

The Use of Amalgam Electrodes to Measure Activity Coefficients of Metal Salts in Multicomponent Salt Solutions

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FOREWORD

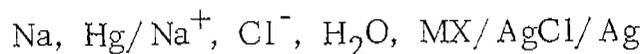
This is one of a continuing series of reports designed to present accounts of progress in saline water conversion and the economics of its application. Such data are expected to contribute to the long-range development of economical processes applicable to low-cost demineralization of sea and other saline water.

Except for minor editing, the data herein are as contained in a report submitted by the contractor. The data and conclusions given in the report are essentially those of the contractor and are not necessarily endorsed by the Department of the Interior.

ABSTRACT

The significance of activity coefficient measurements in connection with current research and engineering in desalination is discussed. The importance of activity as opposed to concentration in the electro dialysis and reverse osmosis processes is shown using the theory of irreversible thermodynamics. The activity of individual components is shown to be the relevant composition factor in processes involving solvent extraction, adsorption or electrosorption, and scale formation.

The principal experiments described in this report are those which measure the activity of NaCl in multicomponent electrolytes using the cell



for added salts (MX) Na_2SO_4 , KCl, LiCl, MgCl_2 , and CaCl_2 . The conditions under which such a cell can be used are discussed.

The thermodynamics and kinetics of the alkali metal amalgam electrode are discussed in detail, with emphasis on factors affecting the accuracy of measurements in cells such as the above. Interference by a second cation such as potassium or lithium is analyzed quantitatively. Measurements of the standard potential of the lithium amalgam electrode, made during the course of this research, are reported.

The alkaline earth amalgam electrodes are discussed, with particular attention to the calcium and barium amalgam electrodes. Standard potentials are calculated for both these electrodes from data of other workers, using the best available thermodynamic data.

The experimental methods used in our research are discussed in detail. Techniques for handling amalgam electrodes, chloride and sulfate-reversible reference electrodes, glass electrodes, and liquid ion exchange electrodes are described.

Results reported include activity coefficient measurements in the aqueous multicomponent systems $\text{NaCl-Na}_2\text{SO}_4$, NaCl-LiCl ,

NaCl-CaCl₂, NaCl-MgCl₂, and NaCl-BaCl₂. Activity measurements using a calcium-sensitive specific ion electrode are reported, and the theory of the activity of calcium ion in multicomponent solutions is discussed. A possible method based on the Brønsted theory for production of activity coefficients in multicomponent mixtures is presented. Experimental studies of the calcium amalgam and barium amalgam electrodes are summarized.

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I. INTRODUCTION

Desalination of sea or brackish waters involves solutions of relatively complex composition. In almost all processes currently under development, the activities of the ionic components of the solution are of paramount importance both in determining the process rate and the final equilibrium composition. Yet, reliable activity data for multicomponent salt solutions are scanty. As a result, concentrations are usually used in theoretical analyses as well as in the design of experiments, and the large differences between activities and concentrations are ignored. Since the activity of a species may be ten times smaller or ten times larger than its concentration, it is apparent that a real need exists for accurate activity data in solutions of interest.

Although the above may appear self-evident, activities have been ignored in actual practice with such consistency that it might be useful to illustrate our assertion with some examples. In reverse osmosis, separation of ionic salts and water is accomplished by applying a pressure differential across a membrane; in electrodialysis, an electric field is used for the same purpose. The general equations governing these processes are given by the theory of irreversible thermodynamics⁽¹⁾. The driving force, X_i , for the separation process is the sum of the chemical potential gradient, $\nabla \mu_i$, the electrical potential gradient, $\nabla \phi$, and the external hydrodynamic or mechanical forces (here represented by Y) imposed on the system:

$$X_i = \nabla \mu_i + \nabla \phi + Y \quad (1)$$

The chemical potential gradient may be expanded as follows:

$$\nabla \mu_i = v_i \nabla p + \sum_k \left(\frac{\partial \mu_i}{\partial C_k} \right) \nabla C_k \quad (2)$$

Where the sum is taken over all the components of a multicomponent electrolyte, v_i is the partial volume of component i , p is the pressure, and C_k is the concentration of each of the various components.

Let us consider a simple case of electro dialysis of a single salt. We can estimate the magnitude of the various terms in eq. (1) by taking some approximate values in a one-dimensional model. Typically Y is of the order of 10^5 joule/mole cm (assuming a potential difference of 10^{-2} v across a membrane 10^{-2} cm thick). The work term $v \nabla p$ is negligible (20 joule/mole cm), and the second term in the chemical potential gradient is thus of the same order as Y .

Now, if we ignore activity coefficients and assume a ratio of concentration across the membrane $C''/C' \sim 2$, we have approximately

$$\nabla \mu_i = RT \nabla \ln \frac{C''}{C'} \quad 1.7 \times 10^5 \text{ joule/mole cm}$$

i. e. as expected, the force applied is of the same order as the force opposing flow of ions in the direction of the field. Let us now assume that the activity coefficient changes from 0.6 to 0.8 we go from the more concentrated to the more dilute solution. Then using the proper ratio $a''/a' = (2)(0.6/0.8) = 1.5$ we find that the correct value of $\nabla \mu_i$ is in fact 1.0×10^5 joule/mole cm; a difference of about 70% in the driving force. This example makes an obvious point, but it must be emphasized that the kinetics as well as the thermodynamics of the over-all process are affected. The flux of component k is

$$J_k = \sum_i L_{ki} X_i$$

where L_{ki} is a generalized conductivity of the membrane. The flux depends directly on the term X_i calculated above and any errors in its estimation will be directly reflected as errors in calculated rates.

The situation is more complex where we deal with multicomponent solutions. In this case, the diagonal coefficients in eq. (2), $(\partial \mu_i / \partial C_i)$ are the largest terms, but since the chemical potential of each component is affected by every other component, particularly in concentrated solutions, the off-diagonal coefficients are not zero. Expressed in terms of activity coefficients (γ_i), these become;

$$\left(\frac{\partial \mu_i}{\partial C_i} \right) = \frac{RT}{C_i} + \frac{RT}{\gamma_i} \left(\frac{\partial \gamma_i}{\partial C_i} \right)$$

$$\left(\frac{\partial \mu_i}{\partial C_k} \right) = \frac{RT}{\gamma_i} \left(\frac{\partial \gamma_i}{\partial C_k} \right) \quad i \neq k$$

Thus, unless we have determined such activity coefficients we may make errors of as much as 100% in the analysis or prediction or the behavior of specific practical systems. Entirely analogous arguments apply to reverse osmosis.

Activity coefficients are of importance in another aspect of desalination by reverse osmosis or by electro dialysis. One of the principal design problems in reverse osmosis is the description and proper evaluation of the effects of a concentrated salt boundary layer formed on the high-pressure side.

The usual approximation in solving the mass transport equations is to replace chemical potential gradients by concentration gradients. Thus, in the partial differential equation for channel flow⁽¹⁾

$$\frac{\partial}{\partial x} (uC) + \frac{\partial}{\partial y} (uC - D \frac{\partial C}{\partial y}) = 0$$

(where u is the velocity, C is concentration, and x and y are coordinates) the activity has been replaced by concentration. The result is to make the diffusion coefficient D a function of the concentration of all components in the electrolyte and, consequently, to limit the usefulness of measurements made in any particular multicomponent electrolyte.

The activity of individual components becomes of still greater significance in processes involving solvent extraction and adsorption (or electrosorption); here, the operative factor is a set of specific chemical and physical equilibria which depend strongly on the nature of the materials involved. Again, concentration rather than activity is normally used with consequent possibilities of substantial errors.

Let us turn to yet another topic of great importance in a desalination process. Scale formation in distillation involves specific ionic equilibria which depend, of course, on activities rather than concentrations. Activities have rarely been used in the analysis of data on scale formation because of the limited availability of activity coefficients, particularly when dealing with concentrated solutions. That activities are important is clear, for example, from the effect of total salt content on the solubility of calcium sulfate or from the more general observation that the solubility of slightly soluble salts strongly increases with the presence in solution of a large number of ions of some other soluble salt. An understanding of such interactions is necessary in order to explain, and thus predict, the wide variability in the nature and thermal resistance of scale formed in different waters. To cite an example again, the thermal resistance of scale formed during boiling of water from the Donets basin is considerably larger than that formed during boiling of Caspian Sea Water, although the concentration of scale-forming agents in Caspian Sea Water is 3 to 4 times larger. The origin of this difference is to be found in the much larger total salt content (about 10 times larger) in the Donets basin water⁽²⁾.

We can generalize all the above examples by drawing an analogy with what we need to know in design and analysis of the most common desalination process, namely distillation. Here, it is clear that accurate knowledge of the activity of water, and hence of the vapor pressure of water as a function of salt content, temperature, etc. is absolutely necessary. In an entirely similar fashion, knowledge of ionic activities in the multicomponent salt solutions processed by other desalination processes is equally indispensable.

The emphasis in this work has been on multicomponent salt solutions containing NaCl, since these are the most relevant to desalination of water. A bibliography of papers⁽³⁻³⁹⁾ concerning

activity coefficients in multicomponent salt solutions is given in Table I. This list does not include measurements on nonaqueous systems nor the very extensive series of measurements on systems containing HCl together with another solute made by Harned and co-workers and well-summarized elsewhere^(40, 41).

Three principal methods have been used to determine activity coefficients of metal salts in multicomponent salt solutions: the amalgam electrode cell, the isopiestic method, and the membrane electrode cell. The amalgam electrode cell was used for much of the early work but has not been used recently because of the experimental difficulties associated with dropping amalgam electrodes. During this contract we have used sodium amalgam electrodes to study the systems NaCl-LiCl, NaCl-CaCl₂, NaCl-MgCl₂, and NaCl-Na₂SO₄⁽³²⁻³⁴⁾. The results of these investigations are given in section VI of this report.

The isopiestic method—based on equilibrating the multicomponent electrolyte vapor pressure with an electrolyte of known vapor pressure—is experimentally simpler, but is restricted to concentrations greater than about 1m. This limitation results because the measurements require accurate values for small changes in weight of solutions; and the calculations involve interpolation of concentration ratios, together with integration of the results of a number of measurements to obtain the activity coefficients of the components. The amalgam electrode method has an important advantage over the isopiestic method in that an emf measurement yields the activity coefficient of a single electrolyte component directly, and the calculations do not depend critically on other measurements.

Recently, some studies have been made using membrane electrodes reversible to only one of the cations in a multicomponent electrolyte. Thermodynamically, such electrodes are equivalent to the amalgam electrodes, but in practice, the selectivity of the electrodes is not perfect and the assymetry potential of the membrane may

TABLE I

Bibliography of Activity Coefficients in Multicomponent
Aqueous Salt Solutions
(excluding systems containing HCl)

<u>Solutes</u>	<u>Method</u>	<u>Authors</u>	<u>Year</u>	<u>Ref.</u>
NaOH + NaCl	Na amalgam - H ₂ electrode	Harned	1925	3
KOH + KCl	K amalgam - H ₂ electrode	Harned	1925	4
LiOH + LiCl	Li amalgam - H ₂ electrode	Harned and Swindells	1926	5
KOH + KBr KOH + KI	K amalgam - H ₂ electrode	Harned and James	1926	6
KOH + KCl NaOH + NaCl	K amalgam - H ₂ electrode Na amalgam - H ₂ electrode	Harned and Harris	1928	7
KNO ₃ , KCl LiNO ₃ , LiCl mixtures	Freezing point	Scatchard and Prentiss	1934	8
NaOH + NaCl	Na amalgam - H ₂ electrode Na amalgam - Ag/AgCl electrode	Harned and Cook	1937	9
KOH + KCl	K amalgam - H ₂ electrode K amalgam - Ag/AgCl electrode			
KCl + LiCl	isopiestic	Owen and Cooke	1937	10
KCl + glycine	Cell with transference, Ag/AgCl electrode	Roberts and Kirkwood	1941	11

TABLE I (cont.)

<u>Solutes</u>	<u>Method</u>	<u>Authors</u>	<u>Year</u>	<u>Ref.</u>
NaCl + CsCl	isopiestic	Robinson	1952	12
KCl + NaCl	isopiestic	Robinson	1953	13, 14
KCl + LiCl NaCl + LiCl LiNO ₃ + LiCl	isopiestic	Robinson and Lim	1953	15
KCl + KBr	isopiestic	McCoy and Wallace	1956	16
NaCl + KCl	isopiestic	Robinson	1961	17
CaCl ₂ + KCl BaCl ₂ + KCl BaCl ₂ + NaCl	organic membrane electrodes reversible to Ba ⁺⁺ or Ca ⁺⁺ , Ag/AgCl or calomel reference	Schonhorn and Gregor	1961	18
MgCl ₂ + KCl SrCl ₂ + KCl SrCl ₂ + MgCl ₂ SrCl ₂ + CaCl ₂	organic membrane electrodes reversible to Mg ⁺⁺ or Sr ⁺⁺ ; Ag/AgCl reference	Gregor, Glatz, and Schonhorn	1963	19
CaCl ₂ + NaCl	organic membrane electrodes reversible to Ca ⁺⁺ ; Ag/AgCl reference	Bagg and Gregor	1964	20
NaCl - MgCl ₂ NaCl - CaCl ₂ NaCl - SrCl ₂ NaCl - BaCl ₂	glass electrode reversible to Na ⁺ ; Ag/AgCl reference	Fitzgerald and Manglesdorf	1964	21

TABLE I (cont.)

