

The Diffusion Potential between Dilute Solutions and Concentrated Solutions of Potassium Chloride plus Potassium Nitrate

K. V. GROVE-RASMUSSEN

*Department of Inorganic Chemistry, Royal Danish School of Pharmacy,
Copenhagen, Denmark*

When used as a salt bridge or a reference electrode solution for emf-measurements, a saturated solution of potassium chloride does not meet the demands of equitransference * to as great an extent as originally supposed.

According to the classic investigations of Hittorf the potassium ion has the transference number 0.498 in potassium chloride. Since then several authors ^{2, 3}, having used both the classic method and the more accurate moving boundary method, have agreed that the transference number, which by the way is not fully independent of the concentration, lies near the value 0.490. As it is known, it is hardly possible to determine the diffusion potential directly and therefore we must generally calculate it. For such a calculation the transference number of potassium chloride is of great importance; this pertains particularly to very dilute solutions, as a consequence results obtained with cells with liquid-liquid junction aiming at an extrapolation to infinite dilution are greatly compromised by the uncertainty of the diffusion potential. This is to a great extent the case because calculation of the diffusion potential is based on the theoretically derived Henderson formula in connection with transference numbers that have been determined by methods which have nothing to do with emf-measurements. The aim of the present work has been:

1) to demonstrate that in accordance with the Henderson formula the diffusion potential increases from a certain limit with increasing dilution when the bridge solution is not equitransferent.

* The term equitransferent has previously been defined by the author ¹ as: "having the same effective cation- and anion-transference".

2) from experiments to determine the order of magnitude of the ratio KCl/KNO_3 which leads to an equitransferent solution; we presume that equitransference is present when the ratio is such that the measurements are in agreement with the activity laws, even in extreme dilution.

3) to give certain indications for the application of such a bridge solution.

Murray and Acree⁴ (1931) and Kline, Meacham and Acree⁵ (1932) have suggested the use of a concentrated solution of potassium chloride plus potassium nitrate in the mole ratio 3 : 1. A more detailed investigation of the problem was made by Manov, DeLollis and Acree⁶ (1944). They found from theoretical viewpoints that the said solution is not completely equitransferent and that equitransference may be obtained by the addition of a small quantity of hydrochloric acid. The present author does not consider this solution of the problem suitable, as the hydrochloric acid may cause protolytic changes in the boundary and if some of the bridge solution enters the test solution the measurement is often totally compromised.

Instead it seems reasonable to try to increase the amount of potassium nitrate in proportion to potassium chloride. The reason that the above authors have not suggested this procedure is possibly that they wanted to keep up a total concentration that was above 4 normal and this is hardly possible at room temperature if the concentration of potassium nitrate is further increased.

CALCULATIONS BASED ON KNOWN TRANSFERENCE NUMBERS

If the cation transference t is known for potassium chloride and potassium nitrate, it is possible to calculate the ratio KCl/KNO_3 which leads to an equitransferent solution.

If u and v denote the mobilities of cations and anions, respectively, we obtain by applying the formula

$$t = \frac{u}{u + v} \quad (1)$$

$$v_{\text{Cl}} = \frac{u(1-t_{\text{KCl}})}{t_{\text{KCl}}} \quad \text{and} \quad v_{\text{NO}_3} = \frac{u(1-t_{\text{KNO}_3})}{t_{\text{KNO}_3}} \quad (2)$$

If we put the total concentration = c we have the following condition for equitransference

$$uc = v_{\text{Cl}}c_{\text{KCl}} + v_{\text{NO}_3}c_{\text{KNO}_3} \quad (3)$$

Equations (2) and (3) lead to

$$\frac{c_{\text{KCl}}}{c_{\text{KNO}_3}} = \frac{(2t_{\text{KNO}_3}-1) t_{\text{KCl}}}{(1 - 2t_{\text{KCl}}) t_{\text{KNO}_3}} \quad (4)$$

We here meet the difficulty that the transference numbers depend to a certain extent on the concentration. Table 1 gives the mole ratio KCl/KNO₃ for some concentrations calculated from equation (4).

