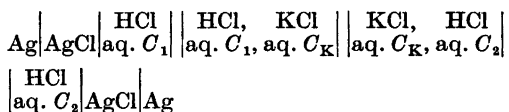# An Experimental and Theoretical Investigation of the Salt Bridge in Concentration Cells

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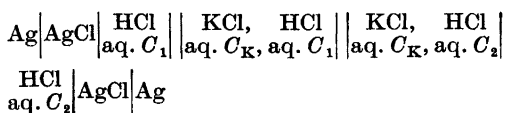
Measured and calculated emfs for the concentration cell

$$\text{Ag}\Big|\text{AgCl}\Big|\begin{matrix}\text{HCl}\\ \text{aq. } C_1\end{matrix}\Big|\Big|\begin{matrix}\text{HCl, KCl}\\ \text{aq. } C_1, \text{aq. } C_K\end{matrix}\Big|\Big|\begin{matrix}\text{KCl, HCl}\\ \text{aq. } C_K, \text{aq. } C_2\end{matrix}\Big|$$
$$\Big|\begin{matrix}\text{HCl}\\ \text{aq. } C_2\end{matrix}\Big|\text{AgCl}\Big|\text{Ag}$$

are compared. The junction between the two half cells is made such that the concentration of HCl(KCl) is kept close to constant over the range where the KCl(HCl) concentration changes. Adopting this specific experimental arrangement and introducing the assumption of constant mobility ratios, calculated and measured potentials agree within 1 % when $C_1$ and $C_2$ are varied between 0.1 M and 0.001 M and $C_K$ is varied from 0 to 4 M.

The salt bridge in concentration cells has been discussed in a previous communication.[1] The emf of a concentration cell containing two HCl solutions separated by a KCl salt bridge was calculated assuming ideal electrolyte solutions or Debye-Hückel activity coefficients (log $\gamma_\pm = -A\omega^{\frac{1}{2}}$ where $\omega$ is the ionic strength).

In the present paper this discussion will be extended to include also experimental data on concentration cells of the above type. The following cell

$$\text{Ag}\Big|\text{AgCl}\Big|\begin{matrix}\text{HCl}\\ \text{aq. } C_1\end{matrix}\Big|\Big|\begin{matrix}\text{KCl, HCl}\\ \text{aq. } C_K, \text{aq. } C_1\end{matrix}\Big|\Big|\begin{matrix}\text{KCl, HCl}\\ \text{aq. } C_K, \text{aq. } C_2\end{matrix}\Big|$$
$$\begin{matrix}\text{HCl}\\ \text{aq. } C_2\end{matrix}\Big|\text{AgCl}\Big|\text{Ag}$$

was studied with varying concentrations of HCl in the two half cells and with varying concentrations of KCl in the bridge. Since the cell

emf is a function of the form of the concentration gradients between the two electrolytes, the experiment should be arranged in such a way that the concentrations as functions of position in the cell are well defined. It is then possible to calculate in a rigorous manner the chemical work carried out in the salt bridge and its contacts with the two HCl solutions.

In the work of Henderson[2] a mixed boundary is assumed in the emf calculation. Guggenheim[3] showed how such boundaries could be obtained experimentally, and his results indicated that the junctions prepared were reproducible with a probable error of less than 0.2 mV. According to Planck[4] a so called restricted diffusion contact may be formed between the solution in the salt bridge. Using this method a rigorous calculation of the concentration gradients and the cell emf would involve an enormous amount of work.

By assuming a mixed boundary and that the activity coefficients of individual ions of an electrolyte are equal in all cases to the mean activity coefficient of that electrolyte (the Guggenheim assumption[5]), Hamer[6] calculated the liquid junction potentials for HCl−KCl junctions for varying concentrations of HCl and KCl. Using the same approximation for single ion activities Maronny and Valensi[7] estimated the HCl−KCl liquid junction potentials from measured potentials without specifying which type of junction they were using. Picknett[8] calculated the junction potential by a numerical method also involving assumptions regarding single ion activities.

It is well known that varying assumptions regarding single-ion activity coefficients will

lead to varying values of a calculated steady-state junction potential, but these differences must be cancelled by corresponding differences in calculated electrode potentials, so that the overall potential remains constant. The calculated junction and electrode potentials therefore have no absolute values. Instead of calculating separately such immeasurable potentials Mac-Innes and Longsworth [9] calculated the total cell potential for the cell

Ag|AgCl|HCl(0.1 M)||KCl(0.1 M)|AgCl|Ag
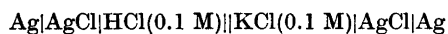
from experimentally determined transport numbers and activity coefficients assuming only a mixed boundary.

