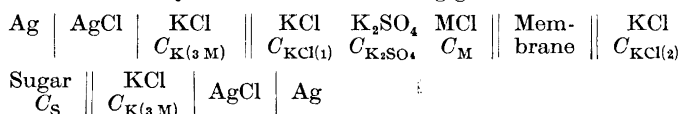# The Donnan Potential II

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The Donnan potential is calculated on the basis of classical irreversible thermodynamics for the following galvanic cell:

$$\text{Ag} \mid \text{AgCl} \mid \underset{C_{\text{K}(3\,\text{M})}}{\text{KCl}} \parallel \underset{C_{\text{KCl}(1)}}{\text{KCl}} \ \underset{C_{\text{K}_2\text{SO}_4}}{\text{K}_2\text{SO}_4} \ \underset{C_{\text{M}}}{\text{MCl}} \parallel \underset{\text{brane}}{\text{Mem-}} \parallel \underset{C_{\text{KCl}(2)}}{\text{KCl}}$$

$$\underset{C_{\text{S}}}{\text{Sugar}} \parallel \underset{C_{\text{K}(3\,\text{M})}}{\text{KCl}} \mid \text{AgCl} \mid \text{Ag}$$

The membrane is permeable to water, K^+ and Cl^- ions, but impermeable to the M^+ and $\text{SO}_4{}^{2-}$ ions. When chemical equilibrium is obtained across the membrane, the emf for the present cell can be approximated by the equation
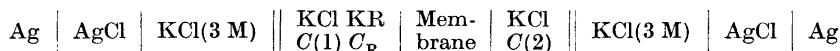
$$E = \frac{RT}{F} \left\{ \ln \frac{C_{\text{Cl}(2)}}{C_{\text{Cl}(1)}} + \frac{u_{\text{K}} - \frac{1}{2}u_{\text{SO}_4}}{u_{\text{K}} - u_{\text{SO}_4}} \ln \left(1 - \frac{u_{\text{SO}_4} - u_{\text{K}}}{u_{\text{K}}} \frac{C_{\text{SO}_4}}{C_{\text{K}(3\,\text{M})}} \right) \right.$$
$$\left. - \ln \left(1 - \frac{C_{\text{M}}(u_{\text{K}} - u_{\text{M}})}{2C_{\text{K}(3\,\text{M})}u_{\text{K}} + 2C_{\text{SO}_4}(u_{\text{SO}_4} - u_{\text{K}})} \right) \right\}$$

In the present cell the concentration of potassium sulfate in the left hand half cell is much smaller than the concentration of potassium chloride in the 3 molar (3 M) potassium chloride salt bridge. The second term on the right hand side of the above equation is therefore negligible. Since the metal chloride concentration in the left hand half cell also is negligible compared to 3 M the third term in the above equation is also negligible and the emf of the above cell can be further approximated by
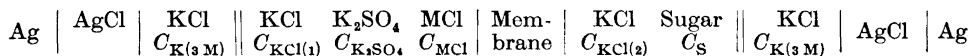
$$E \simeq \frac{RT}{F} \ln \frac{C_{\text{Cl}(2)}}{C_{\text{Cl}(1)}}$$

which is the result obtained experimentally for cells of the above type.

In a recent paper Førland and Østvold[1] calculated the Donnan potential for the following galvanic cell

$$\text{Ag} \mid \text{AgCl} \mid \text{KCl(3 M)} \parallel \underset{C(1)\ C_{\text{R}}}{\text{KCl KR}} \mid \underset{\text{brane}}{\text{Mem-}} \mid \underset{C(2)}{\text{KCl}} \parallel \text{KCl(3 M)} \mid \text{AgCl} \mid \text{Ag}$$

The membrane was considered permeable to water, K^+, and Cl^- ions, but impermeable to the large organic anion R^-. In the calculation of the Donnan potential for the present cell

$$\text{Ag} \left| \text{AgCl} \right| \begin{array}{c} \text{KCl} \\ C_{K(3M)} \end{array} \left\|\, \begin{array}{ccc} \text{KCl} & \text{K}_2\text{SO}_4 & \text{MCl} \\ C_{KCl(1)} & C_{K_2SO_4} & C_{MCl} \end{array} \right| \begin{array}{c} \text{Mem-} \\ \text{brane} \end{array} \left| \begin{array}{cc} \text{KCl} & \text{Sugar} \\ C_{KCl(2)} & C_S \end{array} \right\| \begin{array}{c} \text{KCl} \\ C_{K(3M)} \end{array} \left| \text{AgCl} \right| \text{Ag}$$

the only assumptions introduced are the ideal solution approximation, the assumption of zero mobilities for SO_4^{2-} and M^+ ions in the membrane phase and the assumption of constant relative mobilities in electrolyte solutions. The Donnan potential is a concept very frequently used in the discussion of biological systems, and it is introduced in the calculations of transport processes in biological membranes. Fig. 1 shows a schematic diagram of a galvanic cell with a membrane separating the two half cells. The membrane is permeable to the K^+ and Cl^- ions, but impermeable to the SO_4^{2-} and M^+ ions.