Table 1. The ratio $c_{\text{KCl}}/c_{\text{KNO}_3}$ leading to equitransferent solution.

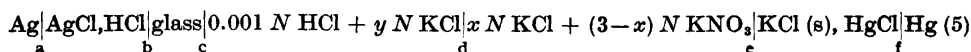
c	Cation transference *		Ratio $c_{\text{KCl}}/c_{\text{KNO}_3}$
	t_{KCl}	t_{KNO_3}	
0	0.4906	0.5072	0.749
0.01	0.4902	0.5084	0.828
0.05	0.4899	0.5093	0.885
0.10	0.4898	0.5103	0.969
0.20	0.4894	0.5120	1.082
1.0	0.4871	unknown	
3.0	0.4858	unknown	

* Values collected by Mc. Innes⁷.

When dealing with a process of this kind which takes place in a boundary between the concentrated bridge solution and a dilute solution, *i. e.* through an interval with varying concentration of the bridge electrolyte, it is not possible to calculate the ratio KCl/KNO₃ according to equation (4). Instead of demanding absolute equitransference in the bridge solution we must claim that the mixture of this solution is such that the boundary between it and a dilute solution on average becomes equitransferent with regard to the ions originally present in the bridge solution. It will hardly be possible to calculate this ratio from known transference numbers.

EXPERIMENTS

Measurements have been made in cells of the type



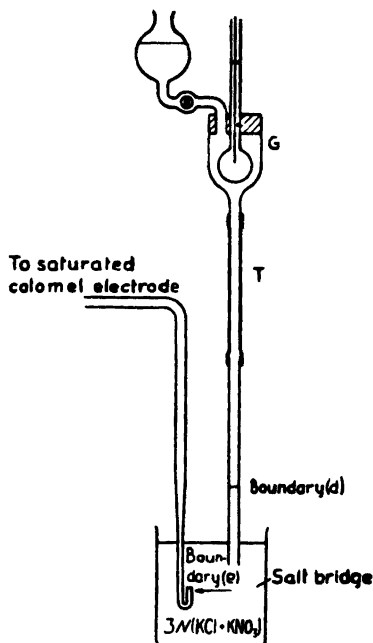


Fig. 1. Experimental arrangement. *G* glass electrode vessel, *T* rubber tubing.

The experiments were carried out in a room where the temperature was kept at $22^{\circ}\text{C} \pm 0.3^{\circ}\text{C}$. Fig. 1 shows the apparatus. A fortnight old Haber electrode with very thin walls was used; it was made by melting 8 cg of Corning 015 glass to the end of a tube of common glass and blowing to a diameter of 2 cm. Measurements have been made with a vacuum tube electrometer (Radiometer, type P.H.M.3).

The test solution ($0.001\text{ N HCl} + y\text{ N KCl}$) was placed in the electrode vessel (*G*) and measurements were first made with 3 N KCl as bridge solution, and then, after washing the vertical tube with the test solution, measurements were made with a mixture of 4 parts of $3\text{ N KCl} + 1$ part 3 N KNO_3 ; then with a mixture of 3 parts $3\text{ N KCl} + 2$ parts of 3 N KNO_3 etc., ending with a pure 3 N KNO_3 solution. And further, for sake of control, a 3 N KCl was again used as bridge solution. A series of such measurements corresponds to a column in Table 2. The values presented are averages of five readings taken just after the boundary has been prepared.

By careful suction (after compression of the rubber tubing (*T*) it is allowed to expand again) the boundary (*d*) between the test solution and the bridge solution has been lifted a few cms into the vertical tube. The object of making the boundary in this manner is to obtain cylindrical symmetry, which is of

Table 2. Potential differences in millivolts.