In the present work we will in a similar manner calculate the total cell potential and we will introduce assumptions which may or may not be verified experimentally.

In the present work we used a junction between the two half cells similar to the one previously discussed [1] where the concentration of HCl is kept approximately constant over the range where the KCl concentration changes. Similarly $C_{KCl}$ is approximately constant when $C_{HCl}$ is changing. Adopting this specific experimental arrangement, calculated and measured potentials may be compared.

In the present calculation some approximations concerning the mobilities of ions and activity coefficients of neutral components have been introduced. The transport numbers of the ions $K^+$, $H^+$, and $Cl^-$ have been measured by Longsworth [10] in the system $HCl-KCl-H_2O$ for a few concentrations at a total concentration of 0.1 M only. It was therefore necessary in the present emf calculations to introduce some simplifying assumptions to obtain transport numbers over the required concentration range. The activity coefficients of HCl and KCl are well known in pure electrolytes and also to some extent in $HCl-KCl-H_2O$ mixtures. The assumptions made with respect to the molar activity coefficients $y_{HCl}$ and $y_{KCl}$ in these mixtures are therefore quite reliable.

The emf of a cell of the above type is frequently expressed by quantities like single electrode potentials, liquid junction potentials, and single ion activities (see MacInnes [11]).

$$E = E_{el} - \frac{1}{F}\int \sum_i \frac{t_i}{z_i}\,d\mu_i = E_{el} - \frac{RT}{F}\int \sum_i \frac{t_i}{z_i}\,d\ln a_i \quad (1)$$

In this equation $E_{el}$ is the contribution to the emf from the electrode reactions, $t_i$ is the ionic transport number, $z_i$ is the singned number of charges of the i'th ion, $\mu_i$ is the chemical potential of that ion, and $a_i$ is the activity of the same ion. The integration is carried out over the whole cell.

For the present cell eqn. (1) may be written

$$E = \frac{1}{F}\Big|_{(1)}^{(2)}\mu_{HCl}t_H + \frac{1}{F}\int_{(1)}^{(2)} (\mu_{HCl}dt_H + \mu_{KCl}dt_K) \quad (2)$$

This equation may also be derived in an alternative way on the basis of classical irreversible thermodynamics where only measureable quantities are introduced. [12]

## EXPERIMENTAL

The hydrochloric acid solutions were made from Titrisol HCl ampullas containing 1 M, 0.1 M and 0.01 M HCl. The relative error in concentrations given in the text are within $\pm 0.05$ %. The potassium chloride-containing hydrochloric acid solutions were prepared by mixing predried potassium chloride and the content of a Titrisol ampulla and diluting with distilled water to a given volume. The silver-silver chloride electrodes were made by electrode-position of silver on 0.5 cm² platinum plates. The electrodes were chloridized by anodization in a dilute solution of HCl. In the same solution the difference in potential between these electrodes never amounted to more than 0.03 mV.

The galvanic cell was made of pyrex. The connection between the two half cells was made through a pyrex tube of 2 cm o.d. split in sections of about 5 cm length by relative coarse pyrex frits (No. 2 porosity $40-60$ $\mu$). Normally ten such sections were used. If we used pyrex frits with fine pores (e.g. No. 5 porosity 2 $\mu$), the potentials of the concentration cells containing HCl only, differed systematically $(0.5-4$ %), depending on the total HCl concentrations) from the theoretical value. This phenomen is probably due to a change in the ionic transport numbers inside the fine-sized pores. The concentrations of HCl and KCl in the central sections of the bridge could be changed in the course of the experiment, and by keeping pure HCl of concentration $C_1$ in the first left and of concentration $C_2$ in the first right hand sections of the bridge, KCl never entered into the electrode compartments which contained 0.75 l solution. The solutions were deoxygenized by bubbling nitrogen through the cell which was tilted so that the heavy KCl-rich solutions allways were at the lower end of the cell.

