrapolation, therefore, the actual diffusion potential in the case of a 3.5N bridge should be 4.3mV. Further, since the diffusion potential across the chain 4.3(ix) is zero, when x=4.12, the difference in the potentials between the cases when x=3.5 and x=4.12 should be equal to 4.3mV. As their measurements showed this latter to be only about 1.3mV, Acree and his co-workers reasoned that the extrapolation was in error by about 330 per cent. They applied this method of reasoning to other systems, and in each case were able to demonstrate an error of similar magnitude.

As general considerations indicated that the assumption of zero potential across the chain

HCl (0.1N) | KCl (4.12N) | KCl (0.1N)......4.3(x)

was invalid, measurements were performed during the present investigation to test it. These showed that this potential is, in fact, 1.67mV (see section 4.6 3). On the basis of this value the error in the Bjerrum method is reduced to the region of 50 per cent.

If the foregoing is viewed in the light of Grove-Rasmussen's suggestion (26) that the accuracy of the predictions of the Bjerrum extrapolation method would be enhanced by the use of equitransferent salt bridges, the need for a revaluation of the method becomes evident. It was considered that this lay within the scope of the present investigation.

The effect of mixed electrolyte bridges on the accuracy of the extrapolations was studied using cell 4.3(vii). Potentials were measured for varying proportions of the constituents of the bridge at constant ional strengths of both 3.5 and 1.75. A comparison of the two sets of readings showed how well the predictions of the Bjerrum method agreed with experiment, and how they were influenced by the use of mixtures of salts in the bridge solution. (See section 4.6 4d.)

The subject was treated from a theoretical point of view using calculated potentials, with two main ends in view. The first of these was to demonstrate the improvement which, in theory, should result from the use of equitransferent bridges: the second was to identify, and, if possible, eliminate other factors which restrict the accuracy of the method. (In this connection "accuracy" is taken to mean the degree to which the calculated diffusion potentials agree with the predictions of the Bjerrum method. It does not refer in any way to the experimental applicability of the method.)

4.3.3a Bjerrum's Treatment.

In his paper of 1911, (16) Bjerrum reasoned as follows:

Consider the junction between solutions of KCl and the hypothetical salt ka, of concentrations c_2 and c_1, respectively, where c_2 is much greater than c_1.

i.e. $$\mathrm{ka}\ (c_1)\ \Big|\ \mathrm{KCl}\ (c_2) \qquad \ldots\ldots\ldots\ldots 4.3(\mathrm{xi}).$$

The Henderson equation (see section 3.1(iii)) can be written as follows for this case:

$$E_j = -\left[\frac{u_K - v_{Cl}}{u_K + v_{Cl}} - \frac{c_1(u_k - v_a)}{c_2(u_K + v_{Cl})}\right]\frac{R\ T}{F\log e}\log\frac{c_2(u_K + v_{Cl})}{c_1(u_k + v_a)}$$

$$\ldots\ldots\ldots\ldots 4.3(\mathrm{xii})$$

if it is assumed that

$$c_1(\ u_k + v_a\ ) \gg c_2(\ u_K + v_{Cl}\ ) \ldots . 4.3(\mathrm{xiia}).$$

i.e.

$$E_j = -\left[\frac{u_K - v_{Cl}}{u_K + v_{Cl}} - \frac{c_1(u_k - v_a)}{c_2(u_K + v_{Cl})}\right]\cdot\eta \qquad \ldots . . 4.3(\mathrm{xiii})$$

where

$$\eta = -\frac{R\ T}{F\log e}\log\frac{c_2(u_K + v_{Cl})}{c_1(u_k + v_a)}$$

If, now, c_2 is halved,

(a) η is practically unaffected. The nett change in the logarithmic factor will be a gain of 0.3010, which is negligible, since c_2 is much greater than c_1.

(b) The first term within the bracket will be unaffected, but, as it is small (u_K is practically equal to u_{Cl}), the resulting error will not be appreciable.

(c) The second term within the bracket will be doubled.

Thus the nett effect is to double E_j.

In this reasoning there are three possible sources of error: -

(a) The error introduced by writing the Henderson equation in the form 4.3(xii)i.e. by the assumption 4.3(xiia).

(b) The error introduced by the term $\frac{u_K - v_{Cl}}{u_K + v_{Cl}}$ i.e. by the non-equitransference of the KCl solution.

(c) The error introduced by the fact that the variation of η with c_2 is not negligible.

4.3 3b. An Extended Treatment.

Let us first reject the highly questionable assumption 4.3(xiia), thereby eliminating error (a), above. The Henderson equation can now be written without approximation, for junction 4.3(xi), as follows:

$$E_j = -\left[\frac{c_2(u_K - v_{Cl})}{c_2(u_K+v_{Cl}) - c_1(u_k+v_a)} - \frac{c_1(u_k - v_a)}{c_2(u_K+v_{Cl}) - c_1(u_k+v_a)}\right]\eta \qquad \ldots\ldots\ldots\ldots 4.3(xiv)$$

For convenience we write this as

$$E_j = (\alpha + \beta)\eta \qquad \ldots\ldots\ldots\ldots 4.3(xv)$$

where $$\alpha = \frac{c_2(u_K - v_{Cl})}{c_2(u_K+v_{Cl}) - c_1(u_k+v_a)}$$

and $$\beta = \frac{c_1(u_k-v_a)}{c_2(u_K+v_{Cl}) - c_1(u_k+v_a)}$$

The values of E_j, α, β and η for the junctions of decinormal solutions of each of HCl, NaCl, and $LiNO_3$ with both 3.5N and 1.75N KCl solutions were calculated. Following the reasoning of Guggenheim and Schindler

(41), the values of u used were those for dilute solutions. The following limiting ion conductivities at 25°C, obtained from Table 1V 4 of "Electrochemical Data" (37) were used as mobilities:

$u_K = 73.52$ $\qquad$ $v_{NO_3} = 71.44$

$u_{Na} = 50.11$ $\qquad$ $v_{Cl} = 76.34$

$u_{Li} = 38.59$

$u_H = 349.8$

The results of these calculations are presented in a convenient form in Table 1.

Table 1.

(a) Solution	(b)	(c)	(d)	(e)	(f)
	Percentage Error				
				Total Error in E_{Bj}	
	η	$\alpha+\beta$	β	Non-Eq't	Eq't
0.1N HCl	26.4	10.2	18.7	62	41
0.1N NaCl	18.7	135	5.9	147	33
0.1N $LiNO_3$	18.1	152	4.1	159	30.

The figures in columns (b), (c), and (d) indicate the deviations in the behaviour of η, $(\alpha + \beta)$, and β, respectively, from the ideal pattern which Bjerrum assumed they would follow as c_2 is halved. Columns (e) and (f) show the error in E_{Bj}, the diffusion potential calculated by the Bjerrum method, when the bridges used are respectively, 3.5N KCl, and a3.5N equitransferent solution whose ionic mobilities are equal to the mean of the mobilities of the potassium and chloride ions. In this latter case, of course

$$\alpha = 0 \quad \text{and} \quad E_j = \beta\eta$$

The data in Table 1 prove that the accuracy of the extrapolation is greatly increased by the use of an equitransferent bridge solution. This improvement is less striking in the case of the HCl solution, as in this case the errors due to α and β tend to cancel, when the bridge solution is non-equitransferent. (see columns (c) and (d).) The residual errors are less than 42 per cent, and, as HCl is an extreme case, this can probably be regarded as an upper limit for decinormal solutions. As the junction potentials at 3.5N bridges are usually not greater than about 3 mV, it can be claimed that the extended extrapolation allows the liquid junction potential to be reduced to within 1 mV.

The error remaining is made up of the error in η and the error in β. The latter is due to the fact that c_1 is not negligible with respect to c_2, and is, therefore, reduced as c_1 decreases. It was found possible to eliminate completely the error due to η by multiplying the potential at the 1.75N bridge by $\frac{\eta_{3.5}}{\eta_{1.75}}$, before applying the extrapolation. (The subscripts denote the concentration of the bridge solution for which the η has been calculated.) This factor was found to vary regularly with $(u_k + u_a)$, as would be expected from the form of the expression for η. On the face if it, therefore, this appears a very effective, and very simple method of reducing the residual error to the region of five per cent. For all practical purposes, however, it is valueless. The extrapolation method is usually applied to junction potentials which are the sum of two separate potentials arising at the ends of the bridge solution i.e. to full bridges, and in this case the factor

$\frac{\eta_{3.5}}{\eta_{1.75}}$ cannot be evaluated from mobility data.

The results of the above analysis must be treated with circumspection. In the first place, little reliance can be placed on Henderson equation calculations, and so it is not at all evident to what extent the figures shown actually apply. In the second place, it must be remembered that for the sake of simplicity, half bridges have been considered.

Nevertheless, while no reliance should be placed on the quantitative aspects of the results shown, the qualitative indications are important:

(a) The use of equitransferent solutions results in a considerable increase in the accuracy of the method.

(b) The other factors governing the accuracy of the Bjerrum method are the concentration and nature of the adjacent solutions.

(c) Further improvements in the method must be evolved empirically.

4.4. PREPARATION AND STANDARDISATION OF MATERIALS.

4.4 1. NITROGEN.

Commercial dry nitrogen was fully deoxegenated by passing it over reduced copper in an electrically heated silica tube. To free it from carbon dioxide and acid impurities, alkaline impurities, sulphides, and water vapour, respectively, it was passed successively through tubes of soda lime, solid metaphosphoric acid solid cupric chloride, and self-indicating silica gel. The resulting pure,dry gas was used in the drying of potassium chloride and the preparation of anaerobic mercury. When used in the deoxygenation of solutions the nitrogen was passed, in addition, through a presaturator containing conductance water at 24°C, and then through one containing the appropriate solution at the correct temperature.

4.4 2. CONDUCTANCE WATER.

Conductance water was used in cleaning glassware, in preparing all solutions, and in the preparation of all chemicals. The water was obtained from an automatic recycling still developed in this laboratory (42), and had a conductance of less than 100 nm per cm.

4.4 3. MERCURY.

Commercial mercury was washed several times by swirling with carbon tetrachloride, and then subjected to aspiration of air, under dilute nitric acid for three days, and under several changes of conductance water for short periods. After drying it was distilled in an all-glass still, under reduced pressure of air (delivered under the surface by means of a capillary), large head and tail fractions being rejected. Immediately before use in the preparation of calomel electrodes, batches were redistilled in a vacuum still swept out with pure, dry nitrogen before evacuation (34).

4.4 4. POTASSIUM CHLORIDE.

(a) Merk G.R. potassium chloride was recrystallised three times from conductance water. During the first of these the hot solution was filtered through sintered glass to eliminate solid impurities. The subsequent recrystallisations were carried out entirely in platinum ware, and the mother liquor removed by decantation. The product was dried at 115° for 24 hours, at 250°C for three days, and stored over silica gel. It was used for preparing the electrolyte for calomel electrodes.

(b) Extreme purity was not necessary in the potassium chloride used for making bridge solutions. Thus, Merk G.R. reagent was dried at 250°C for three weeks, and stored over silica gel, in vaccuo.

4.4 5. POTASSIUM NITRATE.

Merk G.R. potassium nitrate was dried at 115°C for three days, and stored in vaccuo over silica gel.

4.4 6. MERCUROUS NITRATE - $Hg_2(NO_3)_2.2H_2O$.

Difficulty was experienced in finding in the literature an adequate method for the preparation of mercurous nitrate in a pure form. It was felt to be essential that strict precautions be taken to ensure that the product was quite free from the many basic forms and other hydrates which can be produced by the action of nitric acid on mercury. A satisfactory method was finally evolved on the basis of the phase diagram for the system $Hg_2O-H_2O-N_2O5$ drawn up by Denham and Fife (43).

The preparation was carried out in the dark to prevent the formation of mercuric salts. 205 ml of 5N reagent grade nitric acid was allowed to react in the cold with 106 gm pure mercury (see section 4.4 3). After stirring for 22 hours the first crystals appeared. These were allowed to age for 24 hours, filtered off through sintered glass, and recrystallised by slow evaporation from a minimum of 0.6N HNO_3. The product was filtered off, and dried and stored in the dark, in vaccuo over silica gel.

4.4 7. MERCUROUS CHLORIDE -Hg_2Cl_2.

Calomel was prepared according to the precipitation method described by Hills and Ives (34), using a 2N hydrochloric acid solution and a 0.05N solution of mercurous nitrate. It was dried and stored in the dark over phosphorous pentoxide.

4.4 8. CONSTANT-BOILING-POINT HYDROCHLORIC ACID.

Constant-boiling-point hydrochloric acid was prepared by the method of Titus and Smith (44). Reagent grade acid was diluted with conductance water to a specific gravity of 1.10. The resulting solution was allowed to distil in an all-glass still at a rate of about 3ml per minute, until 70 per cent had passed over. The next 10 to 15 per cent was collected, and stored in a glass stoppered Pyrex flask. The concentration of the solution was obtained from the equation

$$\text{Per cent HCl} = 20.245 + (750 - P)0.0024$$

where P is the barometric pressure under which the constant-boiling fraction was collected.

Because hydrochloric acid solutions stored in Pyrex change in concentration due to ion-exchange with the glass, these solutions were freshly prepared every two weeks. The work of Gledhill and Taylor (45) of this department indicates that the change in concentration during this period will be well within the experimental error of the investigation.

4.4 9. CLEANING OF GLASSWARE.

Before use all glassware was thoroughly cleaned by treatment successively with alchohol-nitric acid mixture, and aqua regia, followed by steaming and rinsing with conductance water.

4.4.10. PREPARATION OF SOLUTIONS.

The balances and weights used were carefully standardised and intercompared. Correction was made for the buoyancy of the air in the case of the 0.10000m KCl and 0.09917m HCl solutions.

4.4 10a. 0.09917m HCl Solution.

Using a weight burette of the type described by A.Faure (46), approximately 16.5gm constant-boiling-point hydrochloric acid was weighed into one-litre glass-stoppered flask. To this was added a calculated mass of conductance water.