The potential established over the membrane is called the Donnan potential. As K^+ and Cl^- are free to migrate between the two compartments of the cell separated by the membrane, the chemical potential of KCl, μ_{KCl}, must after some time be equal on both sides of the membrane. If the solutions are sufficiently dilute, they can be treated as ideal ionic solutions, and we may write

$$RT \ln C_{K(1)} C_{Cl(1)} = RT \ln C_{K(2)} C_{Cl(2)}$$

or

$$C_{K(1)} C_{Cl(1)} = C_{K(2)} C_{Cl(2)} \tag{1}$$

which is the Donnan equilibrium. This equation was derived by Donnan and Guggenheim.[2]

When an equation for an electric potential difference, or the emf of a cell, is written, it should be said how it can be measured, and what the electrodes should be like. If the electrodes of the cell in Fig. 1 were reversible to Cl^- (e.g
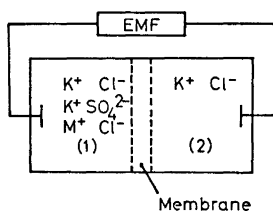

Fig. 1. A schematic diagram of a galvanic cell constructed to study the Donnan potential. The membrane is permeable to water molecules and K^+ and Cl^- ions, but not to the M^+ and SO_4^{2-} ions.

Ag/AgCl electrodes), the total cell reaction would be the transfer of KCl from the left hand side to the right hand side of the cell. (The quantity transferred per Faraday would be given by the transport number of K^+ in the membrane.) But since the chemical potential of KCl is equal on both sides of the membrane, the total cell reaction gives no change in Gibbs energy, and the emf must be zero. The same result would be obtained if the electrodes were reversible to the K^+ ion. This type of reasoning was also used by Babcock and Overstreet[3]

in their discussion of the use of calomel half cells to measure Donnan potentials in 1953, but seems to have been ignored by most scientists discussing Donnan potentials in later years.

Most of the measurements in biology of potentials over membranes are carried out with micro electrodes consisting of a pipette filled with a high concentration KCl-solution, into which an electrode reversible to Cl⁻ is introduced. In such cases it has been assumed that processes taking place in the liquid junction at the tip of the pipettes would not contribute to the measured emf by any significant amount. It will be shown that this assumption is far from beeing valid.
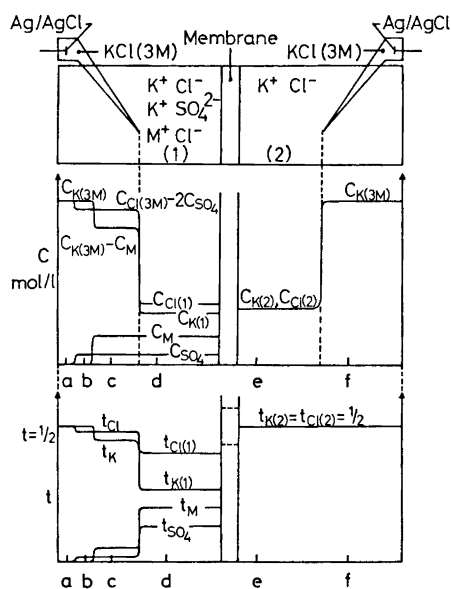
Fig. 2. A schematic diagram of a special galvanic cell constructed to study the Donnan potential together with diagrams of the variations of the concentration of the K^+, M^+, Cl^-, and SO_4^{2-} ions and the transport numbers of the K^+, M^+, Cl^-, and SO_4^{2-} ions through the cell.

To calculate the emf of the cell shown in Fig. 2, a small positive charge, ΔQ, is allowed to pass under reversible conditions from left to right in the cell during a short period of time, Δt. It has been shown in previous papers by Førland [4] and by Førland et al.,[5] that the outer electric work (in the potentiometer) $\Delta Q E$, where E is the emf of the cell, is connected to that part of the Gibbs energy change occurring in the cell which is dependent on ΔQ, but not on Δt. One may thus write

$$\Delta Q E + \frac{\Delta Q}{F} \Delta G_Q = 0 \qquad (2)$$

where ΔG_Q is the change in Gibbs energy following the cell reaction per Faraday of charge transferred. ΔG_Q can be calculated when the cell reaction is known and when the transport number, t_i, and the chemical potentials, μ_i,

of the components of the cell have been measured. ΔG_Q is given by the following equations (see Førland et al. [5]):

$$\Delta G_Q = \Delta G_{el} - \int \sum_i \mu_i dt_i \atop \substack{\text{over} \\ \text{cell}}$$ (3)

where ΔG_{el} is the change in Gibbs energy close to the two electrodes. In the present cell the two electrodes and their close surroundings are identical and $\Delta G_{el} = 0$.

