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### Authors

Smyrl, Wm. H.  
Newman, John.

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William H. Smyrl and John Newman

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POTENTIALS OF CELLS WITH LIQUID JUNCTIONS

William H. Smyrl and John Newman

May, 1968

## Potentials of Cells with Liquid Junctions

William H. Smyrl\* and John Newman  
Inorganic Materials Research Division  
Lawrence Radiation Laboratory, and  
Department of Chemical Engineering  
University of California, Berkeley

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### Abstract

The potential of cells with liquid junctions is affected by diffusion of ions in the junction region. From the laws of diffusion, concentration profiles have been calculated and values of potentials have been determined for several different junctions without the assumption of activity coefficients equal to one. This allows the determination of the magnitude of the diffusion effect in cases where it is desirable that the effect be negligible, as with an electrode of the second kind.

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\* School of Pharmacy, University of California, San Francisco.

## Introduction

The only cells used in electrochemical studies which are strictly without liquid junction are those used to study the thermodynamic properties of alloys. In addition there are cells in which the effect of diffusion in the liquid junction is negligible, for example, a cell with an electrode of the second kind involving a solid salt which is only very slightly soluble. The theoretical analysis of the potential of cells with liquid junctions has been of interest to workers who wish to derive thermodynamic values from such cells by correcting for the effect of diffusion. Some of the basic problems of liquid junctions have been treated adequately (Taylor<sup>1</sup>, Guggenheim<sup>2</sup>, Wagner<sup>3</sup>), and we give here an alternate discussion which emphasizes the quantitative treatment of the transport phenomena. In addition, we shall present a method, with examples, of the calculation of the effect of diffusion on cell potentials without the assumption of ideal-solution behavior and activity coefficients equal to unity.

We shall attempt to give a clear definition of what is meant by liquid-junction potentials and to give a clear treatment of the diffusion phenomena. The expression of cell potentials involves a consideration of electrode equilibria. However, the final result generally requires a knowledge of the concentration profiles and of the effect of diffusion. Therefore, we begin with the treatment of transport in electrolytic solutions and of the determination of the concentration profiles.

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<sup>1</sup> Paul B. Taylor, The Journal of Physical Chemistry, 31, 1478-1500 (1927).

<sup>2</sup> E. A. Guggenheim, The Journal of Physical Chemistry, 33, 842-849 (1929).

<sup>3</sup> Carl Wagner, Adv. in Electrochem. & Electrochem. Engg., 4, 1-46 (1966).

### Transport in Electrolytic Solutions

The difference of the electrochemical potential  $\mu_i$  of an ion between two points (or phases) is the work of transferring one gram ion reversibly at constant temperature and volume from one point (or phase) to the other.<sup>4</sup> If we regard  $c_i \nabla \mu_i$  as the driving force per unit volume for diffusion and migration of species  $i$ , neutral species included, (where  $\nabla \mu_i$  is the gradient of the electrochemical potential of species  $i$ ) and  $K_{ij}(\underline{v}_j - \underline{v}_i)$  is the drag force exerted on species  $i$  by species  $j$  by virtue of their relative motion, then a force balance leads to the multicomponent diffusion equation:

$$c_i \nabla \mu_i = \sum_j K_{ij}(\underline{v}_j - \underline{v}_i). \quad (1)$$

The coefficient  $K_{ij}$  is taken to be independent of the velocity difference  $\underline{v}_j - \underline{v}_i$ , but it may be a function of temperature, pressure, and composition of the solution. The velocity  $\underline{v}_j$  is the average or macroscopic velocity of species  $j$ .

Instead of  $K_{ij}$ , one can define a transport coefficient  $\mathcal{D}_{ij}$  having the dimensions of a diffusion coefficient:

$$K_{ij} = RT \frac{c_i c_j}{c_T \mathcal{D}_{ij}}, \quad (2)$$

where  $c_T$  is the total concentration of the solution. This also serves the goal of accounting for much of the composition dependence of the coefficients  $K_{ij}$ . Equation (1) has been discussed elsewhere (see, for example, Newman<sup>5</sup>).

In this force balance,  $K_{ij} = K_{ji}$  or  $\mathcal{D}_{ij} = \mathcal{D}_{ji}$  by Newton's third

<sup>4</sup> E. A. Guggenheim. Thermodynamics. Amsterdam: North-Holland Publishing Company, 1959, p.374.

<sup>5</sup> John Newman. Adv. in Electrochem. & Electrochem. Engg., 5, 87-135 (1967).

law of motion. This is equivalent to the assumption frequently made in treatments of irreversible thermodynamics. Compare Onsager<sup>6</sup>, who wrote the equation in the form

$$-\nabla\mu_i = \sum_k R_{ik}(c_k v_k - c_{k-1} v_{k-1}). \quad (3)$$

In applications it is frequently desirable to use this equation in an inverted form. Toward this end it is to be noted that there are only n-1 independent velocity differences and n-1 independent gradients of electrochemical potentials in a solution with n species. Therefore, equation (1) can be expressed as

$$c_i \nabla\mu_i = \sum_j M_{ij}(v_j - v_0), \quad (4)$$

where  $v_0$  is the velocity of any one of the species and where

$$M_{ij} = K_{ij} \quad \text{if } i \neq j.$$

$$M_{ij} = K_{ij} - \sum_k K_{ik} \quad \text{if } i = j.$$

It further follows that  $M_{ij} = M_{ji}$ . Bearing in mind that there are n-1 independent equations of the form (4), one can invert this equation to read

$$\frac{v_j - v_0}{c_j} = - \sum_{k \neq 0} L_{jk}^0 c_k \nabla\mu_k \quad \text{for } j \neq 0, \quad (5)$$

where the matrix  $\underline{\underline{L}}^0$  is the inverse of the submatrix  $\underline{\underline{M}}^0$ :

$$\underline{\underline{L}}^0 = (\underline{\underline{M}}^0)^{-1} \quad (6)$$

and where the submatrix  $\underline{\underline{M}}^0$  is obtained from the matrix  $\underline{\underline{M}}$  by deleting the row and the column corresponding to the species 0. The inverse

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<sup>6</sup> Lars Onsager, Annals of the New York Academy of Sciences, 46, 241-265 (1945).



matrix  $\underline{L}^0$  is also symmetric, that is,

$$L_{ij}^0 = L_{ji}^0 . \quad (7)$$

It is to be expected that the  $R_{ij}$ 's and the  $D_{ij}$ 's will be less composition dependent than the  $L_{ij}^0$ 's.

Certain combinations of the  $L_{ij}^0$ 's are related to measurable transport properties and have particular significance in the treatment of cells with liquid junctions. The current density is related to the fluxes of ionic species as follows:

$$\underline{i} = F \sum_i z_i N_{i-1} = F \sum_i z_i c_i \underline{v}_i = F \sum_i z_i c_i (\underline{v}_i - \underline{v}_0) . \quad (8)$$

Substitution of equation (5) yields

$$\underline{i} = -F \sum_{i \neq 0} z_i c_i \sum_{k \neq 0} L_{ik}^0 c_k \nabla \mu_k . \quad (9)$$

In a solution of uniform composition

$$\nabla \mu_k = z_k F \nabla \Phi , \quad (10)$$

where  $\nabla \Phi$  is the gradient of the electric potential. Equation (9) becomes in this case

$$\underline{i} = -F^2 \nabla \Phi \sum_{i \neq 0} z_i c_i \sum_{k \neq 0} L_{ik}^0 z_k c_k . \quad (11)$$

Comparison with Ohm's law, also applicable in this case,

$$\underline{i} = -\kappa \nabla \Phi$$

allows us to identify the conductivity

$$\kappa = F^2 \sum_{i \neq 0} \sum_{k \neq 0} L_{ik}^0 z_i c_i z_k c_k . \quad (12)$$

Although the  $L_{ik}^0$ 's depend upon the reference velocity chosen, the conductivity  $\kappa$  is invariant with respect to this choice.

Next we can identify the transference numbers. Again, for a solution of uniform composition, equation (10) is valid and equation (5) becomes

$$\underline{v}_j - \underline{v}_0 = -FV\Phi \sum_{k \neq 0} L_{jk}^0 z_k c_k . \quad (13)$$

For this case of uniform composition, the species flux is related to the current density and the transference number by the expression

$$t_{j\pm}^0 = z_j F c_j (\underline{v}_j - \underline{v}_0) = -t_j^0 \kappa \nabla \Phi . \quad (14)$$

Comparison shows that the transference number  $t_j^0$  of species  $j$  with respect to species 0 is given by

$$t_j^0 = \frac{z_j c_j F^2}{\kappa} \sum_{k \neq 0} L_{jk}^0 z_k c_k . \quad (15)$$

It is to be noted that the transference number has been defined as the fraction of the current carried by an ion in a solution of uniform composition. In a solution in which there are concentration gradients, the transference number is still a transport property related to the  $L_{ij}^0$ 's by equation (15), but it no longer represents the fraction of current carried by an ion. A different choice of the reference species will change the  $L_{ij}$ 's and hence the transference numbers with respect to a common reference species.

Equation (9) is applicable even in a non-uniform solution, and it can be rewritten in terms of the conductivity and the transference numbers, since  $L_{ij}^0 = L_{ji}^0$ ,

$$\frac{F}{\kappa} \underline{1} = - \sum_1 \frac{t_1^0}{z_1} \nabla \mu_1 . \quad (16)$$

As already noted, a different choice of reference species will change the transference numbers, but equation (16) still applies. However, it is apparent from equation (15) that the ratio  $t_j^0/z_j$  is not zero, even for a neutral species. While the reference velocity can be chosen arbitrarily to be that of any one of the species, charged or uncharged, it is usually taken to be the velocity of the solvent. In this case there is no problem if there are no other neutral components since the ratio  $t_1^0/z_1$  is always zero for the reference species.

Equation (16) also has the same form if other reference velocities, such as the mass-average velocity or the molar-average velocity, are used. Again, care should be exercised since the ratio  $t_1/z_1$  is then not zero for neutral species.

Equation (16) is quite useful in the calculation of the potential of cells with liquid junctions. In the cases of interest the current density is supposed to be zero, but equation (16) also allows one to estimate the effect of the passage of small amounts of current. Equation (16) is generally useful only if the concentration profiles in the liquid junction are known. These are determined not from equation (16), but from the laws of diffusion (equation (1)) and the method of forming the junction.