<u>Solutes</u>	<u>Method</u>	<u>Authors</u>	<u>Year</u>	<u>Ref.</u>
NaCl - NaClO ₄	isopiestic	Scatchard and Yoest	1964	22
NaCl + BaCl ₂	isopiestic	Robinson and Bower	1965	23
KCl + glycine	isopiestic	Bower and Robinson	1965	24
KCl + BaCl ₂	isopiestic	Robinson and Bower	1965	25
CaCl ₂ + NaCl	glass electrode reversible to Na ⁺ ; Ag/AgCl reference	Moore and Ross	1965	26
NaCl + MgCl ₂ NaCl + CaCl ₂ NaCl + SrCl ₂ NaCl + BaCl ₂ NaCl + Na acetate NaCl + NaClO ₄ NaCl + NaNO ₃ NaCl + Na ₂ SO ₄	glass electrode reversible to Na ⁺ ; Ag/AgCl reference	Lanier	1965	27
NaOH - NaCl	Na amalgam - H ₂ electrode	Ferse	1965	28
CaCl ₂ - MgCl ₂	isopiestic	Robinson and Bower	1966	29

TABLE I (cont.)

<u>Solutes</u>	<u>Method</u>	<u>Authors</u>	<u>Year</u>	<u>Ref.</u>
NaCl - CaCl ₂	isopiestic	Robinson and Bower	1966	30
NaCl - Na ₂ SO ₄ NaCl - MgSO ₄	glass electrode reversible to Na ⁺ ; Ag/AgCl reference	Gieskes	1966	31
NaCl - MgSO ₄	isopiestic; Na (Hg) - Ag/AgCl	Platford	1967	31a
NaCl - Na ₂ SO ₄	Na amalgam - Ag/AgCl electrode	Butler, Hsu and Synnott	1967	32
NaCl - LiCl	Na amalgam - Ag/AgCl electrode	Butler, Huston and Hsu	1967	33
NaCl - CaCl ₂ NaCl - MgCl ₂	Na amalgam - Ag/AgCl electrode	Butler and Huston	1967	34
HClO ₄ - LiClO ₄ HClO ₄ - NaClO ₄ LiClO ₄ - NaClO ₄	isopiestic	Rush and Johnson	1968	35
NaCl - Na ₂ SO ₄	isopiestic	Platford	1968	35a
NaCl - Na ₂ SO ₄	glass electrode - Pb(Hg)/PbSO ₄	Synnott and Butler	1968	36
NaCl - MgCl ₂	isopiestic	Platford; Wu et. al.	1968	37
NaCl - Na ₂ SO ₄	isopiestic	Rush	1968	38
NaCl - KCl	isopiestic	Rush and Robinson	1968	39

change with time. Both glass electrodes (for Na^+)^(21, 26, 27) and organic membrane electrodes (for alkaline earth cations)⁽¹⁸⁻²⁰⁾ have been used successfully. We have made measurements with both these types of systems (see section VI-A and VI-B).

In most mixed aqueous electrolytes, the activity coefficient of at least one of the components has been found to obey Harned's Rule^(40, 41):

$$\log \gamma_{12} = \log \gamma_{10} - \alpha_{12} X_2 I$$

where γ_{12} is the activity coefficient of component 1 in the mixed electrolyte of ionic strength I , γ_{10} is the activity coefficient of component 1 alone at ionic strength I , X_2 is the ionic strength fraction of component 2 in the mixed electrolyte, and α_{12} is the Harned Rule coefficient, which depends to some extent on the total ionic strength I , but not on the fraction of the second component X_2 . Among the systems not obeying Harned's Rule within experimental error are the KOH-KCl and NaOH-NaCl mixtures^(3, 4). In the system NaCl- Na_2SO_4 , it was at first believed that Harned's Rule was obeyed for only NaCl⁽²⁷⁾, but independent measurements showed that Harned's Rule is obeyed for both components^(32, 36, 38). These three are the only cases where independent measurements were made of the activity coefficients of each component. Small deviations from Harned's Rule have been observed in very accurate measurements⁽³⁹⁾.

Although the activity coefficient of the second component can be calculated, by the Gibbs-Duhem relation, from measurements of the activity coefficient of the first component over a range of compositions, the final test of thermodynamic consistency is to make independent measurements of the two components by different experimental methods.

This report discusses the use of amalgam electrodes for measurements of activity coefficients in multicomponent salt solutions,

with emphasis on understanding the limitations in our present knowledge of amalgam electrodes and on measuring accurate activity coefficient data relevant to desalination of water.

solutions is obtained by analysis, or by weighing out the required quantities of water and anhydrous salts, and the temperature can be held constant by means of a thermostat, a measurement of the combined emf of the two sodium amalgam-silver chloride cells gives a direct measurement of the ratio of γ_{12} in the mixed electrolyte to γ°_{10} in pure sodium chloride solutions.

Before the present study was begun, the only multicomponent systems studied by the amalgam electrode method were the hydroxide-halide mixtures⁽³⁻⁷⁾, and the most recent work of this type was completed in 1937. In spite of the limited precedent, a large number of multicomponent salt systems can be studied using amalgam electrodes, provided certain conditions are fulfilled. First, the amalgam electrode must be reversible to the desired cation and no others present in the system. Second, the reference electrode must be reversible to the desired anion and to no others present in the system. Third, the cell must be substantially free from liquid junction potentials.

Most of the experimental work described in this report has been carried out using the sodium amalgam-silver chloride cell, which gives the mean activity coefficient of sodium chloride in the mixed electrolyte directly, provided that the other components present in the electrolyte do not interfere with the electrode reactions. To establish the reversibility of amalgam electrodes is a complex problem, discussed in detail in sections III and IV of this report.

The silver/silver-chloride electrode is reversible to chloride ion provided no other anions are present which form silver salts less soluble than AgCl and provided no strongly oxidizing or reducing ions are present which could interfere with the Ag/Ag⁺ electrode reaction. Salts used to prepare the solutions must be highly purified, particularly free from traces of bromide iodide, cyanide, and heavy metal ions. The activity of NaCl can probably be measured in mixtures with many nonreducible anions: NaOH, NaF, NaNO₃, NaClO₃, NaClO₄, Na₂CO₃, NaHCO₃, Na₂SO₄, possibly NaBrO₃ and NaIO₃, as

well as the sodium salts of many organic acids. In section VI-A we have reported our results^(32, 36) on the NaCl-Na₂SO₄ system.

The cells used in the studies we are concerned with are usually described as "cells without liquid junctions." This is at best only an approximation. In fact, cell (1) is better written

$$\text{Na, Hg/Na}^+, \text{Cl}^-, \text{SO}_4^{=} / \text{Na}^+, \text{Cl}^-, \text{SO}_4^{=}, \text{Ag}^+, \text{AgCl}, \text{AgCl}_2^-, \text{etc.} \quad (5)$$

$$/ \text{AgCl(s)}/ \text{Ag}$$

with a well-defined junction between the electrolyte saturated with AgCl and the pure electrolyte which contacts the amalgam electrode. Only because of the low solubility of AgCl in excess chloride can we neglect this liquid junction potential.

Figure 1 shows how the solubility of AgCl and the concentrations of the various silver chloride complexes vary with the concentration of added chloride^(42, 43). Instead of decreasing indefinitely with increasing chloride concentration (as predicted by the solubility product), the solubility of AgCl passes through a minimum value (about 5×10^{-7} M) when the concentration of added chloride is about 4×10^{-3} M. In solutions containing 0.1 to 1 molal chloride, the solubility of AgCl may increase to values greater than 10^{-4} M, and most of the soluble species will be anions of high charge, such as $\text{AgCl}_3^{=}$ and $\text{AgCl}_4^{=}$.

Because the activity coefficients and mobilities of these ions are unknown, it is impossible to calculate the exact value of the liquid junction potential, but a rough approximation can be obtained using the equation (10-6-16 of Ref. 40):

$$E_J = - \frac{RT}{F} \left\{ \sum_i \int_I^{II} t_i d \ln \gamma_i + \sum_i \int_I^{II} t_i d \ln m_i \right\} \quad (6)$$

Here t_i are transference numbers; the sums are performed over all the ions present, and the integration made from the bulk of electrolyte in the left hand compartment (I) to the bulk of the electrolyte in the right-hand compartment (II).

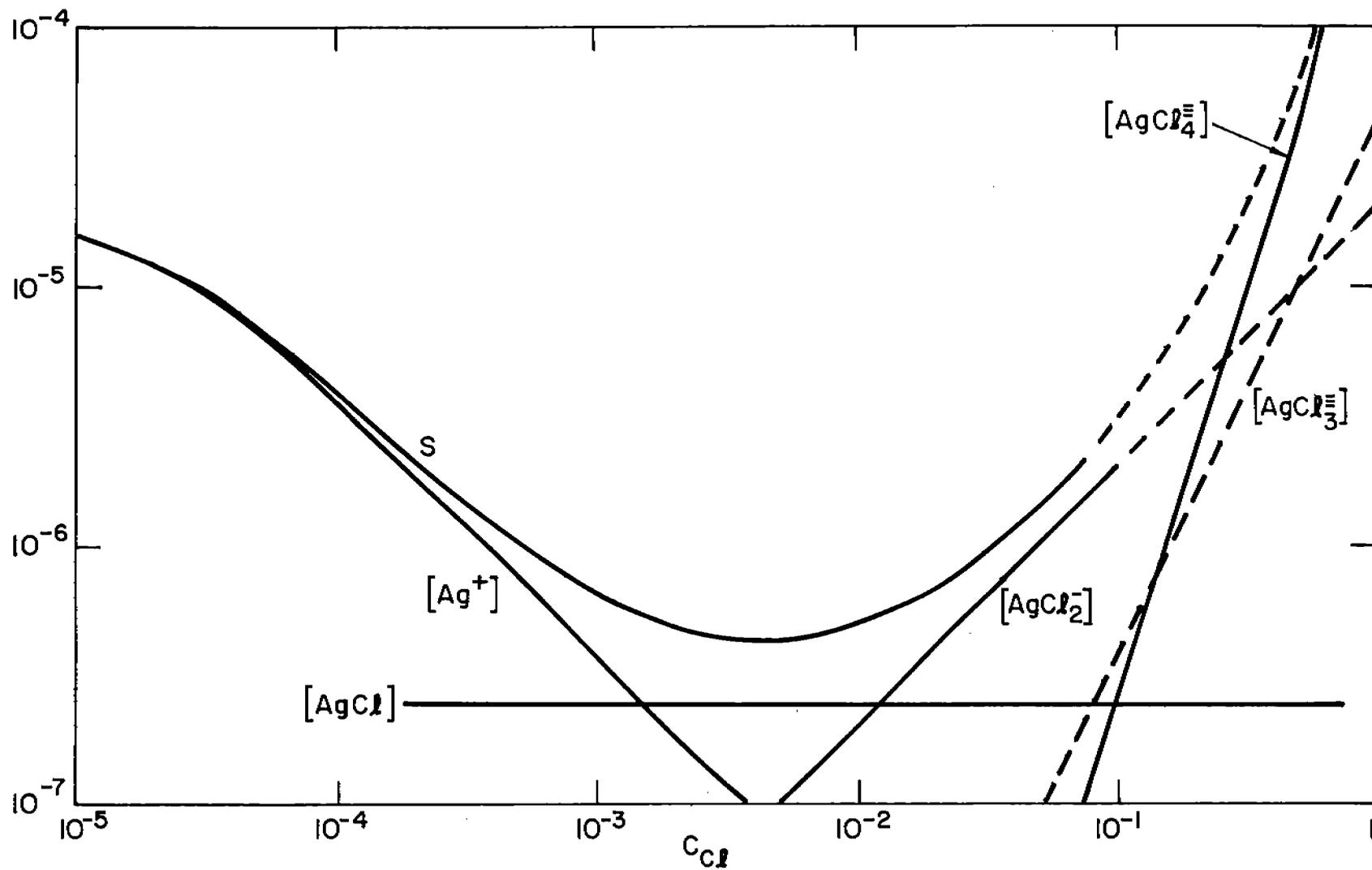


Fig. 1 Solubility of AgCl in excess chloride

Consider a case where a large liquid junction potential is expected, say 1m NaCl containing 0.002 m AgCl_4^- , and make the assumption that the mobility of the silver chloride complex is very small. From equation (6), we obtain $E_J = +0.08$ mv, which is large enough to be a significant systematic error. The calculated value of E_J becomes smaller as the mobility of the complex approaches that of the chloride ion.

Although no detailed investigation of this effect has yet been reported, it may account for a discrepancy of several percent which has been noted between activity coefficients of NaCl measured by the EMF method and by the direct measurement of vapor pressure⁽⁴⁴⁾.

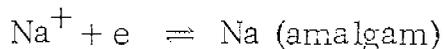
III. ALKALI METAL AMALGAM ELECTRODES

Since the main emphasis in this work has been on solutions containing NaCl, we have devoted most of our effort to measurements with alkali metal amalgam electrodes, particularly sodium amalgam.