The integral $-\int \sum_i \mu_i dt_i$ gives the change in Gibbs energy due to change in composition by charge transfer in the different sections of the cell. In any region where all t_i are constant the change in Gibbs energy is zero. To describe the change in composition of the electrolyte in the different sections of the cell, the choice of frame of reference for all transports have no influence on the final result. For the region of concentration gradients in the electrolyte it is most practical to refer to water as frame of reference.

In the region of the membrane it may sometimes be more practical to refer all transport to the membrane as a frame of reference. Knowing the transport numbers of the components KCl and H_2O one will then be able to tell how much of each component was added to each side of the membrane by the charge transfer. In the present case, however, this is of no interest for the emf calculation since the chemical potential is constant both for KCl and for H_2O in the region from d to e. This may be obtained by adding a neutral molecule like sugar to the right hand side of the cell, or by keeping a pressure difference, which has to be corrected for in the emf. So in the region of the membrane we may just as well use water as frame of reference as was done in the other regions of the cell.

With water as the frame of reference eqn. (3) becomes

$$\Delta G_Q = - \int_a^f \mu_{KCl} dt_{KCl} - \int_a^f \mu_{MCl} dt_{MCl} - \int_a^f \mu_{K_2SO_4} dt_{K_2SO_4}$$ (4)

With electrodes reversible to the Cl^- anions, t_{MCl} obtained from the Hittorf experiment is the same as the transport numbers of M^+ ions, t_M. The transport coefficient for potassium sulfate, $t_{K_2SO_4}$, obtained from the Hittorf experiment, is the same as minus one half times the transport number of SO_4^{2-} ions, t_{SO_4}, because the negative divalent sulfate ion is migrating in the negative direction. The change in KCl content following the Hittorf experiment can be expressed by t_{KCl} and it is easily seen that t_{KCl} is related to the transport numbers of the K^+ and SO_4^{2-} ions through the following equation:

$$t_{KCl} = t_K + t_{SO_4}$$

When ionic transport numbers are introduced eqn. (4) attains the form

$$\Delta G_Q = - \int_a^f \mu_{KCl} d(t_K + t_{SO_4}) - \int_a^f \mu_{MCl} dt_M + \tfrac{1}{2} \int_a^f \mu_{K_2SO_4} dt_{SO_4}$$ (5)

With water as our frame of reference, the membrane (and the walls of the container) will move by the charge transfer. If t_{H_2O} with membrane as frame of reference is positive, then the membrane will move from right to left with water as frame of reference. Since the membrane is assumed to be impermeable to SO_4^{2-} and M^+, this means that MCl and K_2SO_4 must be transported in the same direction as the membrame in a region close to the membrane. As, however, this is transport of components over a region where their chemical potentials are constant, it gives no contribution to the emf.

Principally we should also have a term $-\int \mu_{membrane} dt_{membrane}$ in ΔG_Q. However, the membrane is supposed to be in equilibrium with the KCl and water during the whole process of charge transfer. Thus any movement of these components between d and e with respect to the membrane does not contribute to $\Delta G_Q'$, or any movement, with respect to water, of membrane and KCl within the same region does not contribute to ΔGQ. Therefore the term $-\int \mu_{membrane} dt_{membrane}$ is zero. Further it is sufficient to know the transport coefficient of KCl at the points d and e. The variation in transport coefficient between these points will have no influence on ΔG_Q.

It is thus shown that the change in Gibbs energy by charge transfer can be calculated by eqn. (5) and detailed knowledge about transports in the region from d to e is not needed for the emf calculation.

The transport number t_K is a function of composition and may change along the length of the galvanic cell in a way similar to what is shown in Fig. 2. This means that KCl will be added to the region where the left hand side electrolyte comes in contact with the KCl-solution of the KCl salt bridge. In this region one can observe from Fig. 2 that dt_K is negative. The major change will take place at concentrations close to $C_{KCl(1)}$ since the changes in transport number with distance along the length of the cell is greatest in this region. In this region KCl is transported from a high to a low concentration. This is a source of free energy which is transformed to electric energy in the outer circuit of the galvanic cell.

It should be mentioned that the left hand side KCl salt bridge has been given a MCl and K_2SO_4 content in that part of the bridge which is close to electrolyte(1) of the cell. This is to make the liquid junction reproducible and well defined, and it simplifies the calculation of the integral in eqn. (5), and diffusion data are not needed. It is reasonable to assume that this type of liquid junction will give the same potential as the one usually made. An experimental test of the above assumptions is now in progress. Similar assumptions were made in a previous paper by Førland and Østvold [6] where the emf of a concentration cell containing a KCl salt bridge was calculated.

The major drop in t_K back to the value $\frac{1}{2}$ takes place in the region of the membrane. The quantities of salt coming to either side of the membrane is determined by the transport number, t_K, in the membrane. Due to the Donnan equilibrium established across the membrane μ_{KCl} is constant from one side to the other, and we do not have to know the transport number in the membrane to calculate the chemical work, ΔG_Q, caused by the charge transfer.