### Determination of Concentration Profiles

Several models of liquid junctions are popular, and to these we add one more.

a. Free-diffusion junction. At time zero the two solutions are brought into contact to form an initially sharp boundary in a long, vertical tube. The solutions are then allowed to diffuse into each other, and the thickness of the region of varying concentration increases with the square root of time. Even if the transport properties are concentration dependent and the activity coefficients are not unity, the potential of a cell containing such a junction should be independent of time.

b. Restricted-diffusion junction. The concentration profiles are allowed to reach a steady state by one-dimensional diffusion in the region between  $x=0$  and  $x=L$ , in the absence of convection. The composition at  $x=0$  is that of one solution and at  $x=L$  is that of the other solution. The potential of a cell containing such a junction is independent of  $L$  (as well as time). The condition of no convection is usually not specified (i.e., zero solvent velocity or zero mass-average velocity, etc.).

c. Continuous-mixture junction. At all points in the junction, the concentrations (excluding, we suppose, that of the solvent) are assumed to be linear combinations of those of the solutions at the ends of the boundary. This assumption obviates the problem of calculating the concentration profiles by the laws of diffusion.

d. Flowing junction. In some experiments the solutions are brought

together and allowed to flow side by side for some distance. It is sometimes supposed that observed potentials should approximate those given by a free-diffusion boundary.

e. Electrode of the second kind. To these we add the region of varying composition produced when a sparingly soluble salt is brought into contact with a solution containing a common ion. We might use a model similar to the free-diffusion junction if we imagine the salt to be introduced at the bottom of a vertical tube containing the solution. The sparingly soluble salt will then diffuse up the tube, and the concentration at the bottom will be governed by the solubility product.

The concentration profiles in cases a, b, and e are governed by the laws of diffusion (equation (1)). We propose to treat solutions so dilute that, in equation (1), we can neglect the interaction of the diffusing species with the other components except the solvent:

$$c_1 \nabla \mu_1 = RT \frac{c_1 c_o}{c_T D_{oi}} (v_o - v_1) = RT \frac{c_1}{D_{oi}} (v_o - v_1) \quad (17)$$

or

$$\frac{N_1}{c_1 v_1} = - \frac{c_1 D_{oi}}{RT} \nabla \mu_1 + c_1 v_o \quad (18)$$

However, the activity coefficients will not be assumed to be unity.

The electrochemical potential  $\mu_1$  of an ionic species depends not only on the composition of the phase but also on the electrical state of the phase. For computational purposes it is convenient to express all the electrochemical potentials in terms of one electrical variable. One way to do this is to use the electrochemical potential for one ionic species,  $\mu_n$ , as a reference:

$$\mu_i = \mu_i - \frac{z_i}{z_n} \mu_n + \frac{z_i}{z_n} \mu_n \quad (19)$$

The combination  $\mu_i - z_i \mu_n / z_n$  is then the chemical potential of a neutral combination of ions and is independent of the electrical state, depending only on the local composition.

However, this choice is not convenient, particularly when the concentration of species n goes to zero. Another possibility is to express the electrochemical potential of species n as

$$\mu_n = RT \ln c_n + z_n F \Phi + \mu_n^\theta \quad (20)$$

The potential  $\Phi$  then has some of the characteristics of the commonly used electrostatic potential, and, in fact, has exactly the same properties in infinitely dilute solutions where the activity coefficients of all neutral combinations become equal to one. At higher concentrations, the quasi-electrostatic potential  $\Phi$  is of course arbitrary in the sense that it depends on the designation of the reference species n.

In contrast, the electrochemical potential of species n, or  $\mu_n / z_n F$ , behaves more like the potential of a reference electrode reversible to species n. In a solution of uniform composition, both of these potentials behave like the commonly used electrostatic potential, and, in fact, satisfy Laplace's equation

$$\nabla^2 \Phi = 0 \quad (21)$$

Now, the chemical potential of a neutral combination can be expressed in terms of a well-defined combination of activity coefficients:

$$\begin{aligned} \mu_i - \frac{z_i}{z_n} \mu_n &= \mu_i^\theta - \frac{z_i}{z_n} \mu_n^\theta + RT \ln c_i - \frac{z_i RT}{z_n} \ln c_n \\ &+ RT \left( \ln f_i - \frac{z_i}{z_n} \ln f_n \right) \end{aligned} \quad (22)$$

For the activity coefficients we shall use Guggenheim's expression<sup>7</sup> for dilute solutions of several electrolytes:

$$\ln f_i - \frac{z_i}{z_n} \ln f_n = -\alpha z_i (z_i - z_n) \frac{I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} + 2 \sum_j \left( \beta_{ij} - \frac{z_i}{z_n} \beta_{nj} \right) c_j, \quad (23)$$

where

$$I = \frac{1}{2} \sum_j z_j^2 c_j \quad (24)$$

is the ionic strength,  $c_j$  is in moles/l, and for aqueous solutions  $\alpha = 1.171 (\text{l/mole})^{\frac{1}{2}}$  at 25°C. The values of the coefficients  $\beta_{ij}$  are tabulated by Guggenheim and are zero unless species  $i$  and  $j$  are ions of opposite charge. We shall use these expressions with concentrations instead of molalities, as used by Guggenheim.

Finally, then, the electrochemical potential of an ionic species is expressed as

$$\begin{aligned} \mu_i = RT \ln c_i + z_i F \phi + \mu_i^\theta \\ + RT \left\{ -\alpha z_i (z_i - z_n) \frac{I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} + 2 \sum_j \left( \beta_{ij} - \frac{z_i}{z_n} \beta_{nj} \right) c_j \right\}. \end{aligned} \quad (25)$$

To determine the concentration profiles in liquid junctions involves solving the diffusion equation (18) in conjunction with equation (25) and with the material balance equation,

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \underline{N}_i, \quad (26)$$

the electroneutrality equation,

$$\sum_i z_i c_i = 0, \quad (27)$$

and the condition of zero current. In a following section we illustrate

<sup>7</sup> E. A. Guggenheim. Thermodynamics, North-Holland Publishing Company 1959, p.357.

how to use the concentration profiles or the values of  $\Delta\phi$  to calculate cell potentials. Substitution of equations (18) and (25) into equation (26) yields an equation describing diffusion, migration, and convection of an ionic species but including the activity coefficients in the driving force:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (c_i \mathbf{v}_o) = D_{oi} \nabla^2 c_i + \frac{z_i F D_{oi}}{RT} \nabla \cdot (c_i \nabla \phi) - \alpha z_i (z_i - z_n) D_{oi} \nabla \cdot \left( c_i \nabla \frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} \right) + 2D_{oi} \sum_j \left( \beta_{ij} - \frac{z_i}{z_n} \beta_{nj} \right) \nabla \cdot (c_i \nabla c_j). \quad (28)$$

This equation applies to solutions so dilute that interactions except with the solvent in the multicomponent diffusion equation can be ignored and equation (23) can be used for the activity coefficients.

This problem can be solved numerically for the various models of the liquid junction. In the case of restricted diffusion, the equations are already ordinary differential equations. For free diffusion and for an electrode of the second kind, the similarity transformation  $Y = y/\sqrt{t}$  reduces the problem to ordinary differential equations. These coupled, nonlinear, ordinary differential equations can readily be solved by the method of Newman<sup>8</sup>. The equations can be linearized about a trial solution, producing a series of coupled, linear differential equations. In finite difference form these give coupled, tridiagonal matrices which can be solved on a high-speed, digital computer. The nonlinear problem can then be solved by iteration.

#### Numerical Results

We present here calculated values of  $\Delta\phi$  for the several models for the junctions between solutions of various compositions. No detailed

<sup>8</sup> John Newman. UCRL-17739. August, 1967.



concentration profiles will be given since the potentials of cells with liquid junctions can be calculated directly from the tabulated values of  $\Delta\phi$ , without further reference to the concentration profiles, as indicated in the next section. The tabulation of the values of  $\Delta\phi$ , rather than the potentials of complete cells, is convenient because these values relate to the junction itself, whereas more than one combination of electrodes is possible for a given junction. In addition to  $\Delta\phi$ , only thermodynamic data are needed to calculate potentials of complete cells, the entire effect of the transport phenomena being included in  $\Delta\phi$ .

The value of  $\Delta\phi$  depends upon the choice of the reference ion  $n$ . In each case this is the last ion for a given junction in the tables. For infinitely dilute solutions,  $\Delta\phi$  becomes independent of this choice and, furthermore, depends only on the ratios of concentrations of the ions in the end solutions. Solutions of zero strength ( $f_1=1$ ) are indicated by an asterisk, but the concentrations are given nonzero values so that these ratios will be clear. These junctions also provide a basis for comparison with more concentrated solutions, to indicate the effect of the activity coefficients.

Table 1 gives values of  $\Delta\phi$  for the continuous-mixture, restricted-diffusion, and free-diffusion junctions. Table 2 gives values of  $\Delta\phi$  for an electrode of the second kind, where AgCl, with a solubility product of  $10^{-10}$  (mole/l)<sup>2</sup>, diffuses into hydrochloric acid solutions of various concentrations. For solutions of zero ionic strength, the values of  $\Delta\phi$  for the continuous-mixture and restricted diffusion junctions agree with the values calculated by the methods of Henderson<sup>9</sup> and Planck<sup>10</sup>, respectively. In figures 1-6 are presented the results of more extensive calculations on the HCl-KCl junction.

<sup>9</sup> P. Henderson, Z. physik. Chem., 59, 118 (1907); 63, 325 (1908).

<sup>10</sup> Max Planck, Wied. Ann., 39, 161 (1890); 40, 561 (1890).