A. Factors Affecting Reversibility

For a reversible electrode to be effective in cells used for thermodynamic measurements, three primary criteria must be satisfied: (a) The exchange current for the desired reaction must be high, (b) The activity of reactants must be either constant or accurately known, (c) No other reaction must take place at the electrode.

The first requirement, high exchange current, is well satisfied by the amalgams of all the alkali metals. For example, under the conditions where the sodium amalgam electrode has been used⁽⁴⁵⁾ to determine the activity coefficients of NaCl, the exchange current for the reversible reaction

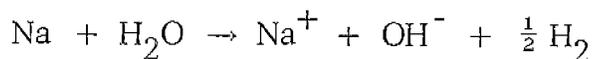


is of the order of 1 a/cm^2 ⁽⁴⁶⁾, comparable to that of the platinum-hydrogen or silver-silver-chloride electrodes⁽⁴⁷⁾.

The second criterion, that the activity of the reactants be either constant or accurately known, is more difficult to satisfy. The composition of the electrolyte can be accurately measured by analysis. However, because of the possibility of contamination by traces of oxygen, the composition of amalgams prepared by electrolysis or by mixing weighed quantities of mercury and alkali metal can be accurately determined only with great difficulty. For this reason, virtually all workers have used two identical cells, with one containing a solution of known activity, as described in the previous section.

The final criterion, the absence of side reactions, is the most difficult to satisfy and is the primary cause of experimental difficulties with amalgam electrodes. Even though the activity of an alkali metal in

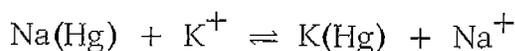
a dilute amalgam (typically 0.05%) may be 10^{-14} times that of the pure metal⁽⁴⁸⁾, the direct dissolution reaction



may still take place at the amalgam-electrolyte interface⁽⁴⁹⁻⁵¹⁾.

Dissolution of the amalgam affects the measured potential in two ways: (a) It shifts the zero-current potential from the reversible value because of the additional electrode process of hydrogen evolution. (b) It increases the concentration of sodium ion in the diffusion layer immediately adjacent to the electrode surface and thus shifts the electrode potential. Both of these shifts are to more positive values. The first of these processes depends of pH but does not depend strongly on salt concentration. The second becomes most important at low salt concentrations, where the concentration in the diffusion layer may be much larger than the bulk concentration of the solution.

In addition to dissolution of the amalgam, reaction can also take place with the cation of the second salt in a mixed electrolyte, if its potential is close to that of the amalgam. For example, the reaction



can shift the potential of a sodium amalgam electrode in solutions containing both sodium and potassium ions.

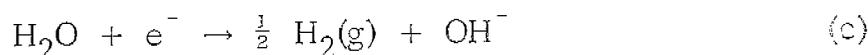
These various effects will be discussed in more detail below.

B. Effect of Hydrogen Evolution

Let us consider first the potential shift due to hydrogen evolution, at a sodium amalgam electrode in an electrolyte consisting only of sodium chloride, water, and an inert sodium salt (such as NaOH or Na_2SO_4). The only anodic process that can take place is the dissolution of sodium from the amalgam:



However, two cathodic processes can take place:



The net current at the electrode will be the difference between the anodic and cathodic currents:

$$i = i_a - i_b - i_c \quad (1)$$

and the potential at which this current is zero will, in general, be different from the reversible potential for the electrode, at which

$$i = i_a - i_b \quad (2)$$

We can obtain an expression for these various currents using independently measured values for the kinetic parameters of the sodium ion discharge reaction and the hydrogen evolution reaction.

Using the Tafel equation, we can express the partial currents for the reactions proceeding at the sodium amalgam electrode in terms of kinetic parameters:

$$i_a = i_0 \exp [F (1 - \alpha) (E - E_e) / RT] \quad (3)$$

$$i_b = i_0 \exp [- F \alpha (E - E_e) / RT] \quad (4)$$

where i_0 is the exchange current, α is the cathodic transfer coefficient, and E_e is the reversible potential for the Na/Na^+ reaction, defined by the equation

$$E_e = E^\circ_{\text{Na(Hg)}} + \frac{RT}{F} \ln \frac{m_{\text{Na}^+} \gamma_{\pm}}{X_{\text{Na}} \gamma_{\text{Na}}} \quad (5)$$

where $E^\circ_{\text{Na(Hg)}}$ is the standard potential of the sodium amalgam electrode (-1.95 volts), m_{Na^+} is the molality of sodium ion in the solution γ_{\pm} is the mean activity coefficient of NaCl (since the reference electrode is reversible to chloride ion), X_{Na} is the mole fraction and γ_{Na} is the activity coefficient of Na in the amalgam (see part E of this section).

Imai and Delahay⁽⁴⁶⁾ have measured exchange currents and transfer coefficients for the alkali metal reactions using the faradaic rectification method, and their results are summarized in Table II in terms of the following equation:

$$i_o = F k_a^o C_{M^+}^{(1-\alpha)} C_M^{(\alpha)} \quad (6)$$

TABLE II
Kinetic Parameters for the Alkali Metal Amalgams⁽³⁸⁾

<u>Metal</u>	<u>α</u>	<u>$F k_a^o$</u> amp l cm ⁻² mole ⁻¹	<u>i_o^*</u> amp/cm ²
Na	0.61	17.4	2.6
K	0.59	5.0	0.57
Li	0.65	8.9	0.0035

* $C_{M^+} = 0.5m$; $E = -1.795$ volts.

The units of $F k_a^o$ given in Table II are such that C_{M^+} and C_M are both in moles/liter, and i_o is in amp/cm². For comparison purposes, Table II gives i_o for conditions corresponding to our experiments.

The concentration of metal ion in solution was fixed at 0.5 m, and the concentration of metal in the amalgam was taken to be the equilibrium amount at a potential of -1.795 volts. Note that the sodium amalgam electrode has the highest rate of the three alkali metals listed.

Reasonable values⁽⁵²⁾ for the kinetic parameters of the hydrogen evolution reaction under the conditions of our experiments are $i_o = 3 \times 10^{-13}$ amp/cm² and $\alpha = 0.50$, independent of pH. The reversible potential of the hydrogen reaction is -0.059 pH volts, so that

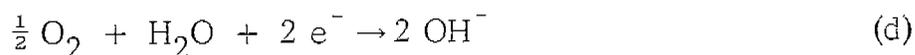
$$i_c = 3 \times 10^{-13} \exp [-19.47 (E + .059 \text{ pH})]$$

Addition of neutral salt decreases the exchange current, so that this is an upper limit.

In Fig. 2 these components of the current are plotted for the potential region near the reversible potential in a typical case at $\text{pH} = 7$. The zero-current potential is shifted approximately 0.75 mv more positive because of the contribution from the hydrogen evolution reaction.

The hydrogen evolution reaction can be diminished in its effect by making the solution more alkaline, which shifts the reversible potential of the hydrogen reaction to more negative values and decreases i_c . For example, at a potential of -1.795 volts with $\text{pH} = 12.0$, the current i_c is calculated to be 2.8×10^{-4} amp/cm². This is only about 0.01% of the current due to the sodium reaction, and produces a negligible shift in potential, less than 0.005 mv.

One crucial point must be considered in this discussion: The current-potential curve for the hydrogen discharge reaction on amalgams is strongly affected by impurities in the solution, notably oxygen and organic materials^(49, 50). It is therefore important to use extremely pure materials and to prepare both the amalgams and the solutions in an inert atmosphere. The presence of traces of oxygen in the solution allows the additional reaction



to take place, adds another cathodic current contribution to the total current, shifts the zero-current potential to more positive values⁽⁵¹⁾ and increases the rate of corrosion of the amalgam. Even in alkaline solutions, then, substantial errors may result unless oxygen is rigorously excluded.

Investigations of hydrogen overpotential on amalgams have shown that in the absence of oxygen, dilute amalgams have a very high hydrogen overvoltage, essentially identical to that of pure mercury^(52, 53). In the presence of traces of oxygen, however, the shape of the current-potential curve is drastically altered, and oxygen reduction becomes

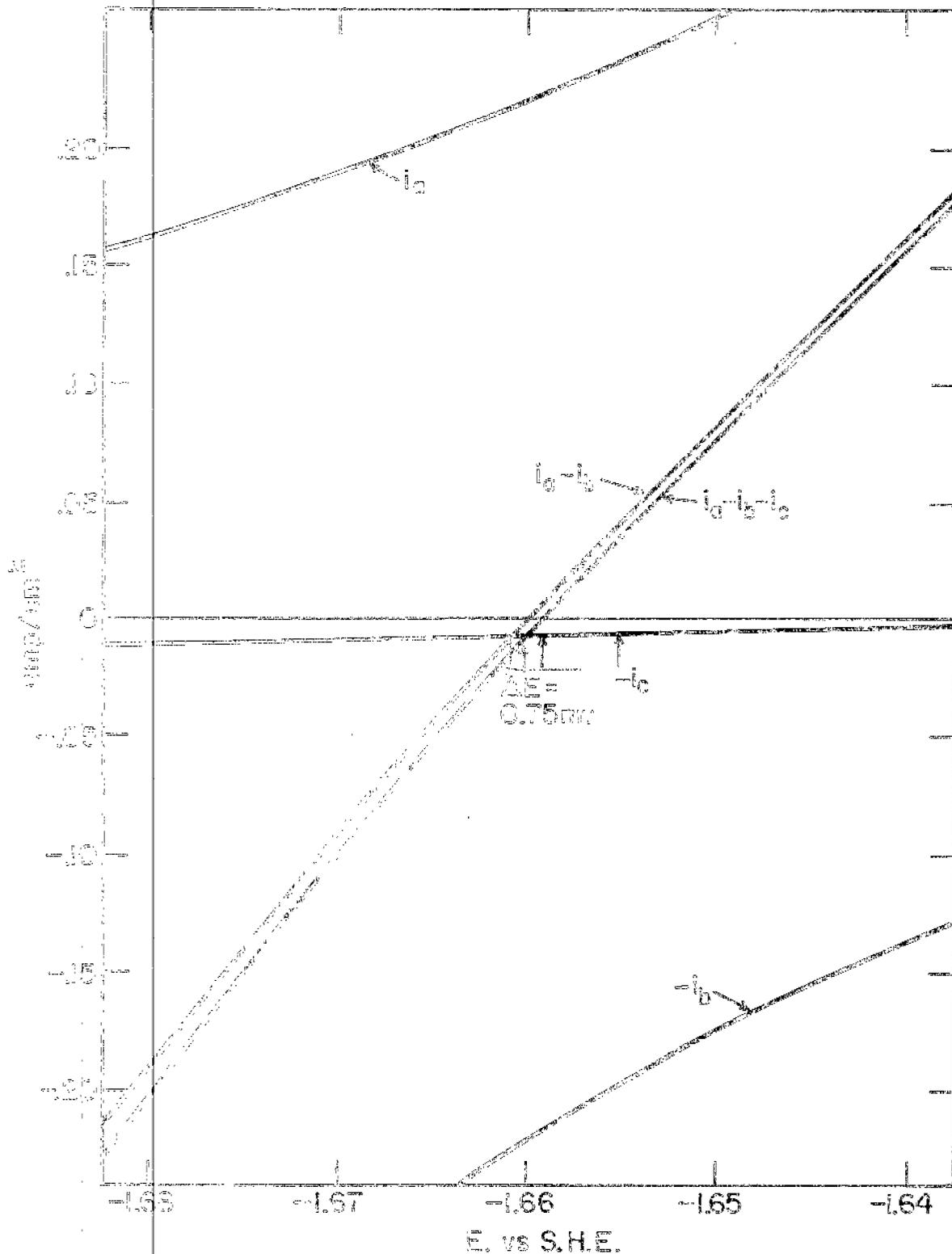


Fig. 2 Components of current at a sodium amalgam electrode, showing the kinetic shift due to hydrogen evolution.

the primary process. Removal of the last traces of oxygen from the solution can be achieved by passing the solution over platinum black, while saturating the solution with pure hydrogen⁽⁵⁴⁾. The platinum black acts as an internally short-circuited fuel cell, a catalyst for the combination of hydrogen with oxygen, and effectively removes the last traces of oxygen from the solution. As discussed later, this type of purification can be carried out without appreciably affecting the electrolyte concentration.

Traces of adsorbable organic material can also be removed by adsorption on platinum-black, but in order for this to be effective, the system must be free of grease or wax, and must be scrupulously clean. Only glass and Teflon appear to be compatible with hydrogen overvoltage measurements of high accuracy⁽⁵³⁾.

Finally, let us consider what the effects of amalgam and electrolyte concentration will be. The exchange current for the amalgam reaction is increased both by increasing the concentration of salt in the solution, and by increasing the concentration of sodium in the amalgam (Eq. 6). The reversible potential of the sodium ion-sodium reaction is shifted to more negative values by increasing the concentration of sodium in the amalgam, and to more positive values by increasing the concentration of sodium salt in the electrolyte (Eq. 5).

