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Ion Transport Across Membranes: I. Definitions of Membrane Electromotive Forces and of Flows of Electrolytic Solutes

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An analysis is given for the treatment of membrane transport phenomena in accord with the theory of steady state thermodynamics. A linear macroscopic theory for discontinuous systems is applied as a postulate. It is shown that as a consequence of the transformation properties of the Onsager reciprocal relations the definition of a membrane electromotive force gives corollary definitions of the flows of electrolytic solutes as a whole in the form of linear combinations of the flows of ionic constituents. It is shown that established conventions which set the activity coefficients of ionic constituents equal to unity at the reference state of infinite dilution lead to a particular definition of the membrane electromotive force which may be applied at any concentration.

1. Introduction

This paper reports the results of a part of a study directed toward the detailed application of the thermodynamics of steady state processes to the investigation of transport phenomena at junctions between electrolytic solutions. The work was undertaken as a part of a research project under the sponsorship of the Office of Saline Water of the U.S. Department of the Interior. This project had the aim of improving the methods of measuring and reporting the electrochemical characteristics of membranes.

In this paper we are concerned with the problem of treating permeability characteristics during steady states involving the transfer of electric charge without introducing the classical uncertainty involving the electrostatic potential difference between two chemical phases of different composition [1, 2, 3, 4].[1] The existence of such an electrostatic potential difference is postulated in discussions of the application of steady state thermodynamics to electrolytic transport problems. The usual practice [5] is to introduce the definition of the differential of the chemical potential of an ionic constituent in the form

$$d\mu_i^{\prime}=(d\mu_i^{\prime})_{d\xi=0}+z_i^{\prime}\mathscr{F}d\xi \tag{1}$$

where $d\mu_i^{\prime}$ is the total differential of the chemical potential; $z_i^{\prime}$ is the electrovalence; $\mathscr{F}$ is the faraday; and $d\xi$ is the differential of the electrostatic potential. The first term on the right, the "nonelectrical part," may be put formally

$$(d\mu_i^{\prime})_{d\xi=0}=-\overline{S}_i^{\prime}dT+\overline{V}_i^{\prime}dP+RTd\ln m_i^{\prime}+RTd\ln \gamma_i^{\prime} \tag{2}$$

where $\overline{S}_i^{\prime}$, $\overline{V}_i^{\prime}$, $m_i^{\prime}$, and $\gamma_i^{\prime}$ are, respectively, the partial molar entropy, the partial molar volume, the molality and the activity coefficient at constant temperature and pressure of the ionic constiuent. We note here that if ion constituents are defined as MacInnis [6] defines them, $m_i^{\prime}$ and hence $d\ln m_i^{\prime}$ are operational quantities without extra-thermodynamic assumptions adopted as arbitrary conventions. The work of Guggenheim [7] as confirmed by de Groot and Tolhoek [8] shows that in ordinary electrochemical systems only the term $d\mu_i^{\prime}$ on the left in eq (1) may be included with $d\ln m_i^{\prime}$ as an operational quantity in a thermodynamic treatment.

de Groot and Tolhoek give demonstrations that, in principle, one may treat transport across junctions between electrolytic solutions without seeking to make the division of chemical potential differentials called for in eq (1). The first object of this paper is to set down a fundamental steady state treatment which makes explicit use of familiar electrochemical quantities but avoids the use of eq (1). The fundamental treatment given here is new only in the sense that it is a unified analysis applicable to the peculiar requirements of membrane studies. It may properly be viewed as first a restriction of Guggenheim's [9] treatment of galvanic cells to discontinuous systems. The treatment is then extended to nonisopiestic systems by including the flow of solvent in a membrane fixed frame of reference. It is further extended to the treatment of stationary states involving flows of electric charge. Finally, by following Temkin and Koroshin [10, 11] and Agar [12] in the treatment of electronic transport entropies we extend the analysis to nonisothermal systems.

In much theoretical and experimental work there appears to be a need to adopt conventions regarding single ion activities, membrane potentials, salt bridges, or ideal "inert" electrodes. In terms of the steady state theory these conventions are viewed as giving definitions to a "force"—the EMF—conjugate to a "flow"—the electric current—in the same sense that a pressure difference is a force conjugate to the flow of fluid volume. In the discussion given in section 10 we show an important case in which the ex-

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[1] Figures in brackets indicate the literature references at the end of this paper.

plicit need for such a convention arises. The second object of this paper is to study the requirements to be met by an EMF convention if it is to lead to an internally consistent treatment of transport phenomena. We will show that the application of the steady state theory leads quite naturally to a particular conventional definition of the membrane EMF. This definition is developed in sections 8 and 9.

2. Analytical Model

In our analysis we will formally treat a one dimensional, discontinuous, open steady state system without chemistry [13]. Flows through a junction are treated as if they took place between two points. The points, α and β, are taken as representative of two parallel planes in a real system at each of which one may assign by experiments a truly representative average value of any intensive property. A "junction" is everything between α and β and its composition need not be defined. We only require flow continuity between α and β. The flow of a conserved quantity, i.e., energy, mass as a chemical constituent, and electric charge, across α in the direction of β must be equal to the flow of that quantity across β toward the surroundings of β. Flows are positive in the direction α to β and are to be measured with reference to α and β.

The postulate of local equilibrium is applied at α and β. A complete set of intensive equilibrium thermodynamic properties can be defined by the local temperature, pressures, and component concentrations when α and β are at the same gravitational potential with no other external fields operating. During a steady state these intensive properties are to be maintained constant by exchanges with the surroundings.

We give *a priori* emphasis to certain consequences of this model. The uncertainty which arises in discussions of transference numbers and diffusion coefficients continues to receive attention in the literature [14, 15, 16]. An analysis of the model chosen gives permeability characteristics as integral characteristics of a junction in a cell fix frame of reference. Thus if the real system were a simple Hittorf transference cell [17], an integral transference number of an ion constituent would be by definition a property of the middle cell region, a solution filled glass tube. A transformation to an ordinary Hittorf or Washburn [12] number given with reference to the center of mass of the solvent would yield another integral property of the solution filled glass tube. The identification of these latter properties as properties of the solution would, in the usual way, require a demonstration that wall effects in large tubes contribute only to the extent that the tube defines the geometry of the solution.

3. Fundamental Steady State Formulation

de Groot gives a detailed discussion of the fundamental principles of the steady state theory. We accept the theory here in the manner of a formal postulate. The material of this section sets forth the way in which quantities of established operational significance are to be employed to define flows and forces in the steady state description of junction processes without resort to eq (1).

The choice of a concentration scale is immaterial to the essential results of this paper. In nonisothermal systems it is generally preferable to avoid volume concentrations [37]. We find it convenient to employ molalities, mole kg^{-1} of solvent. The compositions of the solutions at α and β are defined by the concentrations of r *constituents*. The first m, including the solvent, are nonelectrolytes. The next r-m are ionic constituents. We define a *constituent* composition vector, $\{m^f\}$, the elements of which are the molalities of these constituents. We define the constituent electrovalence vector, $\{z^f\}$, where the elements are the electrovalences of the respective constituents represented in $\{m^f\}$. The restriction of the electroneutrality condition is expressed by

$$\{z^f\}^\dagger \{m^f\} = 0 \tag{3}$$

where the superscript dagger, †, denotes transposition.