In his work on dilute KCl solutions, Faure found that appreciable errors were caused by evaporation of the weighed solution as it was allowed to run from the weight burette, and that he could only eliminate these by carrying out the transfer in a "wet-box." Trial runs with the acid showed that the loss in weight was of the order of 3mg per 16.5gms, which corresponds to an error of about 0.015 per cent in the final solution. As this is less than the experimental error of the investigation, it was not deemed necessary to take precautions to prevent it

4.4 10b. 0.10000m Potassium Chloride.

Potassium chloride, purified and dried as above (see section 4.4 4) still contains traces of mixture which Addink (47) showed can be completely removed by heating to 550°C in an atmosphere of dry nitrogen. It was found that the various batches of KCl recrystallised during the course of the investigation contained from 0.015 to 0.018 per cent water. This agrees with the figure of 0.02 per cent recorded by Addink, but differs widely from Malan's 0.25 per cent (49).

The following procedure was used in making up the solutions: A platinum crucible containing about 7.5 gm of the potassium chloride was placed in a large silica test tube with a loose-fitting Pyrex cap. This was maintained at 550 to 600°C for three-quarters of an hour in a vertical furnace, and the air displaced by a slow current of pure, dry, nitrogen. The potassium chloride was allowed to cool in vaccuo, and the solution made up by weighing.

4.4 10c. Bridge Solutions.

The salt bridges used were mixtures of potassium chloride and potassium nitrate of total ional concentrations 3.5 and 1.75. The salts used were purified as described in sections 4.4 4b and 4.4 5. As these solutions were used in large quantities, and as extreme accuracy was not required, they were made by volume in a two-litre standard flask, the same flask being used in preparing all the solutions.

4.4 11. CALOMEL CELLS.

Calomel half-cells were made by the general method of Hills and Ives (34). The electrode vessels (Figure 2) were cleaned, steamed for three hours, and dried. At a temperature of 60°C, they were filled with a two per cent solution of Dow-Corning No. 200 Fluid in redistilled carbon tetrachloride. They were then emptied, dried in air, and cured at 300°C for 45 minutes. This differs from the Hills and Ives' procedure of baking at 165°C for two hours, but is in accord with the recommendations of the makers of the fluid (48). It was found to produce better siliconing, and to result in more stable electrode potentials. After cooling the electrode vessels were rinsed ten times with carbon tetrachloride, dried, and then five times with conductance water, and again dried.

The vessels were swept out with pure, dry, nitrogen, and a small quantity of freshly distilled, anaerobic mercury added. In a glass-stoppered bottle, a few ml of the mercury were shaken vigorously with a little pure, dry calomel. Small amounts of the resulting grey skin were added to the pool of mercury in the vessel, until the entire exposed surface was covered with the spreading film. It was noted that, when only enough skin was added to form a surface of islands separated by clear mercury, the resulting electrode gave unstable potentials.

The vessel was again swept out with nitrogen, and the electrolyte which had been fully deoxygenated by passing nitrogen through, carefully run in. Finally, nitrogen was bubbled through the cell for eight to twelve hours to bring it to equilibrium.

Calomel electrodes prepared in this way were tested by measuring the resultant potentials, when

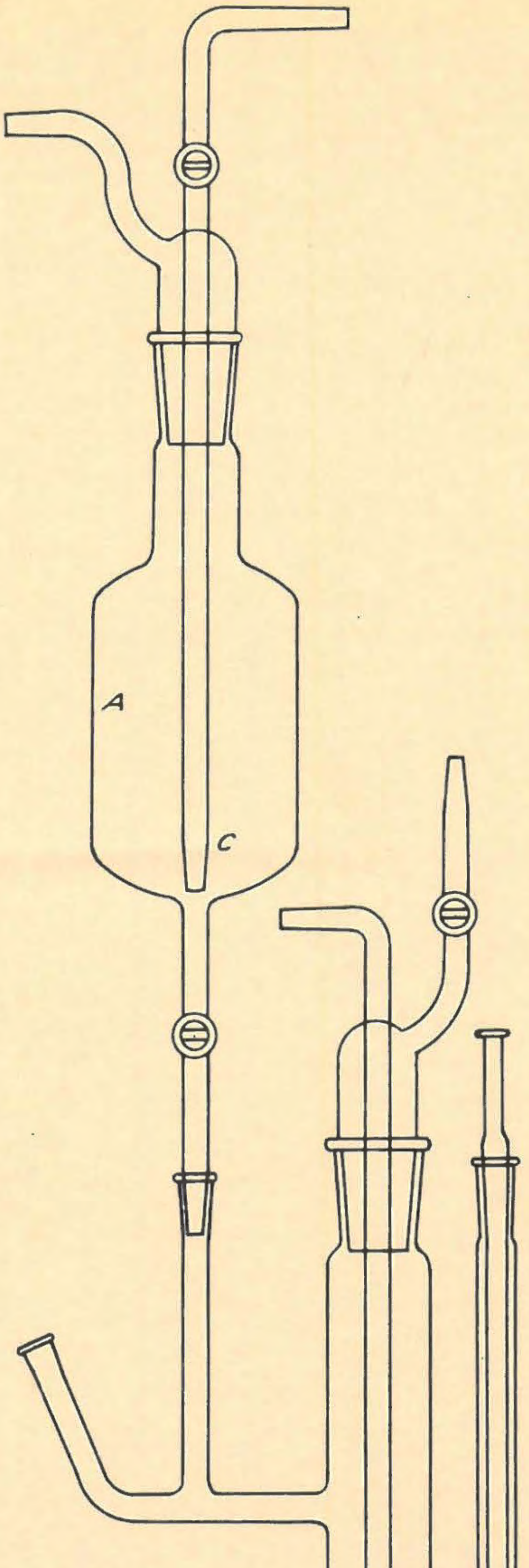


FIG. 2. THE ELECTRODE ASSEMBLY.

two similar cells were opposed, and were found to be stable to at least ± 9 microvolts, and reproducible to within 50 microvolts. They were unaffected by slight shaking, but sometimes suffered small changes in potential when subjected to more vigorous treatment, such as moving from place to place. Their performance is discussed in greater detail in section 4.6 2b.

4.5. DESCRIPTION AND STANDARDISATION OF APPARATUS.

4.5 1. THE CELL.

Experimental work on the cell 4.3(vii) was carried out in an all-glass apparatus designed for the purpose. This consisted of a central "junction assembly" and two "electrode assemblies."

4.5 1a. The Electrode Assembly.

This is illustrated in Figure 2, and is essentially of the same design as the calomel electrode vessel used by Hills and Ives (34). Contact is made with the mercury pool of the electrode by means of a long platinum wire D, as shown in the figure. The end of the nitrogen-bubbling tube, N, was turned upwards to eliminate the effects of bubbling-pressure disturbance on the calomel layer. A is a reservoir containing the electrode solution, and fitted with a nitrogen delivery tube, C.

4.5 1b. The Junction Assembly.

The device used in forming liquid junctions was designed to satisfy two essential conditions: firstly, that it be capable of yielding potentials of the highest accuracy, and, secondly, that results obtained from it, be directly applicable to both high-precision and normal laboratory work involving diffusion potentials.

The second of these requirements was shown to be a matter of cell design by Guggenheim (6). (See section 3.3). His work and that of Ferguson, van Lente, and Hitchins (23) shows, further, that the junction most suitable for this investigation is the free diffusion type. The only other of comparable performance is the flowing junction: The use of the latter is precluded by the fact that in the case of heterionic solutions the effects of bubbling rate and other variable are too unpredictable to allow of free intercomparison of potentials.

For a free diffusion junction to be stable and reproducible, cylindrical symmetry at the boundary is essential, and is only realised when the junction is formed in a tube of regular bore at a point some distance from its extremities. This was effected in this investigation by the use of three-way taps.

In order that a junction formed at one end of the plug of a tap should be quite cylindrically symmetrical, it is necessary that there should be on either side of this point identical tubes of perfectly regular bore. Neither the T-tap used by Ferguson and his co-workers (23) nor the 120°- tap of Owen (17) fully satisfies this condition. The tap designed and used in this work is shown in Figure 3, and was made in this department. It enables ON to be connected either to ML by n_1m_1 or to PQ by n_2p_1. To eliminate the need for a lubricant and to reduce the difficuties of making the bore of a_1m_1 identical with that of ON and ML, it was originally intended that the plug should be of teflon. When after considerable difficulty and

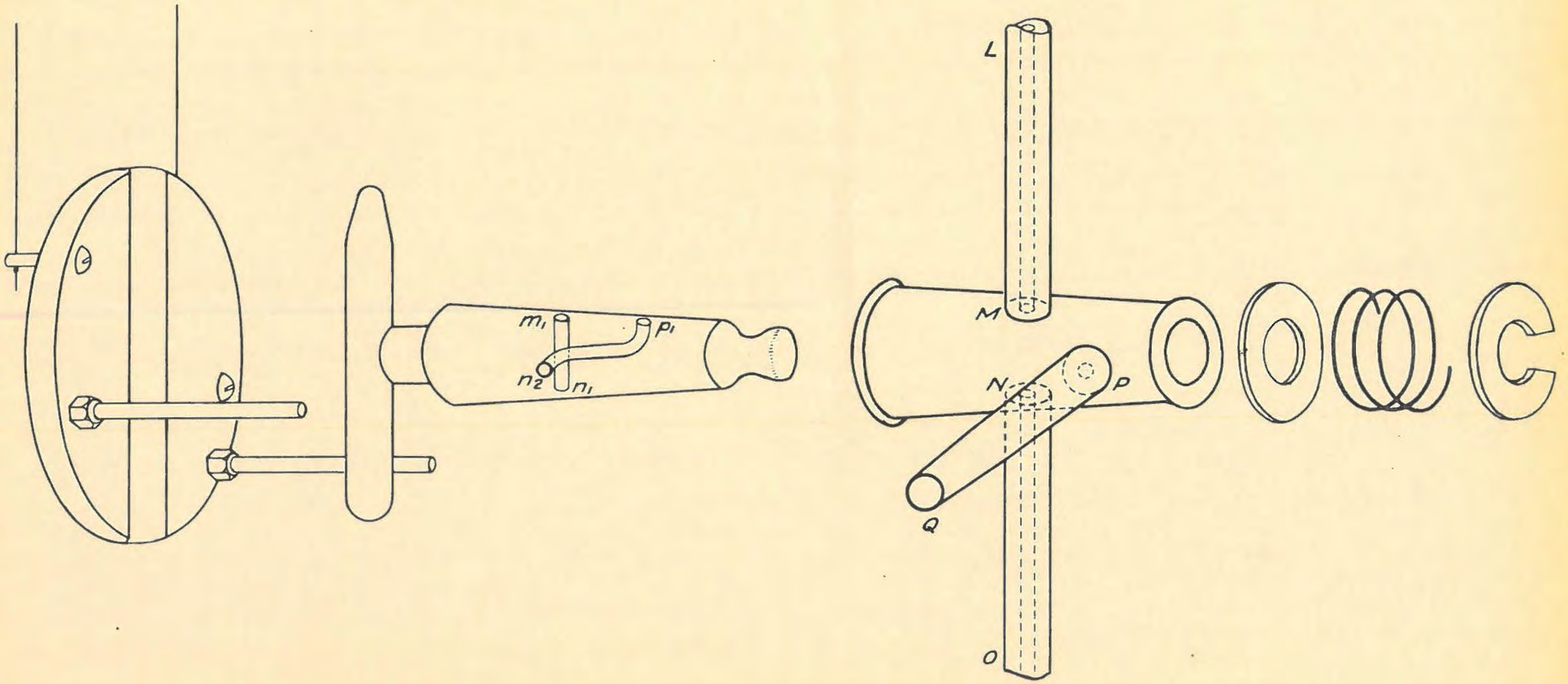


FIG. 3. JUNCTION - FORMING TAP.

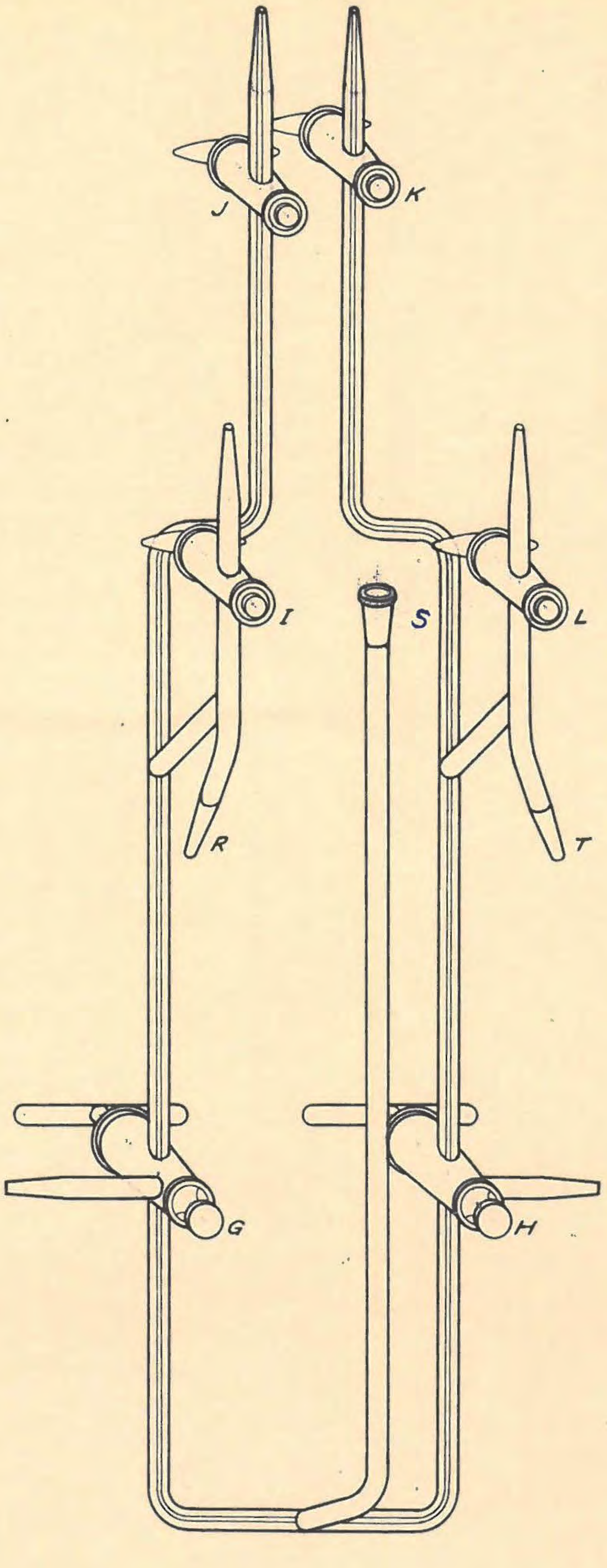


FIG. 4. THE JUNCTION ASSEMBLY.

delay a short length of teflon rod had been procured, it was found to be extremely inhomogeneous. As this precluded the precise machining necessary to prevent leaking, there was no alternative but to use glass. The condition that n_1m_1, NO, and ML form a straight tube of uniform bore makes the construction of an all-glass tap a problem of great technical difficulty, since it necessitates,

(i) that there be no constriction at the seals n_1 and m_1;

(ii) that n_1m_1 be so placed that after grinding and greasing N and n_1, and M and m_1 can simultaneously coincide.