Table 1. Values of  $\Delta\phi$  for various junctions and various models at 25°C. Values for  $f_1=1$  are indicated by an asterisk. The last ion is the reference ion.

ion	soln 1	soln 2	$\phi_1 - \phi_2$ , mV		
			free diffusion	restricted diffusion	continuous mixture
H <sup>+</sup>	0.2	0.1	----	----	-10.31
Cl <sup>-</sup>	0.2	0.1	----	----	-11.43*
K <sup>+</sup>	0.2	0.1	----	----	1.861 (2.05 <sup>11</sup> )
Cl <sup>-</sup>	0.2	0.1	----	----	0.335*
K <sup>+</sup>	0	0.01	-33.50	-32.65	-33.75
H <sup>+</sup>	0.02	0	-34.67*	-33.80*	-34.95*
Cl <sup>-</sup>	0.02	0.01			
K <sup>+</sup>	0	0.1	-27.31 (-27.08 <sup>12</sup> ) (-28.25; 18°C <sup>13</sup> ) (-28.3 <sup>15</sup> )	-27.45	-27.47 (-28.10; 18°C <sup>13</sup> )
H <sup>+</sup>	0.1	0	-26.69*	-26.85*	-26.85*
Cl <sup>-</sup>	0.1	0.1			
K <sup>+</sup>	0	0.2	-27.92	-28.04	-28.09
H <sup>+</sup>	0.2	0	-26.69*	-26.85*	-26.85*
Cl <sup>-</sup>	0.2	0.2			
K <sup>+</sup>	0	0.2	-22.58	-23.03	-22.31
H <sup>+</sup>	0.1	0	-20.24*	-20.74*	-19.96*
Cl <sup>-</sup>	0.1	0.2			
K <sup>+</sup>	0	0.05	-20.70	-21.09	-20.23
H <sup>+</sup>	0.02	0	-18.50*	-18.97*	-18.02*
Cl <sup>-</sup>	0.02	0.05			
K <sup>+</sup>	0	0.1	-18.02	-17.89	-16.84
H <sup>+</sup>	0.02	0	-14.05*	-14.12*	-12.90*
Cl <sup>-</sup>	0.02	0.1			
K <sup>+</sup>	0	0.1	-15.91	-14.99	-14.04
H <sup>+</sup>	0.01	0	-10.85*	-10.30*	-9.09*
Cl <sup>-</sup>	0.01	0.1			

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Table 1. (cont.)

ion	soln 1	soln 2	$\Phi_1 - \Phi_2$ , mV		
			free diffusion	restricted diffusion	continuous mixture
K <sup>+</sup>	0	0.1	-27.24	-27.38	-27.40
			-27.98 <sup>14</sup>		
H <sup>+</sup>	0.09917	0	-26.60*	-26.77*	-26.76*
Cl <sup>-</sup>	0.09917	0.1			
K <sup>+</sup>	0	0.1			
H <sup>+</sup>	0.09917	0	-27.39	-27.48	-27.55
NO <sub>3</sub> <sup>-</sup>	0	0.05	-26.53*	-26.62*	-26.70*
Cl <sup>-</sup>	0.09917	0.05			
K <sup>+</sup>	0.1	0.1	- 0.157	- 0.157	- 0.157
NO <sub>3</sub> <sup>-</sup>	0.05	0	- 0.423*	- 0.423*	- 0.423*
Cl <sup>-</sup>	0.05	0.1			
Na <sup>+</sup>	0.1	0			
H <sup>+</sup>	0	0.05	28.58	29.64	28.10
ClO <sub>4</sub> <sup>-</sup>	0	0.05	26.72*	27.90*	26.22*
Cl <sup>-</sup>	0.1	0			
Na <sup>+</sup>	0.1	0			
H <sup>+</sup>	0	0.1	32.83	33.50	33.05
ClO <sub>4</sub> <sup>-</sup>	0	0.1	32.35*	33.11*	32.57*
Cl <sup>-</sup>	0.1	0			
Na <sup>+</sup>	0.2	0			
H <sup>+</sup>	0	0.2	33.29	33.88	33.53
ClO <sub>4</sub> <sup>-</sup>	0	0.2	32.35*	33.11*	32.57*
Cl <sup>-</sup>	0.2	0			
Na <sup>+</sup>	0.05	0			
H <sup>+</sup>	0	0.1	38.77	38.31	39.26
ClO <sub>4</sub> <sup>-</sup>	0	0.1	39.96*	39.58*	40.48*
Cl <sup>-</sup>	0.05	0			
Cu <sup>++</sup>	0	0.1			
Ag <sup>+</sup>	0.2	0			
NO <sub>3</sub> <sup>-</sup>	0.2	0	- 6.22*	- 6.22*	- 6.22*
ClO <sub>4</sub> <sup>-</sup>	0	0.2			

<sup>11</sup> T. Shedlovsky and D. A. MacInnes, J. Am. Chem. Soc., 59, 503 (1937).

<sup>12</sup> J. B. Chloupek, V. Z. Kanes, and B. A. Danesova, Coll. Czechlov. Chem. Comm., 5, 469, 527 (1933).

<sup>13</sup> E. A. Guggenheim and A. Unmack, Kgl. Danske Vid. Selsk Mat-fys. Medd., 10, #14, 1 (1931).

<sup>14</sup> N. P. Finkelstein and E. T. Verdier, Trans. Faraday Soc., 53, 1618 (1957).

<sup>15</sup> D. C. Grahame and J. I. Cummings, Off. of Nav. Res. Tech. Rep. #5 (1950).

Table 2. Values of  $\Delta\phi$  for a Ag-AgCl electrode in HCl solutions at 25°C. Chloride is the reference ion, and  $\beta$  values are taken to be zero.

HCl bulk, <u>M</u>	$10^{-4}$	$5 \times 10^{-5}$	$2 \times 10^{-5}$	$10^{-5}$	$5 \times 10^{-6}$	$2 \times 10^{-6}$
$\Phi_0 - \Phi_\infty$ , mV	0.0198	0.0737	0.359	0.915	1.780	3.21
$c_{Cl^-}^0 / c_{Cl^-}^\infty$	1.00961	1.0392	1.200	1.604	2.539	5.499
$(\mu_{Cl^-}^\infty - \mu_{Cl^-}^0) / F$ , mV	-0.226	-0.914	-4.32	-11.22	-22.16	-40.58

### Cells with Liquid Junction

Once the concentration profiles are known for a liquid junction region, it is then possible to calculate the effect of the nonuniform composition on the cell potential. This effect is considered in the following subsections for cells of increasingly complex liquid junctions. It will always be assumed that the electrodes are in equilibrium with the adjacent solutions and that regions of nonuniform composition lie outside the immediate vicinity of the electrodes.

The procedure then involves first the treatment of electrode equilibria, in the manner of Guggenheim<sup>16</sup>. This allows the expression of the cell potential in terms of a difference in the electrochemical potential of ions in the solutions adjacent to the two electrodes. The evaluation of this difference involves the integration of equation (16) across the junction region. This equation can be conveniently rewritten in the form

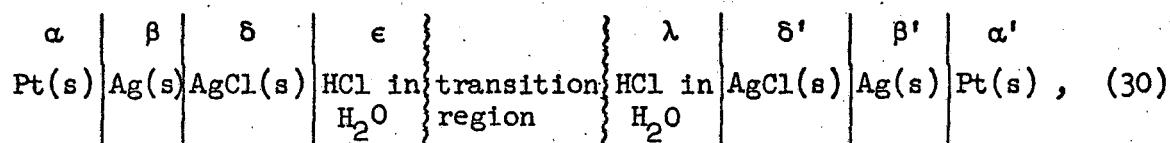
$$\frac{1}{z_j} \nabla \mu_j = - \sum_i \frac{t_i^0}{z_i} \left[ \nabla \mu_i - \frac{z_i}{z_j} \nabla \mu_j \right] - \frac{F}{\kappa} \frac{1}{z_j} \quad (29)$$

<sup>16</sup> E. A. Guggenheim. Thermodynamics. North-Holland Publishing Company, 1959, p.382.

The sum on the right now involves only the gradients of electrochemical potentials of neutral combinations of ions and can be determined from a knowledge of the concentration profiles.

a. Cell with a Single Electrolyte of Varying Concentration

Cells containing a single electrolyte whose concentration varies with location in the cell constitute the simplest of the so-called cells with transference. An example is



where the platinum leads and the silver-silver chloride electrodes have identical compositions on both sides of the cell. In the transition region or liquid junction, the concentration of HCl varies from the value in the  $\epsilon$ -phase to that in the  $\lambda$ -phase.

At both electrodes there is equilibrium among the  $\alpha$ ,  $\beta$ ,  $\delta$ , and  $\epsilon$  phases, for example,

$$\mu_{\text{Cl}^-}^{\delta} = \mu_{\text{Cl}^-}^{\epsilon}, \quad \mu_{\text{Ag}^+}^{\delta} = \mu_{\text{Ag}^+}^{\beta}, \quad \text{and} \quad \mu_{e^-}^{\alpha} = \mu_{e^-}^{\beta}. \quad (31)$$

Combination of these relations with the definitions of the chemical potentials of the neutral silver and silver chloride, for example,

$$\mu_{\text{Ag}}^{\beta} = \mu_{\text{Ag}^+}^{\beta} + \mu_{e^-}^{\beta} \quad \text{and} \quad \mu_{\text{AgCl}}^{\delta} = \mu_{\text{Ag}^+}^{\delta} + \mu_{\text{Cl}^-}^{\delta}, \quad (32)$$

yields an expression for the cell potential

$$-F(\psi^{\alpha} - \psi^{\alpha'}) = \mu_{e^-}^{\alpha} - \mu_{e^-}^{\alpha'} = \mu_{\text{Ag}}^{\beta} - \mu_{\text{AgCl}}^{\delta} + \mu_{\text{Cl}^-}^{\epsilon} - \mu_{\text{Ag}}^{\beta'} + \mu_{\text{AgCl}}^{\delta'} - \mu_{\text{Cl}^-}^{\lambda}, \quad (33)$$

since the difference in electrochemical potential of electrons in the two leads is related to the cell potential as indicated. Since the electrodes are of identical composition, the expression for the cell potential reduces to

$$-F(\psi^{\alpha} - \psi^{\alpha'}) = \mu_{\text{Cl}^-}^{\epsilon} - \mu_{\text{Cl}^-}^{\lambda} \quad (34)$$

This difference in the electrochemical potentials of chloride ions can be evaluated with the aid of equation (29), which becomes in this case

$$\frac{\partial \mu_{\text{Cl}^-}}{\partial x} = t_{\text{H}^+}^{\circ} \frac{\partial \mu_{\text{HCl}}}{\partial x} \quad (35)$$

Equation (34) becomes

$$-F(\psi^{\alpha} - \psi^{\alpha'}) = \int_{\lambda}^{\epsilon} t_{\text{H}^+}^{\circ} d\mu_{\text{HCl}} \quad (36)$$

On the other hand, one could express the difference in electrochemical potentials of chloride ions in terms of the quasi electrostatic potential  $\Phi$  based on chloride ions as the reference ion

$$-F(\psi^{\alpha} - \psi^{\alpha'}) = -F(\Phi^{\epsilon} - \Phi^{\lambda}) + RT \ln (c_{\text{Cl}^-}^{\epsilon} / c_{\text{Cl}^-}^{\lambda}) \quad (37)$$

As shown in equation (36), the cell potential is independent of the method of forming the junction for the case of a single electrolyte of varying concentration, that is, the integral is independent of the detailed form of the concentration profile. From measured cell potentials, equation (36) may be used to determine activity coefficients if the transference number is known, or it may be used to determine the transference number if the activity coefficient is known. Both types of determination are common practice.