Thus, the most favorable conditions for operating the amalgam electrode so that the minimum shift from the reversible potential occurs is to use (1) alkaline solutions, (2) a high concentration of sodium salt in the electrolyte, (3) a moderately low concentration of sodium in the amalgam, and (4) extreme purity of solutions, particularly freedom from oxygen and organic materials.

C. Effect of Concentration Polarization

Now let us turn to another factor which may cause a shift of the measured potential from the true reversible potential for the sodium ion-sodium couple: changes in concentration in the diffusion layer

near the electrode. The potential of the electrode depends on the activity (within a few angstroms of the electrode surface) of sodium ion in the electrolyte and of sodium in the amalgam, not in the bulk, although it is the bulk activity which we want to measure. If an appreciable fraction of the cathodic current is due to hydrogen evolution or oxygen reduction, there will be a net accumulation of sodium ions in the solution and a corresponding depletion of sodium in the amalgam. Eventually, a steady state will be reached, where the interface concentrations are controlled by diffusion of sodium from the interior of the amalgam and by diffusion of sodium ions away from the interface to the bulk solution. Thus, the steady potential observed may differ appreciably from the true reversible potential and depend on the rates of these diffusion processes.

The only experimental studies of this effect published in detail⁽⁵¹⁾ were carried out with concentrated amalgams in solutions containing appreciable oxygen. Thus, the effect was much larger than would be expected for dilute amalgams in an oxygen-free solution such as we have used in our measurements. Nevertheless, these results indicate the type of effect to be expected and give an upper limit to the magnitude of the potential shift which may be obtained.

If the difference in activity of Na^+ at the electrode surface from that in the bulk of the electrolyte is denoted by s , the difference in activity of Na at the electrode surface from that in the bulk of the amalgam is denoted by m , and the diffusion potential resulting from the transport of Na^+ ions away from the electrode by E_{diff} . Then the shift in potential due to the diffusion processes is given by equation (5) to be

$$E = \frac{RT}{F} \ln \left[\frac{1 + \frac{s}{a_{\text{Na}^+}}}{1 + \frac{m}{a_{\text{Na}}}} \right] + E_{\text{diff}} \quad (8)$$

In general, s , m , and E_{diff} depend on the bulk concentrations, temperature, and rate of growth of the drop at a dropping electrode. However, they have been shown to be relatively independent of all these factors⁽⁵¹⁾.

Using a potassium amalgam containing 0.133 mole percent potassium in oxygen-containing solutions, Brauer and Strehlow⁽⁵¹⁾ found that the measured potential was 10 mv too negative in 0.05 M KCl solutions, and 70 mv too negative in 0.005 M KCl solutions when compared to the values extrapolated from high concentrations. However, by using the form of equation (8) with $E_{\text{diff}} = 0$, and $m = 0$, namely:

$$E = 0.05915 \log \left(1 + \frac{7.8 \times 10^{-3}}{C_{\text{K}^+}} \right) \quad (9)$$

the potentials over the entire range of concentration from 0.0005M to 0.2M were fitted, within an error of approximately 2 mv, by a Nernst relation with an activity coefficient for potassium ion which was consistent with the Debye-Hückel theory.

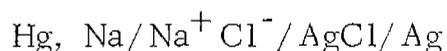
The systematic errors resulting from the diffusion-limited dissolution of the amalgam in Brauer and Strehlow's experiment are very large compared to those in our experimental situation, and the inherent errors in their potential measurements were much larger than we have observed. Even so, it is important to note that with a simple function such as Eq. (9) above, it is possible to correct effectively for the diffusion process.

Since this concentration polarization effect is caused by the corrosion of the amalgam, it can be decreased by the same measures described in the previous section—alkaline solutions, high electrolyte concentration, low amalgam concentration, and purity of solutions. Note, however, that too low an amalgam concentration results in concentration polarization in the amalgam phase. This effect also tends to make the observed electrode potential more positive than the true reversible potential corresponding to the bulk activities. However, unlike the kinetic shift, the concentration shift becomes most important

in dilute solutions, and usually is responsible for the lower concentration limit at which accurate measurements can be obtained.

D. Precision of Measurements with Sodium Amalgam Electrodes

The most careful work previously done with sodium amalgam electrodes was a study by Smith and Taylor⁽⁵⁵⁾, in which they determined the standard electrode potential of sodium. By making measurements in a completely air-free system, they were able to obtain for the potential of the cell



values which were reproducible to within ± 0.02 mv. Their results imply that the large random deviations observed by earlier workers, as much as ± 0.4 mv, may have been caused by a failure to exclude oxygen from the system rigorously.

In our experiments⁽³⁰⁾ we have observed deviations smaller than 0.02 mv under the most favorable conditions. For example, in one experiment we used 1.000m NaCl in one cell and 1.000m NaCl + 1.000m Na₂SO₄ in the other cell. Both solutions were 0.01m in NaOH, and the amalgam contained 0.365 weight % Na. The values obtained for the potential difference between cells, on successive changes of solution, were

$$22.25 \pm 0.05 \text{ mv}$$

$$21.85 \pm 0.05 \text{ mv}$$

$$21.65 \pm 0.01 \text{ mv.}$$

This last value was constant for over an hour without appreciable drift and is considered to be the most reliable value.

Precision of this order of magnitude is comparable to that of the most accurate potentiometric studies which have been carried out in any system^(40, 41, 47), but as we shall see in section VI, experiments are not always this reproducible, nor indeed, this accurate.

E. Systems with Two Different Cations*

Systems which contain a single common cation (such as NaCl-Na₂SO₄ or NaCl-NaOH) require only that the amalgam electrode be reversible to the cation. In systems containing more than one cation, however, a further requirement is that the electrode be reversible to one cation only. This limits the number of systems that can be measured with, say, a sodium amalgam electrode to mixtures with cations whose reduction potentials are considerably more negative than that of Na⁺.

Although the standard potential of pure sodium is over 200 mv more positive than that of potassium and nearly 300 mv more positive than that of lithium⁽⁵⁶⁾, these values cannot be used to predict quantitatively the behavior of amalgams of these metals. The solid phases in equilibrium with dilute alkali metal amalgams are not the alkali metals themselves, but compounds of the alkali metals with mercury: NaHg₄, KHg₁₁, and LiHg₃. The activity of alkali metal in these solid phases may be as much as a factor of 10¹⁴ less than that of the pure metals. The standard potentials of the amalgams, therefore, must be independently measured, and calculations of relative activities of metals in the amalgams at different potentials must be based on these values rather than the standard potentials of the pure metals^(57, 58).

For the dilute amalgams the standard state of activity is that of unit mole fraction in the ideal solution. To obtain activity the experimental values for the emf of amalgam concentration cells are extrapolated to infinite dilution, where, for example, the activity coefficient may be defined to be

$$\gamma_{\text{Na}} = a_{\text{Na}}/X_{\text{Na}} \rightarrow 1. \quad (10)$$

* This section was published as part of the paper "Activity Coefficient Measurements in Aqueous NaCl-LiCl and NaCl-KCl Electrolytes Using Sodium Amalgam Electrodes," by James N. Butler, Rima Huston, and Philomena T. Hsu, *J. Phys. Chem.* 71, 3294-3300 (1967).

At finite concentrations of alkali metal in the amalgam electrode E is then given by equation (5)

$$E = E_{\text{Na(Hg)}}^{\circ} - \frac{RT}{F} \ln \frac{m_{\text{Na}^+} \gamma_{\pm}}{X_{\text{Na}} \gamma_{\text{Na}}} \quad (5)$$

The standard potentials of the amalgams of Na, K, and Li are given in Table III. Note that the standard potentials of Na and K amalgams differ by only 13 mv, whereas the standard potentials of Na and Li amalgams differ by 238 mv. The activity coefficients of the various amalgams are shown in Figs. 3, 4, and 5. These were taken from the calculations of Davies, et al. ⁽⁵⁷⁾, based on the experimental results of Dietrick, et al. ⁽⁵⁹⁾, Bent and Swift ⁽⁶⁰⁾, and Richards and Conant ⁽⁶¹⁾ for sodium amalgams; Armbruster and Crenshaw ⁽⁶²⁾ for potassium amalgams; and Cogley and Butler ⁽⁶³⁾ for lithium amalgams.

TABLE III

Standard Potentials of Amalgams at 25°C
(Reference State: infinite dilution, mole fraction scale)

<u>Metal</u>	<u>Amalgam Standard Potential volts</u>	<u>Reference</u>
Na	-1.9575 ± .0005	(58)
	-1.958 ± .001	(59)
	-1.9574 ± .001	(60)
K	-1.971	(58, 62)
Li	-2.196	This work (section III-F)

The equilibrium potential of an amalgam having the approximate concentration used in our studies can be calculated from these data. For example, a sodium amalgam containing 0.1 mole % Na has an activity coefficient of 1.05 (Fig. 3). If this is in equilibrium with 1.000m NaCl, where $\gamma_{\pm} = 0.657$, then equation (5) gives a potential

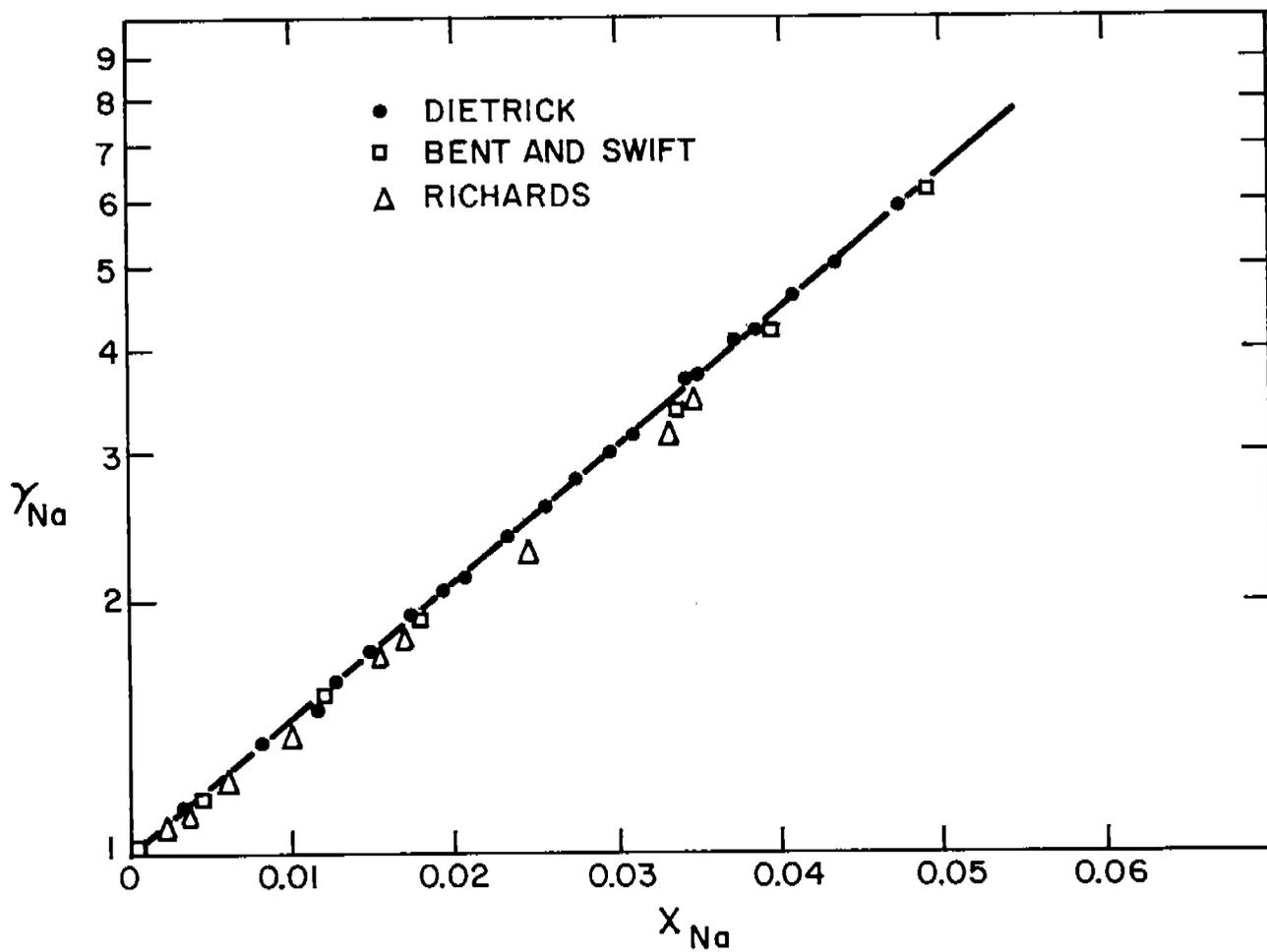


Fig. 3 Activity coefficients of sodium in sodium amalgams at 25.0° C.