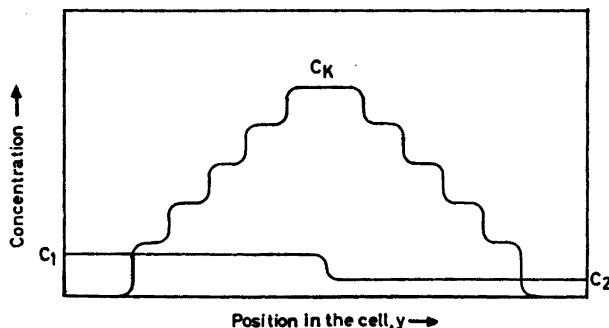The concentrations of the two electrolytes HCl and KCl as functions of the position along
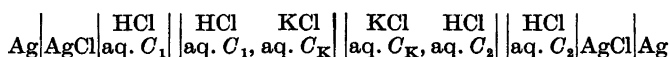
*Fig. 1.* The concentration of the two electrolytes HCl and KCl as functions of position, $y$, in the concentration cell

$$Ag\Big|AgCl\Big|\begin{matrix}HCl\\aq.\ C_1\end{matrix}\Big|\Big|\begin{matrix}HCl\quad KCl\\aq.\ C_1,\ aq.\ C_K\end{matrix}\Big|\Big|\begin{matrix}KCl\quad HCl\\aq.\ C_K,\ aq.\ C_2\end{matrix}\Big|\Big|\begin{matrix}HCl\\aq.\ C_2\end{matrix}\Big|AgCl\Big|Ag$$

the length of the cell, $y$, are shown schematically in Fig. 1. When the cell is assembled, there is a relatively large concentration gradient in KCl across each pyrex frit where $C_{KCl}$ is varying. The interdiffusion of $K^+$ and $H^+$ that starts in these concentration gradients may generate "humps" in the HCl concentrations at each step. These concentration changes will have an influence on the cell potential.

## RESULTS

In Table 1 the experimental potentials are presented. The standard deviation was 0.025 mV for the pure HCl concentration cells and around 0.12 mV for cells containing KCl. With the above mentioned experimental arrangement the cell potential was normally stable for 3 – 10 h after the cell had been assembled. The potential was normally stable from 10 to 20 h. Three typical potential *versus* time curves are shown in Fig. 2 for $C_{KCl} = 0.1$ M, 0.5 M, and 4.0 M in the KCl salt bridges. By constructing cells with approximately constant concentration of HCl throughout the cell and a large KCl gradient on the left and a small KCl gradient on the right side of the bridge, cell potentials around $-5$ to $-7$ mV were observed when the cell was assembled. These potentials decreased with time.[13] When a symmetrical KCl gradient was applied $0 \pm 0.05$ mV was observed after 3 – 10 h.[13] These observations are in agreement with the long times necessary to establish steady state conditions and thus stable potentials in the above concentration cells.

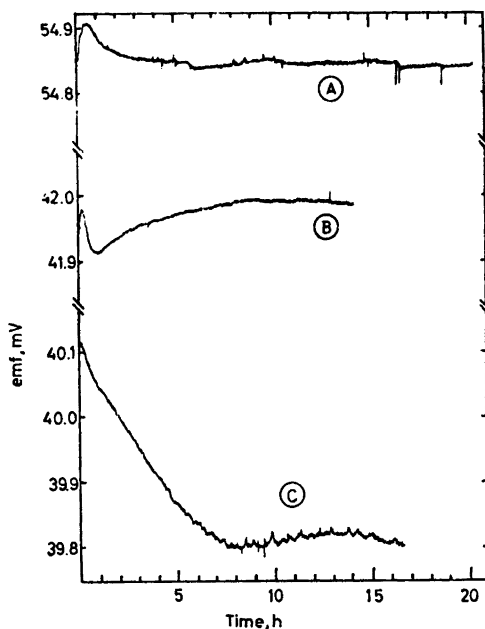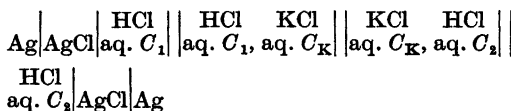In some cases when the concentration of KCl

*Fig. 2.* Potential *versus* time curves for the galvanic cell

$$Ag\Big|AgCl\Big|\begin{matrix}HCl\\aq.\ C_1\end{matrix}\Big|\Big|\begin{matrix}HCl\quad KCl\\aq.\ C_1,\ aq.\ C_K\end{matrix}\Big|\Big|\begin{matrix}KCl\quad HCl\\aq.\ C_K,\ aq.\ C_2\end{matrix}\Big|\Big|$$
$$\begin{matrix}HCl\\aq.\ C_2\end{matrix}\Big|AgCl\Big|Ag$$

at 25 °C.