Thanks to the skill of the University instrument maker, Mr. F. van der Water, these difficulties were overcome. The pair of taps used had no detectable irregularities at the seals, and satisfied the second requirement almost completely. The bore of these taps was 3 mm, and the plug was firmly held in the barrel by means of spring-loaded washers. (see Figure 3).

To the handle of each tap was attached a perspex disc from which projected two short lengths of brass rod. These could be adjusted so that they came into contact with ML or PQ, respectively, when N was joined to M or P, and ensured that the tap was operated with a precision commensurate with the accuracy of its construction. For convenience the taps were manipulated by means of knobs fixed to the frame above the water-line, and connected to them by means of nylon lines.

The complete junction assembly is shown in Figure 4. JGHK which includes the vertically mounted junction taps G and H, is made of 3 mm internal diameter thick-walled tubing. A reservoir identical with those forming part of the electrode units fits

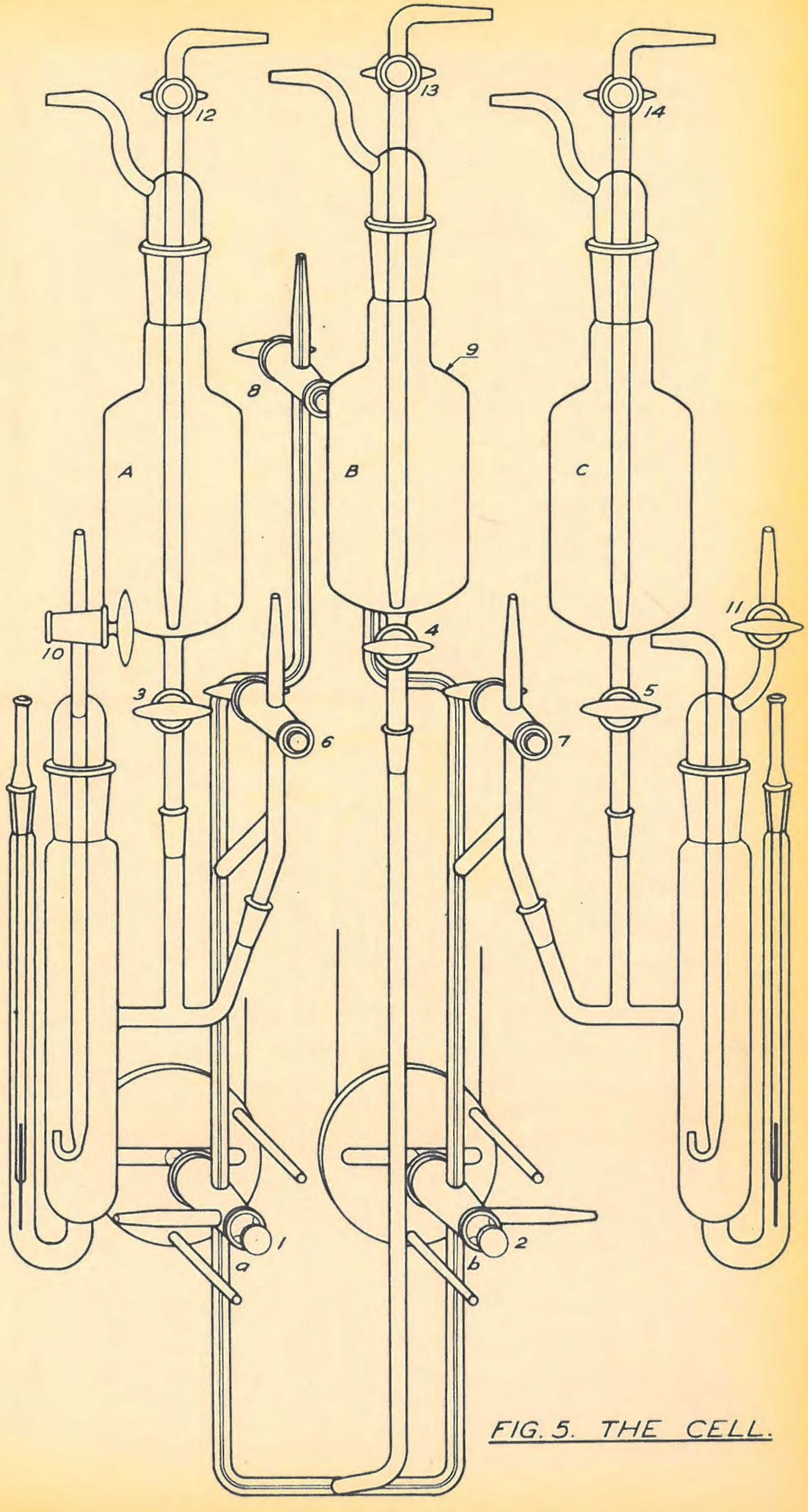


FIG. 5. THE CELL.

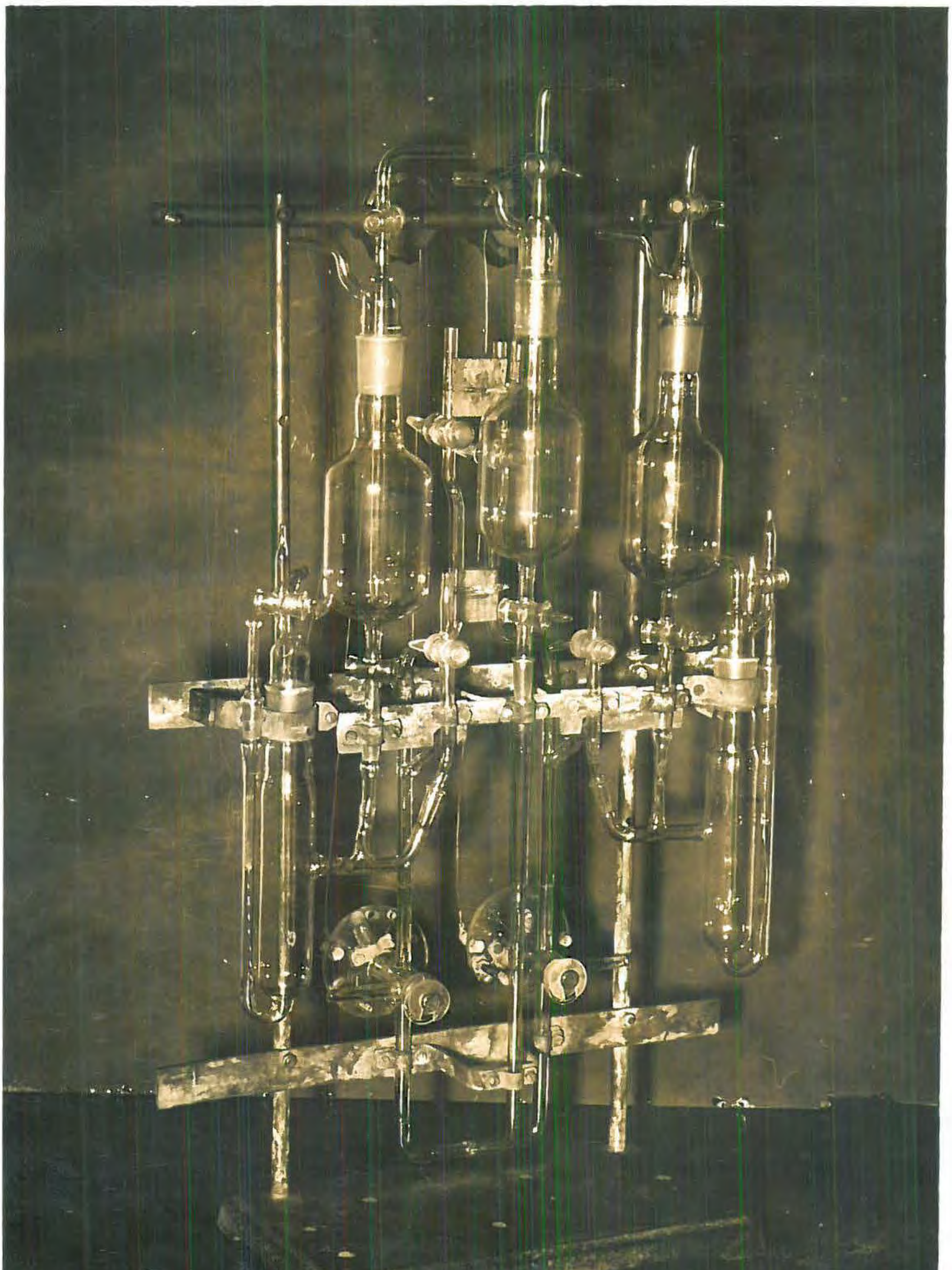


PLATE 1.

into the B10 standard joint, S, and the electrode assemblies are attached at the B7 joints R and T. The function of taps J,K,I, and L is explained in Section 4.6.1.

In Figure 5 and Plate 1 is illustrated the complete cell. The apparatus is rigidly mounted on a brass frame designed so that the electrode vessels are readily removable . When used in the water thermostat (see section 4.5 3) the water level was maintained at a height just below the B10 standard joints holding reservoirs A and C.

4.5 2. POTENTIOMETRIC APPARATUS.

A Tinsley Vernier potentiometer was used to measure cell potentials. A previous worker (49) had standardised two of the three coils of the instrument. This standardisation was checked and found to be satisfactory , and extended to embrace the remaining coil reading the fifth and sixth decimal places of a volt.

The e.m.f.s were expressed in absolute volts with the aid of an Eppley Standard Cadmium Cell. This cell was compared with a similar Eppley cell, recently calibrated to an accuracy of ± 0.02 mV at 24.0°C at the S.A. National Physical Laboratory, and was left undisturbed throughout the course of the work.

A Kipp A75 Light Spot Galvanometer was used as a null-point detector. It had a current sensitivity of 0.3 nano-amps per millimetre scale deflection, and was found to be capable of discriminating one microvolt differences of potential across the cell.

To prevent electrostatic leakage all components of the circuit were mounted on an equipotential surface (50), while shielded leads were used to eliminate errors due to A.C. pick-up.

Reversing switches were employed to investigate the presence of thermal e.m.f s, but at no time were such potentials found to exceed one microvolt.

4.5 3. TEMPERATURE CONTROL.

All apparatus used in making the potential measurements was housed in a constant temperature room maintained at 24.0 ± 0.1°C. This room was constructed in 1940 by Thomas and Gledhill (51) with a mercury-paraffin thermoregulator. During the course of the present investigation this device was replaced by an electronic relay and resistance thermometer. This system will be described elsewhere by Mr. H.S. Govinden (52) who was responsible for the major portion of its design and construction.

The liquid junction cell was immersed in the inner tank of a double bath water thermostat, similar to that used by Gledhill (51). In this work, however, mechanical stirring was not permissible, since the attendant vibrations disturbed the liquid junctions, and prevented their reaching a steady state. It was found that adequate agitation was afforded by compressed air delivered through half a dozen jets at the bottom of the tank. Using a toluene thermoregulator of the type described by Gledhill (51), the temperature of the bath was maintained constant at 25.0 ± 0.01°C, and uniform to within 0.005°C.

4.5 4 THERMOMETERS.

The temperature of the thermostat was determined by means of a solid-stem , mercury-in-glass thermometer calibrated at the British National Physical Laboratory to an accuracy of ± 0.002°C. Fluctuations in temperature were measured using a 5-degree Beckmann thermometer with 0.01°C graduations.

4.6. READINGS AND RESULTS.

4.6 1. TECHNIQUES USED IN TAKING READINGS.

4.6 1a. The Formation of Junctions.

25ml of dilute HCl solution was run from A to waste through tap 2, and 25 ml dilute KCl through tap 1 (see figure 5 for nomenclature used in describing the cell). Any bubbles in the system were allowed to escape through taps 6 and 7. Bridge solution was now run through both 1 and 2, until a total of, approximately 50ml had passed to waste. The cell was allowed to stand for at least an hour to enable the solutions to reach thermal equilibrium at 25°C.

For the boundaries at a and b to be as sharp as possible initially, it is necessary that there should be no hydrostatic pressure difference across them at the moment of junction. In an attempt to meet this requirement, the following procedure was used. All the taps, excluding 12, 13, and 14, and including those in the nitrogen supply lines to the two electrode vessels, were closed. Tap 4 was then opened for a few seconds to allow the bridge solution contained in the section ab to come to equilibrium with the pressure of the atmosphere. Taps 8 and 9 (behind reservoir B in Figure 5) were opened and the levels of both of the dilute solutions in their capillaries adjusted to a height calculated to balance the weight of the denser solution in B. Taps 8 and 9 were again closed, and 1 and 2 turned simultaneously to join the bridge solution with the two electrode solutions at a and b respectively.