Under the restriction imposed by eq (3) it will always be possible to express the composition of solutions α and β in terms of $r-1$ independent components [38]. We define a *component* composition vector, $\{m^*\}$, where the respective elements are the molalities of electrically neutral isolable chemical compounds. These composition vectors must be connected by a relation,

$$[\nu]\{m^*\} = \{m^f\} \tag{4}$$

or, in more detail,

$$\begin{bmatrix} 1 & \cdots & 0 & 0 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & \cdots & 1 & 0 & \cdots & 0 \\ 0 & \cdots & 0 & \nu_{m+1,m+1} & \cdots & \nu_{m+1,r-1} \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & \cdots & 0 & \nu_{r-1,m+1} & \cdots & \nu_{r-1,r-1} \\ 0 & \cdots & 0 & \nu_{r,m+1} & \cdots & \nu_{r,r-1} \end{bmatrix} \left\{ \begin{matrix} m_1^* \\ \cdots \\ m_m^* \\ m_{m+1}^* \\ \cdots \\ m_{r-1}^* \end{matrix} \right\} = \left\{ \begin{matrix} m_1^f \\ \cdots \\ m_m^f \\ m_{m+1}^* \\ \cdots \\ m_{r-1}^f \\ m_r^f \end{matrix} \right\} \tag{5}$$

An element, ν_{ij}, of the matrix $[\nu]$ is zero or a positive integer. It is the number of moles of the ith constituent contained in one mole of the isolated jth neutral component. The particular combinations of ionic constituents chosen as neutral components are a matter of convenience except that the *independence* of the components requires that $[\nu]$ be of rank $r-1$. A unique solution must exist for the molalities of components in terms of molalities of $r-1$ constituents. We note that the requirement of electroneutrality for every component is expressed by

$$\{z^c\}^\dagger[\nu]=[0]. \tag{6}$$

We also note that convenience is best served if $[\nu]$ is chosen such that the elements of the solution vector $\{m^*\}$ of eq (4) satisfy the condition

$$m_j^*\geq 0; \qquad (j=1, 2, \ldots, r-1). \tag{7}$$

It is important to note that in equilibrium thermodynamics one can treat the properties of a three component system such as H_2O-NaCl-KBr. In a steady state treatment of transport processes—"without chemistry"—such as the interdiffusion of the components between solutions with differing concentrations of NaCl and KBr we must regard such solutions as special cases in which the concentration of a fourth component, either KCl or NaBr, is zero. In practice such special cases would be treated as the result of special restraints upon the possible transport processes in a system under study.

Writing

$$\Delta\mu_i=\mu_i^\beta-\mu_i^\alpha, \tag{8}$$

as the difference in chemical potential of a chemical component or constituent between α and β and using the equilibrium property

$$\mu_j^*=\sum_{i=1}^{r}\nu_{ij}\mu_i; \quad (j=1, \ldots, r-1) \tag{9}$$

we secure the equation,

$$[\nu]^\dagger\begin{Bmatrix}\Delta\mu_1^*\\ \cdots\\ \Delta\mu_m^*\\ \Delta\mu_{m+1}^\varepsilon\\ \cdots\\ \Delta\mu_{r-1}^\varepsilon\\ \Delta\mu_r^\varepsilon\end{Bmatrix}=\begin{Bmatrix}\Delta\mu_1^*\\ \cdots\\ \Delta\mu_m^*\\ \Delta\mu_{m+1}^*\\ \cdots\\ \Delta\mu_{r-1}^*\end{Bmatrix} \tag{10}$$

The superscript, *, indicates quantities which are functions of only temperatures, compositions, and pressures in accord with classical thermodynamics. The superscript, ε, indicates quantities requiring an auxiliary electrochemical operation involving measured transfers of electric charge coupled with measured transfers of material constituents [19, 20]. The algebraic theorem that eq (10) possesses no unique solution for the elements of the vector on the left is equivalent to Guggenheim's conclusion that where α and β are formally treated as electrically isolated phases, the elements $\Delta\mu_i^\varepsilon$ have no general thermodynamic significance. However, when α and β are not electrically isolated but communicate through a junction permeable to at least one ion constituent, the elements $\Delta\mu_i^\varepsilon$ are operationally meaningful. Guggenheim considers the case when α and β are at the same temperature and pressure. He shows that when a reversible current can be passed between the terminals of a pair of identical electrodes reversible to the ith constituent, one at α and one at β, the relation

$$\Delta_{T,P}\mu_i^\varepsilon=z_i^c\mathscr{F}(E_i^\beta-E_i^\alpha) \tag{11}$$

defines the chemical potential differences when $E_i^\beta-E_i^\alpha$ is the electric potential difference measured between the electrode terminals. Equation (11) is easily modified to include cases where the temperatures and pressures at the electrodes are not equal. Here we follow Temkin and Koroshin [10, 11], Agar [12], and deBethune [21] by choosing to have the leads from the electrodes at α and β be wires of identical composition which come out to terminals which are at the same temperature, but we specifically require the use of platinum wire for these leads.[2] We write the electrode reaction

$$\sum_k\lambda_{ik}\mathscr{A}_{ik}+\frac{1}{z_i^c}\mathscr{B}_i^c+e^-=0 \tag{12}$$

for an electrode reversible to the ith constituent. $\mathscr{B}_i^c$ denotes the chemical symbol of the constituent corresponding to the ith element of $\{m^c\}$. $\mathscr{A}_{ik}$ denotes neutral components of the electrode which are virtually insoluble in the solutions at the electrodes and, hence, are not represented in the vector $\{m^*\}$. For example, for a silver–silver chloride electrode we write

$$-\mathrm{Ag}+\mathrm{AgCl}-\mathrm{Cl}^-+e^-=0 \tag{12a}$$

with k taking the values 1 and 2. $\mathscr{A}_{i1}$ is silver; $\mathscr{A}_{i2}$ is silver chloride; and λ_{i1} and λ_{i2} are -1 and 1, respectively.

We then write for each ion constituent

$$\Delta\mu_i^\varepsilon=z_i^c\mathscr{F}\Delta\phi_i; \qquad (i=m+1, \ldots, r) \tag{13}$$

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[2] In nonisothermal systems it is necessary to indicate the reference medium implied for electrons when one writes an electrode reaction. The established use of platinum in constructing hydrogen electrodes and in resistance thermometers makes it convenient to regard platinum at 25 °C as the reference medium for electrons.

where $\Delta\phi_i$ is the EMF obtained by correcting the measured EMF, $E_i^\beta - E_i^\alpha$, for the homogeneous thermoelectric effect in the platinum leads and for the chemical potential differences of the insoluble components involved in the electrode reaction, i.e.,

$$\Delta\phi_i = (E_i^\beta - E_i^\alpha) + \frac{\bar{\bar{S}}_{pt}}{\mathscr{F}}\Delta T - \frac{1}{\mathscr{F}}\sum_k \lambda_{ik}\Delta\mu_k \qquad (14)$$

where $\bar{\bar{S}}_{pt}$ is the transported entropy for electrons in platinum.[3]

For silver–silver chloride electrodes under ordinary conditions eq (14) becomes

$$\Delta\phi_{Cl^-} = (E^\beta_{Cl^-} - E^\alpha_{Cl^-}) + \frac{\bar{\bar{S}}_{pt}}{\mathscr{F}}\Delta T$$

$$-\frac{1}{\mathscr{F}}[(\bar{S}_{Ag} - \bar{S}_{AgCl})\Delta T - (\bar{V}_{Ag} - \bar{V}_{AgCl})\Delta P] \qquad (14a)$$

where the term in square brackets is derived from eq (16) below with the condition that

$$\left(\frac{\partial\mu_k}{\partial m_j^*}\right)_{T,P,m} = 0 \qquad (15$$

for compounds in their standard states.

Equation (13) defines the last *r-m* elements of the vector on the left in eq (10). The first *m* elements are defined using the classical equilibrium thermodynamic relation resulting from the choice of temperature, pressure, and molality as independent intensive variables, i.e.,

$$d\mu_i^* = -\bar{S}_i^* dT + \bar{V}_i^* dP + \sum_{j=2}^{r-1}\left(\frac{\partial\mu_i^*}{\partial m_j^*}\right)_{T,P,m} dm_j^* \qquad (16)$$

$\bar{S}_i^*$ denotes the partial molal entropy; $\bar{V}_i^*$ denotes the partial molal volume; and the summation is over the independent solute components represented in the vector $\{m^*\}$. Since we wish to express the thermodynamic "forces", $\Delta\mu_i^*$, as *linear* functions of the experimental "forces" it is convenient to write

$$\Delta\mu_i^* = -\bar{S}_i^*\Delta T + \bar{V}_i^*\Delta P + \sum_{j=2}^{r-1}\Theta_{ij}^*\Delta\log m_j^* \qquad (17)$$

where

$$\Theta_{ij}^* \equiv \left(\frac{\partial\mu_i^*}{\partial\log m_j^*}\right)_{T,P,m} \qquad (18)$$

with log denoting logarithms to the base 10. This gives a condensed symbol for our constant coefficient; we expect $\Delta\mu_i^*$ to be more nearly proportional to $\Delta\log m_j^*$ than to Δm_j^*. We restrict our attention here to steady states representing displacements from a definite reference state of complete equilibrium between α and β when the solutions α and β have the same temperature, pressure, and concentrations of components with no net flows of energy, chemical constituents, or electric charge taking place between them.[4] The vectors $\{m^f\}$ and $\{m^*\}$ are defined at this state.