From tabulated values of  $\Delta\Phi$  (which tabulation requires prior knowledge of the transference number and the activity coefficient) one can calculate the cell potential from equation (37). For example, for  $c_{\text{HCl}}^{\epsilon} = 0.2 \text{ M}$  and  $c_{\text{HCl}}^{\lambda} = 0.1 \text{ M}$  we obtain

$$-(\psi^{\alpha} - \psi^{\alpha'}) = 28.11 \text{ mV} .$$

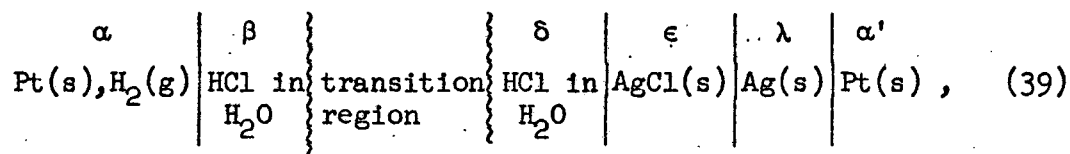
If the silver-silver chloride electrodes were replaced by hydrogen electrodes, the expression for the potential of such a cell would become

$$-F(\psi^\alpha - \psi^{\alpha'}) = \mu_{\text{HCl}}^\lambda - \mu_{\text{HCl}}^\epsilon + \mu_{\text{Cl}^-}^\epsilon - \mu_{\text{Cl}^-}^\lambda, \quad (38)$$

for identical partial pressures of hydrogen over the two electrodes. Equations (34) and (38) thus show the relation between the potentials of two cells with the same liquid junction but different electrodes.

b. Cell with Two Electrolytes, One of Nearly Uniform Concentration

With an electrode of the second kind, as used in the previous example, the solubility of the sparingly soluble salt will, strictly speaking, lead to diffusion of this salt from the electrode. At high concentrations of the other electrolyte, the solubility of the sparingly soluble salt is depressed and the effect on the cell potential is expected to be small. However, this effect becomes more important as the concentration of the second electrolyte is decreased. For the cell



it is assumed that the two platinum electrodes are of identical composition and that the two solutions  $\beta$  and  $\delta$  differ in the concentration of AgCl, phase  $\delta$  being saturated. The transition region, in the model used here, is formed by contacting the solution  $\beta$  with the solid AgCl, and a diffusion layer develops by free diffusion into a stagnant medium. The concentrations of AgCl and HCl in phase  $\delta$ , adjacent to the solid surface, are determined by the laws of diffusion and the conditions of saturation of AgCl and zero flux of hydrogen ions into the solid phase.

From the conditions of phase equilibria at the electrodes and the

definitions of the chemical potentials of neutral species, the cell potential can be written

$$-F(\psi^\alpha - \psi^{\alpha'}) = \frac{1}{2}\mu_{H_2}^\alpha - \mu_{HCl}^\beta - \mu_{Ag}^\lambda + \mu_{AgCl}^\epsilon + (\mu_{Cl^-}^\beta - \mu_{Cl^-}^\delta). \quad (40)$$

If the chemical potentials of hydrogen and HCl are expressed as

$$\mu_{H_2} = \mu_{H_2}^\theta + RT \ln p_{H_2}$$

and

$$\mu_{HCl} = \mu_{HCl}^\theta + 2 RT \ln c_{HCl} f_{HCl},$$

then the standard cell potential  $E^\circ$  can be identified as a collection of thermodynamic quantities,

$$FE^\circ = \frac{1}{2}\mu_{H_2}^\theta - \mu_{HCl}^\theta - \mu_{Ag}^\theta + \mu_{AgCl}^\theta, \quad (41)$$

and the cell potential becomes

$$-F(\psi^\alpha - \psi^{\alpha'}) = FE^\circ + \frac{1}{2} RT \ln p_{H_2}^\alpha - 2RT \ln c_{HCl}^\beta f_{HCl}^\beta + (\mu_{Cl^-}^\beta - \mu_{Cl^-}^\delta). \quad (42)$$

For the evaluation of the difference  $\mu_{Cl^-}^\beta - \mu_{Cl^-}^\delta$ , equation (29) becomes in the absence of current

$$\nabla \mu_{Cl^-} = t_{H^+}^o \nabla \mu_{HCl} + t_{Ag^+}^o \nabla \mu_{AgCl}. \quad (43)$$

Integration gives

$$\mu_{Cl^-}^\beta - \mu_{Cl^-}^\delta = \int_{\delta}^{\beta} t_{H^+}^o \frac{\partial \mu_{HCl}}{\partial x} dx + \int_{\delta}^{\beta} t_{Ag^+}^o \frac{\partial \mu_{AgCl}}{\partial x} dx. \quad (44)$$

The evaluation of these integrals requires a knowledge of the concentration profiles, as well as the transference numbers and thermodynamic properties as functions of the concentrations. For high concentrations of HCl,  $\nabla \mu_{HCl}$  and  $t_{Ag^+}^o$  approach zero, and the term  $\mu_{Cl^-}^\beta - \mu_{Cl^-}^\delta$  may be neglected in comparison to the other terms in equation (42).



The difference in electrochemical potentials of the chloride ion can be expressed in terms of the quasi-electrostatic potentials (referred to the chloride ion), differences of which are given in table 2:

$$\mu_{\text{Cl}^-}^{\beta} - \mu_{\text{Cl}^-}^{\delta} = F(\phi^{\delta} - \phi^{\beta}) + RT \ln c_{\text{Cl}^-}^{\beta} / c_{\text{Cl}^-}^{\delta} \quad (45)$$

For a bulk HCl concentration of  $10^{-4}$  M, one obtains

$$(\mu_{\text{Cl}^-}^{\beta} - \mu_{\text{Cl}^-}^{\delta}) / F = 0.0198 - 0.2457 = -0.226 \text{ mV.}$$

This small error is not of much practical significance since very few measurements have been made in this range of concentration.

Thus, it is seen that the effect of the solubility of the slightly soluble salt will be to cause the potential of the chloride electrode to be more negative with respect to the other electrode than would otherwise be the case. Hence the measured potential of the above cell will be lower than if silver chloride were more insoluble. Smyrl and Tobias<sup>17</sup> have discussed several nonaqueous systems where the effect is much larger in more concentrated solutions, since the effect becomes important for bulk concentrations on the order of the square root of the solubility product. The problem arises because the determination of standard cell potentials involves an extrapolation to infinite dilution. Smyrl and Tobias took the diffusion coefficients to be equal (hence  $\Delta\phi=0$ ) and assumed that the concentration of the second electrolyte is uniform up to the surface of the sparingly soluble salt.

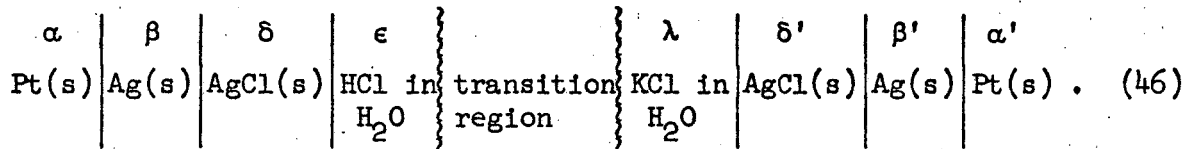
c. Cells with Two Electrolytes, Both of Varying Concentration

Cells of this type may still be divided into two groups according to whether or not the two electrolytes have an ion in common. A junction between  $\text{CuSO}_4$  and  $\text{ZnSO}_4$  is an example where there is a common

<sup>17</sup> W. H. Smyrl and C. W. Tobias, Electrochim. Acta, 13, 1968 (in press).

ion; a junction between NaCl and HClO<sub>4</sub> is an example where there is not. The former class will be discussed first.

Consider the cell



The cell potential is again given by equation (34):

$$-F(\psi^\alpha - \psi^{\alpha'}) = \mu_{\text{Cl}^-}^\epsilon - \mu_{\text{Cl}^-}^\lambda \quad (47)$$

The effect of the nonzero solubility of AgCl, discussed in subsection b, will be ignored here. In this case, however, equation (29) becomes

$$\nabla \mu_{\text{Cl}^-} = t_{\text{H}^+}^0 \nabla \mu_{\text{HCl}} + t_{\text{K}^+}^0 \nabla \mu_{\text{KCl}}, \quad (48)$$

and integration gives

$$\mu_{\text{Cl}^-}^\epsilon - \mu_{\text{Cl}^-}^\lambda = \int_\lambda^\epsilon \left[ t_{\text{H}^+}^0 \frac{\partial \mu_{\text{HCl}}}{\partial x} + t_{\text{K}^+}^0 \frac{\partial \mu_{\text{KCl}}}{\partial x} \right] dx \quad (49)$$

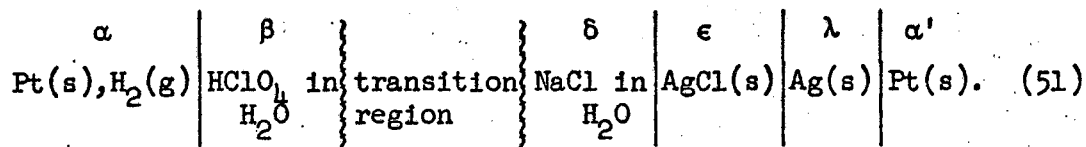
Here, as with equation (44), and in contrast to equation (36), the integral depends on the detailed form of the concentration profiles in the junction region. As in the preceding examples, the cell potential can again be expressed in terms of the quasi-electrostatic potential, referred to the chloride ion:

$$-F(\psi^\alpha - \psi^{\alpha'}) = -F(\phi^\epsilon - \phi^\lambda) + RT \ln (c_{\text{Cl}^-}^\epsilon / c_{\text{Cl}^-}^\lambda), \quad (50)$$

and the values of  $\Delta\phi$  in table 1 allow the cell potential to be calculated. By means of the various models, the detailed form of the concentration profiles has already been taken into account in the tabulated values of  $\Delta\phi$ .