In preliminary experiments with highly coloured potassium permanganate solutions no visible disturbance of the boundary was observed at the moment of junction, when the boundary was made in this way. Other tests proved that 50 ml of bridge solution was sufficient to rinse from ab any traces of the dilute solutions

4.6 1b. Procedure in Taking Readings.

Junctions were prepared as described in the preceeding section, and the potential across the cell read at intervals, until it was constant for more than four and one-half hours (see section 4.6 2a.) This was repeated with each bridge solution, until enough concordant results had been obtained. At the end of each run nitrogen was allowed to bubble through the calomel half cells for some hours, before a fresh junction was established.

In introducing a new bridge solution, reservoir B was removed from the cell and rinsed and filled with the new solution. Then section ab of the junction assembly was drained, rinsed several times, and filled with the new solution.

The dilute solutions were deoxygenated in their respective reservoirs for at least twelve hours before being introduced into the cell.

4.6 1c. The "Reference Junction Potential."

The potentials at the different bridges used can only be intercompared, if it is certain that the nett electrode potential is the same in each case. This was ensured by means of the following device:

The potential of the cell

$$\mathrm{Hg{-}Hg_2Cl_2} \;\Big|\; \begin{matrix}\mathrm{HCl}\\ (0.09917\mathrm{m})\end{matrix} \;\Big|\; \mathrm{KCl}\ (3{,}5\mathrm{N}) \;\Big|\; \begin{matrix}\mathrm{KCl}\\ (0.10000)\end{matrix} \;\Big|\; \mathrm{Hg_2Cl_2{-}Hg} \qquad \ldots\ldots\ldots\ldots 4.6\ (1)$$

was determined with a great deal of care. Several sets of calomel half-cells were used, and both the electrode and bridge solutions changed several times during the course of the long series of runs. The resulting potential was used as a standard for the investigation. Whenever new calomel cells were prepared, and at intervals throughout their working life, their potentials were checked by carrying out runs with a 3.5N KCl bridge solution, and comparing the result with the "reference junction potential."

4.6 1d. Calomel Cells.

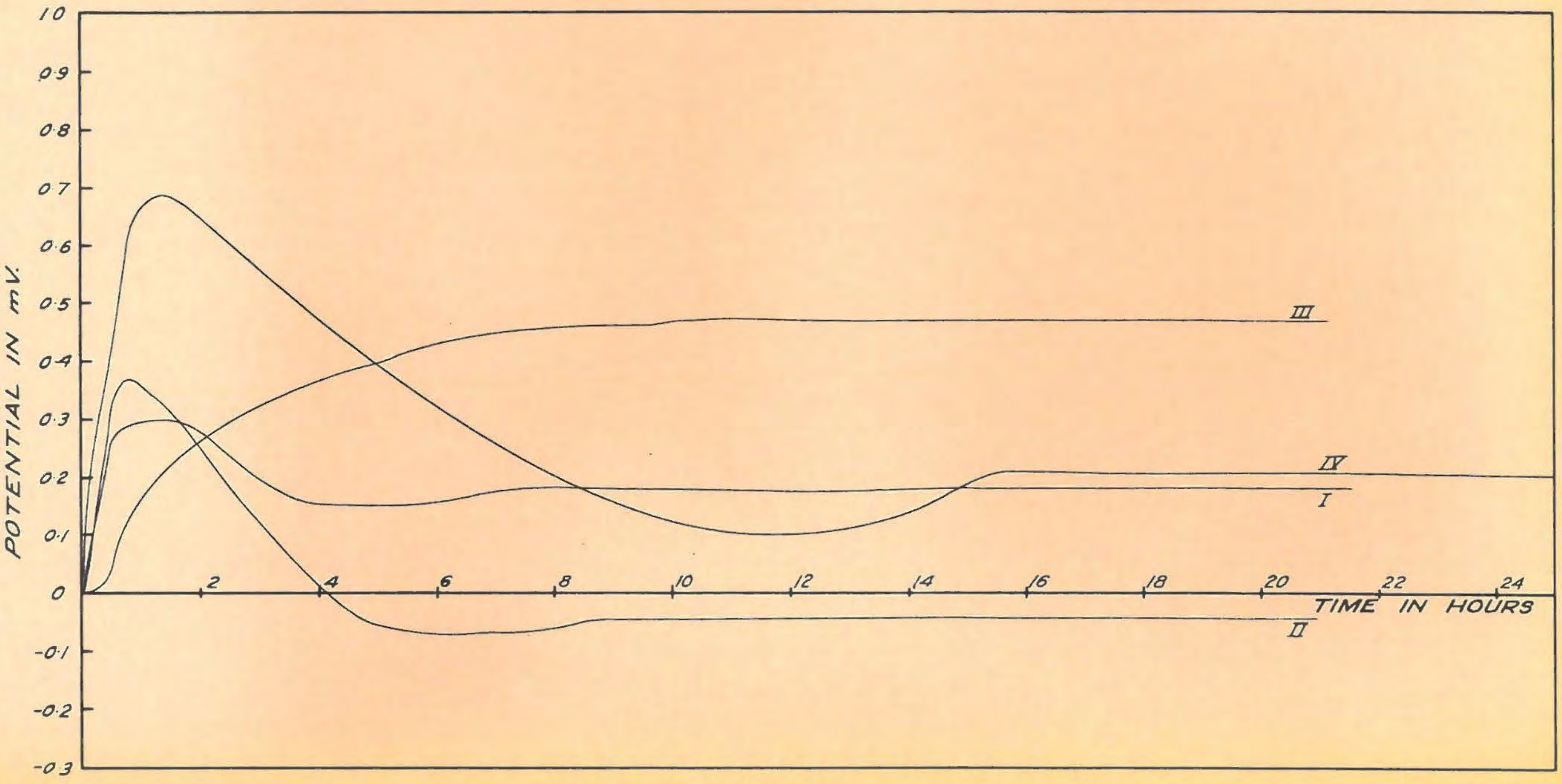
It was found (see section 4.4 11) that changes occurred in the potentials of calomel half-cells, when they were subjected to violent shaking. It was accordingly arranged that the cells should never be moved once they had been prepared. Thus, the apparatus was placed in the water thermostat and securely clamped, before electrolyte was added to the mercury and calomel film of the half-cells. All subsequent manipulation was performed with the cell in this position, and with a minimum of agitation. If it was necessary to move the apparatus from the thermostat fresh calomel cells were made.

Errors occasionally arose in the electrode potentials due to contamination of their electrolytes, or to changes in their concentration caused by inadequate presaturation of the nitrogen. When this occurred cells were drained of electrolyte, rinsed several times, and filled with fresh solution. The resulting electrodes were found to be no less satisfactory than the original.

4.6 le. Leaks.

As it was found that leaks at any of the standard joints or taps of the cell disturbed the liquid junctions, and caused the potentials to drift, care was taken to detect and combat them. When the cell was assembled before preparation of the electrodes, all taps and joints were carefully greased with Fischer "Celloseal", and then tested by applying nitrogen pressure to the cell. Once it had been placed in its thermostat, leaks were revealed by a fall in solution level in the capillaries below taps 8 and 9, when the apparatus was allowed to stand with all the other taps closed. In addition, the depth of fall gave an indication of the location of the fault.

FIG. 6. VARIATION OF MEASURED POTENTIALS WITH TIME. TYPICAL CASES.



4.6 2. THE CHARACTERISTICS OF THE OBSERVED POTENTIALS.

4.6 2a. Stability.

The potentials arising at the ends of the salt bridges, and measured across the terminals of the cell were not initially constant, and underwent considerable fluctuation before reaching a period of stability. The variation with time of the potentials read is shown, for typical cases, in Figure 6. For purposes of comparison these were transposed into the same potential region by taking as zero in each case the potential read immediately after the junction had been made.

The final, stable potentials were constant to within 10 microvolts in the vast majority of cases, although runs were recorded in which the variations were as high as 15 and as low as 1 microvolt. Usually the potential was read at intervals, until it had been constant for $4\frac{1}{2}$ to 12 hours, but even when this was extended to five days, no deterioration of stability was observed. Both the degree and the duration of stability were found to be independent of the concentration and composition of the bridge solution. Even in the case of the junction

$$\mathrm{HCl}\ (0.1N) \,\Big|\, \mathrm{KCl}\ (0.1N) \ldots\ldots\ldots 4.6(ii)$$

there was no deviation in these characteristics, as far as could be judged from the few runs performed with it. It was found that the slightest mechanical disturbance of the cell, such as the vibrations of a motor-driven stirrer, destroyed the stability of the potentials.

The behaviour of the potentials before they reached stability differed from run to run. Nevertheless, a study of more than 200 runs carried out during the investigation revealed certain patterns which it is important to record here.

(i) The potential was at its most unstable immediately after the formation of the junction, and gradually steadied with time.

(ii) The potential-time curves were in many cases very similar in form. The shapes of curve most commonly occurring with 3.5N salt bridges is illustrated by graphs I and II of Figure 6. In other cases, the shape of the curve was substantially different, as in graph III. It was not found possible to correlate the shape of the curve with either the accuracy of the final potential, or with any of its stability characteristics, such as the degree of stability or the time taken to attain it.

(iii) Regions of "false" or transient stability occurred in a large number of runs. It was found that towards the end of the unstable period, the potential would become constant to within 10 microvolts for as long as 2½ hours, and would then begin to vary again. All of the curves in Figure 6 show this behaviour. Truly constant potentials were distinguished by the fact that their stability did not deteriorate with time. It was, therefore, possible to guard against being misled by demanding that a potential remain constant for at least 4½ hours before considering it to be stable.

(iv) The magnitude of the greatest deviation from the stable potential in any run depended on the concentration of the bridge solution. The mean of the maximum deviations observed was 0.29 mV with 3.5N, and 0.40 mV with 1.75N bridges. Insufficient readings were taken with 4.12N bridges and with the junction 4.6 (i) to permit of any comparison.

(v) The time taken for potentials to reach stability also depended on the concentration of the bridge solution. Stability was reached, on the average after $8\frac{1}{2}$ hours with 3.5N bridges, and after $12\frac{1}{2}$ hours with 1.75N bridges.

The behaviour described above is in every way consistent with the theory that the boundaries formed are not initially perfectly sharp, as free diffusion junctions should ideally be, and that certain deviations from sharpness do exist. As unhindered diffusion is allowed is proceed, the transition layer gradually approaches a steady state, and its changing structure is reflected in the variations of potential. Therefore, once the potential reaches stability it does not change unless the steady state of the boundary is in some way disturbed. The initial deviations from sharpness are probably due to mechanical mixing brought about by the motions of the junction-forming taps or by small differences in the hydrostatic pressure across the junction. It is, thus to be expected that the approach to stability should be more rapid when 3.5N than when 1.75N bridges are involved, for the resistance to initial disturbances will be greater, the greater the difference in density of the solutions comprising the junction. It is also to be expected that the shape of the potential-time curve will not be reproducible, for it is not possible in practice to control minutely enough the factors governing the amount of mixing which takes place when the junctions are made. There is no reason, however, why the reproducibility of the final potential should be affected, as this will depend only on the eventual steady state of the system.

4.6 2b. Reproducibility.

An estimate of the precision of the readings was obtained by calculating the standard deviation, and the 95 per cent confidence limits of the replicate determinations with each bridge solution.

The measurements were extremely prone to determinate errors, owing to the sensitivity of the potentials towards slight changes in the concentration of the calomel electrode solutions, which could be brought about by traces of oxygen, or by inadequate presaturation of the nitrogen bubbled through them. Usually these mistakes were revealed during the course of the readings by irregularities of behaviour, and were immediately eliminated. To deal with those that escaped detection, the practice was adopted of rejecting any reading which differed from the average of the set of replicate determinations by more than half the mean deviation from the mean. It was found that in only three of the fourteen sets of readings taken were readings eliminated in this way.

The standard deviations of the potentials at the various bridges used were in the main in the region of 30 microvolts, the greatest being 36 microvolts. The corresponding limits of 95 per cent confidence were of the order of ± 40 microvolts, the largest being ± 44 microvolts. No significant difference in the reproducibility of the potentials at 3.5 and 1.75N bridges could be detected. It can, therefore, safely be claimed that the final potentials were reproducible to within 0.1 mV.

A large proportion of the uncertainty of these potentials undoubtedly arose from instability and irreproducibility in the potentials of the calomel half-cells. These were investigated by opposing two identical calomel electrodes, and measuring the departures of the resultant potentials from zero. It was found that, when allowed to come to equilibrium under the most favourable conditions, the cells yielded potentials stable to less than ± 9 microvolts mean deviation for several days. When subjected to the rather strenuous conditions under which the final potentials were measured, viz, long periods in which there was no deoxygenation or stirring by nitrogen, a fair degree of shaking, and occasional changes of electrolyte, a reproducibility of ± 0.025 mV was obtained.

It was felt that a precision of ±0.025 mV in the electrode potentials was quite adequate for this work, and that, in view of the trying conditions under which it was realised, it compared favourably with the Hills and Ives (34) value of ± 0.010 mV.

4.6 2c. Accuracy.

The following three factors govern the accuracy of the potentials measured:

(i) The accuracy of the electrode potentials.

(ii) The reproducibility of the electrode potentials.

(iii) The reproducibility of the measured potentials.

By the first of these three factors is meant, the degree to which the condition that the two calomel electrodes of cell 4.3(vii) have equal potential, is satisfied. It embraces two distinct sources of error. The first of these lies in the assumption that the difference in the two electrode potentials will be zero, when the ratio of the mean ionic activity of their electrolytes is unity. (See section 4.3 2b). It is not possible to obtain any estimate of the size of the resulting error, for it is bound up with the unrealness of the concept of single ion activities, and single electrode potentials. It should be remembered, however, that, just as this unsatisfactory state of affairs is unavoidable in this work, it is similarly inherent in all measurements to which the findings of this work may be applied. It is, therefore, felt that it should be regarded not as an error, but as a condition under which the determinations were carried out.