It is useful to show how Θ_{ij}^* is to be expressed in terms of the solution compositions and activity coefficients.

We have the defining relation

$$(\mu_i^*)_{T,P} = \mu_i^0 + RT\sum_{k=1}^{r}\nu_{ki}\ln m_k^f\gamma_k^f; \quad (i=1,2,\ldots,r-1) \qquad (19)$$

where the summations are over the elements of $\{m^f\}$. Here, for ion, constituents, γ^f is a single ion activity coefficient[5] which in this paper has no more than the ordinary significance of a formal device. It disappears when eq (19) is written in the meaningful form

$$(\mu_i^*)_{T,P} = \mu_i^0 + RT\sum_{k=1}^{r}\nu_{ki}\ln m_k^f + \nu_i^* RT\ln\gamma_i^* \qquad (20)$$

where

$$\nu_i^* \equiv \sum_{k=1}^{r}\nu_{ki} \qquad (21)$$

and γ_i^* is the molal activity coefficient for nonelectrolytes and the mean molal activity coefficient for electrolytes. From eq (20) and the definition given by eq (18) we find

$$\Theta_{ij}^* = \frac{RT}{0.4343}\left[m_j^*\sum_{k=1}^{r}\frac{\nu_{ki}\nu_{kj}}{m_k^f} + \nu_i^*\left(\frac{\partial\log\gamma_i^*}{\partial\log m_j^*}\right)_{T,P,m}\right]. \qquad (22)$$

There is a real advantage of simplicity and convenience in the form of eq (22) where ionic molalities are retained. The introduction of mean ionic molalities as suggested by textbooks leads to an almost hopelessly unwieldly expression in the general case.

We recognize the experimental fact that the solutions may be of such a composition that no reversible electrode will function as required by eq (14). However, as demonstrated in section 6, if a single pair of reversible electrodes is available to measure $\Delta\phi_i$; for any one of the ion constituents represented in $\{m^f\}$, the added equation supplements eq (10) to give a solution for the remaining terms, $\Delta\mu_i^*$. Thus, given a satisfactory pair of reversible electrodes, we may define every term in eq (10) in terms of operational quantities without resort to eq (1).

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[3] At temperatures near 25 °C the work of Koroshin and Temkin gives

$$\bar{\bar{S}}_{pt} = -8.66\times10^{-4} + 0.044\times10^{-4}T; \qquad (T>220\ ^\circ K)$$

with temperature in degrees Kelvin and $\bar{\bar{S}}_{pt}$ in volt faraday deg^{-1}.

[4] The steady state postulate can be applied with reference to other equilibrium states, e.g., osmotic equilibrium. However, in writing eq (17) we imply the one indicated because we regard $\bar{S}_i^*$, $\bar{V}_i^*$ and Θ_{ij}^* as constants.

[5] It should be noticed that we distinguish γ^s in eq (2) and γ^f here. We regard γ^s as being defined on the basis of a postulate that the electrostatic potential, $\Delta\xi$, can be operationally defined between solutions of different compositions at finite concentrations. This postulate has been rejected.

A fundamental set of phenomenological relations

$$\{J^I\}=[L^I]\{X^I\} \tag{23}$$

with

$$[L^I]=[L^I]^T \tag{24}$$

may now be set down by choosing

$$\{J^I\}=\begin{Bmatrix} J_1^I \\ \cdots \\ J_m^I \\ J_{m+1}^I \\ \cdots \\ J_r \\ J_q \end{Bmatrix}, \text{ and } \{X^I\}=\begin{Bmatrix} -\Delta\mu_1^* \\ \cdots \\ -\Delta\mu_m^* \\ -\Delta\mu_{m+1}^* \\ \cdots \\ -\Delta\mu_r^e \\ -\Delta\ln T \end{Bmatrix} \tag{25}$$

This choice of flows and forces is similar to that employed by Kirkwood [22] in differential form. We have already defined the first r elements of $\{X^I\}$ and grant that $\Delta\ln T$ is a meaningful quantity. The first r elements of $\{J^I\}$ are flows of chemical constituents corresponding to the respective elements of $\{m^I\}$. Since the chemical constituents are defined as having fixed identities in cell processes including exchanges with the surroundings of α and β it may be granted that the first r elements of $\{J^I\}$ are meaningful quantities. It is this conservation of chemical identity in the complete specification of concentrations and of flows of matter which permits the analysis "without chemistry" [13].[5]

The flow of "entropic heat," J_q^I, must be given special notice. We select the name, entropic heat, on the basis of the discussion set down by de Groot [24] who notes that various flows are termed "flows of heat" by different authors. The flow of entropic heat is defined by

$$J_q^I=J_u-\sum_{i=1}^{m}\mu_i^* J_i^I-\sum_{i=m+1}^{r}\mu_i^e J_i^I \tag{26}$$

where J_u is the flow of energy. Energy is of course conserved in all cell processes. Entropic heat is not. However, we cannot rely upon eq (26) alone to define J_q^I since the chemical potential of a single ion constituent, μ_i^e, has been given no meaningful definition. Only its significance in the particular linear combinations of eq (9) has been established. It is necessary to state conditions which are at least sufficient to establish an operational definition of J_q^I.

We first note that by eq (23)

$$J_q^I=-L_{qq}^I\Delta\ln T-\sum_{j=1}^{r}L_{qj}^I X_j^I. \tag{27}$$

A measurement of the thermal conductivity of the junction when all flows of matter are zero gives

$$J_q^I=J_u;\quad (J_{j\neq q}^I=0) \tag{28}$$

from which L_{qq}^I may be determined using

$$L_{qq}^I=-\frac{J_u}{\Delta\ln T}+\sum_{j=1}^{r}L_{qj}^I\frac{X_j^I}{\Delta\ln T};\qquad (J_{j\neq q}=0) \tag{29}$$

when the experiment is designed to simultaneously evaluate the elements of $\{X^I\}$ and the elements L_{qj}^I are already known. Since by eq (24)

$$L_{qj}^I=L_{jq}^I \tag{30}$$

the equations

$$L_{qj}^I=L_{jq}^I=-\frac{J_j^I}{\Delta\ln T}+\sum_{i=1}^{r}L_{ji}^I\frac{X_i^I}{\Delta\ln T} \tag{31}$$

applied to measurements of the flow of each material constituent in the presence of a temperature difference would evaluate each term L_{qj}^I when again the elements of $\{X^I\}$ are simultaneously evaluated and the elements L_{ji}^I are known. We finally require the measurement of a complete set of isothermal permeability characteristics to define the elements of the isothermal admittance matrix in the equation

$$\begin{bmatrix} L_{11}^I & \cdots & L_{1r}^I \\ \cdots & \cdots & \cdots \\ L_{r1}^I & \cdots & L_{rr}^I \end{bmatrix}\begin{Bmatrix} X_1^I \\ \cdots \\ X_r^I \end{Bmatrix}=\begin{Bmatrix} J_1^I \\ \cdots \\ J_r^I \end{Bmatrix} \tag{32}$$

which is obtained from eq (23) by setting $\Delta\ln T$ equal zero. Isothermal measurements dealing with flows of conserved quantities require no special discussion.

This formulation of a *linear* macroscopic theory requires an additional postulate to put a restriction upon the magnitude of any admissible displacement of equilibrium from the reference state. We have chosen to give the treatment of a discontinuous system in order to avoid operational uncertainties which often arise in attempts to apply an analysis of a continuous system [25]. In general we are unable to measure intensive properties at an arbitrarily dense succession of planes lying between α and β. Our choice is in line with the suggestions of Kirkwood [22] and Scatchard [26]. Thus the specification of a junction such as one including a membrane or porous plug must include the specification of the composition of the contacting solutions at the reference state. At the reference state we formally assume that equilibrium is established with respect to all solution components throughout the region α to β. The integral admittance matrix, $[L^I]$, can in principle include linear "polarization" effects in the boundary layers. However, with

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[5] The treatment of water as a nonelectrolytic solvent limits the participation of hydrogen and hydroxyl ions in the net transfer of electric charge to those systems where either a strong acid or strong base is present as a solute. The treatment of weak electrolytes requires the introduction of "chemistry" [23].

reference to Kirkwood's treatment of thed tirec transformation of the analysis of a continuous system into the analysis of a discontinuous system, Schlögl [27] has demonstrated the possibility of "apparently" linear phenomenological relations where the elements of $[L']$ are not proper constants. In such a case the respective elements of a series of differential admittance matrices defined as functions of position between α and β would not, upon integration, give the corresponding elements of $[L']$. In a purely phenomenological approach no basis can exist for distinguishing "really" and "apparently" valid applications of eqs (23) and (24). Schlögl's analysis suggests that no difficulty exists in the limit of the reference state and that if the forces represented in $\{X'\}$ are "sufficiently small," the experimental demonstration of any such distinction would be difficult and would require measurements of the highest accuracy and precision. We require some quantitative criterion for judging what forces are "sufficiently small."