Molar ion concentration c			0.001	0.003	0.01	0.03	0.10	0.3	1.0	3.0	
Composition of the test solution			c_{HCl}	0.001	0.001	0.001	0.001	0.001	0.001	0.001	
			c_{KCl}	0	0.002	0.009	0.029	0.099	0.3	1.0	3.0
System no.	1	Parts 3 N KCl + parts 3 N KNO ₃ in bridge solution	0 + 5	64.9	65.1	65.6	66.1	68.1	68.0	64.6	51.0
	2		1 + 4	62.6	63.3	64.0	64.8	66.7	67.0	64.2	
	3		2 + 3	60.6	61.2	62.1	63.2	65.2	65.9	63.7	
	4		3 + 2	58.0	58.6	59.6	61.1	63.2	64.9	62.8	
	5		4 + 1	55.1	56.1	56.9	58.6	61.1	62.1	62.0	
	6		5 + 0	51.8	53.1	53.9	56.2	58.6	60.7	60.8	50.8
	1		0 + 5	64.8	65.4	65.7	66.7	68.1	68.3	65.0	

importance for reproducing the experiments. The boundary (e) between the bridge solution and the calomel electrode was made by simple submersion, which is considered justifiable as the corresponding diffusion potential is small (maximum 2 mV according to the Henderson formula — also when used in Guggenheim's⁸ modification pertaining to solutions of equal conductance (*i. e.* rendering the quantity C of equation (10) equal to zero)).

It is pointed out that the true electrode potentials are the same in a column of Table 2. The variations through such a column are entirely due to variations in the diffusion potentials at (d) and (e) (formula (5) and Fig. 1). With the weakest solution (0.001 N HCl) using 3 N KCl as bridge solution, 64.9 mV were measured and with 3 N KNO₃ 51.8 mV, *i. e.* a difference of as much as 13 mV. This difference between the extremes decreases as the concentration of the test solution increases and *e. g.* for a 1 N solution we find only a difference of 4 mV.

DISCUSSION OF EXPERIMENTAL FINDINGS

Judging from their transference numbers potassium chloride and potassium nitrate should be equally good as bridge solutions when used in the same concentrations, and the results obtained must be expected to lie on either side of the true value. The latter must be sought somewhere between the two extremes obtained by measurements with pure KCl- and KNO₃ solutions as salt bridges. The bridge solutions given in Table 2 may be evaluated by examining which of the rows of the table is in best agreement with the activity laws. For this object the Debye-Hückel-Brønsted equation has been used:

$$-\log f = 0.5 * \sqrt{c} - \beta c \quad (6)$$

In the following only concentrations of the test solution equal to 0.1 normal or less have been considered. In this concentration-interval equation (6) may be applied with good approximation.

The emf of the cell is equal to the sum of the potential differences at a, b, c, d, e, and f in formula (5). These potential differences are constants at a, b, and f. At (e) the potential difference varies for each of the 6 different bridge solutions, but it is constant in a row of Table 2. Presuming that for the solutions in question the glass electrode acts like the reversible hydrogen electrode, the potential difference at c is equal to a constant minus $(RT/F \log e) \log a_{\text{H}}$. The potential difference at (d) is denoted $-E_j$.

If the constants are combined in one constant K_1 the emf of the cell may be expressed:

$$E = K_1 - \frac{RT}{F \log e} \log a_{\text{H}} - E_j \quad (7)$$

By applying equation (6) this may be written:

$$\frac{E}{k} = K_2 + 0.5 \sqrt{c} - \beta c - \frac{E_j}{k} \quad (8)$$

$$\text{as } a_{\text{H}} = f c_{\text{H}} \text{ and } \frac{RT}{F \log e} = k \text{ and } \frac{K_1}{k} - \log c_{\text{H}} = K_2$$

* After Harned and Owen⁹ the accurate value of the limiting slope is equal to 0.5036 at 22° C.

E_i may be calculated from the Henderson formula, which, as the present systems contain only uni-univalent electrolytes, may here be applied in the simple form:

$$E_i = \frac{RT}{F \log e} \cdot \frac{(U-V) - (U_r - V_r)}{(U+V) - (U_r + V_r)} \log \frac{U_r + V_r}{U+V} \quad (9)$$

where $U = \sum_i u_i c_i$ and $V = \sum_i v_i c_i$

and $U_r = \sum_r u_r c_r$ and $V_r = \sum_r v_r c_r$

u_i and v_i denoting mobilities of cations and anions, respectively, and the indices r and t referring to the bridge solution and the test solution, respectively.