The second source of inaccuracy in the electrode potentials is the uncertainty in the calculation from activity coefficient data of the molalities of the electrode solutions. This has been estimated at, 0.05 mV. (See section 4.3 2c.)

Factors (ii) and (iii) were dealt with in detail above, where it was concluded that they introduced uncertainties of ± 0.025 and ±0.050 mV respectively.

An accuracy of ± 0.05 mV can, therefore, be claimed for the potentials measured across cell 4.3(vii).

4.6 2d. Discussion.

It is of interest to compare the performance detailed above with that recorded by Ferguson, van Lente and Hitchins (22) in what is probably the most accurate investigation in the literature. The significant characteristics of the two investigations are summarised in Table 2.

Table 2.

Characteristic.	A. Ferguson et al	B. Present work:
Stability of electrode potentials.	± 0.02 mV	± 0.009 mV
Reproducibility of electrode potentials.	"Fairly reproducible"	± 0.025 mV
Stability of readings at their constant value	± 0.04 mV	within 0.01 mV
Reproducibility of readings	within 0.1 mV	within 0.1 . mV
Time taken for readings to reach stability.	6 to 26 hours	8½ hours.

Since Ferguson's determinations involved saturated KCl solutions, the data in column B refers, where distinction is necessary, to the measurements in which 3.5N bridges were used. The estimate given in column A of the time taken for readings to reach stability, is based on the graphs appearing in Ferguson's paper, as he did not specifically refer to this characteristic in his discussion.

The comparison shows that, while the diffusion potentials determined in the present investigation are by far the more stable, and appear to reach stability after a shorter time, there is little to choose between the two investigations as far as reproducibility is concerned.

The difference in stability is too great to be accounted for by the difference in the constancy of the two types of calomel electrodes used. It is possibly caused by the fact that the initial mechanical disturbances of the boundary are greater at the 9 mm junction-forming taps used by Ferguson and his co-workers than at the 3 mm ones used here. The fact that the reproducibility of the potentials at these two sizes of taps is approximately the same is in direct contradiction with the theories of Taylor (7) and Cummings and Gilchrist (19), which predicted that free diffusion liquid junction potentials in tubes of small bore would be less reproducible than those in tubes of larger bore.

From the above comparison one concludes, therefore, that 3 mm taps are on the whole more satisfactory than 9 mm taps as junction-forming devices. Whether further improvements would result from continued reduction of the bore cannot be inferred without more experimental evidence.

4.6 3. RESULTS.

In the tables and graphs below are summarised the potentials determined in the course of this investigation. The sign convention used throughout is that of Lewis and Randall (53), viz that the potential is positive if the right-hand electrode (or solution) of the cell (or junction) as written, is positive.

4.6 3a. Measured Potentials.

Table 3 shows the potentials measured as described in the preceding sections, as well as data indicating the precision of the individual sets of readings.

Table 3.

Potentials measured across cell 4.3(vii), at 25°C.

Moles KCl per cent solute.	Mean cell potential (mV).	No. of readings (mV.)	Mean deviation (mV).	Standard deviation (mV).	Limits of 95% confidence. (mV)
		(i) J = 4.12.			
100	1.67(1)	5	0.02(9)	0.03(6)	0.04(4)
		(ii) J = 3.5			
100	2.80(8)	19	0.02(5)	0.02(9)	0.01(4)
75	3.42(8)	5	0.01(7)	0.02(1)	0.02(6)
65	3.75(6)	5	0.01(4)	0.02(1)	0.02(6)
57.15	3.94(1)	6	0.03(1)	0.03(5)	0.03(7)
50	4.18(0)	5	0.01(0)	0.01(7)	0.02(1)
42.85	4.46(3)	5	0.01(9)	0.03(0)	0.03(8)
25	5.12(7)	5	0.02(4)	0.03(1)	0.03(9)
		(iii) J = 1.75.			
100	6.84(0)	5	0.02(7)	0.03(5)	0.04(3)
75	7.21(0)	5	0.02(5)	0.03(3)	0.04(1)
50	7.85(8)	5	0.02(8)	0.03(4)	0.04(2)
25	8.49(4)	5	0.02(2)	0.02(7)	0.03(5)
0	9.26(8)	5	0.02(7)	0.03(4)	0.04(2)
		(iv) No bridge solution.			
-	27.98(1)	5	0.01(5)	0.01(9)	0.03(1)

The first column of the table contains the composition of the bridge solution, expressed as the percentage of potassium chloride in the mixture of

FIG. 7. GRAPH OF DIFFUSION POTENTIAL AGAINST COMPOSITION OF BRIDGE SOLUTE.
$J = 3{\cdot}5$. TEMP. = 25° C.

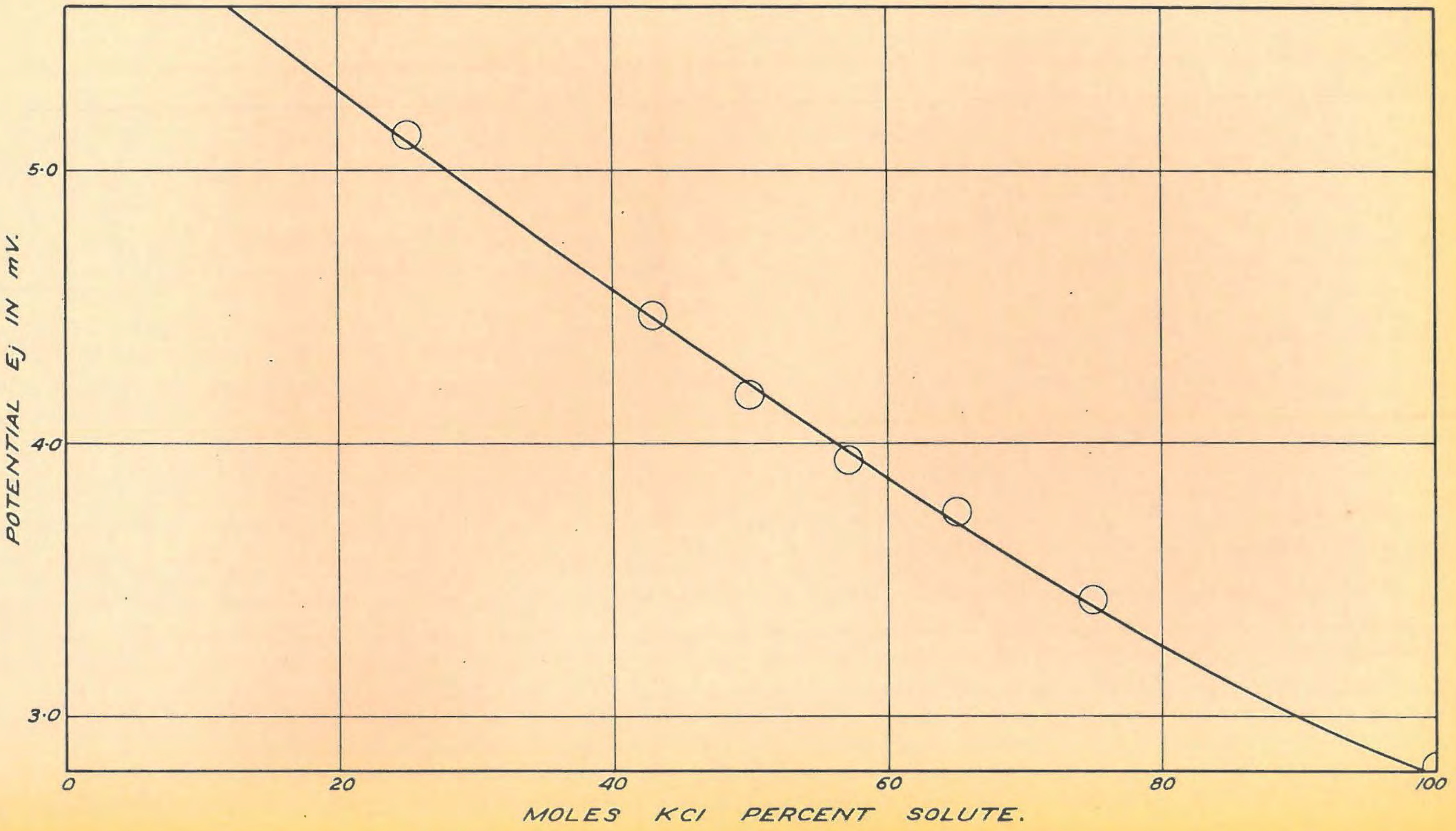
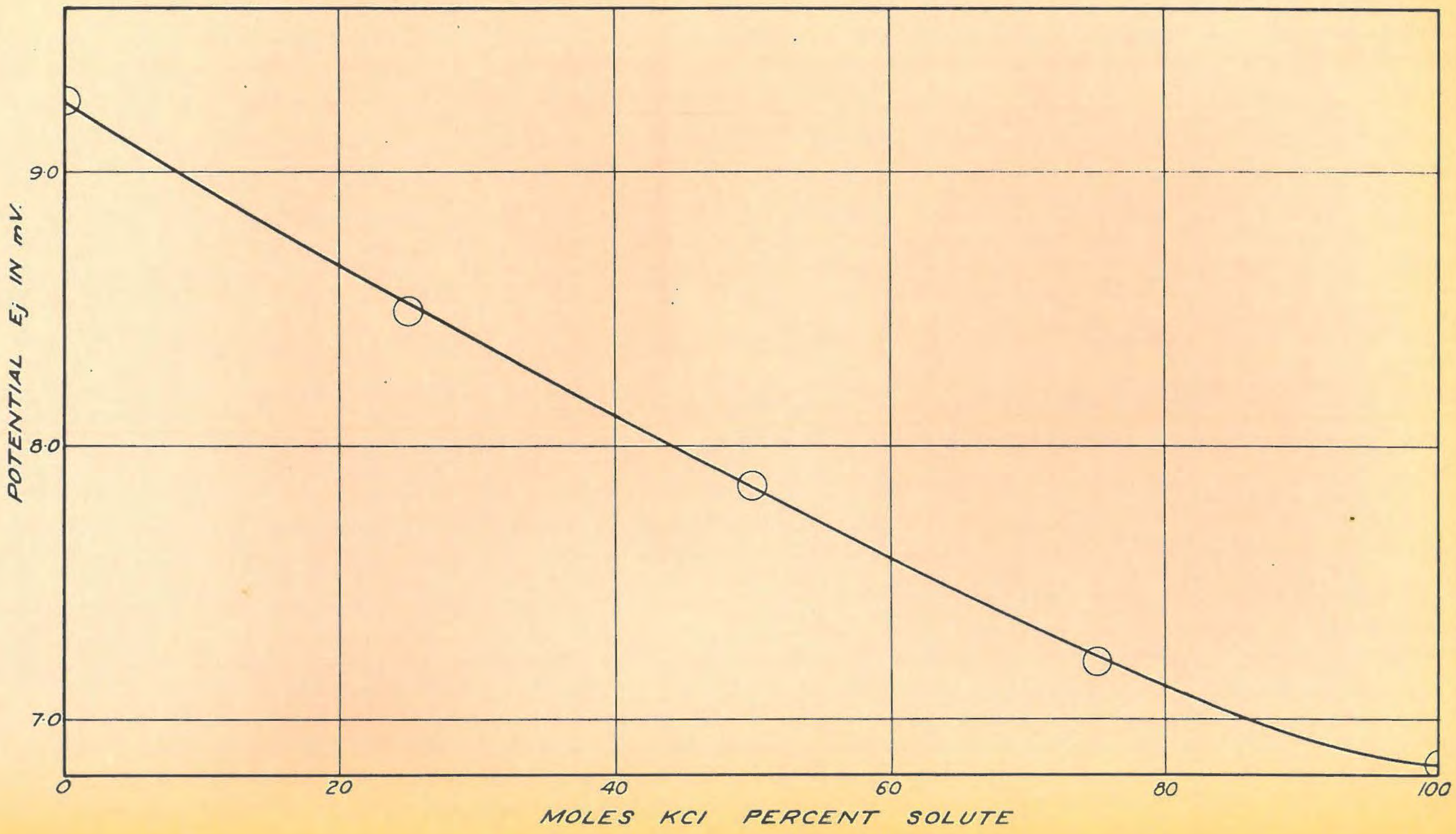


FIG. 8. GRAPH OF DIFFUSION POTENTIAL AGAINST COMPOSITION OF BRIDGE SOLUTE.
J = 1·75. TEMP. = 25° C.



potassium chloride and potassium nitrate comprising the solute. The second column shows the mean of the potentials measured with each bridge colution, while the third indicates the number of readings considered in arriving at this mean. In the fourth and fifth columns are shown, respectively, the mean deviation and standard deviation from the mean of the readings with each bridge solution, and in the sixth the 95 per cent limits of confidence of the mean potential.

Figure 7 shows the graph of the potentials measured against the percentage KCl in the solute of the bridges, at a constant ional concentration of 3.5; Figure 8 contains the corresponding curve for bridges of half this concentration. The radius of the circles is equivalent to 0.044 mV, the highest of the 95 per cent confidence limits.

4.6 3b. Calculated Potentials.

Table 4 shows the values calculated from the Henderson equation of the diffusion potentials at the junctions of decinormal solutions of hydrochloric acid and potassium chloride with mixed (KCl + KNO_3) solutions of different compositionsat total ionic concentrations of 4.12, 3.5 and 1.75, as well as the corresponding potentials across the chains

HCl (0.1N) | Bridge Solution | 0.1N KCl.

Part (iv) of the table shows the calculated potential across the junction 4.6 (ii), i.e. where there is no bridge solution between the two dilute solutions. The values of the mobilities used in the calculations are the same as those listed in section 4.3 3b.