Miller [28] has recently reviewed the experimental evidence which bears upon the validity of the Onsager relations in macroscopic processes. Miller [29] and Dunlop and Gosting [30, 31] have given detailed attention to ternary diffusion in electrolytic solutions. It is clear from a study of these papers that any criterion will necessarily be somewhat arbitrary. Nevertheless, since a major part of the intuitive support for the postulation of a linear macroscopic theory involves the established validity of linear free energy relationships such as eq (17) it is reasonable to assume that the range of validity of eq (17) is of fundamental significance in applications of the theory. Therefore, we choose to apply the following minimum condition:

> It is assumed that determinations of the elements of $[L']$ will involve displacements of equilibrium with forces and flows of such a magnitude that the uncertainty in the value of an element L'_{ij} arising from uncertainties in measurements of temperatures, concentrations, pressures, and potentials will be equal to or greater than the errors introduced by neglecting variations of $\overline{V}_i^*$, $\overline{S}_i^*$, and Θ_{ij}^*.

This criterion has the practical advantage of setting "sufficiently small" at magnitudes consistent with the precision and accuracy of any particular experimental investigation.

4. Transformation Properties

In the fundamental formulation, a flow of electric charge is identified with the flow of each ionic constituent and a conjugate electromotive force is defined for each such flow. However, no net flow of charge or overall electromotive force occurs as an element of the vectors $\{J'\}$ and $\{X'\}$. The thermodynamic theory does not require us to define vectors containing such elements, but the definition of all elements of $\{J'\}$ during all processes including electric charge flows depends upon our extra-thermodynamic definitions of ionic constituents and our use of the established conservation relation

$$\frac{I}{\mathscr{F}}=\sum_{i=n+1}^{r} z\{J\}_i. \qquad (33)$$

The electric current in amperes is denoted by I. Equation (33) suggests a linear transformation of flows to give a new flow vector, say $\{J'\}$, where one element is the flow of electric charge. A corresponding transformation of forces to give a new force vector, $\{X'\}$, would contain an element conjugate to the flow of charge. In this paper we identify such an element of $\{X'\}$ as a junction EMF.

The steady state theory explicitly defines restrictive conditions which must be applied in carrying out linear transformations of flows and forces. The transformation properties are summarized by de Groot [32]. We set them down briefly in the notation of this paper.

We take as given

$$\{J'\}=[L']\{X'\} \qquad (23)$$

with

$$[L']=[L']^{\dagger} \qquad (24)$$

and

$$T\sigma=\{J'\}^{t}\{X'\} \qquad (34)$$

where σ is the rate of entropy production during a steady state process described by the vectors $\{J'\}$ and $\{X'\}$.

We may choose an alternative description of the same steady state process in terms of vectors $\{J'\}$ and $\{X'\}$ where

$$\{J'\}=[L']\{X'\} \qquad (35)$$

with

$$[L']=[L']^{\dagger} \qquad (36)$$

and

$$T\sigma=\{J'\}^{t}\{X'\} \qquad (37$$

The entropy production, σ, must be invariant under a linear transformation of flows and forces. We must define a new force vector by

$$\{X'\}=[b''']\{X'\} \qquad (38)$$

where the order of the superscripts in the matrix of the linear transformation indicates the direction of the transformation, i.e.,

$$[b'']=[b''']^{-t} \qquad (39)$$

The elements of the vector $\{X'\}$ must be linearly independent combinations of the elements of $\{X'\}$, i.e.,

$$det\,[b''']\neq 0 \qquad (40)$$

where the prefix, *det*, denotes the determinant of the matrix. The corresponding transformation of flows is uniquely defined by

$$\{J'\}=[a'']\{J'\} \tag{41}$$

where

$$[a'']=[\![b'']\!]^{\dagger-1} \tag{42}$$

Alternatively, since the reciprocal of the transpose of a matrix is the same as the transpose of its reciprocal the transformations may be defined in reverse order with

$$[\![b'']\!]=[a'']^{\dagger-1} \tag{43}$$

The matrix $[a'']$ takes the role of de Groot's matrix β and we note that an application of the transformation

$$[\![L']\!]=[a''][\![L]\!][a'']^{\dagger} \tag{44}$$

is required to complete the definition of an alternative set of phenomenological relations to replace eq (23).

Finally, we note that in the general case we are dealing with a force vector whose elements are formally linearly independent in terms of their definitions from measurements of intensive properties. We may state that if not all the elements X_i^f are zero,

$$\sum_{j=1}^{q} \epsilon_i X_i^f \neq 0 \tag{45}$$

for any choice of constants, ϵ_i. The transformation properties given remain valid regardless of the permeability characteristics of any junction permeable to at least one ion constituent. In a real system if any one flow or a linear combination of flows is identically zero in all steady state flow processes, the elements of $\{J'\}$ will not be linearly independent. We will study such a special case in section 7 below and set a linear combination of forces to zero. de Groot demonstrates that the *a priori* definition of independent forces secures the validity of the transformation properties despite any linear dependence of flows in a special case.

5. Restrictive Condition Upon a Defined EMF

We consider first a matrix $[\![a'']\!]$. Certain general restrictions upon the form of this matrix may be adopted on the basis of elementary considerations. The nonelectrolytes are *independent* components of conserved chemical identity. The law of conservation of mass is applied to the flow of each such nonelectrolyte. The flows of $r-m-1$ electrolytes and of electric charge are an interdependent group subject to the laws of conservation of mass and of electric charge, but the electroneutrality condition only operates as a restriction upon the flow of ionic constituents with respect to other ionic constituents. It does not restrict the independence between flows of nonelectrolytes and electrolytes. We take these points into consideration when we write

$$[\![a'']\!]=\left[\!\!\left[\begin{array}{ccc|cccc|c}
1 & \dots & 0 & 0 & \dots & 0 & 0 & 0 \\
\dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\
0 & \dots & 1 & 0 & \dots & 0 & 0 & 0 \\
\hline
0 & \dots & 0 & a_{m+1,m+1} & \dots & a_{m+1,r-1} & a_{m+1,r} & 0 \\
\dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\
0 & \dots & 0 & a_{r-1,m+1} & \dots & a_{r-1,r-1} & a_{r-1,r} & 0 \\
0 & \dots & 0 & z_{m+1}^f & \dots & z_{r-1}^f & z_r^f & 0 \\
\hline
0 & \dots & 0 & 0 & \dots & 0 & 0 & 1
\end{array}\right]\!\!\right] \tag{46}$$

where the last column and the last row indicate that we retain the flow of entropic heat as a fundamental flow. It is convenient to have the rth element of our new vector $\{J'\}$ equal to the flow of electric current. This is indicated in the matrix where

$$a''_{rj}=0; \quad (j=1,\ldots,m,q); \tag{47}$$

and

$$a''_{rj}=z_j^f; \quad (j=m+1,\ldots,r). \tag{48}$$

The rth flow defines the flow of electric charge. The flows J'_1 through J'_m are the flows of neutral components not involving a transfer of electric charge. It is natural to inquire into the possibility of defining as set of $r-m-1$ independent flows of the neutral electrolytic components represented by the last $r-m-1$ elements of the vector $\{m^*\}$ in such a way that these flows do not imply a flow of electric charge. On the most elementary rational grounds a net transfer of a quantity of an electrolytic component from α to β must represent some combination of the transfers of ionic constituents. It is not obvious that any established rules or conventions dictate these combinations, but we identify the respective conjugate forces defined by a matrix $[b'']$ with the chemical potential differences of neutral electrolytic components defined as linear combinations in eq (10). The fact that the eq (42) describes a unique operation permits us to carry out an inverted development.