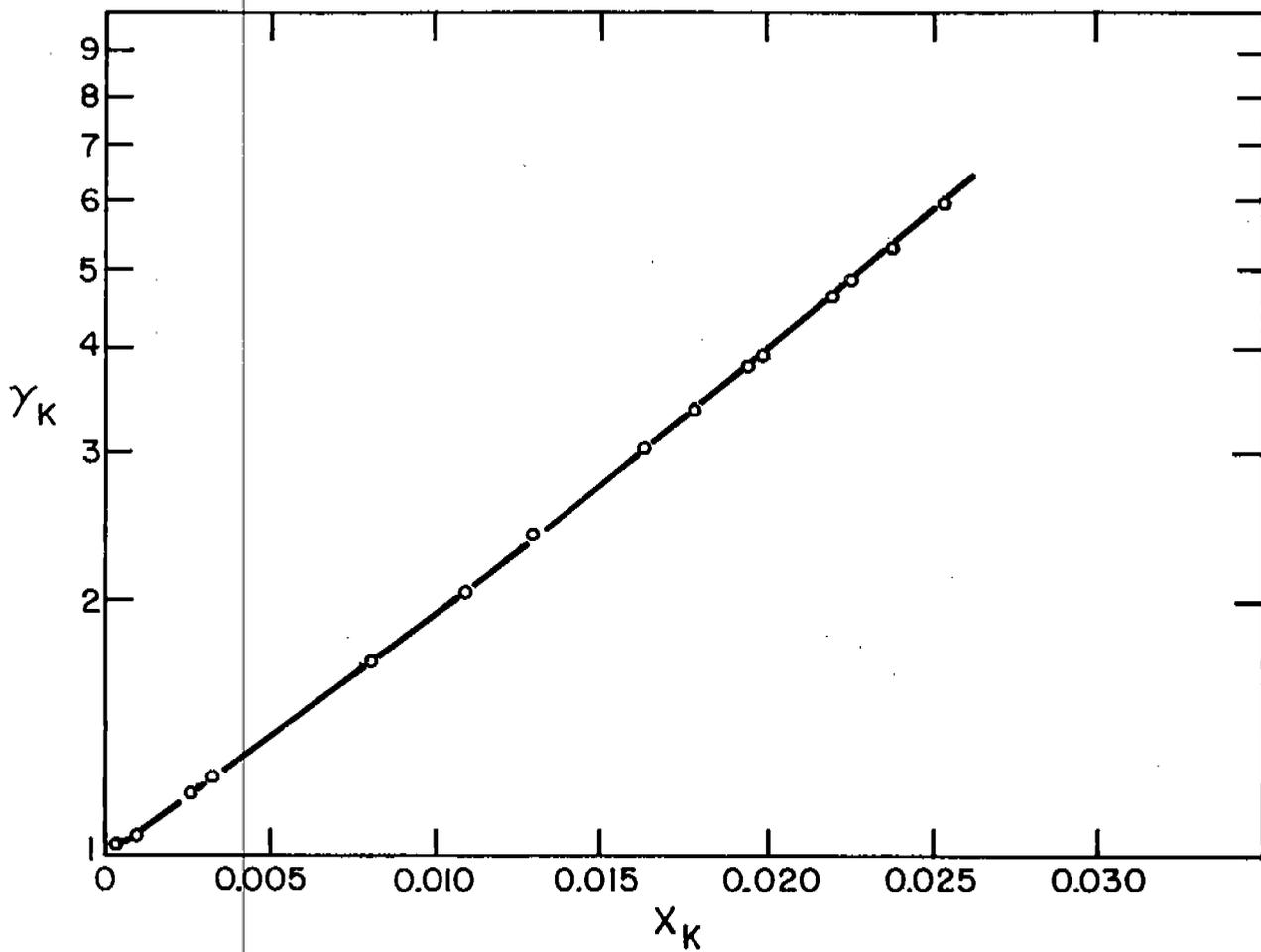


Fig. 4 Activity coefficient of potassium in potassium amalgam at 25.0°C.

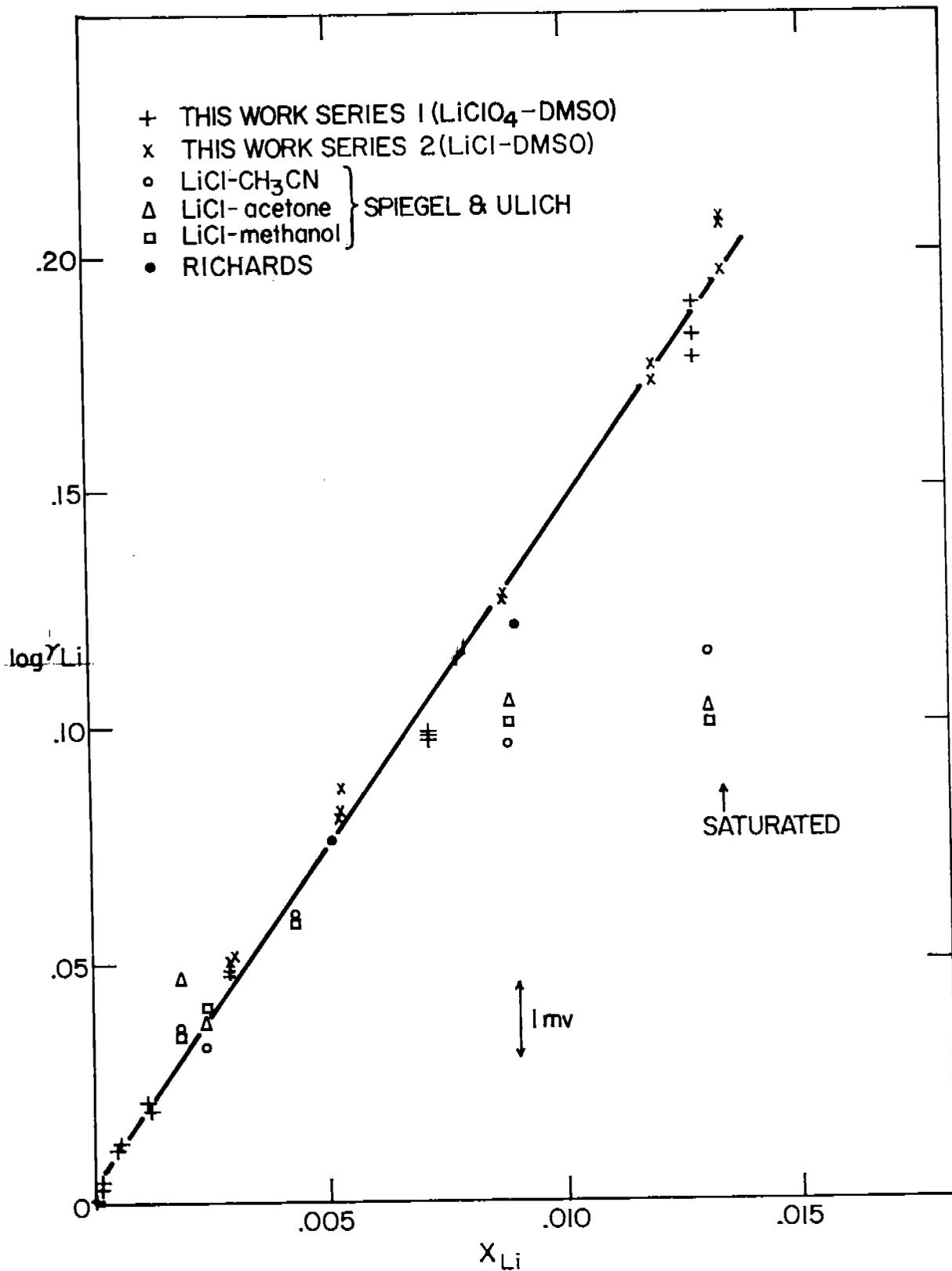
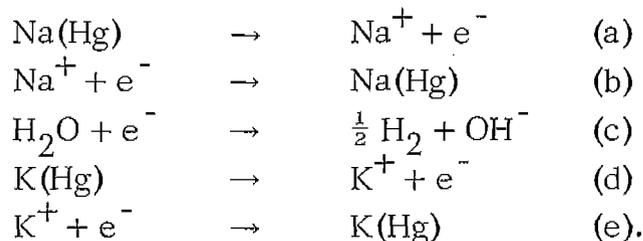


Fig. 5 Activity coefficients of lithium in lithium amalgam at 25.0°C from EMF measurements in various solvents.

of -1.793 volts. A potassium amalgam of the same concentration in an electrolyte containing 1m KCl would have a potential of -1.808 volts, only 15 mv more negative.

The interaction of the electrode processes at amalgam electrodes in solutions containing more than one cation, such as the KCl-NaCl or LiCl-NaCl solutions we have studied, may have a profound influence on the potentials measured at these electrodes. This interaction depends not only on the equilibrium potentials of the amalgams, but also on the rates of the various electrode processes. The situation is further complicated by the fact that a dropping amalgam electrode is continually growing in area, dropping off, and being renewed. The transient behavior of the dropping electrode may also modify the effect of the reaction kinetics on the electrode potential.

If a sodium amalgam electrode is in contact with an electrolyte containing sodium and potassium ions, the amalgam will quickly acquire some small but finite concentration of potassium, so that the electrode reactions occurring may be summarized as follows:



As we discussed in section III-B, the total current (anodic = positive) flowing at a given potential is given by

$$i = i_a - i_b - i_c + i_d - i_e \quad (11)$$

where currents are given by Tafel equations of the type

$$\begin{aligned}
 i_a &= i_o^{(\text{Na})} \exp \left[\frac{F}{RT} (1 - \alpha^{(\text{Na})}) (E - E_e^{(\text{Na})}) \right] \\
 i_b &= i_o^{(\text{Na})} \exp \left[- \frac{F}{RT} \alpha^{(\text{Na})} (E - E_e^{(\text{Na})}) \right]
 \end{aligned}$$

$$\begin{aligned}
 i_c &= i_o^{(H)} \exp \left[- \frac{F}{RT} \alpha^{(H)} (E - E_e^{(H)}) \right] \\
 i_d &= i_o^{(K)} \exp \left[- \frac{F}{RT} (1 - \alpha^{(K)}) (E - E_e^{(K)}) \right] \\
 i_e &= i_o^{(K)} \exp \left[- \frac{F}{RT} \alpha^{(K)} (E - E_e^{(K)}) \right]
 \end{aligned}
 \tag{12}$$

E_e is the equilibrium potential (see Table III), i_o is the exchange current, and α is the cathodic transfer coefficient for the reaction indicated by the superscript (see Table II). If reactions (d) and (e) are ignored, equations (12) become the same as those used in Section III-B. As we have already seen, the shift of potential due to hydrogen evolution at pH = 12 is negligible, less than 0.005 mv, so let us ignore reaction (c) for the moment.

Potassium ions, on the other hand, produce an effect which cannot be made negligible. Consider what happens when a 0.1 mole % sodium amalgam is introduced into a solution containing 0.5 m NaCl and 0.5 m KCl. Initially, the concentration of potassium in the amalgam is very small and the equilibrium potential for potassium, according to eq. 5, is very positive. From eq. 12 we see that the predominant reactions initially will be eq. a, b, and e, but even in this initial stage the potential measured at the amalgam electrode is not the equilibrium potential of the Na-Na⁺ couple. The zero current potential is more positive than the true equilibrium potential of sodium in that solution, because reaction a must compensate for the additional cathodic current of reaction e. This is shown in Fig. 6. The partial currents at a sodium amalgam electrode containing a small amount of potassium, in a solution containing both Na⁺ and K⁺, were calculated using eq. 1, 5, 6, 11, and 12 and the data in Tables II and III. Note that the zero current potential is shifted by 4.2 mv in the presence of potassium.