Table 4.

Potentials calculated by means of the Henderson equation at 25°C.

Moles KCl per cent bridge solute	Diffusion potential at the junction (mV):		
	HCl|Bridge	KCl|Bridge	HCl|Bridge|KCl
	(i) J = 4.12.		
100	4.66	1.79	2.87
	(ii) J = 3.5		
100	5.04	1.78	3.26
75	4.43	0.94	3.49
65	4.05	0.47	3.58
57.15	4.00	0.36	3.64
50	3.86	0.16	3.70
42.85	3.73	-0.03	3.76
25	3.31	-0.60	3.91
0	2.68	-1.42	4.10
	(iii) J = 1.75.		
100	6.88	1.40	5.48
75	6.45	0.75	5.70
65	6.27	0.49	5.78
57.15	6.15	0.31	5.84
50	6.03	0.13	5.90
42.85	5.88	-0.09	5.97
25	5.61	-0.51	6.12
0	5.16	-1.18	6.34
	(iv) No bridge solution.		
—	—	-	26.85

4.6 4. DISCUSSION OF RESULTS.

4.6 4a. Comparison with previous measurements.

Before proceeding to discuss the implications of the results set out in section 4.6 3, it is of interest to see how the potentials determined here compare with previous measurements.

The only heteroionic junction to have been studied at all generally is junction 4.6(ii). This is very similar to the junction

HCl (0.09917m) | KCl (0.10000m).......4.6(iii)

whose potential is recorded in Table 3 (iv). As calculations with the Henderson equation indicate that the difference in the potentials at these two junctions will, in fact, be less than 0.1 mV, they can be regarded as identical for the present purpose. In Table 5 are summarised the results of the various measurements of this diffusion potential.

Table 5.

Worker	Reference	Type of Junction	Potential. (mV)
Present investigation		Free diffusion.	27.98
Chloupek,Daneš, and Danešova.	54	Free diffusion.	27.08
Lewis, Brighton and Sebastian.	21	Dipping tube.	27.8
Ghosh.	55	Drop contact.	28.27
Bjerrum	16	In sand.	27.8
Meyers and Acree	56	In sand.	27.79
Roberts and Fenwick.	57	Flowing.	28.00
MacInnes and Yeh.	58	Flowing	26.78

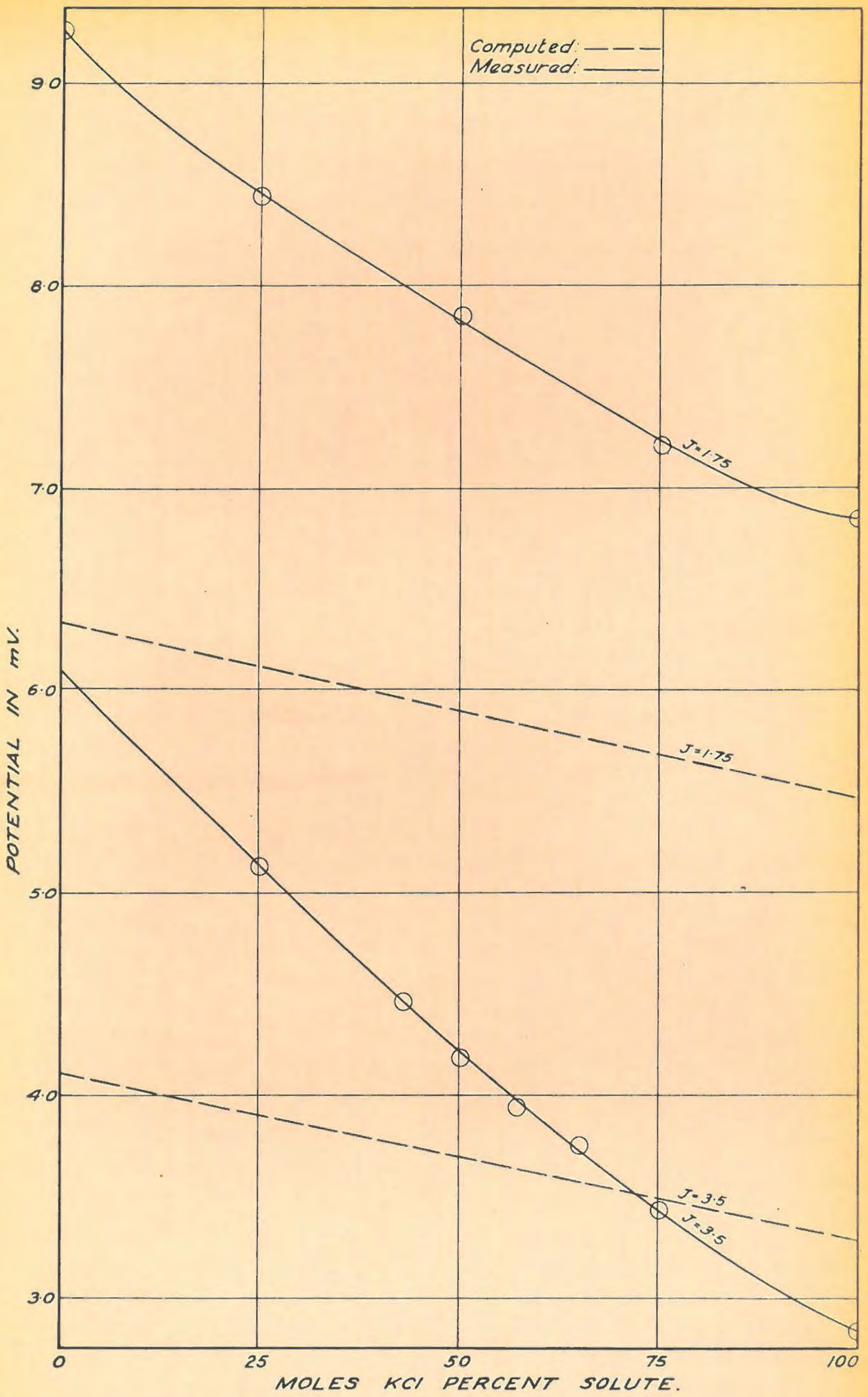


FIG. 9. COMPARISON OF MEASURED AND COMPUTED DIFFUSION POTENTIALS AT 25° C.

These results show considerable variation, due in part, possibly, to the different types of junctions used. Nonetheless, it can be seen that the value obtained in the present investigation is of the correct order of magnitude, and is in no way markedly inconsistent.

Another comparison may be made which involves more directly the potentials at full salt bridges. Kline, Meacham, and Acree (13) collated the values obtained by different investigators for the difference in the potentials across the chains

HCl (0.1N) | KCl (3.5N) | KCl (0.1N)
and
HCl (0.1N) | KCl (1.75N) | KCl (0.1N)

and arrived at a mean of 4.3 mV. Here again, therefore, the potential observed in this work (4.04 mV) agrees with previous estimates.

4.6 4b. Comparison of Calculated and Experimental Potentials.

In Table 6 and Figure 9 are compared the observed potentials and those calculated from the Henderson equation (equation 3.1 (iii)).

In considering these figures, it must be borne in mind that the Henderson equation gives potentials at continuous mixture boundaries, while the potentials measured are at a free diffusion junctions. Thus, the two are strictly not comparable. Nevertheless, the comparison is not without value. In the first place, evidence exists (6) that the two types of transition layer give potentials which differ by only a few tenths of a millivolt; in the second place, there is the fact that in practice the equation is used to estimate potentials at all types of junctions, including free diffusion. The comparison, therefore, indicates the order of the errors commonly incurred.

Table 6.

Temp.= 25°C.

Moles KCl Per cent Solute	Measured Potential (mV)	Computed Potential (mV)	Difference (mV)
	(i) J = 4.12.		
100	1.67	2.87	-1.10
	(ii) J = 3.5.		
100	2.81	3.26	-0.45
75	3.43	3.49	-0.06
65	3.76	3.58	0.18
57.15	3.94	3.64	0.30
50	4.18	3.70	0.48
42.85	4.46	3.76	0.70
25	5.13	3.91	1.22
0	6.1@	4.10	2.0
	(iii) J = 1.75		
100	6.84	5.48	1.36
75	7.21	5.70	1.51
65	7.50@	5.78	1.72
57.15	7.66@	5.84	1.82
50	7.86	5.90	1.96
42.85	8.03@	5.97	2.06
25	8.49	6.12	2.37
0	9.27	6.34	2.93
	(iv) No bridge solution.		
-	27.98	26.85	1.13

Potentials marked with a superscript @ were obtained from the graphs in Figures 7 and 8.

The errors range from zero to three millivolts, and are less in bridges containing higher proportions of potassium chloride. This would appear to indicate that the many approximations involved in the derivation of the equation hold more nearly in the case of KCl than KNO_3. Since the equation is derived for ideal solutions, and since limiting values of the mobilities at infinite dilution were used in the calculations, one would expect that its accuracy would increase with dilution of the bridge solution. However, the figures in Table 6 do not agree with this deduction. If we consider the three sets of values given for pure potassium chloride bridges, we see that the error passes through a minimum in the region of 3.5N. It is not possible to explain this behaviour on the basis of the limited number of measurements available.

However, the important point arising from the comparison is that the Henderson equation is accurate, in the case under consideration, to within 3 mV. Furthermore, since the case is in no way a special or particularly favourable one, it is reasonable to expect that this is the general order of accuracy for all salt bridges linking decinormal or more dilute solutions.

It is, therefore, uncertain whether any increase in accuracy results, when the equation is used in correcting for the residual potentials at salt bridges. On the other hand, the accuracy shown is great enough to justify the use of the Henderson equation in indicating the general trend of diffusion potentials. This is of great importance; for it is only by means of this equation that one is able to gain an insight into the working of the diffusion potentials, and how they are affected by changes in the ionic concentrations and mobilities in the two solutions. It is in this semi-quantitative way that the equation has been employed in the present investigation.

A note of caution should be sounded, however, Too great a trust should not be placed upon the indications given by the equation, unless some degree of experimental support is available. In certain cases it is found that the trends shown are completely erroneous. (See section 4.6 4d.)

Taylor (7) used the equation which he derived (equation 3.1 (iv)) to calculate the diffusion potential at the junction 4.6 (ii), and obtained the value 27.6 mV which agrees more closely with the potential observed during this investigation (27.97 mV) than does the Henderson equation's estimate of 26.85 mV. An attempt was, accordingly, made to extend the comparison of observed and calculated potentials to those computed from the Taylor equation. It was found, however, that Taylor's description of the calculation of the quantity W_H did not agree with the method he actually used in working out the example, and that the latter was not generally applicable. Various other methods of obtaining this quantity were tried, and gave quite unreasonable values for the correction term of the equation. The attempt had, therefore, to be abandoned.

4.6 4c. The Variation of the Measured Potentials with the Composition of the bridge solution.

Parts (ii) and (iii) of Table 3, and Figures 7 and

8 show how the potential of cell 4.6 3(vii) reacts as the relative proportions of potassium chloride and potassium nitrate in the solute of the bridge solution are varied at constant ional concentration. In Figure 9 this variation is compared with that predicted by the Henderson equation.

As the percentage of KCl in the bridge solution is increased, the potential falls along a smooth curve whose form in the two cases, J = 3.5 and J = 1.75, is very similar. The curvature of these graphs, although not very great, is too pronounced to be accounted for by experimental error.

On the other hand, the corresponding graphs for computed potentials appear to be straight lines of identical slope. This linearity is, at first sight, anomalous, for the Henderson equation contains a logarithmic factor. In practice, however, it was found that the variation of this quantity was small (less than one per cent over the range of mixtures), and was, therefore, swamped by the large change in the value of the other factor. Thus, the curves are probably not strictly linear, but have a curvature so slight that it is concealed by uncertainties in the computation. Whatever the true case may be, they will be regarded as linear for the purposes of this discussion.

The difference in the degree of curvature of the measured and calculated graphs could be due either to salt effects, or to a deviation from the simple mixture rule for transport numbers in mixtures of electrolytes,caused by some specific interaction between the chloride and nitrate ions. In the present state of knowledge of the properties of concentrated mixtures of electrolytes, it is not possible to judge whether, indeed, either of these effects would bring about the difference observed. Little is known of the variation of activity coefficients in concentrated KCl-KNO_3 mixtures, and, while van Rysselberge and his co-workers (59) have shown that the simple mixture rule for conductivities is well obeyed by KCl and KNO_3 at a total concentration of 1 molal, no indication is available as to whether the simple rule for transport numbers is also obeyed.

A further point of variance between the curves for measured and calculated potentials is clearly shown in Figure 9: the former are much steeper than the latter. The reason for this probably lies in the fact that the variation of the quantity $\sum_{i} t_i^+ - \sum_{i} t_i^-$ with change in composition of the solute is different in the two cases; and this in turn is probably caused by the inaccuracy of the values used for the mobilities of the two anions.

From the practical point of view, however, the most significant property of the potentials listed in Tables 3 and 4, and illustrated in Figures 7, 8 and 9, is their failure either to pass through zero, or to reach a minimum at any point along the range of mixtures. This means that at no stage does the addition of KNO_3 to the KCl of the bridge solute result in a lowering of the residual liquid junction potential. In actual fact, a substantial increase is caused.

This might at first appear to be a denial of the principle of the use of mixed electrolyte salt bridges (see section 4.1), but further consideration shows this interpretation to be incorrect, and to rest on what will be proved to be a widespread misconception.

It must be remembered that it is full bridges rather than half bridges which are being studied, for this is one of the instances when clear distinction must be made between the two types. They will thus be treated separately.

Let us first consider half bridges. The figures in the third column of Table 4 show how, in the case of the junction KCl (3.5N) | KCl (0.1N), the addition to the concentrated solution of a salt whose most mobile ion(K^+) is of the opposite sign to the most mobile ion of KCl (Cl^-), results in a reduction and change of sign of the diffusion potential. The junctions

KNO_3 (3.5N) | KCl (0.1N)
KCl (1.75N) | KCl (0.1N)
KNO_3(1.75N) | KCl (0.1N)

show similar behaviour.