As the major part of the transport takes place in concentration ranges around $C_{KCl(1)}$ and since the activity coefficients are usually not known for

such systems, we may operate with low values of C_{KCl} and assume that the solutions are close to ideal. We will then have from eqn. (5) remembering that

$$t_K + t_{SO_4} = 1 - t_{Cl}$$

$$\Delta G_Q = \int_a^b (\mu^\circ_{KCl} + RT \ln C_K C_{Cl}) dt_{Cl} + \tfrac{1}{2}\int_a^b (\mu^\circ_{K_2SO_4} + RT \ln C_K{}^2 C_{SO_4}) dt_{SO_4}$$

$$- \int_b^e (\mu^\circ_{KCl} + RT \ln C_K C_{Cl}) d(t_K + t_{SO_4}) - \int_b^e (\mu^\circ_{MCl} + RT \ln C_M C_{Cl}) dt_M$$

$$+ \tfrac{1}{2}\int_b^e (\mu^\circ_{K_2SO_4} + RT \ln C_K{}^2 C_{SO_4}) dt_{SO_4} \tag{6}$$

or

$$\Delta G_Q = RT\{\int_a^b \ln C_K C_{Cl} dt_{Cl} + \tfrac{1}{2}\int_a^b \ln C_K{}^2 C_{SO_4} dt_{SO_4} - \int_b^e \ln C_K C_{Cl} dt_K$$

$$- \int_b^e \ln C_M C_{Cl} dt_M + \int_b^e (\tfrac{1}{2} \ln C_K{}^2 C_{SO_4} - \ln C_K C_{Cl}) dt_{SO_4}\} \tag{7}$$

If we assume that the mobility ratios u_i/u_j of the ions K^+, M^+, $SO_4{}^{2-}$, and Cl^- are independent of the concentrations, the transport number of these ions will be simple functions of the concentrations. We thus have

$$t_K = \frac{u_K C_K}{u_K C_K + u_{Cl} C_{Cl} + u_M C_M + 2u_{SO_4} C_{SO_4}} \tag{8}$$

and similarly for the other transport numbers. These transport numbers will change in the following regions of the galvanic cell; $(a-b)$, $(b-c)$, $(c-d)$ and $(d-e)$ (see Fig. 2). In the region $(a-b)$ we have

$$dt_{Cl} = -\frac{2u_{K_2SO_4} u_{Cl} C_{K(3\,M)}}{[C_{K(3\,M)} u_{KCl} + 2C(u_{SO_4} - u_{Cl})]^2} dC \tag{9}$$

$$dt_{SO_4} = \frac{2u_{KCl} u_{SO_4} C_{K(3\,M)}}{[C_{K(3\,M)} u_{KCl} + 2C(u_{SO_4} - u_{Cl})]^2} dC \tag{10}$$

In these equations $u_{KCl} = u_K + u_{Cl}$, $u_{K_2SO_4} = u_K + u_{SO_4}$ and C is the concentration of $SO_4{}^{2-}$ in the electrolyte. In the region $(b-c)$ we have

$$dt_K = -\frac{u_K(C_{K(3\,M)} u_{MCl} + 2C_{SO_4}(u_{SO_4} - u_{Cl}))}{[C_{K(3\,M)} u_{KCl} + C(u_M - u_K) + 2C_{SO_4}(u_{SO_4} - u_{Cl})]^2} dC \tag{11}$$

$$dt_M = \frac{u_M[C_{K(3\,M)} u_{KCl} + 2C_{SO_4}(u_{SO_4} - u_{Cl})]}{[C_{K(3\,M)} u_{KCl} + C(u_M - u_K) + 2C_{SO_4}(u_{SO_4} - u_{Cl})]^2} dC \tag{12}$$

$$dt_{SO_4} = -\frac{2u_{SO_4}(u_M - u_K) C_{SO_4}}{[C_{K(3\,M)} u_{KCl} + C(u_M - u_K) + 2C_{SO_4}(u_{SO_4} - u_{Cl})]^2} dC \tag{13}$$

In eqn. (11) to eqn. (13) $u_{MCl} = u_M + u_{Cl}$ and C is the concentration of M^+ in the electrolyte.

In the region (c − d) the M^+ and SO_4^{2-} concentrations are constant and we can express the variation the ionic transport numbers as functions of the variations in the concentration of K^+ ions.

We thus have

$$dt_K = \frac{u_K(C_M u_{MCl} + 2C_{SO_4}(u_{SO_4} - u_{Cl}))}{[Cu_{KCl} + C_M u_{MCl} + 2C_{SO_4}(u_{SO_4} - u_{Cl})]^2} \, dC \tag{14}$$

$$dt_M = -\frac{C_M u_M u_{KCl}}{[Cu_{KCl} + C_M u_{MCl} + 2C_{SO_4}(u_{SO_4} - u_{Cl})]^2} \, dC \tag{15}$$

$$dt_{SO_4} = -\frac{2C_{SO_4} u_{SO_4} u_{KCl}}{[Cu_{KCl} + C_M u_{MCl} + 2C_{SO_4}(u_{SO_4} - u_{Cl})]^2} \, dC \tag{16}$$

In these equations C is the concentration of K^+ ions in the electrolyte.