The concentration of potassium in the amalgam grows with time and the potential $E_e^{(K)}$ becomes more negative. Since the anodic

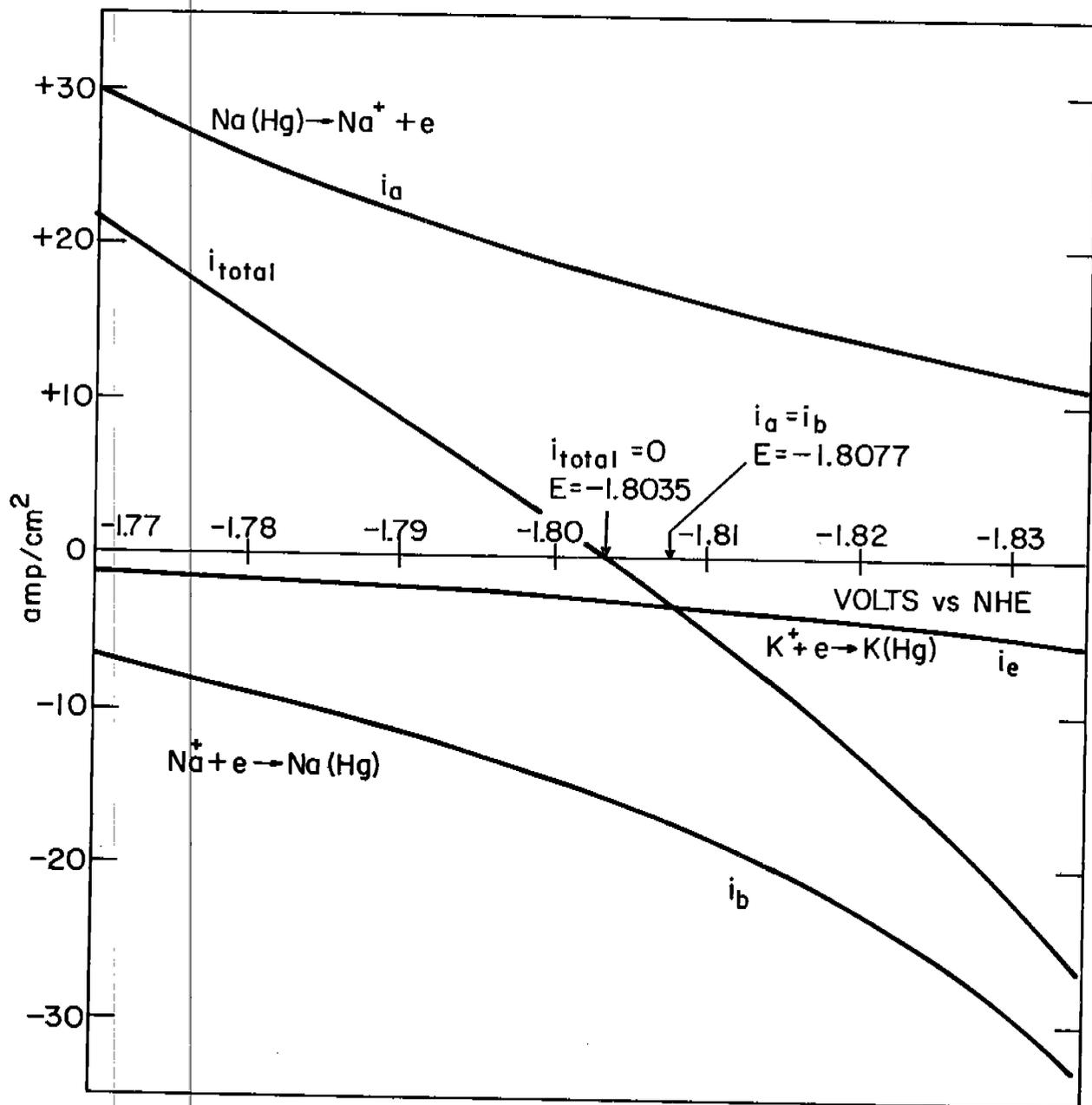
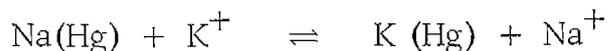


Fig. 6 Initial partial currents at a sodium amalgam electrode (0.1 mole %) in contact with an electrolyte containing 0.5 m Na⁺ and 0.5 m K⁺, pH 12. The partial currents for hydrogen evolution and potassium dissolution are less than 10⁻³ amp/cm². Note that the zero current potential (-1.8035 v) is 4.2 mv more positive than the equilibrium potential (-1.8077 v) expected for the Na(Hg)/Na⁺ couple if there were no influence from potassium ion.

reaction of sodium dissolution (eq. a) is required (at zero net current) to balance not only the sodium deposition (eq. b) but also the potassium deposition (eq. e), the sodium content of the amalgam is depleted and the potential $E_e^{(Na)}$ becomes more positive. Eventually, an equilibrium potential is reached which is defined by eq. 11, with $i = 0$, and with the various partial currents given by eq. 12. This potential is neither the equilibrium potential for sodium nor the equilibrium potential for potassium. In the limit where $i_o^{(K)}$ is very small compared to $i_o^{(Na)}$, or $E_e^{(K)}$ is much more negative than $E_e^{(Na)}$, the equilibrium value reached will be essentially $E_e^{(Na)}$; but in the case we are considering, such an assumption is not valid.

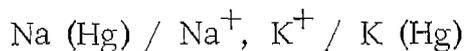
A simplified solution to this rather complex problem can be obtained by considering an infinite reservoir of electrolyte and a limited amount of sodium amalgam and permitting the reaction



to go to equilibrium. Because the electrolyte supply is infinite, the concentrations of the ions will not change, but because the amount of the amalgam is finite, its concentrations are subject to the restriction

$$X_K + X_{Na} = X_{Na}^o \quad (13)$$

where X_{Na}^o is the initial mole fraction of sodium in the amalgam and X_K and X_{Na} are the concentrations at equilibrium. The concentration ratio in the amalgam can be estimated from the standard potentials of the amalgams. Applying the Nernst equation to the cell



with $E = 0$, using known activity coefficients for the electrolytes⁽⁴¹⁾ and amalgams⁽⁵⁸⁾, and combining with eq. 13 we obtain $X_{Na}^o / X_{Na} = 1.565$. By eq. 5 this corresponds to a shift of the sodium amalgam electrode potential to a value 11.5 mv more positive than if K^+ had not been present. Figure 7 shows the partial currents at equilibrium, calculated using equations 5, 6, 11, and 12.

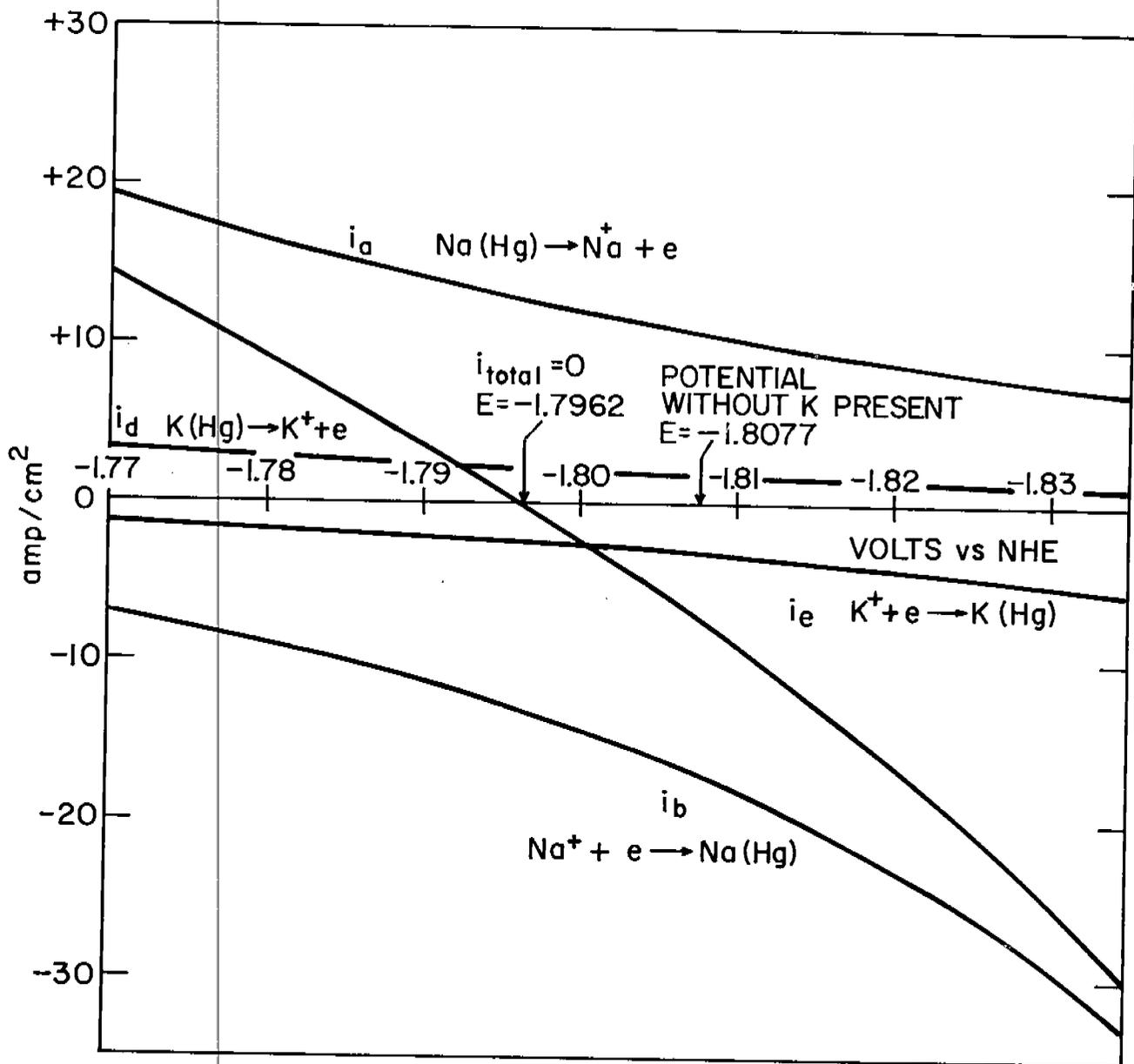
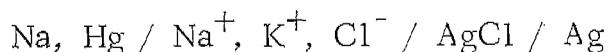


Fig. 7 Equilibrium partial currents at a sodium amalgam electrode (0.1 mole %) in contact with a large excess of electrolyte containing 0.5 m Na⁺ and 0.5 m K⁺, pH 12. The partial current for hydrogen evolution is less than 10⁻³ amp/cm². The equilibrium composition of the amalgam is 0.064 mole % Na and 0.036 mole % K. The zero current potential (-1.7962 v) is 11.5 mv more positive than the equilibrium potential (-1.8077 v) expected for the Na(Hg)/Na⁺ couple if there were no influence from potassium ion.

Our experiments (conducted as described below in section V) using the cell



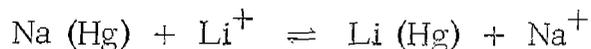
have confirmed the conclusion reached theoretically: activity coefficient measurements cannot be made with sufficient accuracy in NaCl-KCl electrolytes using sodium amalgam electrodes. The general scheme proposed in our theoretical discussion has also been confirmed, although extensive experiments were not made. The results of three experiments made with NaCl-KCl electrolytes are summarized in Table IV. Our experimental potential values are listed in the third column. The potential calculated on the assumption that the sodium amalgam electrode reached equilibrium with the NaCl-KCl electrolyte is listed in the fourth column and the potential calculated from the isopiestic data^(13, 14, 17) on the assumption that the sodium amalgam electrode was reversible to Na^+ , with no effect of K^+ , is listed in the fifth column.

The observed potential fluctuated irregularly as the amalgam drops fell from the capillaries and not smoothly as in solutions containing only Na^+ . Note that the experimental values agree to within a few millivolts with those calculated assuming that the amalgam electrode reached equilibrium with the solution. However, the uncertainty in this correction is in most cases larger than the activity coefficient variation described by Harned's rule and it is clear that accurate measurements on the activity coefficients of sodium salts in the presence of potassium salts (or vice versa) cannot be made by the amalgam electrode method.

Of course, the real situation is much more complicated, as we have indicated, but this shift we have calculated probably represents a reasonable upper limit. If the ratio of Na^+ to K^+ in the electrolyte is larger or if the measurements are made before the full equilibrium is established, then the potential shift may be smaller; if the ratio of Na^+ to K^+ is smaller, the potential shift may be even larger. In the limit where $X_{\text{Na}^+} \rightarrow 0$, the potential at equilibrium is that of the potassium amalgam electrode, which corresponds to a

negative shift in potential.

A totally analogous argument may be made for solutions containing Na^+ and Li^+ , but the conclusion is more favorable. From Table III, we can see that the standard potential of Li amalgam is 230mv more negative than that of Na amalgam and from Table II that the exchange current is smaller than that for sodium. Using eq. 5 and 13 with K replaced by Li, we find that for Li^+/Na^+ ratios less than 30, the error due to the reaction



is less than 0.1 mv. Thus we predict that no appreciable systematic errors may be observed in Li^+/Na^+ mixtures (using sodium amalgam electrodes) if more than 3% of the cations present are Na^+ . Because of the lower exchange current of the lithium reaction (Table II), we expect that the effect will be even smaller than predicted. This is borne out by our experimental measurements, which are presented in section VI-A.

TABLE IV

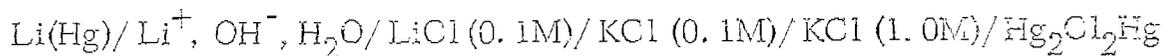
Measurements in NaCl-KCl Electrolytes

m_{NaCl}	m_{KCl}	Measured	Potential cal'd from isopiestic data, *	
			Including amalgam effect	Neglecting amalgam effect
0.50	0.50	9.2 ± 0.3	7.3	18.79
0.200	0.200	26.6 ± 0.2 28.0 ± 0.5	25.6	14.13

* Reference cell for the first set contained 1.00 m NaCl; reference cell for the second set contained 0.200 m NaCl. Solutions contained 5×10^{-4} m NaOH. Isopiestic data from Refs. 13, 14, and 17.

F. The Standard Potential of the Lithium Amalgam Electrode*

The only experimental measurement of the standard potential of the lithium electrode in aqueous solutions is that by Lewis and Keyes⁽⁶⁴⁾ in 1913. They measured the EMF of the two cells



The liquid junction potentials were eliminated by corrections made using the Lewis and Sargent⁽⁶⁵⁾ formula based on conductivity. With these corrections, the standard potential of the lithium electrode was reported as -3. 3044 volts vs. the Normal Calomel Electrode. This corresponds to -3. 0243 volts vs. a Normal Hydrogen Electrode. However, the correction for liquid junction potentials was 25. 9 mv and could be in error by several millivolts. In a later publication, Lewis and Argo⁽⁶⁶⁾ reported the standard potential of lithium as -3. 027 volts. Still later, Lewis and Randall⁽⁶⁷⁾ and Latimer⁽⁶⁸⁾, incorrectly quoted Lewis' s experimental value for the standard potential of lithium as -2. 957 volts.