It will be noticed that this behaviour is not fully duplicated by the values in the second column of the table. The reason for this is that, where the junctions involve decinormal HCl solutions, it cannot be considered that the bridge solution controls the liquid junction potential: so great is the transport number of the hydrogen ion, that it exerts a major influence on the potential at the junction. To reduce the potential, therefore, a salt must be used whose most mobile ion has the same sign as the hydrogen ion, and which will, consequently, tend to nullify the effects of its diffusion. Thus, when KNO_3 is added to the KCl solution the diffusion potential is reduced. It does not change sign, however, as it is not powerful enough to counter the high mobility of the hydrogen ion in decinormal solution, even when the 3.5N solution contains no KCl.

We have shown, therefore, that by varying the composition of the more concentrated solution , it is always possible to reduce the diffusion potential at a half bridge. Whether or not this reduction extends to and through zero depends on the nature and concentration of the ions in the dilute solution, and on the relative mobilities of the ions in the added salt.

We now go on to consider full bridges. Here the position is more complicated, for there are two liquid junctions each producing, for all practical purposes, its own potential. To reduce to zero the total potential across the bridge, the composition of the bridge solution must be adjusted to make these two potentials equal and opposite.

If the adjacent solutions are so dilute relative to the bridge solution that both junctions can be considered to be swamped, the individual diffusion potentials are practically identical in magnitude, and have opposite signs, for all mixtures. Thus, there is no advantage to be gained by the use of equitransferent solutions. (In practice it can be considered that a 3.5N bridge solution will swamp solutions more dilute than 10^{-3}N.)

In the general case it is found that, although the concentrated bridge solution may contribute the major portion of the two separate potentials, the potential across the full bridge is mainly determined by

FIG. 10. VARIATION OF DIFFUSION POTENTIALS AT MIXED ELECTROLYTE HALF BRIDGES AT 25° C.

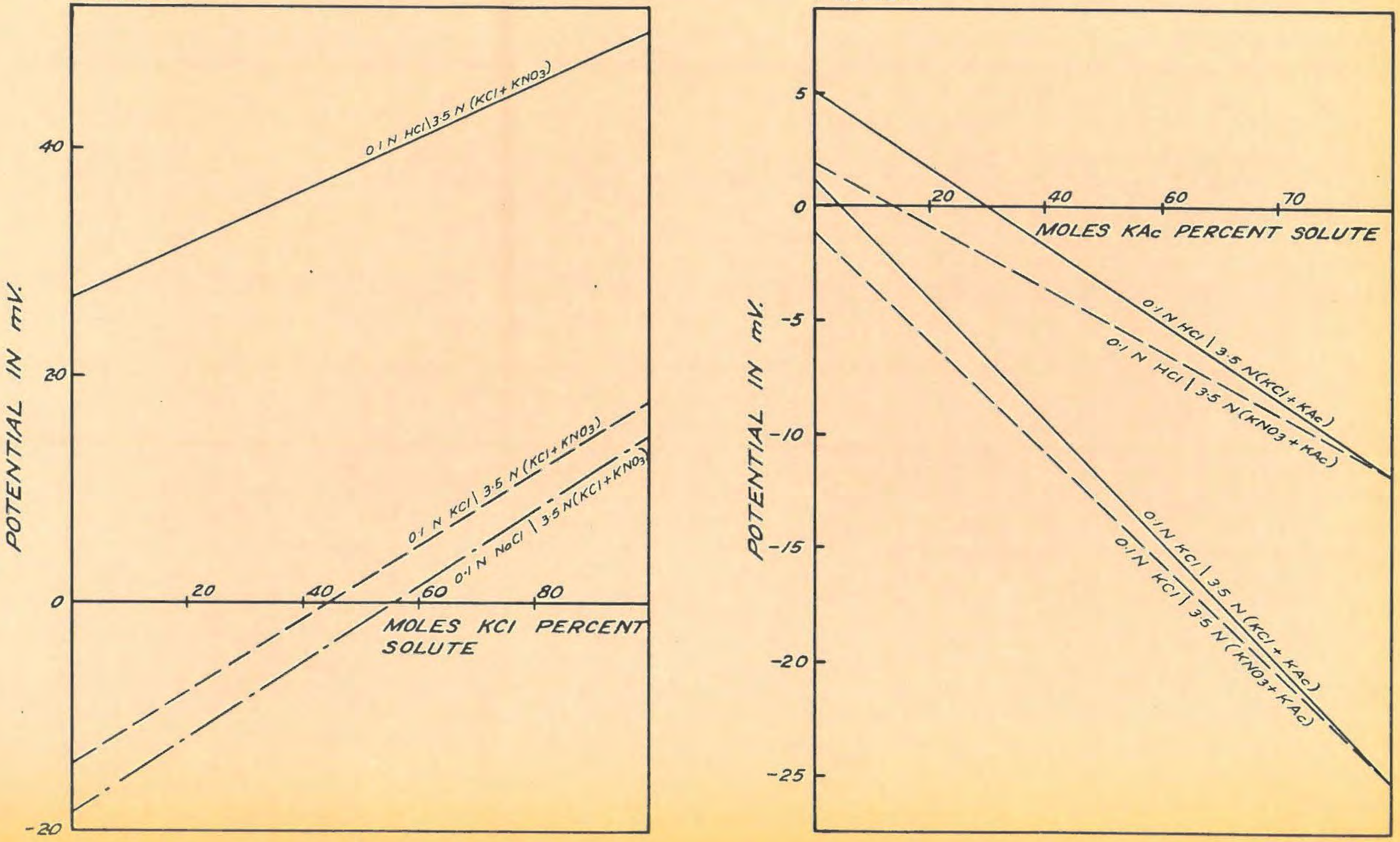


FIG. 10a.

FIG. 10b.

the dilute solutions. A change in composition of the bridge may result in large variations in the half bridge potentials, but the direction of these variations, and to some degree their magnitude, will be independent of the dilute solution concerned. As a result, their effects on the full bridge potential will tend to cancel. This point is clearly illustrated in Figure 10a. The graphs in this figure represent the variation with bridge solution composition of the calculated diffusion potential at the junctions

$$\begin{array}{l} \mathrm{HCl\ (0.1N)} \,\big|\, (\mathrm{KCl} + \mathrm{KNO_3})\ \ 3.5\mathrm{N} \\ \mathrm{KCl\ (0.1N)} \,\big|\, (\mathrm{KCl} + \mathrm{KNO_3})\ \ 3.5\mathrm{N} \\ \mathrm{NaCl(0.1N)} \,\big|\, (\mathrm{KCl} + \mathrm{KNO_3})\ \ 3.5\mathrm{N}. \end{array}$$

From these lines, as well, the potentials across the three possible series of full bridges can be determined. For example, the potential at the bridge

$$\mathrm{HCl\ (0.1N)}\ \left|\ \begin{matrix} 3.5(1 - 0.60)\mathrm{N\ KCl,} \\ 3.5\ .\ 0.40\mathrm{N\ KNO_3} \end{matrix}\ \right|\ \mathrm{KCl\ (0.1N)}$$

is given by the difference between the potentials at its two constituent half bridges,

i.e. $4.1 - 0.5 = 3.6$ mV.

It can be seen that, for all the examples illustrated, the variation of diffusion potential is considerably less for full bridges than for half bridges (the changes in the latter case are all in the same direction and tend to cancel.) The graphs in Figure 10b show the same behaviour. In these potassium acetate (KAc) is introduced as one of the components of the bridge solute.

In considering the graphs in Figure 10, it should be noticed that in no case does a line representing the variation of diffusion potential with the composition of a concentrated solution, cross or touch another line representing potentials at the same concentrated solution. This means that in none of these examples can diffusion potentials be eliminated by varying the composition of the bridge solution.

The examples shown are widely distributed, and embrace extremes as regards the solutes of both bridge and adjacent solutions. Furthermore, although this discussion has been developed on the basis of computed potentials, it should be borne in mind that it is in complete agreement with the experimental evidence obtained during the present investigation. Consequently, it is felt that the reliance placed on the predictions of the Henderson equation is in this instance justified.

It can thus be stated as a general rule that in no case can the residual liquid junction potential at a full salt bridge be eliminated by the use of mixtures of electrolytes as the bridge solute.

This conclusion is directly opposed to beliefs held widely both by workers in this field, and by other electrochemists. The following examples support this statement:

Acree and his co-workers recommended repeatedly (13,31,32) a mixture of KNO_3 and KCl in a molar ratio of 1 to 3 as being more efficient as a "contact potential eliminator" than pure KCl solution, for solutions of pH between 3 and 10. Admittedly this mixture was sometimes mentioned in context with half bridges, when, of course, the claims made for it might possibly be justified. Other cases can only be construed as applying to full bridges. Furthermore, this solution is quoted by reviewers as being an improvement on the conventional saturated potassium chloride salt bridge. (e.g. see Bates' "Electrometric pH Determinations" page 188 (60)).

Grove-Rasmussen, on page 456 of his second paper (33) states that "...by using an equitransferent bridge solution we gain partly the advantage.....that we are working on the whole with smaller diffusion potentials ......". On page 422 of his third paper (26), he claims that".....an equitransferent solution of KCl and KNO_3 will probably be better suited for the elimination of the diffusion potential than the saturated potassium chloride solution usually used for this purpose."

The root of this misconception almost certainly lies in the failure to recognise the necessity for distinguishing between single junctions and full salt bridges. It appears that, once workers have realised the advantages of using mixtures in the former case, they have without question extended the technique to the latter.

From this discussion, therefore, we must conclude that no reduction in the residual liquid junction potential at full salt bridges is, in general, effected by the use of mixed electrolyte bridge solutions, although there probably are considerable advantages in using equitransferent solutions at half bridges. As a result, it is not possible to determine the composition of equitransferent mixtures by measurements of the diffusion potentials at full bridges.