A: $C_1 = 0.1$ mol/l, $C_2 = 0.01$ mol/l, and $C_K = 0.5$ mol/l

B: $C_1 = 0.001$ mol/l, $C_2 = 0.005$ mol/l, and $C_K = 0.1$ mol/l

C: $C_1 = 0.001$ mol/l, $C_2 = 0.005$ mol/l, and $C_K = 4.0$ mol/l

in the central part of the bridge was low (0.1 M), a steady increase in cell potential was observed after some time ($\simeq 0.05$ mV/h). This increase was due to a dilution of KCl in the central section of the bridge.

## DISCUSSION

We will now briefly go through the emf calculation and present the approximations introduced. As mentioned previously, the water framed ionic transport numbers $t_{K^+}$, $t_{H^+}$, and $t_{Cl^-}$ are not very well known in the KCl−HCl−H$_2$O system. We will therefore assume that the ionic transport numbers can be expressed by eqn. (3).

$$t_i = [(u_i/u_{Cl})C_i]/\sum_i (u_i/u_{Cl})C_i \qquad (3)$$

In this equation $u_i$ and $C_i$ represent ionic mobilities and concentrations, respectively. In our calculation we will assume that the mobility ratios $u_H/u_{Cl}$ and $u_K/u_{Cl}$ are independent of concentration.

Transport numbers calculated from eqn. (3) agree within 1 % with transport numbers measured by Longsworth [10] for a total concentration of 0.1 M HCl and KCl in the present ternary system. The mobility ratios used in eqn (3) to compare calculated and measured transport numbers, are average values of the mobility ratios in 0.1 M pure electrolytes and at infinite dilution. Using data from Longsworth,[14] these mobility ratios are $u_H/u_{Cl} = 4.773$ and $u_K/u_{Cl} = 0.9605$. We know that the ionic mobilities vary considerably with concentration. The variation in mobility ratios are, however, smaller $u_H/u_{Cl} = 4.618$ at infinite dilution and 4.928 in 0.1 M HCl. $u_K/u_{Cl} = 0.9621$ at infinite dilution and 0.9589 in 0.1 M KCl.

The approximation of constant mobility ratios are questionable at least for HCl solutions where the variation is about 6 % going from infinite dilution to 0.1 M HCl solutions. Even so we believe that a calculation of cell potentials of the above cell using eqn. (3) are worth while doing until accurate experimental transport numbers are known. The activity coefficients of HCl and KCl in water are very well known, and the following expression for $y_{HCl}$ in the system HCl-H$_2$O was based on the equation given by MacInnes [11] and formation cell data given by Harned and Ehlers [15]

($y_{HCl} = a_{HCl}/C_H C_{Cl}$, $y_{HCl} \to 1$ when $C_{HCl} \to 0$)

$$\ln y_{HCl} = -\frac{2.3284\,C_{HCl}^{\frac{1}{2}}}{1+1.1382\,C_{HCl}^{\frac{1}{2}}} + 0.8932\,C_{HCl} \qquad (4)$$

The molar activity coefficients calculated from eqn. (4) agree very well with experimental results for concentrations up to 0.1 M.

In the mixed system KCl−HCl−H$_2$O the following equation for the molar activity coefficient of HCl was used

$$\ln y_{HCl} = -\frac{2.3284\,\omega^{\frac{1}{2}}}{1+1.350\,\omega^{\frac{1}{2}}} + 0.4472\,C_{HCl} + 0.3050\,C_{KCl} \qquad (5)$$

where $\omega$ is the ionic strength of the solution.[11] This equation is based on work of Harned [16] and the coefficients are adjusted to fit experimental activity coefficients in the mixed KCl−HCl−H$_2$O system at 0.1 M and 0.01 M HCl concentrations at varying ionic strength.[16,17] At concentrations of KCl greater than 3 M, ln $y_{HCl}$ is roughly constant for constant HCl concentrations. This is accounted for in eqn. (5) by setting $C_{KCl} = 3$ M in solutions of higher potassium chloride concentrations. For KCl the following molar activity coefficient expression was used

$$\ln y_{KCl} = -\frac{2.3444\,\omega^{\frac{1}{2}}}{1+1.294\,\omega^{\frac{1}{2}}} + 0.04738\omega + 0.01985\omega^2 \qquad (6)$$

Experimental molar activity coefficients of KCl in mixtures with water may be accurately represented by this equations.[18] In the ternary HCl−KCl−H$_2$O system the experimental activity coefficients will deviate most markedly from coefficients calculated from eqn. (6) in the low potassium chloride concentration regions. Data are not available to construct equations of the form given by eqn. (5) for the KCl activity coefficient.

