# The Potential across a Membrane

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A general treatment is presented for the thermodynamics of a
cell with a membrane.
Further, two special cases are treated in details. In one case the
membrane is permeable to two kinds of cations. In the other case
the membrane is permeable to one kind of cations, one kind of anions,
and to water molecules.

Transport across membranes and the electrical work associated with the
transport are of interest in several fields of chemistry. Processes of this
kind are important in biochemistry, for the investigations of cells having ion
exchange resins as membranes, and in high temperature chemistry where
glass membranes have been used in galvanic cells.

In the present treatment of processes in membranes the use of unmeasure-
able quantities like single ion activities, single electrode potentials, and phase-
boundary potentials (Donnan potentials) have been avoided. This also seems
to simplify the calculations.

### GENERAL TREATMENT OF A CELL HAVING A MEMBRANE

The galvanic cell shown in Fig. 1 will be considered. The composition of
any section of the cell may be expressed by the number of moles of electrically
neutral components (1, 2, 3,...). When a charge $\Delta Q$ is transferred through the
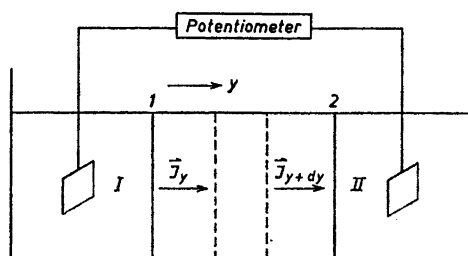


*Fig. 1.* I and II indicate the two electro-
lytes, while 1 and 2 indicate the two
interfaces between membrane and electro-
lytes.

cell during the time $\varDelta t$, there will be a transport of all components which can migrate in the cell. These transports can be expressed by fluxes of the neutral components, $(\vec{J}_1, \vec{J}_2, \vec{J}_3,....)$ in moles/cm² sec. If the value of a flux varies along the $y$-direction in the cell, e.g. if $\vec{J}_{1,y} > \vec{J}_{1,y+dy}$, the content of component 1 will increase in the volume element between the two planes indicated by dotted lines in the figure, and similar changes will occur for the other components being transported. The changes in the content of all components in the volume element may be multiplied by their respective chemical potentials $(\bar{G}_1, \bar{G}_2, \bar{G}_3,...)$ and summed up for all components and over all volume elements from inside electrolyte I to inside electrolyte II. To this one may further add the changes taken place at the two electrodes and in their close vicinity, to obtain the total change in Gibb's free energy of the cell during the time $\varDelta t$.

If no irreversible reactions take place at the electrodes, the free energy change at and close to the electrodes is proportional to $\varDelta Q$ and independent of $\varDelta t$.

The free energy change in the membrane and any other region of the cell having concentration gradients may be calculated from equations correlating fluxes and forces (grad $\bar{G}_1$, grad $\bar{G}_2$ .... grad electrostatic potential) based on the postulate that there is a linear relation between fluxes and forces.[1] From these equations one obtains the following equation for the free energy change in the cell region dealt with:

$$\varDelta G' = \varDelta G_t' + \varDelta G_Q'$$

where $\varDelta G_t'$ contains the time, $\varDelta t$, and not the transferred charge $\varDelta Q$, and

$$\varDelta G_Q' = -\frac{\varDelta Q}{F} \int \sum_i \bar{G}_i dt_i$$

is independent of time. Here $F$ is the Faraday number, $t_i$ is a transport coefficient of component i defined by $t_i = \vec{J}_i/\vec{I}$, where $\vec{I}$ is current density (in Faraday/sec cm²). The integrations are carried out over the volume ranging from inside electrolyte I to inside electrolyte II.

The total change in free energy in the cell during the rime $\varDelta t$ may thus be expressed by the equation:

$$\varDelta G_{\text{total}} = \varDelta G_t' + \frac{\varDelta Q}{F} \left( \varDelta G_e - \int \sum_i \bar{G}_i dt_i \right)$$
$$= \varDelta G_t' + \varDelta G_Q$$

where $(\varDelta Q/F)\varDelta G_e$ is the free energy change at and close to the electrodes.

Both $\varDelta G_Q$ and the outer electric work, $\varDelta Q \times E$, ($E$ is the emf of the cell) are proportional to $\varDelta Q$ and will change sign if $\varDelta Q$ changes sign (by small changes in $E$, the current in the cell may be reversed). The electric work $\varDelta Q \times E$ carried out by an external source has no effect on $\varDelta G_t'$, but it creates the free energy change $\varDelta G_Q$ in the cell. Conversely the free energy change $-\varDelta G_Q$ produces the electric energy $\varDelta Q \times E$. Therefore the change in free

energy due to the transfer of charge must be balanced by the electric energy produced in the outer circuit when the current through the cell is very small.

$$\Delta Q \times E + \Delta G_Q = 0$$

or
$$E \times F = -\Delta G_e + \int \sum_i \bar{G}_i \mathrm{d}t_i \qquad (1)$$

The transport coefficients $t_i$ are defined for electrically neutral components, but it may of course in many cases be more practical to describe the concentration changes by means of ionic transport numbers. The chemical potential $\bar{G}_i$ for electrically neutral components will, however, be maintained.