Since potassium chloride is the only component transported across the membrane during charge transfer the integral from d to e in eqn. (7) can be simplified. Since μ_{KCl} is constant from one side of the membrane to the other, that part of the integral which is due to potassium chloride transport can be simplified to $-RT(t_{KCl(2)} - t_{KCl(1)}) \ln C_{K(1)} C_{Cl(1)}$. The metal chloride, MCl, is transported to the membrane at the left hand side and since the transport numbers of the metal ion is zero in the membrane the chemical work occurring at the membrane interface due to MCl-transport is given approximately by $-RT(-t_{MCl(1)}) \ln C_M C_{Cl(1)}$. The contribution to the integral from d to e in eqn. (7) from potassium sulfate transport is analogously given by $-RT(-t_{K_2SO_4(1)}) \ln C_{K(1)}{}^2 C_{SO_4}$.

In the half cell on the right hand side the concentrations of potassium and chloride are equal and as a consequence of this t_K is constant in this region. Introducing these results and eqns. (8 − 16) into eqn. (7) gives the following equation for the change in Gibbs energy per Faraday for the cell reaction (see Appendix for calculations):

$$\Delta G_Q = RT\left[\ln\frac{C_{Cl(1)}}{C_{Cl(2)}} - \frac{u_{Cl} - \frac{1}{2}u_{SO_4}}{u_{Cl} - u_{SO_4}}\ln\left(1 - \frac{u_{SO_4} - u_{Cl}}{u_{Cl}}\frac{C_{SO_4}}{C_{K(3\,M)}}\right)\right.$$
$$\left. + \ln\left(1 - \frac{C_M(u_{Cl} - u_M)}{2C_{K(3\,M)}u_{Cl} + 2C_{SO_4}(u_{SO_4} - u_{Cl})}\right)\right] \tag{17}$$

and the emf of the cell is

$$E = \frac{RT}{F}\left[\ln\frac{C_{Cl(2)}}{C_{Cl(1)}} + \frac{u_{Cl} - \frac{1}{2}u_{SO_4}}{u_{Cl} - u_{SO_4}}\ln\left(1 - \frac{u_{SO_4} - u_{Cl}}{u_{Cl}}\frac{C_{SO_4}}{C_{K(3\,M)}}\right)\right.$$
$$\left. - \ln\left(1 - \frac{1}{2}\frac{C_M(u_{Cl} - u_M)}{C_{K(3\,M)}u_{Cl} + C_{SO_4}(u_{SO_4} - u_{Cl})}\right)\right] \tag{18}$$

The last two terms in this equation are very small since $C_{SO_4}{}^{2-}$ and $C_M{}^+$ are very small compared to 3 M and they can therefore probably be neglected in view of the approximation introduced by assuming ideal solution behaviour of the electrolyte. We thus obtain an equation for the emf of the cell which

is identical to an equation usually presented as the Donnan potential equation. This equation is, however, constructed by operating with single ion activities which are not measurable quantities and by neglecting processes taking place at the liquid junction of the KCl bridge (see, e.g., Aidly [7]), processes which in this case are the major sources of free energy change contributing to the emf.

In the paper mentioned above by Førland and Østvold [1] the Donnan potential was calculated for the cell containing KCl and KR only. Zero mobility for the R^- ion in the membrane was assumed. The following result was obtained

$$E = \frac{RT}{F}\left[\ln\frac{C_{\text{Cl}(2)}}{C_{\text{Cl}(1)}} + \ln\left(1 + \frac{u_R - u_{\text{Cl}}}{2u_{\text{Cl}}}\frac{C_R}{C_{\text{K}(3\,\text{M})}}\right)\right] \qquad (19)$$

showing that the emf of the cell can be approximated by the first term in this equation as long as $C_R \ll 3\,\text{M}$. If we had used saturated KCl salt bridges in these emf calculations, the equation for the emf would have been slightly different, but the difference can be neglected in view of the ideal solution approximation used in the calculations.

Yuasa et al. [8] measured the emf of the cell

$$\text{Hg}\ \bigg|\ \text{Hg}_2\text{Cl}_2\ \bigg|\!\begin{array}{c}\text{KCl}\\(\text{satd.})\end{array}\!\bigg|\!\bigg|\!\begin{array}{c}\text{K}^+\text{PSS}^-(x)\\\text{K}^+\text{Cl}^-\end{array}\!\bigg|\ \text{Membrane}\ \bigg|\ \text{KCl (C)}\ \bigg|\!\bigg|\!\begin{array}{c}\text{KCl}\\(\text{satd.})\end{array}\!\bigg|\ \text{Hg}_2\text{Cl}_2\ \bigg|\ \text{Hg}$$

where the membrane is permeable to water K^+ and Cl^- but not to the polystyrene-sulfonate ion. The emf of the cell was measured as a function of C (concentration of KCl in the right hand half cell) and X (concentration of potassium polystyrenesulfonate in the left hand half cell). Their results agree with eqn. (19) within 0.2 mV. Instead of making the emphasis on undefined or irrelevant local electric potential differences in the galvanic cell by the calculation of an emf, as is very frequently done, it is demonstrated in this paper that the emphasis should be on the gradients of chemical potential of neutral components of the cell and how the concentration of these components is changed by charge transfer, that means on the coupling between transport of charge and transport of components.