Many cells of practical importance contain two electrolytes of

varying concentration with no common ion. Such a cell is



From the conditions of phase equilibria at the electrodes and the definitions of the chemical potentials of neutral species, the cell potential can be written

$$-F(\psi^\alpha - \psi^{\alpha'}) = \frac{1}{2}\mu_{\text{H}_2}^\alpha - \mu_{\text{Ag}}^\lambda + \mu_{\text{AgCl}}^\epsilon - (\mu_{\text{H}^+}^\beta + \mu_{\text{Cl}^-}^\delta) \quad (52)$$

The cell potential is again related to the thermodynamic properties of electrically neutral components, but a new term has appeared. Instead of the difference of electrochemical potential of a single ion between the two solutions, there is now a combination of electrochemical potentials of two ions. This, more complicated situation can be analyzed if the ionic strength does not go to zero anywhere in the junction (as must also be the case with the junctions treated earlier). Choose some solution in the junction and denote it as I. The quantities  $\mu_{\text{Cl}^-}^\delta - \mu_{\text{Cl}^-}^{\text{I}}$  and  $\mu_{\text{H}^+}^\beta - \mu_{\text{H}^+}^{\text{I}}$  are both well defined if the intermediate solution I has nonzero concentrations of both ions  $\text{Cl}^-$  and  $\text{H}^+$ . The cell potential can be written, then,

$$-F(\psi^\alpha - \psi^{\alpha'}) = \frac{1}{2}\mu_{\text{H}_2}^\alpha - \mu_{\text{Ag}}^\lambda + \mu_{\text{AgCl}}^\epsilon - (\mu_{\text{H}^+}^\beta - \mu_{\text{H}^+}^{\text{I}}) - (\mu_{\text{Cl}^-}^\delta - \mu_{\text{Cl}^-}^{\text{I}}) - \mu_{\text{HCl}}^{\text{I}} \quad (53)$$

The electrochemical potential differences in equation (53) can now be related through equation (29) to integrals of transference numbers multiplied by gradients of chemical potentials of neutral combinations. The integrals can be evaluated from the concentration profiles in the junction along with the concentration dependence of the transport and

thermodynamic properties. The cell potential is, of course, independent of the choice of the intermediate solution I.

In this case it may be particularly convenient to use the quasi-electrostatic potential, here referred to the chloride ion. This allows one to write

$$\mu_{H^+}^{\beta} + \mu_{Cl^-}^{\delta} = \mu_{HCl}^{\theta} + RT \ln (c_{H^+}^{\beta} c_{Cl^-}^{\delta}) + F(\phi^{\beta} - \phi^{\delta}) + RT \ln f_{H^+}^{\beta} f_{Cl^-}^{\beta} \quad (53)$$

The last term in equation (53) is well-defined, although it is somewhat unusual. Here  $f_{H^+}^{\beta} f_{Cl^-}^{\beta}$  represents the activity coefficient of hydrogen ions referred to chloride ions in a solution of vanishing chloride concentration. According to equation (23), this term would be given by

$$\ln f_{H^+}^{\beta} f_{Cl^-}^{\beta} = \frac{-2\alpha I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} + 2(\beta_{HClO_4} + \beta_{HCl}) c_{H^+}^{\beta}, \quad (54)$$

where I now refers to the ionic strength in solution  $\beta$ . This procedure is justified by the fact that it is no longer necessary to select an intermediate solution in the junction.

The cell potential can now be written

$$\begin{aligned} -F(\psi^{\alpha} - \psi^{\alpha'}) &= FE^{\circ} + \frac{1}{2}RT \ln p_{H_2}^{\alpha} - RT \ln c_{H^+}^{\beta} c_{Cl^-}^{\delta} \\ &+ F(\phi^{\delta} - \phi^{\beta}) - RT \ln f_{H^+}^{\beta} f_{Cl^-}^{\beta}, \end{aligned} \quad (55)$$

where the standard cell potential has been identified:

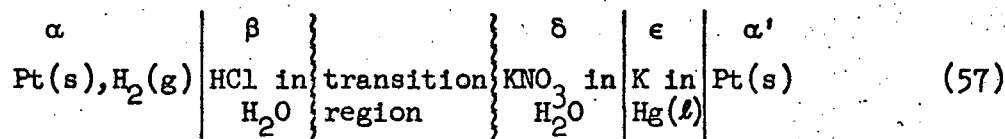
$$FE^{\circ} = \frac{1}{2}\mu_{H_2}^{\theta} - \mu_{Ag}^{\theta} + \mu_{AgCl}^{\theta} - \mu_{HCl}^{\theta} \quad (56)$$

A determination of the standard cell potential by means of this cell would be affected by the uncertainties in the values of  $\Delta\phi$  and  $f_{H^+}^{\beta} f_{Cl^-}^{\beta}$ , a problem which is avoided with the cell discussed in subsection b.

If  $E^0$  is known from measurements with that cell, any uncertainty in the calculated value of  $\Delta\phi$  will cause a consequent uncertainty in any value of  $f_{H^+}^\beta f_{Cl^-}^\beta$  obtained from measurements on the present cell. This discussion reveals some of the difficulties involved in the use of such cells for thermodynamic measurements.

We could check the calculated value of  $\Delta\phi$  in table 1 by subtracting from the cell potential the standard cell potential and the terms in activity coefficients and concentrations. The potentials of such cells have, unfortunately, not been measured.

The cell



is very similar to that of the previous example, but differs in that both electrodes involve phase equilibria of cations. Again, from the phase equilibria and the relevant thermodynamic identities, the cell potential may be written

$$\begin{aligned}
 -F(\psi^\alpha - \psi^{\alpha'}) &= \frac{1}{2}\mu_{H_2}^\alpha - \mu_K^\epsilon + \mu_{K^+}^\delta - \mu_{H^+}^\beta \\
 &= \frac{1}{2}\mu_{H_2}^\alpha - \mu_K^\epsilon + (\mu_{K^+}^\delta - \mu_{K^+}^I) - (\mu_{H^+}^\beta - \mu_{H^+}^I) + (\mu_{K^+}^I - \mu_{H^+}^I), \quad (58)
 \end{aligned}$$

where I denotes an intermeditait solution where both  $K^+$  and  $H^+$  ions are present. The quantities  $(\mu_{K^+}^\delta - \mu_{K^+}^I)$  and  $(\mu_{H^+}^\beta - \mu_{H^+}^I)$  can be related through equation (29) to integrals of transference numbers multiplied by gradients of chemical potentials of neutral combinations. The last term in equation (58) is well defined and is given by

$$\mu_{K^+}^I - \mu_{H^+}^I = \mu_{KCl}^I - \mu_{HCl}^I.$$

To demonstrate the usefulness of tabulated values of  $\Delta\Phi$ , let the quasi-electrostatic potential be based on the chloride ion. Equation (58) can be rewritten

$$-F(\psi^\alpha - \psi^{\alpha'}) = \frac{1}{2}\mu_{H_2}^\alpha - \mu_K^\epsilon + \mu_{KCl}^\theta - \mu_{HCl}^\theta + RT \ln c_{K^+}^\delta / c_{H^+}^\beta + RT \ln (f_{K^+}^\delta f_{Cl^-}^\delta / f_{H^+}^\beta f_{Cl^-}^\beta) + F(\Phi^\delta - \Phi^\beta). \quad (59)$$

Any uncertainty in  $\Delta\Phi$  and  $f_{K^+}^\delta f_{Cl^-}^\delta$  would be reflected in the uncertainty in a derived value of a standard cell potential. Thus, the use of such a cell to determine standard cell potentials is justified only if the junction is well characterized and if the thermodynamic properties of one of the end solutions are well known.

Other cells could be analyzed, but the analysis would involve only the principles and procedures which have been used above.

#### Discussion

The analysis of the cells in the previous section revealed the relation between measured cell potentials and the thermodynamic and transport properties of the materials in the cells. For cells with liquid junctions, the cell potential depends on the concentration profiles in the liquid junction and the transport and thermodynamic properties of the junction region in addition to the standard cell potential and the composition and activity coefficients of the end solutions. Alternatively, for the junction one could specify the concentration profiles, the value of  $\Delta\Phi$  which characterizes the junction, and the ion to which  $\Phi$  is referred. Once single junctions have been characterized, the behavior of combinations of these junctions in other cells, e.g., cells with salt bridges, may be predicted.

Calculations for several single junctions have been made and the results given in Table 1. The only one of the junctions for which our calculations may be compared with other calculations and with experimental results is the 0.1M HCl - 0.1M KCl junction. MacInnes and Longworth<sup>18</sup> have made calculations for this junction of the free diffusion type, and report 28.19 millivolts to compare to 27.31 millivolts of the present study. Spiro<sup>19</sup> has discussed cells with liquid junctions, including salt bridges, for junctions of constant ionic strength across the junction, and of the continuous mixture type, and has included activity coefficient corrections. For this HCl-KCl junction Spiro calculates 29.07 millivolts and we calculate 27.47 millivolts. The experimental results are given in Table 1.

MacInnes and Longworth used equation (29) and the known activity coefficients and transference numbers for this junction and an assumed concentration profile to make their calculation. From this, it is not clear whether the difference between their results and ours is due to our assumption about activity coefficients, or our assumptions about the ionic diffusion coefficients. We propose that it is the latter, on the basis of our analysis of Spiro's calculations.

Spiro calculates about the same activity coefficient correction as we do (i.e., 0.62 mV) but his calculation neglecting activity coefficients is higher than our (i.e., -26.85 mV) by about 1.5 mV. We have assumed the ionic diffusion coefficients to be constant and have used the values corresponding to infinite dilution in making the Henderson calculation. Spiro has used the Lewis and Sargent equation and has utilized conductivity data for the 0.1M solutions. It is known<sup>20</sup> that  $D_{\text{OCl}}$  is about 17% higher in KCl at this concentration than in HCl, whereas it is the

<sup>18</sup> M. Spiro, Electrochim. Acta, 11, 569 (1966).

<sup>19</sup> D. A. MacInnes and L. G. Longworth, Cold Spring Harbor Symposium on Quantitative Biology, 4, 18 (1936).