In the following calculations on membrane-cells, we assume that diffusion in the membrane is very slow compared to diffusion and convection in the electrolyte (due to stirring), so that concentration gradients in the electrolytes can be neglected. It will further be assumed that the exchange reactions at the two electrolyte-membrane interfaces are at equilibrium. The validity of these assumptions may be tested by using membranes of different thickness. If the assumptions are valid, an increase in membrane thickness should not have an effect on the emf of the cell.

Under these conditions it may be practical to include in $\Delta G_e$ all the free energy changes in electrolyte I and II, both those at the electrode-electrolyte interfaces and those at the membrane-electrolyte interfaces. The integration is then carried out over the membrane only.

## THE POTENTIAL ACROSS A MEMBRANE PENETRABLE TO TWO KINDS OF CATIONS

The following type of cell will be considered:

$$\mathrm{Cl_2|(NaCl)_I|glass|(NaCl + KCl)_{II}|Cl_2}$$
$$\quad\quad\quad {}_1\quad\quad {}_2$$
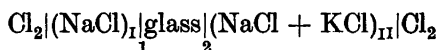
This is a high temperature cell having fused salts as electrolyte and a silicate glass as membrane. The ions $\mathrm{Na^+}$ and $\mathrm{K^+}$ can migrate through the membrane.[2,3]

According to eqn. (1) one can write:

$$EF = -(\bar{G}_{\mathrm{NaCl}}t_{\mathrm{Na}} + \bar{G}_{\mathrm{KCl}}t_{\mathrm{K}})_1 + (\bar{G}_{\mathrm{NaCl}}t_{\mathrm{Na}} + \bar{G}_{\mathrm{KCl}}t_{\mathrm{K}})_2 + \int_1^2 (\bar{G}_{\mathrm{Na-sil}}\mathrm{d}t_{\mathrm{Na}} + \bar{G}_{\mathrm{K-sil}}\mathrm{d}t_{\mathrm{K}})$$

where the subscripts 1 and 2 mean that the functions inside the parentheses have the values of these functions at the interfaces 1 and 2, respectively. $\bar{G}$ with subscript is chemical potential of the indicated component. The glass membrane may, for the present process, be described as a two component system: Na-silicate and K-silicate. $t$ with subscript is transport number in membrane.

The equation may be given the form:

$$EF = -|(\bar{G}_{\mathrm{NaCl}}t_{\mathrm{Na}} + \bar{G}_{\mathrm{KCl}}t_{\mathrm{K}})\int_1^2 (\bar{G}_{\mathrm{Na-sil}} - \bar{G}_{\mathrm{K-sil}})\mathrm{d}t_{\mathrm{K}}$$

Integration by parts and rearrangement give:

$$EF = -|\bar{G}_{NaCl} \Big|_1^2 + |(\bar{G}_{NaCl} - \bar{G}_{KCl} - \bar{G}_{Na-sil} + \bar{G}_{K-sil})t_K \Big|_1^2$$

$$+ \int_1^2 t_K d(\bar{G}_{Na-sil} - \bar{G}_{K-sil}) \tag{2}$$

Equilibrium at the salt-glass interface gives:

$$\bar{G}_{NaCl} - \bar{G}_{KCl} = \bar{G}_{Na-sil} - \bar{G}_{K-sil} \tag{3}$$

which means that the second term of eqn. (2) is zero.

In experimental series it would be convenient to use pure NaCl as electrolyte I and also refer to this as the standard state for sodium chloride in electrolyte II. For a small change in the composition of electrolyte II, the change in emf of the cell is given by:

$$F \times dE = -d\bar{G}_{NaCl} + t_K(d\bar{G}_{Na-sil} - d\bar{G}_{K-sil})$$

However, using eqn. (3) for equilibrium at interface (2), one obtains:

$$F \times dE = -d\bar{G}_{NaCl} + t_K(d\bar{G}_{NaCl} - d\bar{G}_{KCl}) = -t_{Na}d\bar{G}_{NaCl} - t_K d\bar{G}_{KCl} \tag{4}$$

Combining with the Gibbs-Duhem equation

$$x_{NaCl}d\bar{G}_{NaCl} + x_{KCl}d\bar{G}_{KCl} = 0$$

where $x$ with subscript is molefraction in electrolyte II, one obtains:

$$F \times dE = \frac{t_K - x_{KCl}}{x_{KCl}} d\bar{G}_{NaCl}$$

which solved with respect to $d\bar{G}_{NaCl}$ and integrated gives:

$$\varDelta\bar{G}_{NaCl} = F \int_1^2 \frac{x_{KCl}}{t_K - x_{KCl}} dE \tag{5}$$

Thus for a given composition of electrolyte II one can measure $E$ and the transport number of potassium ions in a glass membrane, which is in equilibrium with an electrolyte of the same composition as electrolyte II. By plotting corresponding values of $x_{KCl}/(t_K - x_{KCl})$ and $E$, the chemical potential, $\varDelta\bar{G}_{NaCl}$, is obtained from the area under a curve.