Before setting down a matrix $[b'']$ we note that in the matrix $[a'']$ given above the dashed lines show how the matrix may be partitioned to give a pseudo-diagonal matrix;

$$[a'']=\left[\!\!\left[\begin{array}{ccc} M & 0 & 0 \\ 0 & N & 0 \\ 0 & 0 & Q \end{array}\right]\!\!\right] \tag{49}$$

The submatrices $[\![M]\!]$ and $[Q]$ are identity matrices, and the submatrices $[\![0]\!]$ are zero matrices. It results as a property of such forms [33] that when the matrix $[N]$ is not singular,

$$[b''] = [a'']^{\dagger -1} = \begin{bmatrix} M & 0 & 0 \\ 0 & N^{\dagger -1} & 0 \\ 0 & 0 & Q \end{bmatrix} \qquad (50)$$

with

$$det\,[b''] = det\,[N]^{\dagger -1} \qquad (51)$$

Thus we write the pseudodiagonal form

$$[b''] = \left[\begin{array}{ccc|cccc|c} 1 & \cdots & 0 & 0 & \cdots & 0 & 0 & 0 \\ 0 & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & \cdots & 1 & 0 & \cdots & 0 & 0 & 0 \\ \hline 0 & \cdots & 0 & \nu_{m+1,m+1} & \cdots & \nu_{r-1,m+1} & \nu_{r,m+1} & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & \cdots & 0 & \nu_{m+1,r-1} & \cdots & \nu_{r-1,r-1} & \nu_{r,r-1} & 0 \\ 0 & \cdots & 0 & b''_{r,m+1} & \cdots & b''_{r,r-1} & b''_{r,r} & 0 \\ \hline 0 & \cdots & 0 & 0 & \cdots & 0 & 0 & 1 \end{array}\right] \qquad (52)$$

with the matrix $[\nu]^{\dagger}$ from eq (10) comprising the first $r-1$ rows and first r columns. Only the elements, b''_{rj}, in the rth row and columns $m+1$ through r are left to be determined.

The restriction upon $[b'']$ can be demonstrated. For the moment we assume that $det\,[b'']$ does not vanish. The definition of an element of the ith row of the reciprocal of a transposed matrix is [33],

$$a''_{ij} = \frac{cof\; b''_{ij}}{det\,[b'']}, \qquad (53)$$

where the numerator on the right is the cofactor of the element indicated. Following eq (53) we write the definitions of the elements of $[a'']$ within the submatrix $[N]$ as

$$a''_{ij} = \frac{cof\; N^{\dagger -1}_{i-m,j-m}}{det\,[N]^{\dagger -1}} \qquad (54)$$

The electrical neutrality of each component represented in the vector $\{m^*\}$ as stated in eq (6) gives the condition,

$$\sum_{j=m+1}^{r} z'_j N^{\dagger -1}_{i-m,j-m} = 0; \qquad (i = m+1, \ldots, r-1) \quad (55)$$

Equation (55) applied in the first $r-m-1$ rows of $det\,[N]^{\dagger -1}$ gives zeros as the first $r-m-1$ elements of any column when the other $r-m-1$ columns are added to it. The last element of that column then becomes

$$\sum_{j=m+1}^{r} z'_j N^{\dagger -1}_{r-m,j-m} = \sum_{j=m+1}^{r} z'_j b''_{rj} \qquad (56)$$

for any jth column. It then follows that

$$det\,[b''] = \frac{cof\; b''_{rj}}{z'_j} \left(\sum_{j=m+1}^{r} z'_j b''_{rj} \right) \qquad (57)$$

for any jth column $m+1$ through r. Substituting from eq (57) for $det\,[b'']$ in eq (53) gives

$$a''_{rj} = z'_j \left(\sum_{j=m+1}^{r} z'_j b''_{rj} \right)^{-1} \qquad (58)$$

Clearly, if

$$\sum_{j=m+1}^{r} z'_j b''_{rj} = 1, \qquad (59)$$

eqs (47) and (48) will be satisfied provided $[b'']$ is not singular. The nonsingularity of $[b'']$ is assured by the requirement that $[\nu]$ be of rank $r-1$. At least one $cof\; b''_{rj}$ will not vanish. When the condition of eq (59) is applied the determinant will be given by

$$det\,[b''] = \frac{cof\; b''_{rj}}{z'_j} \neq 0. \qquad (60)$$

6. Reference Ion Electromotive Force

An extremely important class of experimental systems including concentration cells and various cells with transference have identical reversible terminal electrodes [1] and can be designed to fall into the class of systems discussed in section 2. It is proper to inquire as to whether or not the EMF between a single pair of identical reversible probe electrodes, one at ϕ and one at β, may be formally regarded as the junction electromotive force. We may choose to order the elements of $\{m'\}$, $\{X'\}$ and $\{J'\}$ to have the rth constituent be that one to which the electrode pair is reversible. We define a "reference ion" force vector with

$$X^*_i = X'_i; \qquad (i = 1, \ldots, m); \qquad (61)$$

$$X^*_i = \sum_{j=m+1}^{r} \nu_{ji} X'_j; \qquad (i = m+1, \ldots, r-1); \quad (62)$$

$$X^*_r = \frac{X'_r}{z'_r} \qquad (63)$$

and

$$X^*_q = X'_q. \qquad (64)$$

The matrix $[b'']$ is thus of the class of $[b'']$ in eq (52). The elements

$$b''_{rj} = 0; \qquad (j = 1, \ldots, r-1, q) \qquad (65)$$

and

$$b''_{rr} = \frac{1}{z'_r}. \qquad (66)$$

clearly satisfy the restriction imposed by eq (59). Therefore, any one of the $r-m$ EMF's $\Delta\phi_i$ defined by eq (14) may be chosen as *the* junction EMF.

This reference ion formulation is important for practical applications. In most systems one can at best discover a single pair of adequate reversible electrodes. Experimental flows will normally be expressed most directly in terms of the vector $\{J''\}$ with the forces being in terms of the vector $\{X''\}$, A transformation,

$$\{X'\}=[b'']\{X''\}, \tag{67}$$

must be applied with

$$[b'']=[b'']^{-1}. \tag{68}$$

7. Junctions With Zero Electric Current Flow

Treatments of electromotive forces acting across junctions are most often encountered in discussions of the thermodynamics of galvanic cells. In such treatments one is concerned with the apparently reversible EMF measured at the limit of zero electric current flow. Guggenheim [9] has given a treatment of isothermal, isopiestic cells with liquid-liquid junctions without employing eq (1). The treatment is one of a continuous steady state system without chemistry in a solvent fixed frame of reference. His work is an exception to the apparent universal practice of using eq (1) or its equivalent. Therefore, some indication must be given of the relationship between the treatment here and the more common treatments. In addition the treatment of junctions at states of zero current gives an important relationship for use in connection with eq (10).

It can be shown [34] that when no electric current is flowing through the junction,

$$\sum_{j=1}^{r}\tau_j^f\Delta\mu_j=0\,; \qquad \left(\frac{I}{\mathscr{F}}=0\right). \tag{69}$$

The coefficients, τ_j^f, are the integral stoichiometric transference numbers in a cell fixed frame of reference when no difference of temperature, pressure, or composition exists between α and β, i.e.,

$$\tau_j^f=J_j^f\left(\sum_{j=1}^{r} z_j^f J_j^f\right)^{-1}; \qquad (\Delta T=\Delta P=\{\Delta m^*\}=0). \tag{70}$$

The numbers τ_j^f are properties of the junction defined as functions of the elements of the admittance matrix $[L^f]$.
These functions are

$$\tau_j^f=\frac{1}{L_E}\sum_{i=1}^{r} z_i^f L_{ji}^f \tag{71}$$

where

$$L_E=\sum_{j=1}^{r}\sum_{i=1}^{r} z_j^f z_i^f L_{ji}^f \tag{72}$$

with

$$\sum_{j=m+1}^{r} z_j^f\tau_j^f=1. \tag{73}$$

The detailed manipulations leading to the above relations need not be repeated. However, in existing analyses the use of eq (1) as an elementary postulate gives a familiar result in differential form as

$$-\mathscr{F}d\xi=\sum_{j=1}^{r}\tau_j^f(d\mu_j)_{d\xi=0}=RT\sum_{j=1}^{r}\tau_j^f(d\ln a_j)_{d\xi=0} \tag{74}$$

which because of uncertainties in notation may appear to be inconsistent with eq (69). The relationship may be seen clearly if we write

$$\Delta\mu_j=(\Delta\mu_j)_{\Delta\xi=0}+z_j^f\mathscr{F}\Delta\xi \tag{75}$$

and substitute for $\Delta\mu_j$ in eq (69). The use of eq (73) to reduce the coefficient of $\mathscr{F}\Delta\xi$ then gives

$$-\mathscr{F}\Delta\xi=\sum_{j=1}^{r}\tau_j^f(\Delta\mu_j)_{\Delta\xi=0}. \tag{76}$$

Of course this only demonstrates a formal abstract relationship since the operational significance of eq (1) has not been established for ordinary electrochemical systems.