Introducing eqns. (3, 4, 5, and 6) into the expression for the emf of the cell, eqn. (2), and integrating over the concentration gradient as outlined in a previous communication [1] the following result is obtained

$$E = (RT/F)\left[ (2u_K/u_{Cl}) \ln (C_1/C_2)/[(u_K/u_{Cl}) + 1] + 2\{[(u_H/u_{Cl}) - (u_K/u_{Cl})]/[(u_H/u_{Cl}) + 1] \times [(u_K/u_{Cl}) + 1]\} \times \right.$$
$$\left. \ln \frac{1 + [(u_H/u_{Cl}) + 1]C_1/[(u_K/u_{Cl}) + 1]C_K}{1 + [(u_H/u_{Cl}) + 1]C_2/[(u_K/u_{Cl}) + 1]C_K} \right] + E^{corr} \qquad (7)$$

*Table 1.* Emf of the concentration cell

$$\text{Ag}\Big|\text{AgCl}\Big|\overset{\text{HCl}}{\text{aq. }C_1}\Big|\Big|\overset{\text{HCl, KCl}}{\text{aq.}C_1,\text{ aq. }C_K}\Big|\Big|\overset{\text{KCl, HCl}}{\text{aq. }C_K,\text{ aq. }C_2}\Big|\Big|\overset{\text{HCl}}{\text{aq. }C_2}\Big|\text{AgCl}\Big|\text{Ag}$$

as a functions of the HCl and KCl concentrations at 25 °C.

| Concentrations | | | Calculated potentials | | | Observed potentials $E^{obs}$ |
|---|---|---|---|---|---|---|
| HCl | | KCl | "Electrode potential" | Ideal | Debye-Hückel | |
| $C_1$ mol/l | $C_2$ mol/l | $C_K$ mol/l | eqn. (8) mV | $E$(eqn. (7)]$-E^{corr}$ mV | $E$(eqn. (7)) mV | mV |
| 0.1 | 0.02 | 0 | | 68.30 | 64.59[a] | 64.59 |
| | | 0.1 | | 56.17 | 53.03 | 53.21 |
| | | 4.0 | 38.95 | 41.40 | 35.59 | 35.51 |
| 0.1 | 0.01 | 0 | | 98.01 | 92.63[a] | 92.65 |
| | | 0.1 | | 77.42 | 73.02 | 73.22 |
| | | 0.5 | | 65.06 | 60.23 | 60.59 |
| | | 1.5 | | 60.76 | 54.51 | 54.84 |
| | | 4.0 | 55.94 | 59.07 | 51.81 | 51.78 |
| 0.1 | 0.005 | 0 | | 127.28 | 120.83[a] | 120.82 |
| | | 0.1 | | 96.79 | 91.74 | 92.07 |
| | | 0.4 | 73.09 | 76.56 | 68.48 | 68.27 |
| 0.1 | 0.001 | 0 | | 195.66 | 187.21[a] | 187.11 |
| | | 0.1 | | 139.18 | 133.42 | 133.20 |
| | | 4.0 | 113.46 | 117.12 | 108.19 | 108.70 |
| 0.02 | 0.01 | 0 | | 29.41 | 28.04[a] | 28.05 |
| | | 0.1 | | 20.97 | 19.98 | 20.11 |
| | | 4.0 | 16.99 | 17.59 | 16.22 | 16.35 |
| 0.005 | 0.001 | 0 | | 68.09 | 66.39[a] | 66.36 |
| | | 0.1 | | 42.19 | 41.61 | 41.71 |
| | | 4.0 | 40.37 | 40.38 | 39.71 | 39.81 |

[a] The potentials for the pure HCl//HCl concentration cell are calculated from the equation

$$E= \frac{1}{F}\Big|_{(1)}^{(2)} \mu_{HCl}t_H + \frac{1}{F}\int_{(1)}^{(2)} \mu_{HCl}dt_H$$

using experimental transport numbers [14] and chemical potentials.[15]

In this equation the term $E^{corr}$ is due to activity coefficient corrections. The mobility ratios $u_H/u_{Cl}$ are average values and the numbers used in the present calculations are given in Table 2. The ionic mobility ratio $u_K/u_{Cl}$ seems to be relatively constant with varying concentration of KCl [10] and we have adopted the value 0.96.