It should be noted that a requirement for the above integration is that the composition of the membrane is uniform, except for the cations, from 1 to 2.


### THE POTENTIAL ACROSS A MEMBRANE PENETRABLE TO ONE KIND OF CATIONS AND ONE KIND OF ANIONS AND TO WATER MOLECULES

The following type of cell will be considered:

$$Ag|AgCl|KCl_{(c_1)}|Membrane|KCl_{(c_2)}|AgCl|Ag$$
$$\qquad\qquad\qquad 1 \qquad\qquad\qquad 2$$
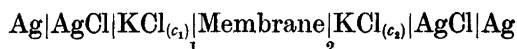
The electrolytes are water solutions of potassium chloride and the membrane is an ion exchange resin allowing potassium and chloride ions and water molecules to migrate through itself if placed in an electric field. From eqn. (1) one has:

$$EF = -|_1^2 (\bar{G}_{KCl} t_K + \bar{G}_{H_2O} t_{H_2O}) + \int_1^2 (\bar{G}_{KCl(m)} dt_K + \bar{G}_{H_2O(m)} dt_{H_2O})$$

Where $\bar{G}_{KCl}$ and $\bar{G}_{KCl(m)}$ are the chemical potentials of KCl in, respectively, the electrolyte and the membrane. $\bar{G}_{H_2O}$ and $\bar{G}_{H_2O(m)}$ have similar meaning, $t$ with subscript are transport coefficients in membrane.

Integration by parts and assumption of equilibrium at the electrolyte-membrane interfaces give:

$$EF = -\int_1^2 (t_K d\bar{G}_{KCl(m)} + t_{H_2O} d\bar{G}_{H_2O(m)}) \tag{6}$$

Keeping the concentration $c_1$ constant and changing $c_2$ by a small amount, the change in the emf is given by:

$$F \times dE = -t_K d\bar{G}_{KCl(m)} - t_{H_2O} d\bar{G}_{H_2O(m)}$$

Before rearranging and integrating this equation, we will introduce an additional assumption. We will assume that to any set of values $\bar{G}_{KCl(m)}$ and $\bar{G}_{H_2O(m)}$ for the membrane there exists a set of values $\bar{G}_{KCl}$ and $\bar{G}_{H_2O}$ for a water solution so that $\bar{G}_{KCl} = \bar{G}_{KCl(m)}$ and $\bar{G}_{H_2O} = \bar{G}_{H_2O(m)}$. In other words, it is always possible to find a KCl-H$_2$O mixture which at normal pressure is in equilibrium with potassium chloride and water in the membrane. This again means that the membrane could be split vertically at some point, and it should be possible to find a KCl-H$_2$O mixture, which could be introduced in between the two parts of the membrane without changing its composition. Suppose the concentration of potassium chloride in this mixture is $c_3$, and an Ag/AgCl-electrode is inserted into this electrolyte. We will then have two cells, one over the concentrations $c_1$ to $c_3$ and one over $c_3$ to $c_2$. The sum of the emf's of these two cells must be equal to the emf of the cell over the concentrations $c_1$ to $c_2$. Our assumption can thus be checked by investigation, whether or not the emf's of cells over different concentration ranges are additive.

With the above assumption we may substitute $d\bar{G}_{KCl(m)}$ by $d\bar{G}_{KCl}$ and $d\bar{G}_{H_2O(m)}$ by $d\bar{G}_{H_2O}$ and integrate for changes in concentration of KCl, $(c_{KCl})$ from $c_1$ to any fixed value of $c_2$.
We have:

$$F \times dE = -t_K d\bar{G}_{KCl} - t_{H_2O} d\bar{G}_{H_2O} \tag{7}$$

Introduction of the Gibbs-Duhem equation

$$c_{KCl} d\bar{G}_{KCl} + c_{H_2O} d\bar{G}_{H_2O} = 0$$

rearrangement and integration give

$$\bar{G}_{\text{KCl}(c_2)} - \bar{G}_{\text{KCl}(c_1)} = -F \int\limits_{c_{\text{KCl}}=c_1}^{c_{\text{KCl}}=c_2} \frac{1}{t_{\text{K}} - t_{\text{H}_2\text{O}}(c_{\text{KCl}}/c_{\text{H}_2\text{O}})} \; \text{d}E \qquad (8)$$

Thus by measuring corresponding values of $t_{\text{K}}$ and $t_{\text{H}_2\text{O}}$ and $E$ for different values of $c_{\text{KCl}}$, the chemical potential of potassium chloride in the KCl-$H_2O$ mixture can be obtained as a function of composition, the left hand side electrolyte being the reference state.

## REFERENCES

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