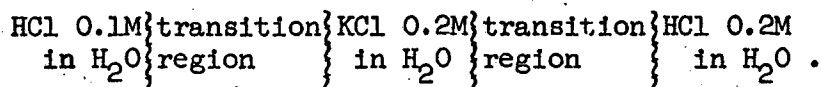
<sup>20</sup> T. W. Chapman, Ph.D. Thesis, Univ. of Calif., Berkeley, 1967.

same in both solutions at infinite dilution. Therefore we may conclude that at least our calculation is consistent, but Spiro's is not, although it is quite likely that our calculation is in error. We propose that this error is caused by inaccuracies in our assumptions about the diffusion coefficients.

Unfortunately, it has not been possible to compare all our results with experimental measurements. This is because our calculations are made for dilute solutions whereas most measurements (on salt bridges, for example) have been made for concentrated solutions. Therefore we can only propose that all other calculations will be at least as accurate as for the HCl-KCl junction.

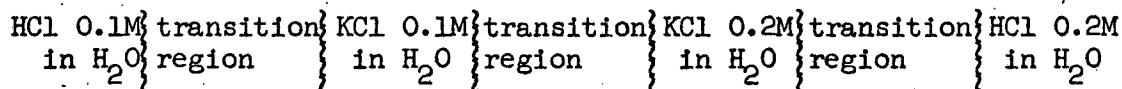


A salt bridge is often used to separate two electrolytic solutions, and sometimes the stated purpose is "to eliminate liquid junction potentials." We should now be in a position to evaluate whether this purpose is achieved, if we could define the liquid junction potential which is supposed to be eliminated. Such a salt bridge might be



It seems clear that the salt bridge does not make the value of  $\mu_{\text{Cl}^-}$  equal in the two hydrochloric acid solutions. The value of  $\Delta\phi$  (referred to the chloride ion) for this combination of junctions is 5.78 mV if the junctions are of the continuous mixture type. This can be compared with the value  $\Delta\phi = 10.31$  mV for a single, direct junction between 0.1 and 0.2 M HCl solutions.

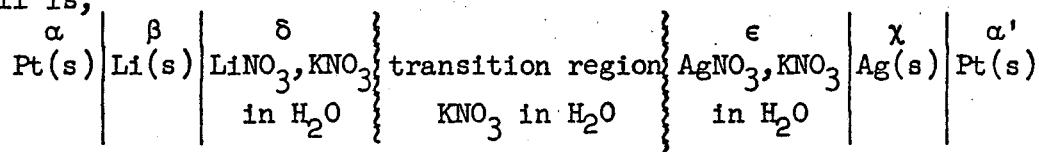
If the transference numbers of KCl were equal to 0.5 and if departures of activity coefficients from unity could be ignored, the liquid junction potential of the combination of two junctions of the salt bridge should decrease as the concentration of KCl increases. If one insists on using salt bridges, one might consider as an alternative the series of junctions



for which  $\Delta\phi = 1.24$  mV and for which the value of  $\Delta\phi$  would approach zero as all the concentrations were reduced in proportion if the transference numbers of KCl were 0.5.

Although cells with salt bridges are not useful for determining activity coefficients, they are useful for determining standard cell

potentials. A cell which is particularly appropriate for such studies, but which has not been utilized extensively, is one in which the electrolyte of the salt bridge is present throughout. An example of this cell is,



in which  $\text{KNO}_3$  is present throughout the cell at the same concentration.

The transition region contains concentration gradients of both  $\text{LiNO}_3$  and  $\text{AgNO}_3$ . The cell potential may be expressed as

$$-F(\psi^\alpha - \psi^{\alpha'}) = \mu_{\text{Li}}^\beta - \mu_{\text{LiNO}_3}^\delta - \mu_{\text{Ag}}^\chi + \mu_{\text{AgNO}_3}^\epsilon - \mu_{\text{NO}_3^-}^\epsilon + \mu_{\text{NO}_3^-}^\delta .$$

We adopt the following approximations which essentially fix the range of concentrations:

$$t_{\text{Ag}^+}^0 = 0$$

$$t_{\text{Li}^+}^0 = 0$$

$$c_{\text{Ag}^+}^\epsilon = c_{\text{Li}^+}^\delta \ll c_{\text{K}^+} ,$$

$$(c_{\text{Ag}^+}^\epsilon)^{\frac{1}{2}} = (c_{\text{Li}^+}^\delta)^{\frac{1}{2}} \ll c_{\text{K}^+}^{\frac{1}{2}} .$$

The expression for the cell potential becomes

$$-F(\psi^\alpha - \psi^{\alpha'}) = FE^0 + 2RT (\beta_{\text{AgNO}_3} - \beta_{\text{LiNO}_3}) c_{\text{NO}_3^-} .$$

Thus the measured cell potential should be a linear function of  $c_{\text{NO}_3^-}$ .

As

$$c_{\text{NO}_3^-} \rightarrow 0 ,$$

the standard cell potential may be determined from the intercept. It would not be necessary to extrapolate to the low concentrations which are necessary for cells without transference.

### Conclusions

A general treatment of the effect of diffusion on the electrical potential of cells with liquid junctions has been given. It was found that such cells have a potential which is related to a difference (or sum) of the electrochemical potential of an ion (or ions). It has been shown that this characteristic combination of electrochemical potentials can be determined from a knowledge of the concentration profiles and the transport and thermodynamic properties in the junction region. From the laws of diffusion, the concentration profiles have been calculated and values of  $\Delta\phi$  determined for several different junctions without the assumption of activity coefficients equal to one. These results have been applied to specific cells. Such an analysis has made it possible to determine the magnitude of the diffusion effect in cases where it is desirable that the effect be negligible.

The cell potential can still be obtained from contributions of various phase boundaries and liquid junctions if certain conventions are adopted. This procedure makes simpler the tabulation of the properties of electrochemical cells.

### Acknowledgment

This work was supported by the United States Atomic Energy Commission.

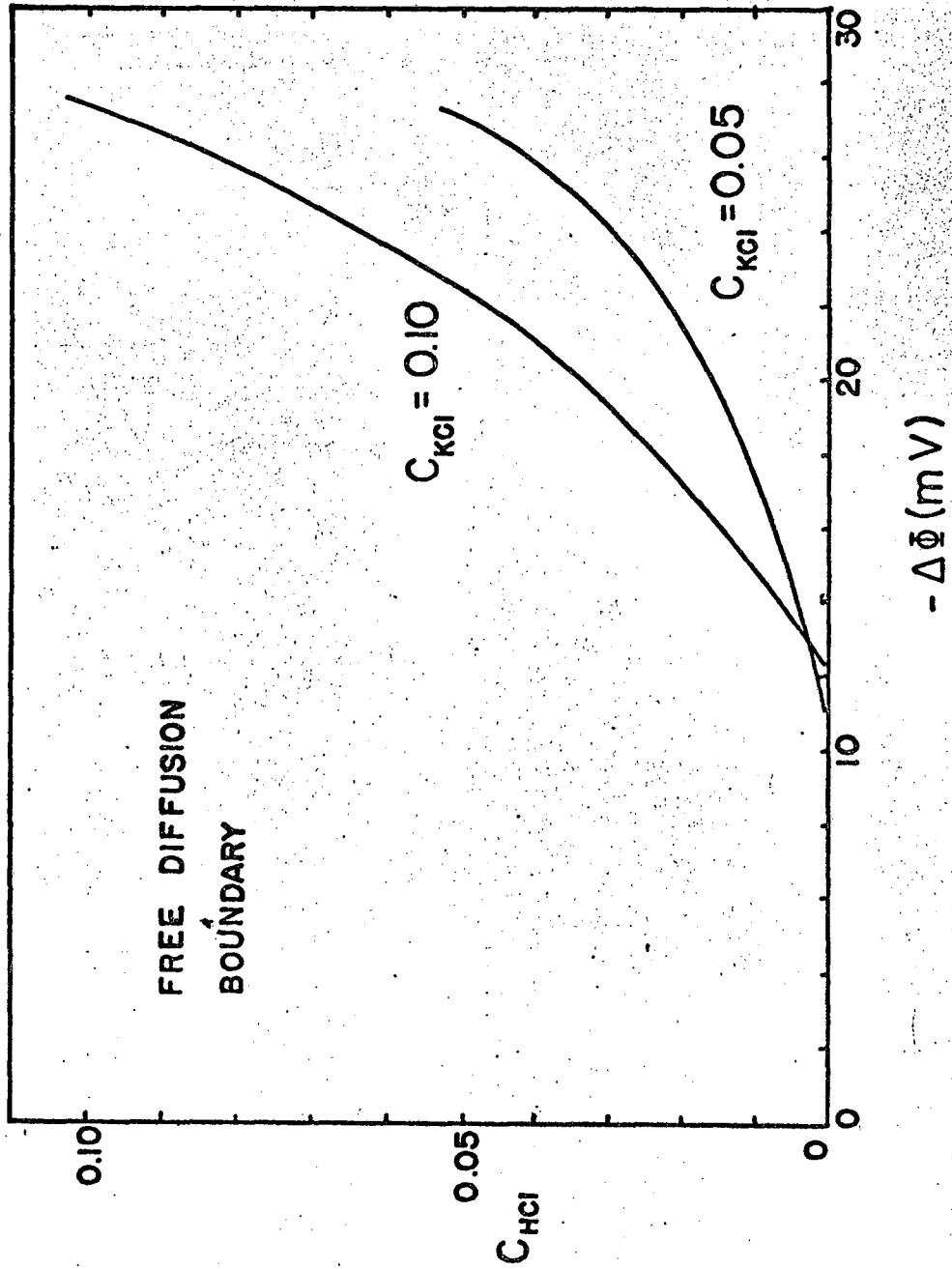
### Nomenclature

- $c_i$  - concentration of species  $i$  (mole/cm<sup>3</sup>).
- $D_{ij}$  - diffusion coefficient for interaction of species  $i$  and  $j$  (cm<sup>2</sup>/sec).
- $E^\circ$  - standard cell potential (V).
- $f_i$  - activity coefficient.
- $F$  - Faraday's constant (coul/equiv).
- $i$  - current density (amp/cm<sup>2</sup>).

- I - ionic strength (mole/l).
- $K_{ij}$  -
- $L_{ij}^0$  -
- $M_{ij}$  -
- $\underline{N}_i$  - flux of species i (mole/cm<sup>2</sup>-sec).
- p - pressure (dyne/cm<sup>2</sup>).
- R - universal gas constant (joule/mole-°K).
- $R_{ij}$  -
- t - time (sec).
- $t_i^0$  - transference number of species i with respect to species 0.
- T - absolute temperature (deg K).
- $\underline{v}_i$  - velocity of species i (cm/sec).
- x - distance (cm).
- $z_i$  - charge number of species i.
- $\alpha$  - Debye-Hückel constant ( $[\text{l/mole}]^{\frac{1}{2}}$ ).
- $\beta_{ij}$  - constant, independent of concentration (l/mole).
- $\kappa$  - conductivity (mho/cm).
- $\mu_i$  - electrochemical potential of species i (joule/mole).
- $\Phi$  - electric potential or quasi electrostatic potential (V).
- $\Psi$  - potential of an electrode (V).