The method outlined above will be applied to other potential calculations related to biological membranes.

APPENDIX

When eqns. (8 – 16) are introduced into eqn. (7) and the integral over the membrane from d to e is calculated as outlined in the text, the change in Gibbs energy per Faraday in the above galvanic cell following the transfer of positive charge from the left to the right hand electrode at equilibrium conditions is given by the following equation:

$$\frac{\Delta G_Q}{RT} = - \frac{2u_{K_2SO_4}u_{Cl}C_{K(3\,M)}}{4(u_{SO_4} - u_{Cl})^2} \int\limits_0^{C_{SO_4}} \frac{\ln C_{K(3\,M)} + \ln (C_{K(3\,M)} - 2C)}{\left(C + \dfrac{u_{KCl}}{2(u_{SO_4} - u_{Cl})}C_{K(3\,M)}\right)^2}\,dC$$

$$+ \frac{u_{SO_4}C_{K(3\,M)}}{4(u_{SO_4} - u_{Cl})^2} \int\limits_0^{C_{SO_4}} \frac{2\ln C_{K(3\,M)} + \ln C}{\left(C + \dfrac{u_{KCl}}{2(u_{SO_4} - u_{Cl})}C_{K(3\,M)}\right)^2}\,dC$$

$$+ \frac{u_K(C_{K(3\,M)}u_{MCl} + 2C_{SO_4}(u_{SO_4} - u_{Cl})}{(u_M - u_K)^2} \times$$

$$\int\limits_0^{C_M} \frac{\ln (C_{K(3\,M)} - C) + \ln (C_{K(3\,M)} - 2C_{SO_4})}{\left(C + \dfrac{2C_{SO_4}(u_{SO_4} - u_{Cl}) + C_{K(3\,M)}u_{KCl}}{u_M - u_K}\right)^2}\,dC$$

$$- \frac{u_M[C_{K(3\,M)}u_{KCl} + 2C_{SO_4}(u_{SO_4} - u_{Cl})]}{(u_M - u_K)^2} \times$$

$$\int\limits_0^{C_M} \frac{\ln C + \ln (C_{K(3\,M)} - 2C_{SO_4})}{\left(C + \dfrac{2C_{SO_4}(u_{SO_4} - u_{Cl}) + C_{K(3\,M)}u_{KCl}}{u_M - u_K}\right)^2}\,dC$$

$$- \frac{u_{SO_4}C_{SO_4}}{u_M - u_K} \int\limits_0^{C_M} \frac{2\ln (C_{K(3\,M)} - C) + \ln C_{SO_4}}{\left(C + \dfrac{2C_{SO_4}(u_{SO_4} - u_{Cl}) + C_{K(3\,M)}u_{KCl}}{u_M - u_K}\right)^2}\,dC$$

$$+ \frac{2u_{SO_4}C_{SO_4}}{u_M - u_K} \int\limits_0^{C_M} \frac{\ln (C_{K(3\,M)} - C) + \ln (C_{K(3\,M)} - 2C_{SO_4})}{\left(C + \dfrac{2C_{SO_4}(u_{SO_4} - u_{Cl}) + C_{K(3\,M)}u_{KCl}}{u_M - u_K}\right)^2}\,dC$$

$$- \frac{u_K[C_M u_{MCl} + 2C_{SO_4}(u_{SO_4} - u_{Cl})]}{u_{KCl}^2} \times$$

$$\int\limits_{C_{K(3\,M)} - C_M}^{C_{K(1)}} \frac{\ln C + \ln (C + C_M - 2C_{SO_4})}{\left(C + \dfrac{C_M u_{MCl} + 2C_{SO_4}(u_{SO_4} - u_{Cl})}{u_{KCl}}\right)^2}\,dC$$

$$+ \frac{C_M u_M}{u_{KCl}} \int\limits_{C_{K(3\,M)} - C_M}^{C_{K(1)}} \frac{\ln C_M + \ln (C + C_M - 2C_{SO_4})}{\left(C + \dfrac{C_M u_{MCl} + 2C_{SO_4}(u_{SO_4} - u_{Cl})}{u_{KCl}}\right)^2}\,dC$$

$$- \frac{C_{SO_4}u_{SO_4}}{u_{KCl}} \int\limits_{C_{K(3\,M)} - C_M}^{C_{K(1)}} \frac{2\ln C + \ln C_{SO_4}}{\left(C + \dfrac{C_M u_{MCl} + 2C_{SO_4}(u_{SO_4} - u_{Cl})}{u_{KCl}}\right)^2}\,dC$$