Latimer' s (and the U. S. Bureau of Standards) preferred value for the standard potential of lithium is based on his own entropy calculations⁽⁶⁹⁾ and is -3. 045 volts. Since the measurement of the standard potential of lithium amalgam was never repeated, we felt it desirable to make this measurement in a cell without liquid junction, and thereby eliminate the uncertainty in the liquid junction potential corrections of Lewis' s early work. Furthermore, the recent measurements in this laboratory⁽⁶³⁾ of the cell



* Submitted for publication as "The Standard Potential of the Lithium Electrode in Aqueous Solutions," by Rima Huston and James N. Butler. Accepted by the Journal of Physical Chemistry.

gave an accurate standard potential difference between the lithium amalgam and solid lithium electrodes, of 0.8438 volts, which differs slightly from the Lewis and Keyes measurements (0.8412 volts).

LiOH solutions were prepared, in a glove box under nitrogen atmosphere, from a sample of the monohydrate containing less than 5 ppm Na, K or heavy metals (Foote Mineral Co.) and triply distilled conductivity water. The solutions were analyzed volumetrically with standard HCl using phenolphthalein indicator, and deoxygenated by passing hydrogen over a large platinum black electrode for 2 hours. Solutions thus prepurified were also saturated with hydrogen.

Lithium amalgam was prepared from 99.9% pure lithium ribbon (K & K Laboratories) and triply distilled mercury (Doe and Ingalls) in a dry box under argon atmosphere. The liquid mixture thus prepared was saturated at 25° and was analyzed to be 1.335 mole % Li. Various concentrations of lithium amalgam were obtained by diluting the saturated amalgam and checked by analyzing it after each experiment. The amalgam electrodes were constructed as described in section V-B.

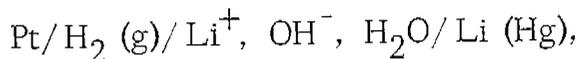
The hydrogen electrode was prepared by attaching to a piece of 99.9% Pt wire a 1 cm² Pt screen platinized by cathodizing in a chloroplatinic acid solution. The electrode was kept in triple-distilled water prior to measurement. Hydrogen used for the electrode as well as for purification and saturation of solutions was obtained from an ultra-pure hydrogen generator (Matheson Co.) by electrolysis of water in a cell with silver-palladium cathode and contained less than 0.1 ppm oxygen. All measurements were conducted in a thermostat at 25.00 ± 0.02°.

The experimental measurements are given in Table V. The limits on E indicate the approximate variation of values obtained, but do not include any estimates of systematic errors.

The standard potential of the lithium amalgam electrode $E_{\text{Li(Hg)}}^{\circ}$ (vs. the Normal Hydrogen Electrode) was calculated by the following equation

$$E_{\text{Li(Hg)}}^{\circ} = E + 0.05915 \log \frac{X_{\text{Li}} \gamma_{\text{Li}} a_{\text{H}_2\text{O}} K_{\text{W}}}{m^2 (P_{\text{H}_2})^{\frac{1}{2}} \gamma_{\pm}^2}$$

where E is the experimentally measured potential (IUPAC convention) of the cell



$K_{\text{W}} = 1.00 \times 10^{-14}$ is the ion product of water, X_{Li} is the mole fraction of lithium in the amalgam and m is the molal concentration of LiOH in the solution. The activity of water was calculated from the osmotic coefficient of LiOH (ϕ_{LiOH}) using the equation⁽⁴¹⁾

TABLE V

Measurements of the Standard Potential of Lithium Amalgams

LiOH Solution (a)		Lithium Amalgam (b)		E	E ^o
<u>m</u>	<u>γ_{\pm}</u>	<u>X_{Li}</u>	<u>γ_{Li}</u>	<u>(v)</u>	<u>Li(Hg)</u>
0.026	0.866	3.25×10^{-3}	1.122	$-1.406 \pm .002$	-2.183
0.026	0.866	1.08×10^{-3}	1.043	$-1.397 \pm .010$	-2.209
0.518	0.589	13.35×10^{-3}	1.574	$-1.317 \pm .001$	-2.183
1.293	0.537	4.46×10^{-3}	1.175	$-1.254 \pm .002$	-2.196
2.669	0.501	3.25×10^{-3}	1.122	$-1.212 \pm .002$	-2.197

(a) Values taken from Robinson and Stokes⁽⁴¹⁾ or calculated (below 0.1 m) from Debye-Hückel theory with $a = 6$ Angstroms.

(b) From Reference 63.

$$\ln a_{\text{H}_2\text{O}} = 0.018 m \phi_{\text{LiOH}}$$

The barometric pressure was corrected for the vapor pressure of the solution to obtain the hydrogen pressure P_{H_2} . Activity coefficients of LiOH were taken from Robinson and Stokes⁽⁴¹⁾ except where the concentration was lower than 0.1 m in which case the Debye-Hückel equation was used with $a = 6$.

The most reliable measurements in Table V are expected to be those with a LiOH concentration which is not too small, and a concentration of amalgam which is not too large. Under these circumstances corrosion of the amalgam would have the least effect on the measured potential. For these reasons we have weighted the entries in Table V by the factor m/X_{Li} and calculated the weighted mean to obtain an estimate for the best value of the standard potential of lithium amalgam

$$E_{\text{Li(Hg)}}^{\circ} = 2.1963 \pm 0.0016 \text{ volts}$$

(The error is the standard deviation.) This may be combined with our previously measured value⁽⁶³⁾

$$E_{\text{Li(Hg)}}^{\circ} - E_{\text{Li}}^{\circ} = 0.8438 \pm 0.0002 \text{ volts}$$

to give, as the best experimental value for the standard potential of lithium in aqueous solutions:

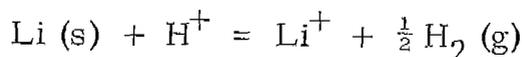
$$E_{\text{Li}}^{\circ} = -3.0401 \pm 0.0016 \text{ volts}$$

Note that this value is 5 mv more positive than Latimer's theoretical value, and 16 mv more negative than the Lewis and Keyes⁽⁶⁴⁾ value.

From this standard potential value, the standard free energy of the lithium ion is calculated to be

$$\Delta G^{\circ} = -70.11 \pm 0.04 \text{ kcal}$$

and using the enthalpy of lithium ion ($\Delta H^{\circ} = -66.554 \text{ kcal}$) obtained from the heat of dissolution of lithium in acid^(68,69) we obtain the entropy of the reaction



to be $\Delta S^{\circ} = +11.9 \pm 0.1 \text{ cal/mole deg}$. Finally, this leads to the standard entropy of the lithium ion (relative to H^{+} being zero) of

$$S^{\circ} = 3.0 \pm 0.1 \text{ cal/mole deg.}$$

This is probably more accurate than the currently accepted value⁽⁶⁸⁾ of 3.4, with an implied error of several tenths of an entropy unit.

IV. ALKALINE EARTH METAL AMALGAM ELECTRODES

A. General Considerations

Salts of magnesium and the alkaline earth metals are of great importance in desalination research and technology, but no previous studies of multicomponent systems containing these ions have been made by the amalgam electrode method.

Magnesium, calcium, strontium and barium all form liquid amalgams with mercury at room temperature, containing 0.5 to 2.5 atom % of the metal⁽⁷⁰⁾. Such concentrations are adequate to use these amalgams as electrodes, if the electrode reaction is reversible. Some early thermodynamic work was done with the calcium, strontium, and barium amalgam electrodes, but no reliable measurements have been made of the potential of a magnesium amalgam electrode.

Table VI summarizes some of the information available about the potentials of the alkaline earth metal amalgam electrode. Proceeding from magnesium to barium, the reduction potential of the pure elements become more negative, but the reduction potential of the amalgams becomes more positive because of the formation of stronger compounds with mercury. Detailed kinetic studies have not been made, but the polarographic reversibility, together with our own measurements (see Section VI) indicate that the barium amalgam is the most reversible electrode (highest exchange current) and magnesium amalgam is the least reversible.

Although measurements of activity coefficients using barium and strontium amalgams agree closely with those obtained by other methods, measurements using calcium amalgams are in some doubt. The activity coefficients of BaCl_2 measured by the isopiestic method⁽⁷⁵⁾ agree to within $\pm 0.5\%$ with two independent measurements by the emf method^(73,76,77), over the concentration range from 0.1 to 1.5m. Similarly, isopiestic measurements of the activity coefficients of SrCl_2 ⁽⁷⁵⁾ agree with the emf method^(76,77) to within $\pm 0.5\%$ over the concentration range from 0.1 to 2.0m.

TABLE VI

Reduction Potentials of Divalent Cations at 25°C
(volts vs. normal H₂ electrode)

<u>Element</u>	Solubility in Hg at 25°C ⁽⁷⁰⁾ <u>Atom %</u>	Standard Potential for Pure Element ⁽⁵⁶⁾	Standard Potential for Amalgam	Polarographic ⁽⁷⁴⁾ <u>E_{1/2}</u>
Mg	2.5	-2.37	-2.1 (?)	-2.06 (irrev.)
Ca	1.5	-2.87	-1.996 ⁽⁷¹⁾	-1.98
Sr	2.5	-2.89	1.9 (?) ⁽⁷²⁾	-1.87
Ba	0.55	-2.90	1.727 ⁽⁷³⁾	-1.696

In contrast, the measurements of activity coefficients of CaCl₂ are quite discordant, as can be seen from Table VII. The activity coefficients listed in this table have been multiplied by an arbitrary factor to make them all equal at $m = 0.1$. Over the range from 0.1 to 1.0m, the isopiestic and freezing point methods give the same values to within 1%, which is acceptable. The emf measurements of three independent investigators give values which are nearly 50% higher and which disagree with each other by approximately 5%. At higher concentrations, the disagreement is even worse. Robinson⁽⁷⁵⁾ attributed this disagreement to the irreversibility of the calcium amalgam electrode, and data on the activity coefficients of calcium salts obtained by the emf method has generally been discredited^(40, 41). Activity coefficients of magnesium halides have been measured by the isopiestic method⁽⁸⁰⁾ but not the emf method.

TABLE VII

Activity Coefficients of CaCl_2 at 25°C Obtained
by Different Methods⁽⁷⁵⁾

<u>m</u>	<u>EMF (76)</u>	<u>EMF (78)</u>	<u>EMF (79)</u>	<u>Isopiestic (75)</u>	<u>Freezing Point (corr. to 25°C) (75)</u>
0.1	0.531	0.531	0.531	0.531	0.531
0.5	0.513	0.516	0.535	0.457	0.447
1.0	0.730	0.704	0.737	0.509	0.505
1.5	---	1.181	1.080	0.626	---
2.0	1.565	---	---	0.807	---

The possibility of using amalgam electrodes to determine activity coefficients in mixtures containing magnesium or calcium salts, depends primarily on the standard potentials of the calcium and magnesium amalgam electrodes. Some estimates of these values can be made from the data in Table VI.

The polarographic reduction of Mg^{++} occurs at the dropping mercury electrode at a half-wave potential of -2.06 volts vs. NHE, but the reduction appears to be irreversible⁽⁷⁴⁾. From this value, the standard potential of the amalgam can be estimated to be approximately -2.1 volts, which is considerably more negative than that of sodium (-1.958 v).

In spite of the apparent irreversibility of the calcium amalgam electrode (as indicated by the data in Table VII), measurements^(78, 81) have been made from which a standard potential can be calculated. These calculations are summarized in the next section; and similar calculations for the barium amalgam electrode follow.

By means of an analysis such as we carried out in section III-E, we can conclude that a sodium amalgam electrode will respond reversibly to 0.05m Na^+ in the presence of 1m divalent cation with an error of less than 0.1 mv , if the standard potential for the divalent metal amalgam is more negative than -2.025 volts . A similar argument may be made for the use of potassium amalgam in the presence of divalent cations, since the potassium and sodium amalgams have almost identical standard potentials.

From the estimated values in Table VI for the standard potential of calcium and magnesium amalgams, it appears to be possible to make measurements with sodium amalgam electrodes in the presence of calcium or magnesium salts, provided the ratio of calcium or magnesium to sodium is not larger than about 10 to 20. One mitigating factor operates, however, which improves the accuracy and extends the range of the measurements: The rate of the calcium and magnesium reactions is much slower than that of the sodium reaction, and thus less interference is obtained than from an ideally reversible reaction. An external check on measurements using amalgam electrodes in NaCl-MgCl_2 or NaCl-CaCl_2 mixtures can be obtained from glass electrode data^(21, 27, 31), or from isopiestic^(24, 30) measurements. Our measurements using sodium amalgam electrodes in NaCl-CaCl_2 and NaCl-MgCl_2 mixtures are given in Section VI.