LIST OF FIGURE CAPTIONS

- Figure 1. -  $\Delta\Phi$ (mV) for free diffusion boundary between HCl and KCl, calculated for two different concentrations of KCl.
- Figure 2. Calculated values of -  $\Delta\Phi$ (mV) for free diffusion boundary between HCl and KCl, at a constant ratio of  $C_{KCl}$  to  $C_{HCl}$ . The dashed line represents the (constant) ideal-solution calculation, the solid line includes activity coefficient corrections.
- Figure 3. Results for the restricted diffusion boundary HCl/KCl, given for two different concentrations of KCl.
- Figure 4. Results for the restricted diffusion boundary HCl/KCl, for a constant ratio of  $C_{KCl}$  to  $C_{HCl}$ . The dashed line represents the ideal-solution calculation, the solid line includes activity coefficient corrections.
- Figure 5. Values of -  $\Delta\Phi$ (mV) for the continuous mixture boundary. The dashed line corresponds to the Henderson calculation; the solid line includes activity coefficient corrections.
- Figure 6. Continuous mixture boundary calculations for a constant ration of  $C_{KCl}$  to  $C_{HCl}$ . The dashed line is the ideal-solution calculation, the solid line includes activity coefficient corrections.



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FIG. 1.

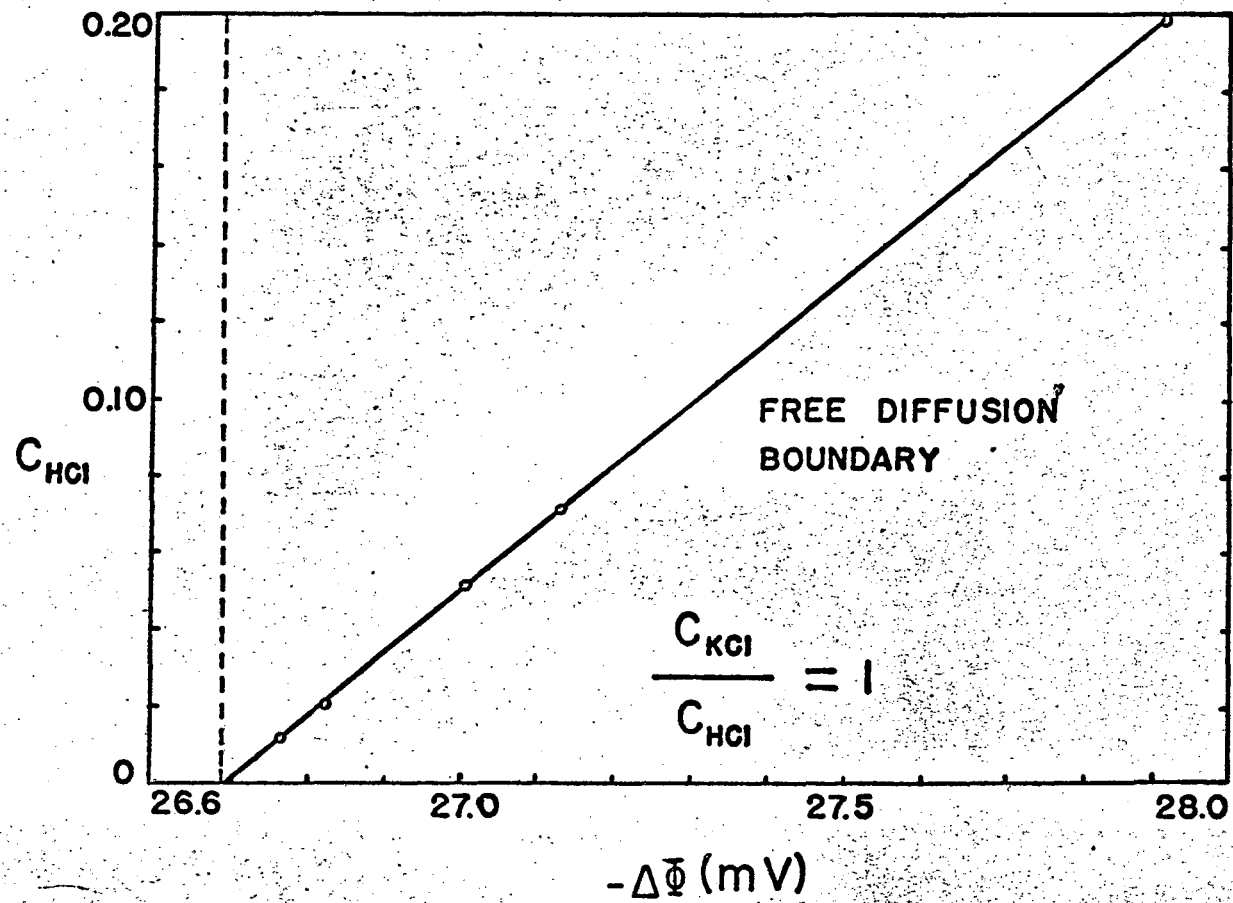
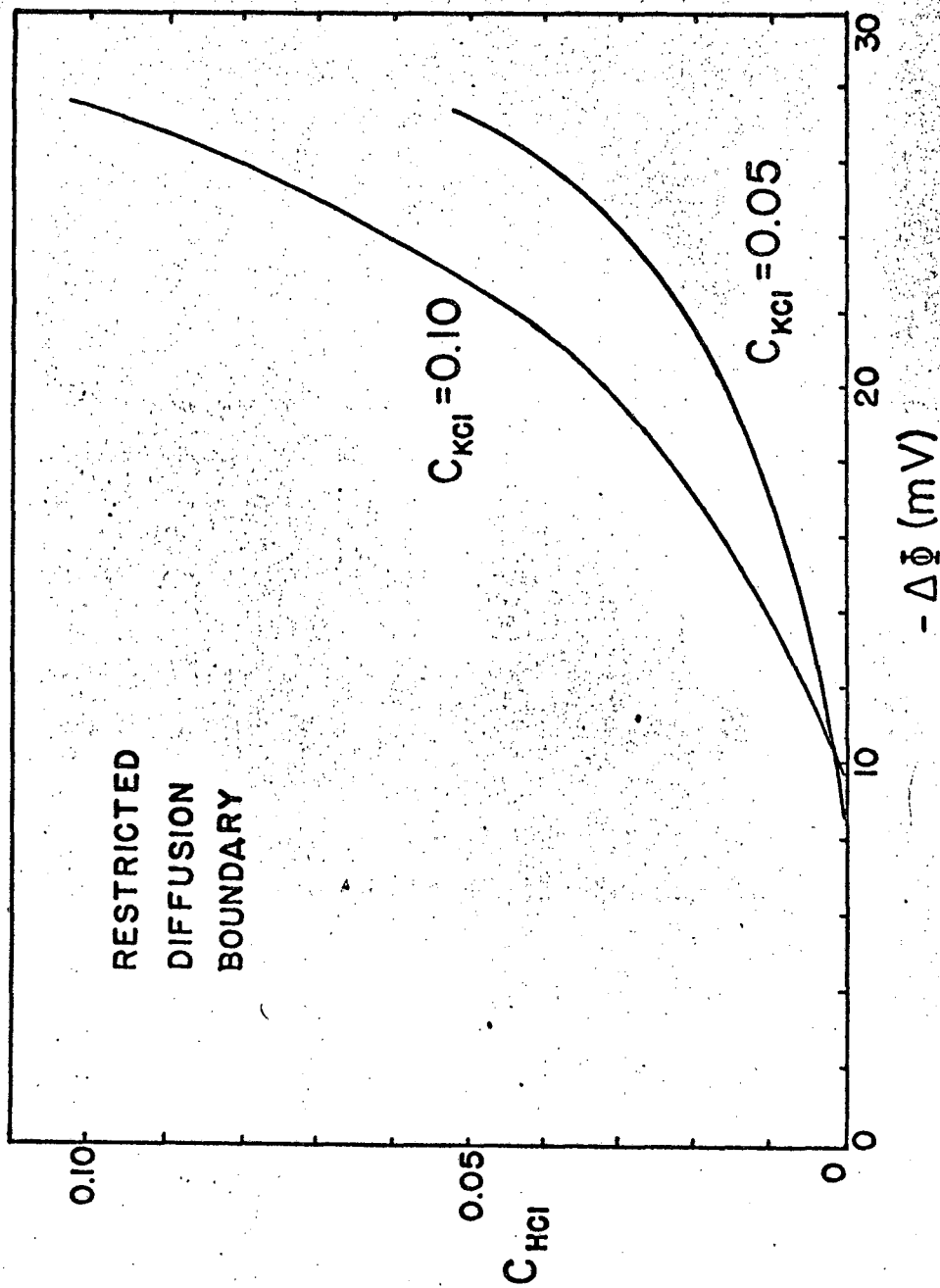


Fig. 2.

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Fig. 3.