Equation (9) may be written:

$$E_i = k \cdot \left(\frac{U-V}{\underset{A}{(U+V) - (U_r + V_r)}} - \frac{U_r - V_r}{\underset{B}{(U+V) - (U_r + V_r)}} \right) \log \frac{U_r + V_r}{\underset{C}{U+V}} \quad (10)$$

$$\text{or } E_i = kAC + kBC \quad (11)$$

When the test solution is of low concentration in comparison with the bridge solution we may reason as follows:

The denominator of the fraction A is large compared with the numerator and is relatively independent of the conditions in the test solution. The numerator, on the other hand, depends greatly on the proportions between the ionic mobilities in the test solution and is proportionate to the concentration of the latter solution. The quantity C increases as the test solution becomes more diluted, but this increase is of a lesser order of magnitude than the corresponding decrease in fraction A . Therefore the product kAC will decrease as the test solution becomes more diluted. If dilution becomes infinite the limiting value is equal to zero.

The denominator of the fraction B is approximately constant and the numerator is constant. Therefore, as the test solution becomes more diluted the product kBC increases proportionately with the logarithm of the conductance of the test solution.

In the present experiments the composition of the test solution has been chosen in such a manner that for concentrations below or equal to 0.1 normal

the product kAC does not exceed 0.2 Vm. Thus, in equation (11) variations in the diffusion potential may be considered due to the product kBC alone. Equation (10) may thus be reduced to:

$$E = \frac{-k(U_r - V_r)}{(U + V) - (U_r + V_r)} \log \frac{U_r + V_r}{U + V} \quad (12)$$

or

$$E_i = \frac{-k(U_r - V_r) \log (U_r + V_r)}{(U + V) - (U_r + V_r)} + \frac{k(U_r - V_r) \log (U + V)}{(U + V) - (U_r + V_r)} \quad (13)$$

As the concentration of the test solution in the present investigation did not exceed 0.1 normal the error we introduce by putting $((U + V) - (U_r + V_r))$ equal to $-(U_r + V_r)$ does not exceed 3.5 %; as further the quantity $(U_r - V_r)$ is constant for each of the 6 bridge solutions, equation (13) may with good approximation be reduced to:

$$E_i = K_3 - k D \log (U + V) \quad (14)$$

where

$$D = \frac{U_r - V_r}{U_r + V_r} \quad (15)$$

and
$$K_3 = \frac{-k(U_r - V_r) \log (U_r + V_r)}{(U + V) - (U_r + V_r)}$$

If equation (14) is substituted in equation (8) we obtain:

$$\frac{E}{k} = K + 0.5 \sqrt{c} - \beta c + D \log (U + V) \quad (16)$$

the constant terms being combined in the constant K .

The bridge solution which eliminates the diffusion potential best leads to the value zero of the quantity $(D \log (U + V))$, *i. e.* equation (16) becomes:

$$\frac{E}{k} - 0.5 \sqrt{c} = -\beta c + K \quad (17)$$

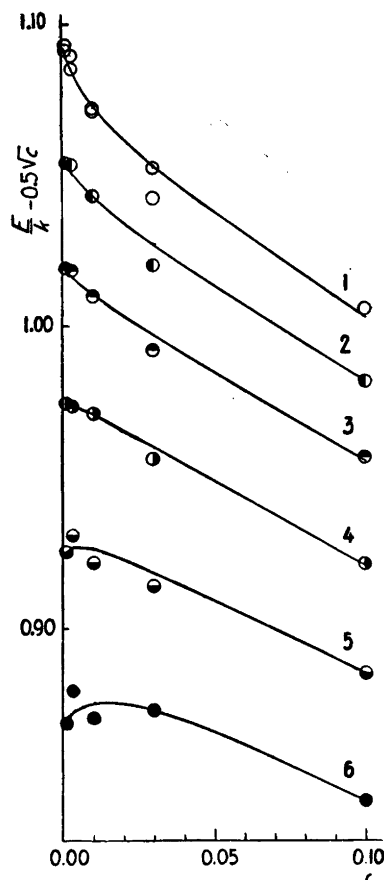


Fig. 2. Curves given by equation (17). Each curve corresponds to a given value of the ratio KCl/KNO_3 in the salt bridge. Presuming that the Debye-Hückel-Bronsted equation is valid, the curve should be a straight line. A straight line is best realized between curves (3) and (4), corresponding to the mol ratio $KCl/KNO_3 = 1$.

In order to examine in which of the 6 systems of Table 2 this elimination is best realized, the quantity $((E/k) - 0.5\sqrt{c})$ has been plotted as a function of c in Fig. 2. This should lead to a straight line with slope $-\beta$. The ordinates corresponding to the curves have been entered in columns (a) of Table 3.

Fig. 2 shows that systems (3) and (4) lead to almost straight lines; at the lowest concentrations, however, they deviate slightly in different directions. Thus, it seems reasonable to assume that a straight line would have been obtained between systems (3) and (4), *i. e.* corresponding to approximately equimolar concentrations of potassium chloride and potassium nitrate. Even though the present experiments do not allow of an accurate determination of the ratio between potassium chloride and potassium nitrate, they seem to indicate that mole ratios between 2 : 3 and 3 : 2 are able to eliminate the diffusion potential

Table 3. Column a gives the values of $E/k - 0.5 \sqrt{c}$ corresponding to equation (17) and Fig. 2. Column b gives the values of $E/k - 0.5 \sqrt{c} + 0.584 c$ corresponding to equation (18) and Fig. 3.

Concentration		0.001		0.003		0.01		0.03		0.1	
		a	b	a	b	a	b	a	b	a	b
System no.	1	1.093	1.094	1.085	1.086	1.071	1.077	1.042	1.060	1.005	1.063
	2	1.054	1.055	1.054	1.055	1.043	1.049	1.020	1.037	0.981	1.039
	3	1.019	1.020	1.019	1.020	1.010	1.016	0.992	1.010	0.956	1.014
	4	0.975	0.975	0.974	0.975	0.971	0.977	0.956	0.974	0.921	0.979
	5	0.925	0.926	0.931	0.933	0.922	0.928	0.914	0.932	0.885	0.943
	6	0.869	0.870	0.880	0.881	0.871	0.877	0.873	0.890	0.843	0.901
	1	1.091	1.092	1.090	1.091	1.072	1.078	1.052	1.069	1.005	1.063
log (U + V)			-0.398		-0.173		0.203		0.618		1.101

to such a degree that — even in extreme dilution — the results obtained are in good agreement with the activity laws.

The curves (3) and (4) have the slopes -0.632 and -0.535 , respectively; the mean of these slopes, -0.584 we denote $-\beta$. Substituting in equation (16) this leads to:

$$\frac{E}{k} - 0.5\sqrt{c} + 0.584 c = K + D \log (U + V) \quad (18)$$

In Fig. 3 the quantity $((E/k) - 0.5\sqrt{c} + 0.584 c)$ has been plotted as a function of $\log (U + V)$. Thus, D denotes the slope of the obtained lines. The coordinates corresponding to Fig. 3 have been entered in the columns (b) of Table 3. The values of $(U + V)$ have been calculated from data collected by