Nevertheless, we note that eq (69) is a linear combination of chemical potential differences defined as a function of the permeability characteristics of the junction. Thus when this relation is added to the set of equations in eq (10) we have a set of r equations in r unknowns,

$$\begin{bmatrix} 1 & \cdots & 0 & 0 & \cdots & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & \cdots & 1 & 0 & \cdots & 0 & 0 \\ 0 & \cdots & 0 & \nu_{m+1,m+1} & \cdots & \nu_{r-1,m-1} & \nu_{r,m-1} \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \\ 0 & \cdots & 0 & \nu_{m+1,r-1} & \cdots & \nu_{r-1,r-1} & \nu_{r,r-1} \\ \tau_1^f & \cdots & \tau_m^f & \tau_{m+1}^f & \cdots & \tau_{r-1}^f & \tau_r^f \end{bmatrix} \left\{\begin{matrix} \Delta\mu_1^* \\ \cdots \\ \Delta\mu_m^* \\ \Delta\mu_{m+1}^* \\ \cdots \\ \Delta\mu_{r-1}^* \\ \Delta\mu_r^* \end{matrix}\right\} = \left\{\begin{matrix} \Delta\mu_1^* \\ \cdots \\ \Delta\mu_m^* \\ \Delta\mu_{m+1}^* \\ \cdots \\ \Delta\mu_{r-1}^* \\ 0 \end{matrix}\right\} \tag{77}$$

The elements τ_{m+1}^f through τ_r^f obey eq (73); therefore the condition of eq (59) required for $b_{r,m+1}''$ through $b_{r,r}''$ in treating the matrix $[b'']$ applies. It may be shown by a treatment similar to that applied to $[b'']$ that the matrix here does not vanish unless

$$\tau_{m+1}^f=\ldots=\tau_r^f=0 \tag{78}$$

Thus if the junction is permeable to at least one ionic constituent of the solutions at α and β, eq (77) possesses a unique solution. This result confirms the statement given after eq (10).

It should be noted that eq (77) has the distinct practical advantage of unifying the treatment of galvanic cells having identical terminal electrodes in compartments separated by a defined junction through which flow continuity is established. It is clear that a solution for any $\Delta\mu_i^\xi$ will after applying eq (13) give the EMF, $\Delta\phi_t$, at the limit of zero electric current flow in terms of the transference numbers and the thermodynamic properties of independent isolable components.

8. Electromotive Force at Infinite Dilution

The reference state of unit activity coefficient established for treating the thermodynamic properties of solutes is infinite dilution in pure solvent. In the limit of infinite dilution aqueous solutions of strong electrolytes are "nearly" insulators and the Debye-Hückel limiting law is valid for electrolytic solutes as a whole. In accord with the discussion of Tolhoek and de Groot [8] and Guggenheim [7] we may regard it as meaningful to speak of a difference of electrostatic potential acting as a part of the "force" conjugate to the transfer of an ionic constituent between solutions of infinitesimally different compositions in the neighborhood of infinite dilution. To define this "force" we make use of several commonly used extrathermodynamic conventions, and we need only consider isothermal, isopiestic systems.

We assume that the activity coefficients of solute nonelectrolytes approach unity much more rapidly than their concentrations approach zero in the limit as a solution is diluted with pure solvent. We write

$$(d\mu_i^*)_{T,P}=RTd\ln m_i^*;\quad (i=2,\ldots,m). \tag{79}$$

For ionic solute constituents we apply the same assumption and write

$$(d\mu_i^\xi)_{T,P}=RTd\ln m_i^\xi+z_i^\xi\mathscr{F}d\xi;\quad (i=m+1,\ldots,r) \tag{80}$$

It will be noted that the Debye-Hückel theory supports the assumption underlying eq (80) since the limiting law

$$(\ln\gamma_i^\xi)_{T,P,d\xi=0}=-A(z_i^\xi)^2\sqrt{\mathrm{u}} \tag{81}$$

where u is the ionic strength, i.e.,

$$\mathrm{u}=\frac{1}{2}\sum_{j=m+1}^{r}(z_j^\xi)^2m_j^\xi, \tag{82}$$

suggests that $(\ln\gamma_i^\xi)_{T,P,d\xi=0}$ approaches zero in the limit of infinite dilution as $\ln m_i^\xi$ approaches minus infinity.

Using the relation.

$$d\ln m_i^\xi=\frac{dm_i^\xi}{m_i^\xi} \tag{83}$$

in eqs (79) and (80) and then applying the electroneutrality condition

$$\sum_{j=m+1}^{r}z_j^\xi dm_j^\xi=0 \tag{84}$$

gives a set of r equations in r unknowns.

$$\begin{bmatrix} \frac{RT}{m_2^\xi} & \ldots & 0 & 0 & \ldots & 0 & 0 \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\ 0 & \ldots & \frac{RT}{m_m^\xi} & 0 & \ldots & 0 & 0 \\ 0 & \ldots & 0 & \frac{RT}{m_{m+1}^\xi} & \ldots & 0 & z_{m+1}^\xi \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\ 0 & \ldots & 0 & 0 & \ldots & \frac{RT}{m_r^\xi} & z_r^\xi \\ 0 & \ldots & 0 & z_{m+1}^\xi & \ldots & z_r^\xi & 0 \end{bmatrix}$$

$$\left\{\begin{matrix} dm_2^\xi \\ \ldots \\ dm_m^\xi \\ dm_{m+1}^\xi \\ \ldots \\ dm_r \\ \mathscr{F}d\xi \end{matrix}\right\}=\left\{\begin{matrix} (d\mu_2^*)_{T,P} \\ \ldots \\ (d\mu_m^*)_{T,P} \\ (d\mu_{m+1}^\xi)_{T,P} \\ \ldots \\ (d\mu_r^\xi)_{T,P} \\ 0 \end{matrix}\right\} \tag{85}$$

The coefficient matrix is nonsingular; its determinant is given by

$$2(RT)^{r-2}\mathrm{u}\left(\prod_{j=2}^{r}m_j^\xi\right)^{-1}>0. \tag{86}$$

The solution,

$$\mathscr{F}d\xi=\sum_{j=m+1}^{r}\frac{z_j^\xi m_j^\xi}{2\mathrm{u}}(d\mu_j^\xi)_{T,P}, \tag{87}$$

gives the differential of the electrostatic potential at infinite dilution as a linear combination of the differentials of chemical potential. The coefficients in eq (87) satisfy eq (59).

It is clear from the form of eq (80) that $d\xi$ is introduced as the "force" conjugate to any infinitesimal transfer of electric charge, hence, eq (87) defines the electromotive force at infinite dilution. We use eq (87) to define the elements of the rth row of the linear transformation matrix in

$$[b^{rd}]\{X^r\}=\{X^d\} \tag{88}$$

where $[b^{rd}]$ is of the class required by eq (52). By eqs (41) and (43) we have the transformation

$$[a^{rd}]\{J^r\}=\{J^d\} \tag{89}$$

where each element J^d_{m+1} through J^d_{r-1} is a linear combination of the flows of ionic constituents defining the "flow" conjugate to the "force" acting on an isolable electrolytic component as a whole. The combinations are necessary consequences of established extra-thermodynamic conventions and assumptions. They are implicit in our established methods of treating the properties of completely dissociated electrolytes.