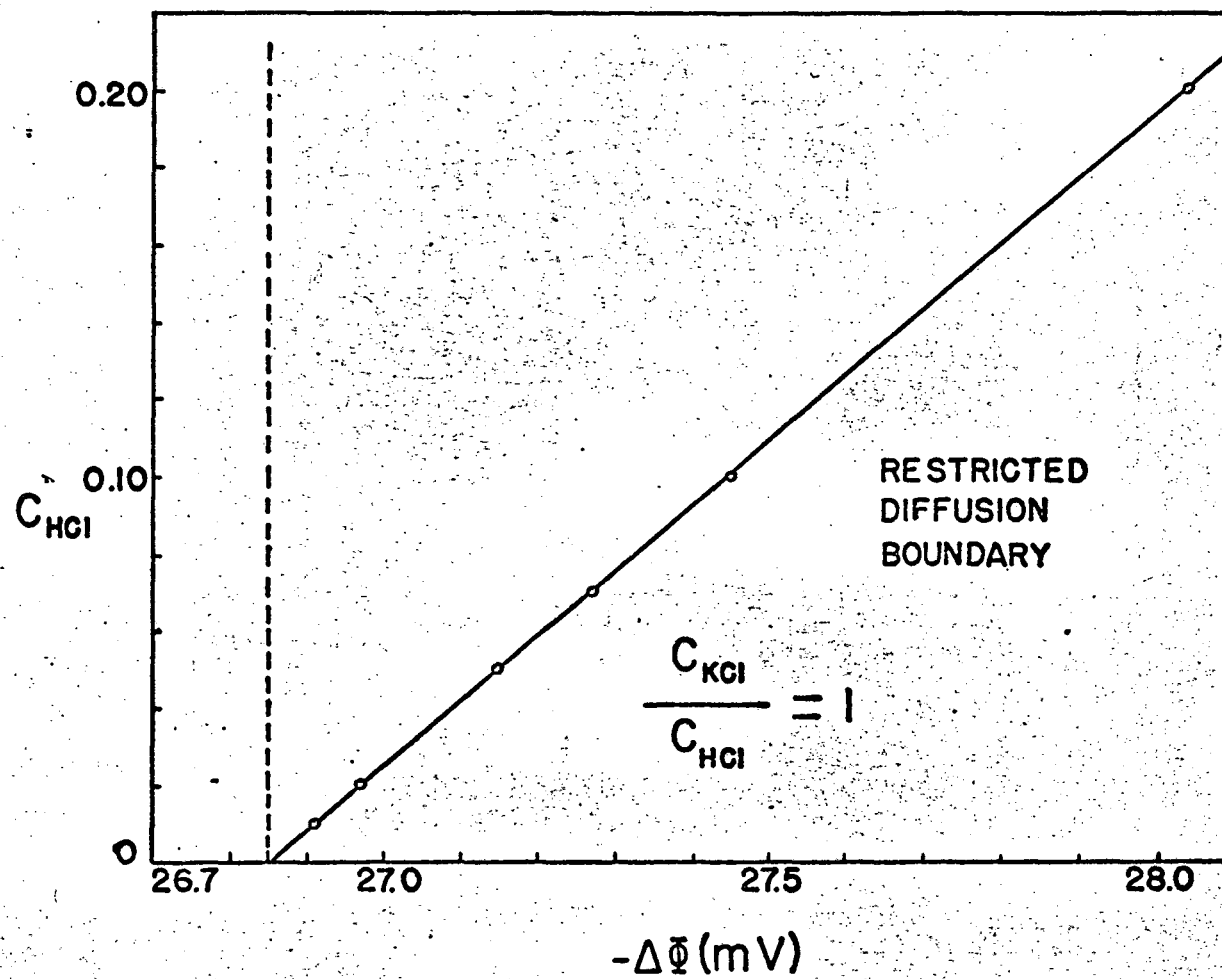
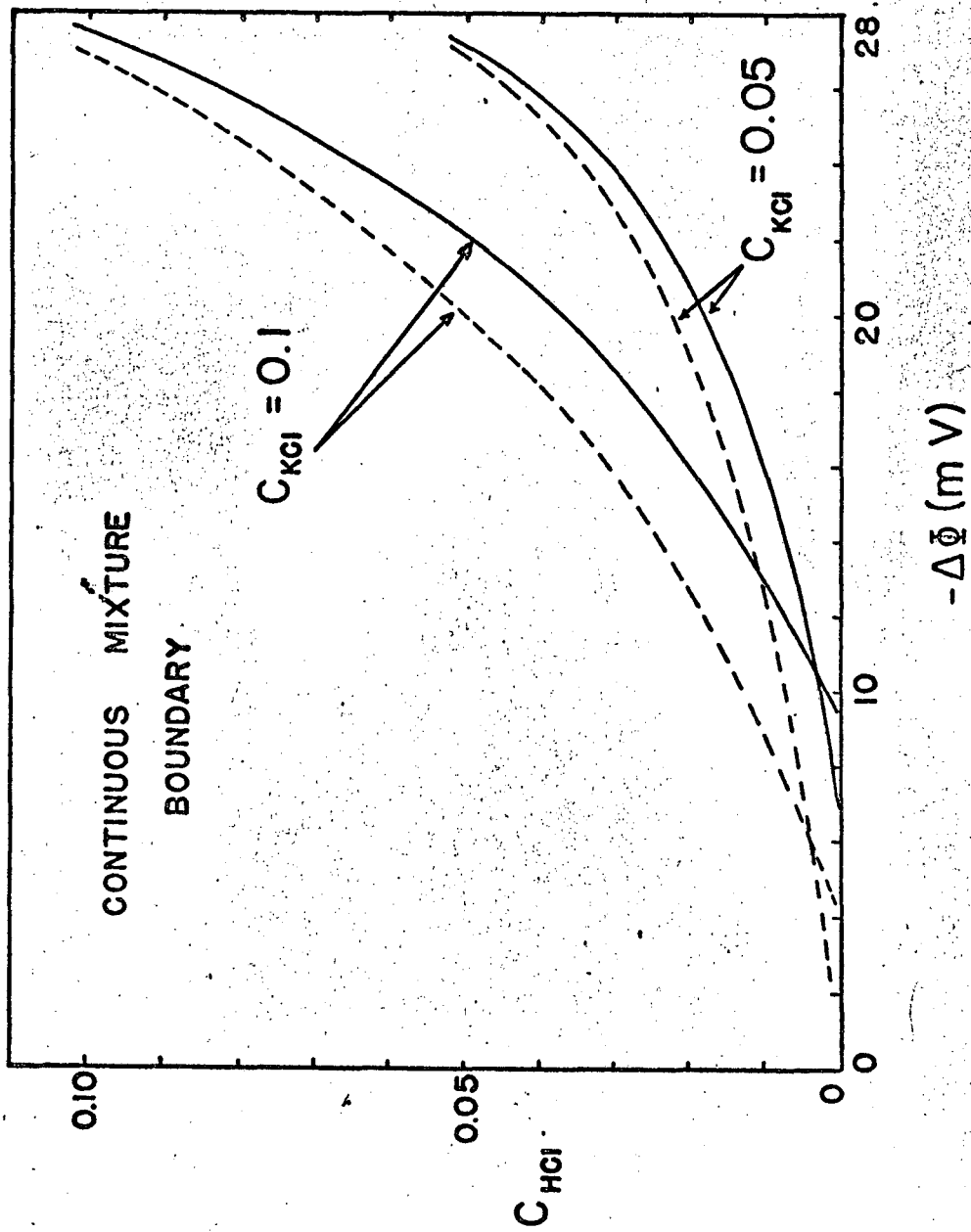


Fig. 4.

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Fig. 5.

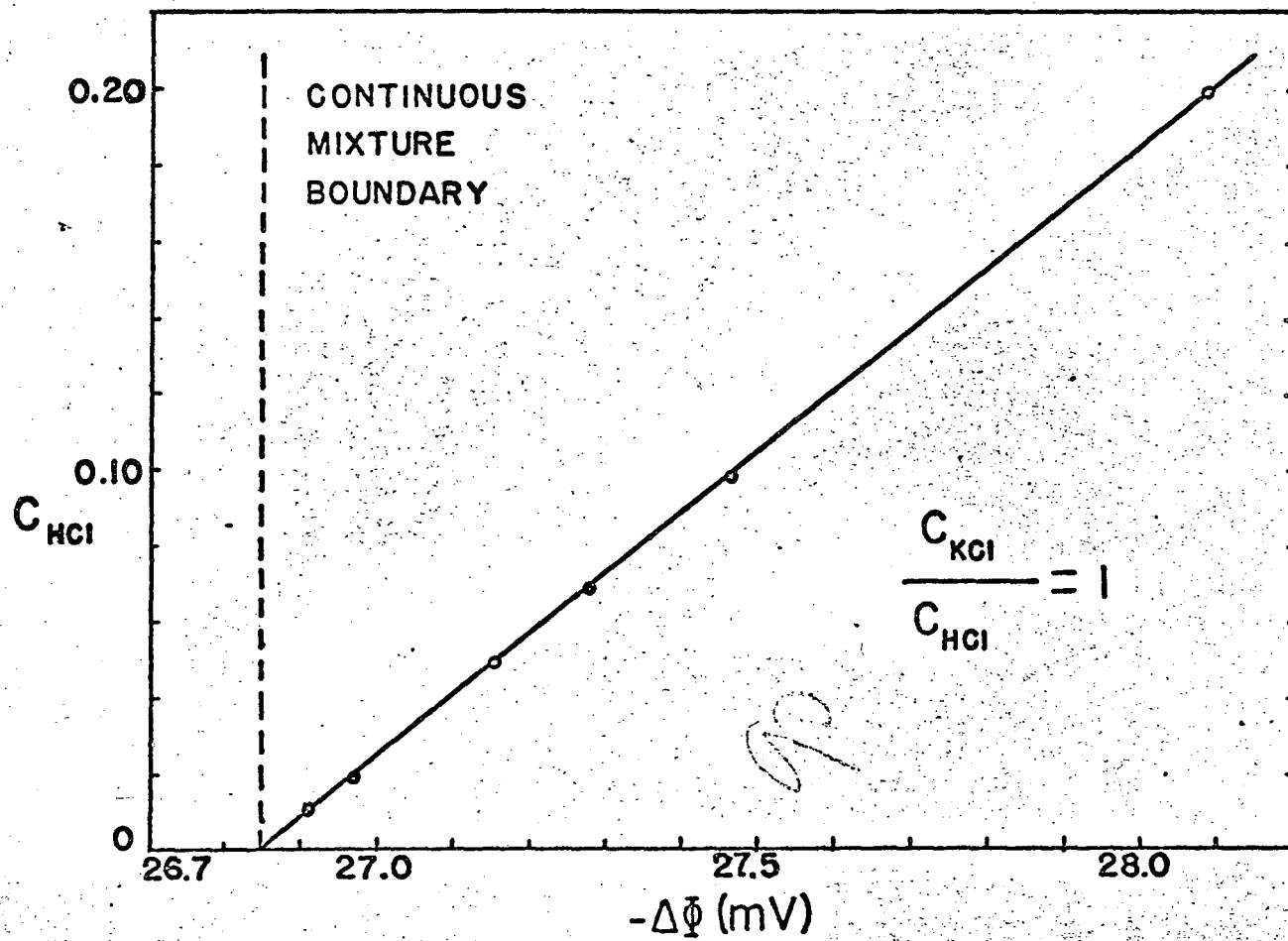


Fig. 6.

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