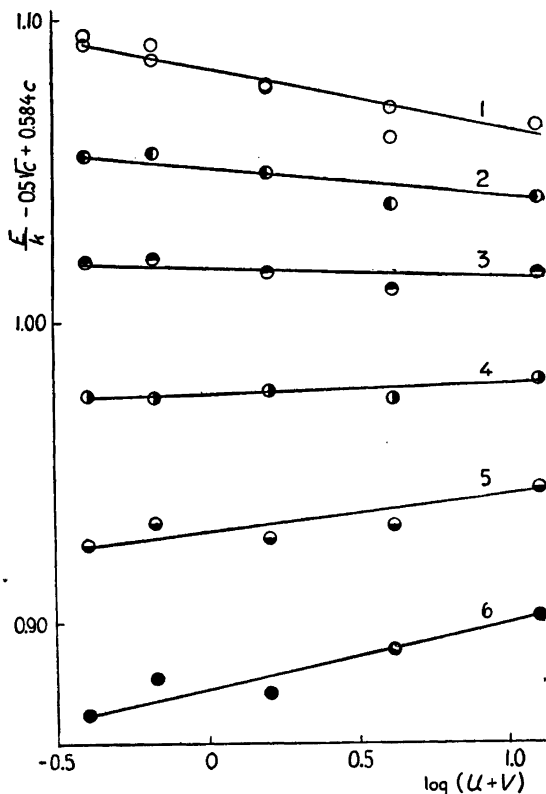


Fig. 3. Transformation of Fig. 2 corresponding to equation (18). The figure justifies the plotting of the curves in relation to the given points. Further, it is possible to calculate the cation transference for each of the bridge solutions used from the slope of the curves. The accuracy of this calculation, however, depends on the accuracy of the value chosen for β .

Harned and Owen⁹. Their values applied to 25° C and have here been corrected to 22° C by subtracting 5 %.

The slopes of the lines plotted for the 6 bridge solutions have been calculated as: $D_1 = -0.0203$, $D_2 = -0.0102$, $D_3 = -0.0036$, $D_4 = 0.0028$, $D_5 = 0.0118$, and $D_6 = 0.0213$.

From these values it is possible to calculate the cation transferences of the bridge solutions. Equation (1) and (15) lead to

$$t = \frac{1 + D}{2}$$

and we thus find the following 6 values for the cation transferences: $t_1 = 0.490$, $t_2 = 0.495$, $t_3 = 0.498$, $t_4 = 0.501$, $t_5 = 0.506$, and $t_6 = 0.511$.

If we compare the value t_1 (pure KCl) and t_6 (pure KNO_3) with the values given in Table 1 we find an agreement which may be considered a good veri-

fication of Henderson's formula. It must be emphasized that the transference values obtained cannot be attributed to any well-defined concentration but must be looked upon as representing the average condition of the boundary.

The slopes of the curves in Fig. 3 and the transference numbers calculated from them are dependent on the value allotted to the quantity β . This implies that the transference numbers determined are not appropriate to a calculation of the optimal ratio KCl/KNO_3 . The main use we can make of Fig. 3 is hereafter to find the course of the curves on Fig. 2 in relation to the plotted points, as one of these is a transformation of the other.

The choice of the mole ratio 1 : 1 is solely based on the estimate that the curvatures of the curves (3) and (4) in Fig. 2 take opposite directions and are equal in size. Unfortunately, it is not possible with the technique used here to obtain results so accurate as to allow a computation of the optimal ratio from the curvatures of the curves. It must therefore suffice to know that both curves (3) and (4) give a comparatively good agreement with the activity laws. When we consider how sensitive such very dilute solutions as we are dealing with here are to influences from without it seems doubtful whether the use of another kind of electrode could verify our presumption. It is a fact that in so diluted solutions it is often difficult to use the hydrogen electrode with satisfactory accuracy. Even though the glass electrode is known to give less reproducible results in general than the hydrogen electrode the present author has found that the former gives better results than the latter in solutions that are very dilute with respect to hydrochloric acid.

APPLICATION

By using an equitransferent bridge solution instead of saturated potassium chloride we gain partly the advantage that the formula for calculation is simplified, partly that we are working with smaller diffusion potentials on the whole, and it is not the least consequence that the diffusion potential decreases as the test solution becomes more diluted. As already mentioned the simplification obtained is that in equation (11) the quantity kBC becomes zero. In the above the problem has been elucidated through an example with univalent ions. If the test solution contains polyvalent ions the equation corresponding to equation (10) takes the form:

$$E_i = k \left(\frac{U - V}{(\bar{U} + \bar{V}) - (U_r + V_r)} - \frac{U_r - V_r}{(\bar{U} + \bar{V}) - (U_r + V_r)} \right) \log \frac{U_r + V_r}{\bar{U} + \bar{V}} \quad (19)$$

A
B
C

where $\bar{U} = \sum_i u_i z_i c_i$ and $\bar{V} = \sum_i v_i z_i c_i$

c denotes the molarity of the test solution and z the valency of the ions, taken positive.