$$+ \frac{2C_{SO_4}u_{SO_4}}{u_{KCl}} \int_{C_{K(3\,M)} - C_M}^{C_{K(1)}} \frac{\ln C + \ln (C + C_M - 2C_{SO_4})}{\left(C + \dfrac{C_M u_{MCl} + 2C_{SO_4}(u_{SO_4} - u_{Cl})}{u_{KCl}}\right)^2} \, dC$$

$$+ \ln C_{K(1)} C_{Cl(1)} \left(\frac{C_{K(1)}u_K + 2C_{SO_4}u_{SO_4}}{C_{K(1)}u_{KCl} + C_M u_{MCl} + 2C_{SO_4}(u_{SO_4} - u_{Cl})} - \tfrac{1}{2} \right)$$

$$+ \ln C_M C_{Cl(1)} \frac{C_M u_M}{C_{K(1)}u_{KCl} + C_M u_{MCl} + 2C_{SO_4}(u_{SO_4} - u_{Cl})}$$

$$- \tfrac{1}{2} \ln C_{K(1)}{}^2 C_{SO_4} \frac{2C_{SO_4}u_{SO_4}}{C_{K(1)}u_{KCl} + C_M u_{MCl} + 2C_{SO_4}(u_{SO_4} - u_{Cl})} \tag{A1}$$

When the above integrals are solved * the following result is obtained

$$\frac{\Delta G_Q}{RT} = \frac{2u_K(u_{SO_4} - u_{Cl})C_{SO_4}\ln C_{K(3\,M)}}{u_{KCl}[C_{K(3\,M)}u_{KCl} + 2C_{SO_4}(u_{SO_4} - u_{Cl})]} - \frac{u_{Cl}}{u_{KCl}}\ln C_{K(3\,M)}$$

$$+ \frac{u_{Cl}}{u_{SO_4} - u_{Cl}}\ln\left(1 + \frac{2C_{SO_4}}{C_{K(3\,M)}}\frac{u_{SO_4} - u_{Cl}}{u_{KCl}}\right)$$

$$+ u_{Cl}\frac{(C_{K(3\,M)} - 2C_{SO_4})\ln(C_{K(3\,M)} - 2C_{SO_4})}{C_{K(3\,M)}u_{KCl} + 2C_{SO_4}(u_{SO_4} - u_{Cl})}$$

$$+ u_{SO_4}\frac{C_{SO_4}\ln C_{SO_4}}{C_{K(3\,M)}u_{KCl} + 2C_{SO_4}(u_{SO_4} - u_{Cl})}$$

$$- \tfrac{1}{2}\frac{u_{SO_4}}{u_{SO_4} - u_{Cl}}\ln\left(1 + \frac{2C_{SO_4}}{C_{K(3\,M)}}\frac{u_{SO_4} - u_{Cl}}{u_{KCl}}\right) - \frac{u_M a}{u_M - u_K}\left[\frac{C_M \ln C_M}{a(a + C_M)}\right.$$

$$- \frac{1}{a}\ln\left(1 + \frac{C_M}{a}\right)\bigg] - \frac{u_K d}{(u_M - u_K)(C_{K(3\,M)} + a)}\left[\frac{(C_{K(3\,M)} - C_M)\ln(C_{K(3\,M)} - C_M)}{C_M + a}\right.$$

$$- \frac{C_{K(3\,M)}\ln C_{K(3\,M)}}{a} + \ln\left(1 + \frac{C_M}{a}\right)\bigg]$$

$$+ \frac{C_M}{a(u_K - u_M)}\left(u_{Cl}\frac{(C_{K(3\,M)} - 2C_{SO_4})\ln(C_{K(3\,M)} - 2C_{SO_4})}{C_M + a} + u_{SO_4}\frac{C_{SO_4}\ln C_{SO_4}}{C_M + a}\right)$$

$$- \frac{u_K}{u_{KCl}}\left(\frac{C_{K(1)}\ln C_{K(1)}}{C_{K(1)} + b} - \frac{(C_{K(3\,M)} - C_M)\ln(C_{K(3\,M)} - C_M)}{C_{K(3\,M)} - C_M + b}\right.$$

$$+ \ln\frac{C_{K(3\,M)} - C_M + b}{C_{K(1)} + b}\bigg) + \frac{u_{Cl}}{u_{KCl}}\left(\frac{C_{Cl(1)}\ln C_{Cl(1)}}{C_{K(1)} + b}\right.$$

$$- \frac{(C_{K(3\,M)} - 2C_{SO_4})\ln(C_{K(3\,M)} - 2C_{SO_4})}{C_{K(3\,M)} - C_M + b} + \ln\frac{C_{K(3\,M)} - C_M + b}{C_{K(1)} + b}\bigg)$$