9. The Membrane EMF at Higher Concentrations

The definition of the membrane EMF at higher concentrations follows directly from the definition at infinite dilution. In order to remove any implication of a definition of an electrostatic potential difference at finite concentrations and concentration differences we write

$$\mathscr{F}\psi=\sum_{i=m+1}^{r}\frac{z_i\{m_i\}}{2u}\Delta\mu_i^* \tag{90}$$

where ψ is the electromotive force between α and β. We regard ψ as representing the action of an electric field in the sense that it denotes a force acting to produce a flow of electric charge, but it is not a gradient of an external electrostatic potential field [35]. The EMF, ψ, is fully meaningful since every term on the right hand side is meaningful. It is arbitrary in the sense that our choice of the reference state of infinite dilution and the applications of eqs (79) and (80) are arbitrary. It depends upon our definitions of the elements of the vector $\{m^r\}$ and our use of these ion constituent concentrations in writing the ionic strength, u, given in eq (82) and the electroneutrality condition given as eq (3). It is, however, quite independent of any arbitrary choice of the matrix $[\nu]$ to give the elements of $\{m^*\}$. The matrix $[a^{rd}]$ of eq (89) defined at infinite dilution fixes the stoichiometry governing exchanges of radical chemical constituents. The most elementary considerations of internal consistency dictate the use of this same stoichiometry regardless of the absolute concentrations of the solutions.

10. Discussion

The need for defining a membrane electromotive force and the corollary flows of electrolytes as a whole arises quite naturally if we consider the treatment of electrokinetic phenomena. However, we must first establish certain points in terms of a specific example.

Consider a membrane cell with compartments filled with HCl solutions. Let it be arranged in the manner of a four lead resistor with a pair of probe electrodes close to the membrane—one on each side. These probe electrodes establish the positions of the planes, α and β, indicated in section 2. They are potential indicating devices and carry no steady electric currents. Let each compartment also be provided with a working or current electrode more remote from the membrane than α and β. The electrode reactions at the current electrodes are to involve virtually insoluble components and either the chloride or the hydrogen ion constituent of the solution. Let us also provide for continuous, adjustable flows through each compartment utilizing feed solutions of adjustable composition.

A little reflection will show that we can establish a particular steady state—defined by giving the elements of $\{X^r\}$—regardless of whether it is the hydrogen ions or the chloride ions which are exchanged with the solutions at the current electrodes. The adjustments of feed solution compositions and rates of flow serve as our compensating variables. If the phenomenological relations, eq (23), describe a steady state process taking place between α and β, they describe it independently of the specific nature of the processes at current electrodes which may in practice be at virtually infinite distances from the region between α and β. This statement of independence, the independence of dissipative processes occuring in different regions of space, expresses an elementary requirement of the steady state theory [39]. Processes which are described as coupled—having phenomenological relations with cross coefficients—in the production of entropy must take place in the same system. By system we mean an open system, the region of space between α and β as defined in section 2. If we wish to describe a particular process in terms of some set of phenomenological relations resulting from a linear transformation of eq (23), the second form of the phenomenological relations will describe the *same* and *only the same* process if and only if it is defined so as not to include *external* dissipative processes. This elementary requirement is expressed in the steady state theory when we state that the rate of entropy production given by eq (34) must be independent of a linear transformation of the forces and flows.

Ordinary isothermal electrokinetic phenomena at membranes are investigated by making experimental measurements—in a membrane fixed frame of reference—of flows of fluid volume and electric current under the influence of their conjugate forces—pressure difference and electric potential difference. We can site, for example, de Groot's [40] and Guggenheim's [36] demonstrations of the application of the steady state theory in the special case where no differences of temperature or of composition are present to act as forces. They show that the well known experimental relation, the Saxén relation, between the streaming potential and the electroosmotic transport, i.e.,

$$\left(\frac{\Delta\xi}{\Delta P}\right)_{I=\Delta T=\{\Delta m^*\}=0}=\left(\frac{J_V}{I}\right)_{\Delta P=\Delta T=\{\Delta m^*\}=0} \qquad (91)$$

may be regarded as a consequence of the Onsager reciprocal relations. J_V is the rate of flow of fluid volume and $\Delta\xi$ is, as before, the difference in electrostatic potential. The electrostatic potential, $\Delta\xi$, is of course a meaningful quantity when measured between phases of identical composition and temperature; it is the EMF measured between the terminals of any pair of identical electrodes. Hence, neither of the treatments cited makes any reference to the nature of the electrodes employed to measure $\Delta\xi$. The fact that these analyses impose the restriction

$$\Delta T=\{\Delta m^*\}=0 \qquad (92)$$

and the fact that in practice the experimental measurements do not include measurements of the flows of heat and of the relative flows of constituents obscures certain features of the phenomena involved. J_V is computed from the measured rate of change of the volume of solution in a cell compartment with due allowance for the change of the volume of a compartment arising from the reactions of insoluble components at the working electrodes. In such treatments there is normally an implicit understanding that the reactions at the probe and working electrodes are identical. The problem of separating electrode and membrane processes simply does not arise in such a restricted case. However, we may, for example, study Guggenheim's [9] treatment of concentration cells with transference. This is a case where $\{\Delta m^*\}$ is not restricted to zero. Although our formulation is first to be distinguished from his treatment of concentration cells by the fact that his is in a Hittorf, i.e., solvent fixed, frame of reference, the essential point is that Guggenheim explicitly requires the use of electrodes reversible to one of the ionic constituents. Such a treatment avoids the classical uncertainty involving $\Delta\xi$. Since he restricted his treatment to steady states not involving flows of electric charge, the requirement of specific electrodes does not introduce any difficulty with respect to the separation of electrode and junction processes.

Since the phenomenological relations of eq (23) describe processes which involve electrokinetic effects as well as diffusion effects, we are led immediately to attempt to set down a treatment in which heat flows and temperature differences and diffusion flows and concentration differences are added to the flows and forces of the electrokinetic treatment. However, we find that not only the meaning of $\Delta\xi$ but also the meaning of J_V, is uncertain. We must require our formulation to describe the processes in the "membrane", i.e., α to β, region. It is to result from a linear transformation of the fundamental phenomenological relations, eq (23).

At first glance it appears that we would write

$$J'_V=\sum_{i=1}^{m}\overline{V}'_iJ'_i+\sum_{i=m+1}^{r}\overline{V}^*_iJ'_i \qquad (93)$$

where the terms $\overline{V}'_i$ are the partial molal volumes of the nonelectrolytes and the terms $\overline{V}^*_i$ are the partial molal volumes of ionic constituents represented in the vector $\{m'\}$. However, we have already indicated in the discussion of eq (2) that $\overline{V}'_i$ has no operational meaning when we reject the postulate that $\Delta\xi$ is operationally defined. We could consider a convention which defines $\overline{V}'_i$ for any constituent. Such a convention would permit us to retain the distinction between electrode and membrane processes. However, there is an alternative approach which has to be considered.

We recognize that in the study of combined hydrodynamic and diffusion flow processes during steady states not involving net flows of electric current, we have by definition

$$(J'_V)_{I=0}\equiv\sum_{j=1}^{r-1}\overline{V}^*_j(J^*_j)_{I=0} \qquad (94)$$

where $(J^*_j)_{I=0}$ are the flows of the neutral components represented in the vector $\{m^*\}$ and $\overline{V}^*_j$ are their partial molal volumes. We recognize that in practice the flows $(J^*_j)_{I=0}$ will be computed from experimental measurements of changes of ion constituent concentrations with explicit dependence upon the requirement of electroneutrality, i.e., as linear combinations of the flows $(J'_i)_{I=0}$. We are thus led to write

$$J'_V=\sum_{j=1}^{r-1}\overline{V}^*_jJ'_j;\ I\neq0 \qquad (95)$$

where the flows J'_j are linear combinations of the flows of ion constituents which represent flows of electrolytes as a whole. It was necessary to discover what conditions are to be met in defining J'_j.

In section 5 of this paper we showed that we are first led to the conclusion that when we define the membrane EMF in terms of the potentials measured between pairs of identical probe electrodes with specific electrode reactions, we at the same time define, by implication, a particular method of combining the flows of ionic constituents into the flows of neutral electrolytes as a whole. Thus, by implication, we establish the definitions of J'_j and, hence, J'_V in eq (95). Therefore, we conclude that it is not proper to introduce any auxiliary convention which defines $\overline{V}'_i$ in eq (93) when we set down a transformation of eq (23) into an electrokinetic formulation.