In equation (19) the quantity B will be equal to zero. Thus we have the following general equation for the diffusion potential between an equitransferent uni-univalent bridge solution and a diluted solution:

$$E_t = \frac{RT}{F \log e} \cdot \frac{U - V}{(\bar{U} + \bar{V}) - (U_r + V_r)} \log \frac{U_r + V_r}{\bar{U} + \bar{V}} \quad (20)$$

Equation (20) shows that the diffusion potential decreases as the concentration of the bridge solution increases. In the above experiments the concentration has been 3 normal on account of the solubility of potassium nitrate. For equimolar mixtures of potassium chloride and potassium nitrate it is possible to use somewhat higher concentrations. In a thermostat at 25°C it is possible to use a 4 normal solution, but this has the drawback that the solution crystallises when it is left at room temperature. A 3.6 normal solution (1.8 N KCl + 1.8 N KNO_3) may be recommended because it is stable also at room temperature.

The present work cannot be concluded without an emphatic warning against the use of the common standard values for calomel electrodes in connection with the bridge solution suggested here, as these values are based on the use of saturated potassium chloride and thus include the corresponding diffusion potentials. The error which this implies may be estimated from Fig. 2 in which an unit in the ordinate is equal to one pH-unit. We must possibly except the E_0 -value given by Guggenheim and Schnindler¹⁰ for the decinormal calomel electrode as this value has been corrected for the diffusion potential with application of the new value for the transference number of potassium chloride.

Acree and collaborators⁶ have demonstrated that it is possible to obtain constant and reproducible calomel electrodes with mixtures of potassium chloride and potassium nitrate. The present author is not so far able to state an accurate E_0 -value for such a calomel electrode when using the above suggested bridge solution as reference electrode solution. This, however, does not prevent the use of such an electrode for ordinary work; *e. g.* when measuring hydrogen ion concentrations, a determination is simply made in a solution with known hydrogen ion activity and then the E_0 -value is calculated or the pH-value is calculated directly from the difference between the potentials of the standard and the test-solutions (due allowance being made for the diffusion potential).

The order of magnitude of the diffusion potentials found when we are working with equitransferent bridge solutions will be investigated later. Probably they are often so small that it is justifiable to disregard them altogether if the desired accuracy allows it.

On the whole when saturated potassium chloride is used as salt bridge or as reference electrode solution it has been recommended to standardise the determination of the hydrogen ion concentrations with standard buffer solutions instead of using the E_0 -value of a calomel electrode ^{7, 11, 12}. It seems probable that in certain cases the results obtained will equal those obtained with an equitransferent bridge solution or reference electrode solution, namely when the conductance of the standard- and the test-solution are of the same order of magnitude. If this is the case the contribution to the diffusion potential which is due to the differences between the cation and anion mobilities in the bridge solution (the quantity kBC in equation (11)) will be of no consequence as it will appear as a positive correction in one measurement and a negative one in another.

SUMMARY AND CONCLUSIONS

1. If the bridge solution is not equitransferent the diffusion potentials are large in very dilute solutions.

2. A concentrated equimolar solution of potassium chloride and potassium nitrate is considered equitransferent; since when it is used as bridge solution, the measurements are in agreement with the activity laws even when the test solution is extremely dilute. A 3.6 normal solution (1.8 *N* KCl + 1.8 *N* KNO₃) is suggested as bridge solution or reference electrode solution.

3. The bridge solution suggested should not be applied in connection with the known standard values for calomel electrodes. A solution of known hydrogen ion activity should be used as standard.

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