$C_1$ and $C_2$ are the HCl concentrations in the left and right solution, respectively, and $C_K$ is the concentration of KCl in the salt bridge. In Table 1 the potentials calculated by eqn. (7) are compared with experimental values.

For the above cell the following equation for the cell potential is often written

$$E = (RT/F) \ln [C_{Cl}(1)y_\pm(1)/C_{Cl}(2)y_\pm(2)] \qquad (8)$$

when the liquid junction potential across the salt bridge is neglected [*cf.* eqn. (1)]. This

*Table 2.* Average ionic mobility ratios at 25 °C in the ternary system HCl−KCl−H$_2$O calculated from experimental mobilities by Longsworth.[10]

| Concentration of HCl in mol/l | | Average ionic mobility ratios | |
|---|---|---|---|
| $C_1$ | $C_2$ | $u_H/u_{Cl}$ | $u_K/u_{Cl}$ |
| 0.1 | 0.01 | 4.826 | 0.96 |
| 0.1 | 0.02 | 4.846 | 0.96 |
| 0.1 | 0.001 | 4.775 | 0.96 |
| 0.1 | 0.005 | 4.775 | 0.96 |
| 0.01 | 0.02 | 4.741 | 0.96 |
| 0.005 | 0.001 | 4.62 | 0.96 |
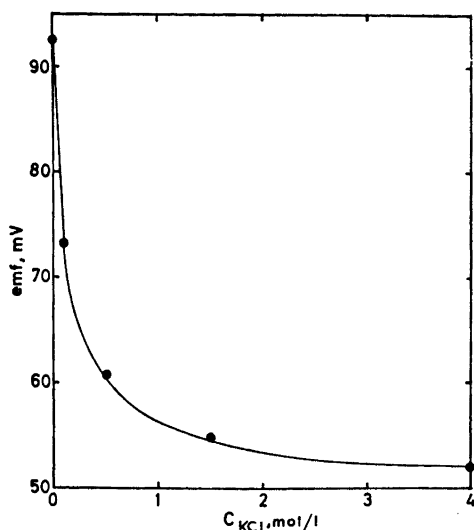
*Fig. 3.* Potential *versus* concentration of KCl, $C_{KCl}$, in the salt bridge for the galvanic cell

$$Ag\Big|AgCl\Big|\begin{matrix} HCl \\ 0.1\,M \end{matrix}\Big|\Big|\begin{matrix} HCl,\ KCl \\ 0.1\,M,\ C_K \end{matrix}\Big|\Big|\begin{matrix} HCl,\ KCl \\ 0.01\,M,\ C_K \end{matrix}\Big|\Big|\begin{matrix} HCl \\ 0.01\,M \end{matrix}\Big|$$

$$AgCl\Big|Ag$$
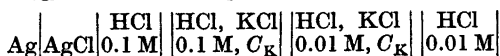
at 25 °C. Full drawn line, calculated; ●, experimental.

potential is also compared with experimental potentials in Table 1.

From Table 1 it is observed that while both the potential given by eqn. (8) and the ideal solution potential, $E$[eqn. (7)] $- E^{corr}$, deviate markedly from the experimental potentials, there is a very good agreement between observed potentials and potentials calculated by eqn. (7).

In Fig. 3 calculated and measured potentials for cells containing 0.1 M HCl and 0.01 M HCl in the two half cells and varying concentration of KCl in the salt bridge are plotted *versus* $C_{KCl}$. At low potassium chloride concentrations the cell potential is very dependent on $C_{KCl}$ while the variation in emf is rather small at concentrations higher than $C_{KCl} = 2$ M. It is therefore important to use high concentration of KCl in standard salt bridges of the above type.

We know that the mobility ratios $u_i/u_{Cl}$ do vary with concentration, and the use of constant mobility ratios therefore probably represents the most serious error in the above calculations. With experimentally known activities

and ionic transport numbers we should probably be able to come even closer to the experimentally obtained potentials than is the case in the present calculation. The degree of consistency between experimentally and theoretically obtained potentials, would then give an indication on the reliability of the assumption regarding the concentration gradients made in the emf calculations.

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