FIG. 11b CALCULATED POTENTIALS

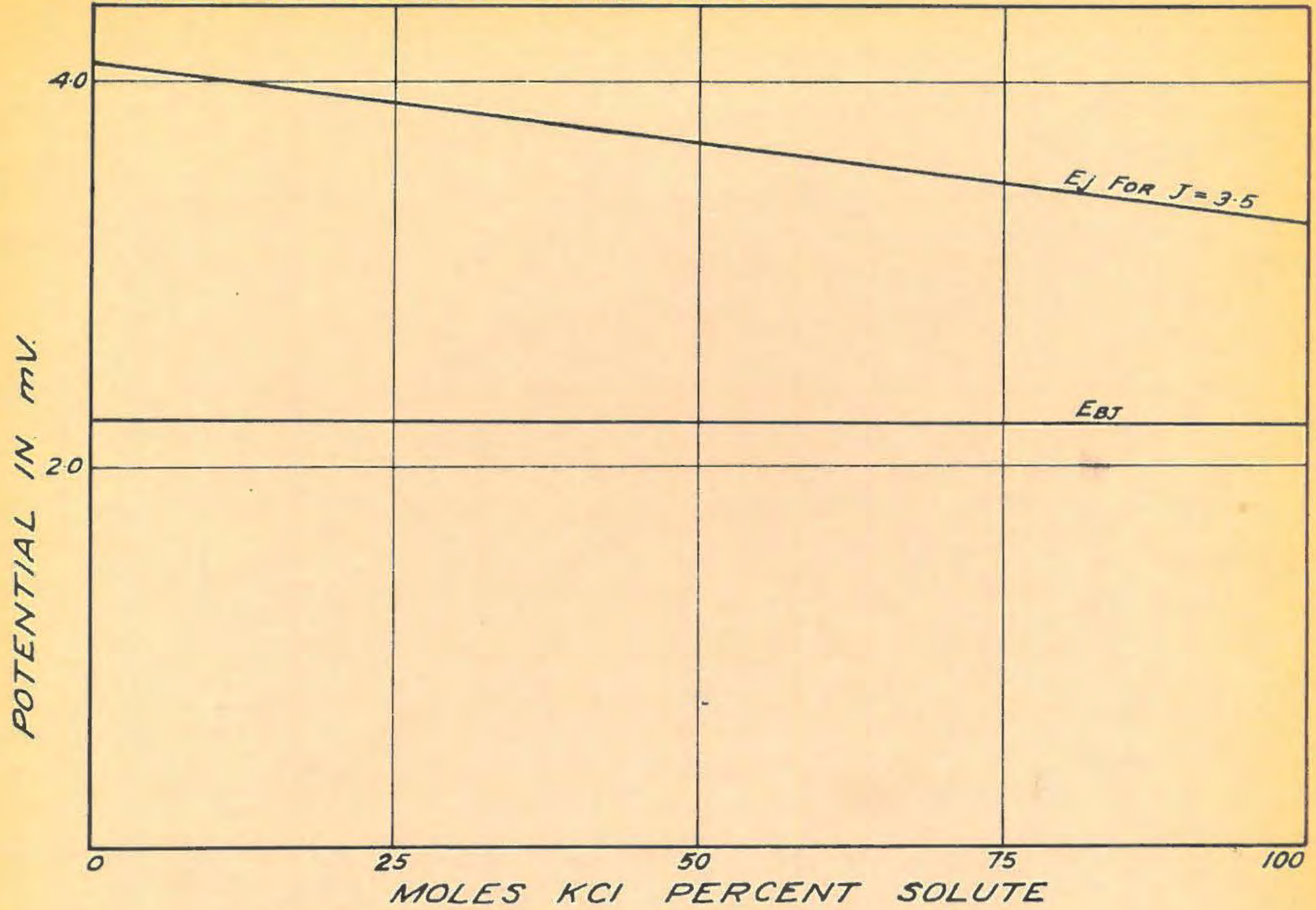


FIG. 11a MEASURED POTENTIALS

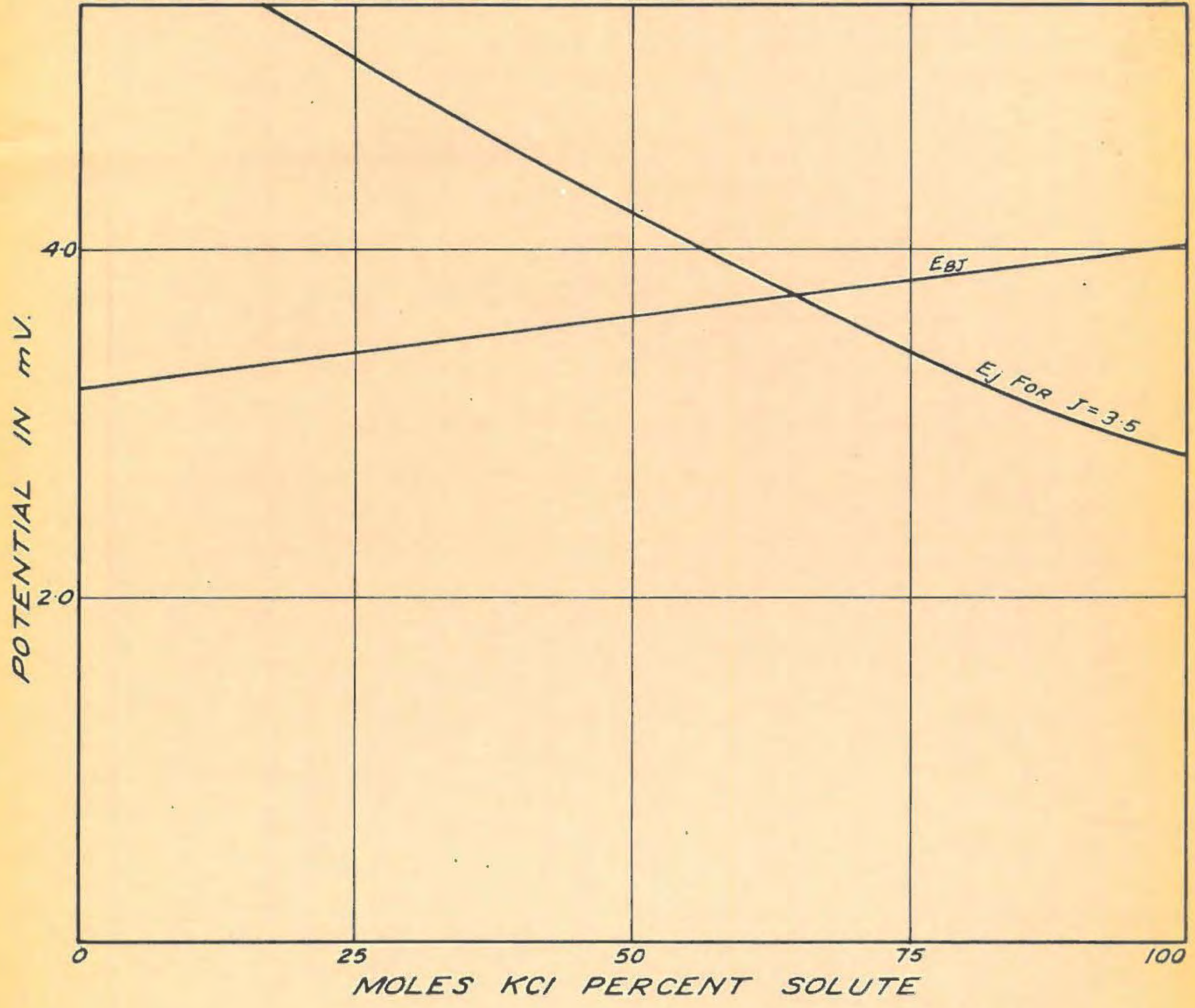


FIG. 11. COMPARISON OF E_{BJ} WITH, (a) MEASURED AND (b) CALCULATED DIFFUSION POTENTIALS AT 25° C.

4.6 4d. The Bjerrum Extrapolation.

Using the values given in Table 3 for the residual potentials at 3.5N and 1.75N mixed electrolyte salt bridges, an indication can be obtained of how the accuracy of the Bjerrum extrapolation method is affected by changes in the composition of the salt bridge. This method predicts that the potential at a 3.5N bridge will be half that at one of normality 1.75. Hence, the potential, E_{Bj}, estimated by means of the method for a 3.5N solution of any mixture of KCl and KNO_3, is equal to the difference between the potentials at 1.75 and 3.5N bridges of that composition.

i.e. $E_{Bj} = E_{1.75} - E_{3.5}$..........4.6 (iv)

If the method is accurate, E_{Bj} should be equal to the liquid junction potential at the 3.5N bridge, $E_{3.5}$.

In Figure 11a the variation of E_{Bj}, calculated from the values in Table 3 (ii) and (iii), is compared with the variation of E_j at 3.5N bridges. Figure 11b shows corresponding curves for potentials calculated by means of the Henderson equation. (See Table 4). It should be emphasised that these comparisons are for a single case, and care should, therefore, be taken in drawing generalised conclusions.

The curves in Figure 11a intersect. This, of course, means that for some mixture of KCl and KNO_3, the Bjerrum extrapolation applies exactly. If, furthermore, we use either pure KCl or pure KNO_3 as bridge solute and gradually increase the proportion of the second component, the predicted potentials become progressively more accurate. It can, therefore, be stated that in the case of the chain

$$\mathrm{HCl}\ (0.09917\mathrm{m})\ \Big|\ \text{Bridge solution}\ \Big|\ \mathrm{KCl}\ (0.10000\mathrm{m})$$

the accuracy of the Bjerrum extrapolation method can be greatly increased by the use of mixed electrolyte salt bridges.

The theoretical curves in Figure 11b do not intersect. Thus, the Henderson equation has here failed to show even the qualitative behaviour of the diffusion potentials, although it demonstrated clearly the superiority of equitransferent solutions in the case of half bridges. (See section 4.3 3.) We have here a clear instance of the need - a need which has been stressed throughout this thesis - for theoretical predictions to be supported experimentally, before too great a reliance is placed on them.

What significance can be attached to the value of the ratio $KCl : KNO_3$ (= 1 : 2.2) at which E_{Bj} is equal to $E_{3.5}$? It is unlikely that it defines the equitransferent mixture of the salts, as it is probable that the adjacent solution will have had some influence in determining the point of intersection of the two graphs. How great this influence will have been is difficult to estimate. No prediction based on the Henderson equation is, of course, admissible in view of its failure in this matter. It is to be expected, nevertheless, that the intersect will lie in the general vicinity of the equitransferent mixture, and, therefore, we can use the value of this ratio to obtain a tentative estimate of the composition of the mixture. In the opinion of the present author, the equitransferent mixture will lie between 50 and 80 moles KCl per cent.

This can be compared with the estimates of Murray and Acree (31) and Grove-Rasmussen (33) of, respectively, 75, and 40 to 60 moles KCl per cent. It lies in the same region, but, as neither of these previous estimates is based on particularly satisfactory work, it is not certain what value can be placed on this agreement.

It is impossible to draw any more definite conclusions from the graphs in Figure 11a. Before a general verdict can be given as to the possibilities of the use of the Bjerrum extrapolation in conjunction with mixed electrolyte bridges, more experimental work is necessary to show firstly, whether the intersection is obtained in all cases, and secondly, how it is affected by the nature of the adjacent solutions. The results of this investigation do, however, indicate that the possibility exists of the extrapolation's being developed into a general method of great accuracy.

4. 7 CONCLUSIONS.

The conclusions of this investigation, as developed in the discussion in section 4.6 4, are summarised below. It should be borne in mind that these apply strictly only to the cell studied (cell 4.3 (vii)), and under the conditions stated in section 4.6 2c.

(i) The variation of the diffusion potential at mixed KCl - KNO_3 salt bridges is, as shown in Figure 7 and 8, almost but not quite linear.

(ii) Residual junction potentials at full salt bridges are not, in general, reduced as the mixed electrolyte salt bridge approaches equitransference. It is extremely unlikely that they can be completely annulled through the agency of mixtures of electrolytes in any possible case.

(iii) It is probable that the diffusion potentials at half bridges can be eliminated by the use of the correct proportions of suitable salts in the bridge solutions, although this has not yet been proved experimentally.

(iv) In the specific case studied, the Bjerrum extrapolation method for the estimation of residual diffusion potentials is greatly improved by the use of mixed electrolyte salt bridges. The experimental data obtained is too restricted to allow this result to be generalised, but it does indicate the possibility of there being developed along these lines a highly accurate method of eliminating the error due to liquid junction potentials.

(v) It is not possible to determine the composition of equitransferent solutions using cells involving full salt bridges.

(vi) Diffusion potentials across salt bridges linking decinormal or more dilute solutions, and estimated by means of the Henderson equation, are accurate to within 3 mV. Too great a reliance should not be placed on the qualitative indications of the equation, unless some degree of experimental support is available.

4.8 SUGGESTIONS FOR FURTHER WORK.

The present investigation indicates that there is a definite possibility of developing a general method of eliminating the effects of liquid junction potentials using mixed electrolyte salt bridges. A considerable amount of further work is still necessary, and this must all be performed experimentally. Research should be concentrated on the Bjerrum extrapolation method, for it is clear that any general device developed will be of this type. In this connection, three important questions must be answered:

(a) Does the behaviour shown in the experimental curve in Figure 11 occur in all cases?

(b) Is a general Bjerrum-type method possible, and, if so, sufficiently accurate to be worth while?

(c) Has the property of the equitransference any significance in regard to this general method?

The question of whether the intersection of curves observed in Figure 11 occurs in general can only be answered by determining these curves from other systems, that is, chains consisting of KCl - KNO_3 bridges linking various combinations and concentrations of adjacent solutions. This will undoubtedly be a laborious process. However, the work involved, will be less than a consideration of the present investigation might lead one to expect, as two or three points on each curve should suffice to indicate whether intersection will occur. Greater care will, however, be required in determining the exact point of intersection in each case, but this is a later problem. It will probably be wise at first to keep one dilute solution constant as 0.1m KCl, and vary the other. The conclusions of this study could then be extended to a more general case. If this were, for some reason not possible, a method applying only to this particular case could still find a wide application in the field of measurements.

Once this generality has been established, the next step will be to develop and test a method based on it. The obvious way in which the former could be tackled would be to find a relation between the composition at which the graphs of observed and extrapolated potentials cut, and the mobilities of the ions of the dilute solutions. General considerations lead one to believe that some relation must exist, and that it will most simply be revealed by plotting accurately determined compositions against various functions of the ionic mobilities.

The findings of the present investigation tend to diminish the importance of truly equitransferent solutions, but considerable interest does still pertain to them. In the first place, a relation between equitransference and the point of intersection would provide a contact between theory and experiment, and in the second place, equitransferent solutions could find direct application in cells involving half bridges, on account of the behaviour shown in Figures 1a and 1b. The problem of determining them is certain to present difficulties: they would have to be found from measurements on cells with only one liquid junction; and the consequent problem of the value of the electrode potentials involved could only be satisfactorily overcome by finding the single electrode potentials by measurements on cells without liquid junction.

5.0 SUMMARY.

(i) The field of diffusion potentials at heteroionic junctions is reviewed. It is shown that, whereas considerable advances have been made in certain directions, notably in the practical preparation of reproducible liquid junctions, there still exists the need for accurate methods of estimating or eliminating the error due to liquid junction potentials. The Henderson equation is the only expression which it is practicable to use in the calculation of diffusion potentials, but although it is widely used, there is little direct evidence as to the accuracy which may be expected from it.

(ii) The principle of the use of mixed electrolyte salt bridges is developed, and the advantages of using equitransferent mixtures demonstrated on theoretical grounds.

(iii) Previous work on mixed electrolyte salt bridges is reviewed. It is shown that too great a reliance has been placed on approximate theoretical relations, and that very little is at present known about the subject.

(iv) An apparatus is described by means of which liquid junction potentials were measured with a precision greater than any yet recorded. The main feature of this cell is a new type of three-way tap which allows cylindrically symmetrical, free diffusion junctions to be set up simply and conveniently.

(v) Using this apparatus, a series of measurements was carried out on the cell

$$\mathrm{Hg{-}Hg_2Cl_2}\left|\begin{array}{l}\mathrm{HCl}\\ 0.09917\mathrm{m}\end{array}\right|\begin{array}{l}\mathrm{KCl}\ \ J(1-x),\\ \mathrm{KNO_3}\ \ Jx\end{array}\left|\begin{array}{l}\mathrm{KCl}\\ 0.10000\mathrm{m}\end{array}\right|\mathrm{Hg_2Cl_2{-}Hg}$$

with total ional concentrations, J, of 4.12, 3.5 and 1.75, and values of x ranging from zero to one. A few measurements were also made with the two dilute solutions in direct contact.

(vi) Discussion of the measurements leads to the following conclusions:

(a) Diffusion potentials vary with the composition of mixed KCl-$\mathrm{KNO_3}$ bridges at constant total ional concentration along a smooth curve, which is not quite linear.

(b) Residual junction potentials at full salt bridges are not, in general, reduced as the mixed electrolyte salt bridge approaches equitransference. It is extremely unlikely that they can be completely annulled through the agency of mixtures of electrolytes in any possible case.

(c) It is probable that the diffusion potentials at half bridges can be eliminated by the use of the correct proportions of suitable salts in the bridge solution, although this has not yet been proved experimentally.

(d) In the specific case studied, the Bjerrum extrapolation method for the estimation of residual diffusion potentials is greatly improved by the use of mixed electrolyte salt bridges. The experimental data obtained is too restricted to allow this result to be generalised, but it does indicate the possibility of their being developed along these lines a highly accurate method of eliminating the error due to liquid junction potentials.

(e) It is notpossible to determine the composition of equitransferent solutions using cells involving full salt bridges.

(f) Potentials calculated from the Henderson equation are accurate to within 3mV.

(vii) Suggestions are made for further work.

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