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* To solve these integrals we used the equation

$$\int \frac{\ln x}{(a + x)^2}\, dx = \frac{x \ln x}{a(a + x)} - \frac{1}{a}\ln(a + x)$$

$$+ \frac{u_{SO_4}C_{SO_4}\ln C_{SO_4}}{C_{K(1)}u_{KCl} + C_M u_{MCl} + 2C_{SO_4}(u_{SO_4} - u_{Cl})}$$

$$- \frac{u_{SO_4}C_{SO_4}\ln C_{SO_4}}{C_{K(3\,M)}u_{KCl} + C_M(u_M - u_K) + 2C_{SO_4}(u_{SO_4} - u_{Cl})}$$

$$+ \frac{u_M C_M \ln C_M}{C_{K(3\,M)}u_{KCl} + C_M(u_M - u_K) + 2C_{SO_4}(u_{SO_4} - u_{Cl})}$$

$$- \frac{u_M C_M \ln C_M}{C_{K(1)}u_{KCl} + C_M u_{MCl} + 2C_{SO_4}(u_{SO_4} - u_{Cl})}$$

$$- \frac{u_{SO_4}C_{SO_4}\ln C_{SO_4} - u_M C_M \ln C_M}{C_{K(1)}u_{KCl} + C_M u_{MCl} + 2C_{SO_4}(u_{SO_4} - u_{Cl})}$$

$$+ \left(\frac{C_{K(1)}u_K}{C_{K(1)}u_{KCl} + C_M u_{MCl} + 2C_{SO_4}(u_{SO_4} - u_{Cl})} - \tfrac{1}{2} \right) \ln C_{K(1)}$$

$$+ \tfrac{1}{2} \frac{C_{K(1)}(u_K - u_{Cl}) + C_M(u_M - u_{Cl}) + 2C_{SO_4}(u_{SO_4} - u_{Cl})}{C_{K(1)}u_{KCl} + C_M u_{MCl} + 2C_{SO_4}(u_{SO_4} - u_{Cl})} \ln C_{Cl(1)} \qquad \text{(A2)}$$

In this equation

$$a = \frac{C_{K(3\,M)}u_{KCl} + 2C_{SO_4}(u_{SO_4} - u_{Cl})}{u_M - u_K}, \quad b = \frac{C_M u_{MCl} + 2C_{SO_4}(u_{SO_4} - u_{Cl})}{u_{KCl}}$$

and $d = \dfrac{C_{K(3\,M)}u_{MCl} + 2C_{SO_4}(u_{SO_4} - u_{Cl})}{u_M - u_K}$

In aqueous electrolytes $u_{Cl} \simeq u_K$. If this approximation is introduced in the above equation and terms with the same logaritmic functions are gathered, the following result is obtained

$$\frac{\Delta G_Q}{RT} = \tfrac{1}{2}\ln\frac{C_{Cl(1)}}{C_{K(1)}} - \frac{u_{Cl} - \tfrac{1}{2}u_{SO_4}}{u_{Cl} - u_{SO_4}}\ln\left(1 - \frac{u_{SO_4} - u_{Cl}}{u_{Cl}}\frac{C_{SO_4}}{C_{K(3\,M)}}\right)$$

$$+ \ln\left(1 - \tfrac{1}{2}\frac{C_M(u_{Cl} - u_M)}{C_{K(3\,M)}u_{Cl} + C_{SO_4}(u_{SO_4} - u_{Cl})}\right) \qquad \text{(A3)}$$

The Donnan equilibrium is established across the membrane, and the chemical potential of potassium chloride is therefore the same on both sides of the membrane. Using eqn. (1) we get

$$\frac{C_{Cl(1)}}{C_{K(1)}} = \frac{C^2_{Cl(1)}}{C_{K(1)}C_{Cl(1)}} = \frac{C^2_{Cl(1)}}{C^2_{Cl(2)}} \qquad \text{(A4)}$$

Combining eqns. (A3 and A4) we have

$$E = -\frac{\Delta G_Q}{F} = \frac{RT}{F}\left[\ln\frac{C_{Cl(2)}}{C_{Cl(1)}} + \frac{u_{Cl} - \tfrac{1}{2}u_{SO_4}}{u_{Cl} - u_{SO_4}}\ln\left(1 - \frac{u_{SO_4} - u_{Cl}}{u_{Cl}}\frac{C_{SO_4}}{C_{K(1\,M)}}\right)\right.$$

$$\left. - \ln\left(1 - \tfrac{1}{2}\frac{C_M(u_{Cl} - u_M)}{C_{K(3\,M)}u_{Cl} + C_{SO_4}(u_{SO_4} - u_{Cl})}\right)\right] \qquad \text{(A5)}$$

Since the concentration of metal chloride and potassium sulfate is very small compared to 3 M, the electromotive force of the above cell can be expressed by the equation

$$E = \frac{RT}{F} \ln \frac{C_{Cl(2)}}{C_{Cl(1)}} \qquad\qquad (A6)$$

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