In section 6 we showed that we can choose a "reference ion" EMF, $\Delta\phi_r$, by choosing to employ probe electrodes reversible to some particular ion constituent. Formally, there will be $r-m$ distinct choices possible. In general there will be a family of $r-m$ pairs of matrices $[b'^r]$ and $[a'^r]$. The definition of the flow of any jth neutral electrolyte

$$J_j^r=\sum_{i=m+1}^{r} a_{ji}^r J_i' ;\; (j=m+1,\ldots,r-1) \qquad (96)$$

will in general be different for each choice of a "reference ion." Although the arbitrariness of a "reference ion" electromotive force is objectionable, one can always employ such a device in order to define electrokinetic effects in terms of a general treatment. We can employ the essentially "direct experimental variables" such as appear in Saxén's relation, eq (91), in conjunction with diffusion flows and concentration difference forces without including *external* dissipative processes in our description of membrane processes.

The arbitrariness of a "reference ion" treatment can only be removed by adopting an additional convention—an "averaging" convention. In Sections 8 and 9 we showed that such a convention is implicit in the conventions already established for the treatment of the thermodynamic properties of electrolytic solutions. A general treatment which is consistent with the elementary defining stoichiometric relationships employed at the reference state of infinite dilution results when we write

$$J_v^\psi=\sum_{j=1}^{r-1}\overline{V}_j^* J_j^\psi \qquad (97)$$

where J_j^ψ is defined by the transformation given in eq (89).

It is important to emphasize that the treatment which defines ψ is complete only with respect to the requirement of consistency with established convention. We have implied that ψ is a physically significant quantity. The developments of this paper are not adequate to demonstrate any real physical significance. Our development in sections 8 and 9 follows the formal procedure of defining the Lagrangian multiplier corresponding to the electroneutrality condition.[7] Although as a formal device in section 8 ψ is uniquely defined when we write eq (85), the approach to ideal behavior implied by eq (80) is not subject to an adequate experimental test [42]. The use of the concept of "almost" insulators is not satisfying as a basis for attaching physical significance to $\Delta\xi$ in extremely dilute solution and, hence, to ψ in more concentrated solutions.

An important problem for further investigation is the comparison of experimentally determined values of ψ with the EMF's measured between pairs of saturated calomel electrodes. A study of representative attempts to set down meaningful conventions for junctions potentials [4, 43, 44] based upon established common practice shows that saturated solutions of potassium chloride are regarded as special experimental devices. It is abundantly clear that they are assumed to represent a practical approach to some ideal of "inert" behavior in experimental systems. We can, for example, accept ψ as a physically significant quantity if a general study of a large class of experimental systems shows that saturated calomel electrodes can be regarded as experimental devices which measure ψ directly with a degree of accuracy which is adequate for most practical purposes—"to within a few millivolts." We suggest this hypothesis here because our first tests support it, but we regard it, for the present, as only an example.

11. Summary of Symbols and Notation

a_i	Activity of a constituent, eq (74).
$[a'']$	Matrix of transformation of $g=r+1$ flows, r of chemical constituents and one of entropic heat, into the flows of $r-1$ chemical components, electric current, and entropic heat, eq (46).
$[\alpha'']$	$[a'']^{-1}$, the reciprocal of $[a'']$.
$[a^\psi]$	Matrix of the class $[a'']$ consistent with the conventional EMF, ψ, section 9.
$[a^r]$	Matrix of the class $[a'']$ consistent with a particular reference ion EMF, $\Delta\phi_r$, section 6.
$\mathscr{A}_u$	Chemical symbol of electrode component, eq (12).
$[b'']$	Matrix of transformation of forces, eqs (50) and (52); $[b'']=[a'']^{\dagger-1}$.
$[b^\psi]$	Matrix of the class $[b'']$; $[b^\psi]=[a^\psi]^{\dagger-1}$.
$[b^r]$	Matrix of the class $[b'']$; $[b^r]=[a^r]^{\dagger-1}$.
$\mathscr{B}_i'$	Chemical symbol of ion constituent, eq (12).
cof a_{ij}''	Cofactor of ijth element of $[a'']$.
det$[a'']$	Determinant of matrix $[a'']$.
$E_\phi^\beta-E_\phi^\alpha$	EMF measured between electrode terminals.
$\mathscr{F}$	Faraday.
I	Electric current.
J_i'	$i=1, \ldots, r$; rate of flow of a chemical constituent.
J_i'', J_i^ψ, J_i^r	$i=1, \ldots, r-1$; rate of flow of a neutral component.
J_r'', J_r^ψ, J_r^r	$I/\mathscr{F}$, eq (33).
$(J_i^\psi)_{I=0}$	$i=1, \ldots, r-1$; rate of flow of a neutral component when $I=0$, eq (94).
$J_q', J_q'', J_q^\psi, J_q^r$	$g=r+1$; rate of flow of entropic heat.
J_v	Rate of flow of fluid volume, section 10.
$[L'], [L'']$	Admittance matrices.
$\{m'\}$	Constituent composition vector having r elements which are the molalities of m nonelectrolytes and $r-m$ ion constituents.
$\{m^*\}$	Component composition vector having $r-1$ elements which are the molalities of m nonelectrolytes and $r-m-1$ neutral electrolytes.
P	Pressure.

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[7] Lagrangian multipliers as physically significant quantities are common in statistical mechanics. Onsager [41] suggests the use of such a multiplier to represent the electric potential in electrochemical systems. However, he gives no explicit definition and, further, he chooses to have his dissipation function include electrode processes.

R	Gas constant.
$\bar{S}_i^*$	Partial molal entropy of ith component in $\{m^*\}$.
$\bar{S}_i^e$	(Undefined) partial molal entropy of an ion constituent.
T	Temperature.
$\bar{V}_i^*$	Partial molal volume of ith component in $\{m^*\}$.
$\bar{V}_i^e$	(Undefined) partial molal volume of an ion constituent.
$X_i^f, X_i', X_i^*, X_i^r$	$i=1, \ldots, m$; forces, $-\Delta\mu_i^*$, acting conjugate to the flows of nonelectrolytes.
X_i^f	$i=m+1, \ldots, r$; forces, $-\Delta\mu_i^f$, acting conjugate to the flows of ion constituents.
X_i', X_i^*, X_i^r	$i=m+1, \ldots, r-1$; forces, $-\Delta\mu_i^*$, acting conjugate to the flows of neutral electrolytes.
X_r^*	Conventionally averaged force, $-\mathscr{F}\psi$, acting conjugate to the flow of electric charge, section 9.
X_r^r	Force, $-\mathscr{F}\Delta\phi_r$, acting conjugate to the flow of electric charge in accord with a reference ion convention, section 6.
$X_q^f, X_q', X_q^*, X_q^r$	$q=r+1$; force, $-\Delta \ln T$, acting conjugate to the flow of entropic heat.
z_i^f	Electrovalence of a constituent.
α, β	Denote boundaries of membrane region; α to β positive.
γ_i^*	$i=1, \ldots, m$; molal activity coefficient of a nonelectrolyte; and $i=m+1 \ldots, r-1$; mean molal activity coefficient of an electrolyte.
γ_i^e	(Undefined) electrostatic molal activity coefficient of an ion constituent.
γ_i^f	Formal device denoting the molal activity coefficient of an ion constituent; eq (19).
Θ_{ij}^*	Thermodynamic composition coefficient, eq (18).
$\lambda_{\alpha i}$	Stoichiometric coefficient of a neutral component in an electrode reaction, eq (12).
μ_i^f	Formal device denoting the chemical potential of an ion constituent.
$\Delta\mu_i^f$	Difference in the chemical potential of an ion constituent between α and β, eq (13).
μ_i^*	The chemical potential of a component represented in $\{m^*\}$.
$\{\nu\}$	The stoichiometry matrix, eq (4).
τ^f	The integral stoichiometric transference number of a constituent in a cell fixed frame of reference; eq (69).
ξ	(Undefined) the absolute electrostatic potential.
$\Delta\phi_i$	Equation (13).
ψ	Conventionally defined EMF, section 9.

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