B. The Standard Potential of the Calcium Amalgam Electrode*

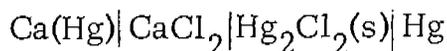
Although a number of determinations of the potentials of calcium amalgam electrodes in aqueous solutions have been made^(74, 78, 81, 82, 83), no critical evaluation of this data presently exists, and in general it is ignored in compilations of thermodynamic data on the potential of the calcium electrode in aqueous solution^(68, 84, 85), or discredited as being

* Published as "The Standard Potential of the Calcium Amalgam Electrode," by James N. Butler, in *J. Electroanal. Chem.* 17, 309-317, (1968).

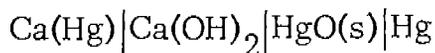
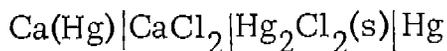
unreliable^(40, 56, 75). However, recent experiments on the kinetics of the calcium amalgam electrode in aqueous calcium formate at high pH-values have shown that the electrode is apparently reversible⁽⁸⁶⁾, in contrast to previous statements that it is irreversible⁽⁷⁵⁾.

Previous workers did not apply consistent corrections for activity coefficients to their data, did not in general extrapolate to infinite dilution, and did not in general apply any corrections for temperature, liquid junction potentials, or ion-pairing, where these were applicable. Thus in order to compare these data we recalculated them completely, beginning with the actual experimental measurements, and applying the most recent data on activity coefficients, liquid junction potentials, reference electrode potentials, and ion-pairing equilibria. The results are summarized below. We have divided this discussion into measurements involving cells without liquid junction, cells with liquid junction, and non-aqueous cells.

Cells Without Liquid Junction. The simplest measurement of the standard potential is made in a cell without liquid junction. Two sets of measurements have been made: Tamele⁽⁸²⁾ used the cell:



and Shibata⁽⁸³⁾ used the cells:

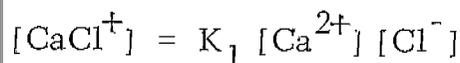


Taking the CaCl_2 cell as an example, we shall describe the method used for calculation. The potential of the cell is given by

$$E = E_{\text{ref}}^0 - E_{\text{Ca(Hg)}}^0 - \frac{RT}{2F} \ln \left\{ \frac{[\text{Ca}^{2+}] [\text{Cl}^-]^2 \gamma_{\pm}^3}{X_{\text{Ca}} \gamma_{\text{Ca}}} \right\}$$

The potential E is positive according to the IUPAC convention. The experimental measurements consist of the total concentration of $\text{CaCl}_2(M)$, the reference electrode standard potential, E_{ref}^0 , the mole fraction of calcium in the amalgam (X_{Ca}), the temperature T , and the measured potential E . To calculate a value of the amalgam standard potential, one must make assumptions about the activity coefficients of the ions and about the possibility of ion-pairing, and about the activity coefficient of calcium in the amalgam.

In the case of solutions containing only CaCl_2 in water, ion-pairing is probably quite small⁽⁴⁰⁾ and we assumed that the ion-pair equilibrium constant, K_1 , was 0.1 for all our calculations concerning CaCl_2 :



The activity coefficient of the ions was assumed to be given by the Davies equation:

$$\log \gamma_{\pm} = -\frac{A Z_+ Z_- \sqrt{I}}{1 + \sqrt{I}} + 0.1 Z_+ Z_- I$$

where

$$I = 2 [\text{Ca}^{2+}] + \frac{1}{2} [\text{CaCl}^+] + \frac{1}{2} [\text{Cl}^-]$$

is the ionic strength. This equation represents the experimental activity coefficients satisfactorily in dilute solutions, and provides a rational basis for calculating single-ion activity coefficients in the cells involving liquid junctions.

The activity coefficient of calcium in the amalgam was provisionally assumed to be unity, since there were no data or theory available which would predict this quantity. Since the amalgams are dilute, it was expected (by analogy with alkali-metal amalgams) that the activity coefficient of calcium would be within a few percent of unity. If the standard potential

was found to vary with amalgam concentration, it could be extrapolated to zero concentration.

The standard potential of the calomel electrode was taken to be⁽⁸⁷⁾

$$E_{\text{ref}}^0 = + 0.27082 - 0.000254 (T - 15.0)$$

The amalgam standard potentials calculated from Tamele's data, are plotted in Fig. 8.

Similar calculations were made for Shibata's measurements on the Ca(OH)_2 cell. For this calculation, the ion-pairing constant was taken to be⁽⁸⁸⁾ $K_1 = 10^{+1.20}$, and the standard potential of the HgO/Hg electrode was taken to be⁽⁸⁹⁾

$$E_{\text{ref}}^0 = + 0.0977 - 0.000288 (T - 25.0)$$

The standard potentials are also plotted in Fig. 8.

With the exception of two points, all the data fit a single straight line (Fig. 8) giving E^0 as a function of M . There does not appear to be any systematic trend with temperature or with amalgam concentration, within the ranges covered, and there appear to be negligible differences between CaCl_2 and Ca(OH)_2 as electrolyte. This latter observation is quite important, since the pH of the CaCl_2 solution was probably about 6 or 7, and the pH of the Ca(OH)_2 solution was about 12. If there had been interference from the hydrogen evolution reaction, we would have expected the CaCl_2 measurements to give E^0 -values which were systematically more positive than the Ca(OH)_2 measurements, both because of amalgam corrosion (which increases Ca^{2+} concentration near the electrode) and because of kinetic interference. Although the CaCl_2 measurements of Tamele are two or three millivolts more positive than those of Shibata, this difference is within experimental error. The fact that Tamele's CaCl_2 value at 0.005 M agrees with Shibata's Ca(OH)_2

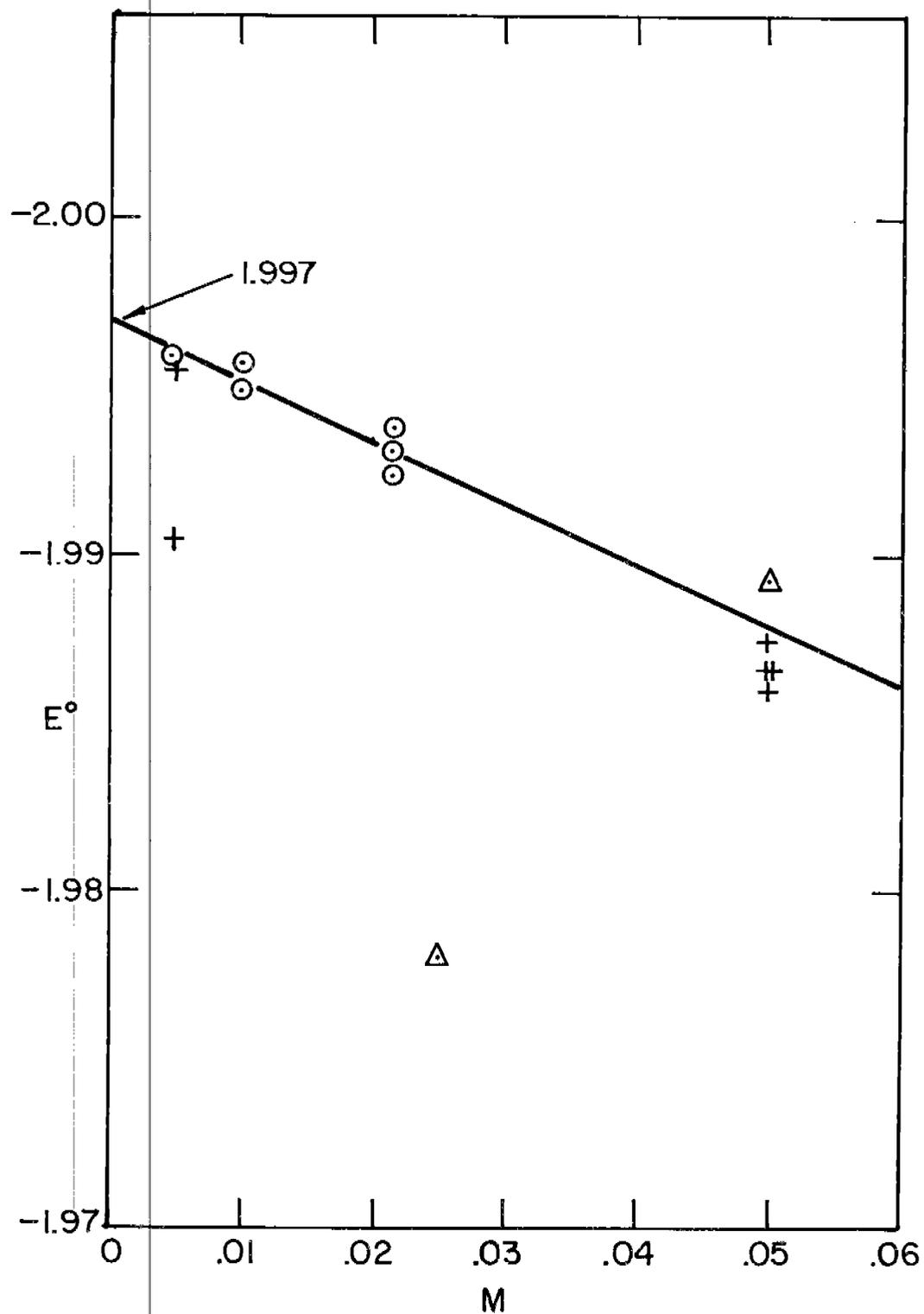
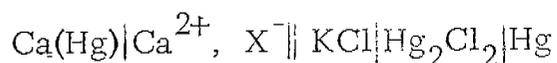


Fig. 8 Standard potential of Ca(Hg) electrode. (\circ), Shibata (Ca(OH)_2); (Δ), Shibata (CaCl_2); (+), Tamele (CaCl_2).

value at the same concentration is perhaps the strongest evidence that the electrode potentials measured are indeed thermodynamic values.

The trend of calculated E^0 with concentration simply reflects the use of the Davies equation as an extrapolation function; and extrapolation of the E^0 -values to zero concentration gives a thermodynamic potential of -1.997 ± 0.001 V.

Cells With Liquid Junction. Almost one hundred measurements were made by Drucker and Luft⁽⁸¹⁾ and by Fosbinder⁽⁷⁸⁾, using the cell:



In this cell, the nature of the anion has relatively little influence. Fosbinder used CaSO_4 , Ca(OH)_2 , CaCl_2 calcium lactate, and calcium acetate. Drucker and Luft used only CaCl_2 . Their cell was slightly different, in that they used a normal calomel electrode connected to the CaCl_2 solution by a 3M KCl salt bridge. Fosbinder used a saturated calomel electrode and a saturated KCl salt bridge. In either case, the potential of the cell is given by

$$E = E_{\text{ref}}^0 - E_{\text{Ca(Hg)}}^0 - \frac{RT}{2F} \ln \frac{[\text{Ca}^{2+}] \gamma_{2+}}{X_{\text{Ca}} \gamma_{\text{Ca}}} + E_j$$

For our calculations, we assumed (as before) that γ_{Ca} , the activity coefficient of calcium in the amalgam was unity and that the activity coefficient of the calcium ion was given by the Davies equation:

$$\log \gamma_{2+} = - 4A \sqrt{I}/(I + \sqrt{I}) + 0.4 I$$

$$I = 2 [\text{Ca}^{2+}] + \frac{1}{2} [\text{CaX}^+] + \frac{1}{2} [\text{X}^-] \text{ for salts of the type } \text{CaX}_2$$

$$I = 2 [\text{Ca}^{2+}] + 2 [\text{SO}_4^{2-}] \quad \text{for } \text{CaSO}_4$$

The ion-pairing equilibrium constants used are given in Table VIII.

TABLE VIII

Ion-Pairing Equilibrium Constants

Ion Pair	$\log K_1$	Reference
$\text{Ca}^{2+} - \text{Cl}^-$	-1	40
$\text{Ca}^{2+} - \text{acetate}$	+0.77	90
$\text{Ca}^{2+} - \text{OH}^-$	+1.20	88
$\text{Ca}^{2+} - \text{lactate}$	+1.42	91
$\text{Ca}^{2+} - \text{SO}_4^{2-}$	+2.31	92

The combined potential of the reference electrode and liquid junction was taken to be the value given by Ives and Janz⁽⁴⁷⁾

$$E_{\text{ref}}^0 + E_j = +0.283 - 0.0003 (T - 25) \text{ for normal calomel}$$

$$= +0.2445 - 0.00066 (T - 25) \text{ for saturated calomel.}$$

In calculating the activity coefficients, it was usually necessary to make several iterations, since the presence of the ion-pairs had a substantial influence on the ionic strength.

Figure 9 summarizes all the E^0 -values for the calcium amalgam electrode which were calculated from Fosbinder's data. Though one set of the CaSO_4 data shows an upward trend with increasing concentration, and the CaCl_2 data show a downward trend, all the data can be combined to give a standard potential

$$E^0 = -1.992 \pm 0.001 \text{ V.}$$

This is 5 mv more positive than the value obtained from cells without liquid junction.

The data of Drucker and Luft⁽⁸¹⁾ were less precise. Though the temperature varied substantially, there appeared to be no obvious trend with temperature. The slight trend of E^0 with electrolyte concentration was accounted for by extrapolation to $M = 0$. These extrapolated values are plotted in Fig. 10, along with all the other data, as a function of amalgam concentration. If the first two series of Drucker and Luft's data are ignored (since they show wide scatter) all the data from the four separate investigators lies between -1.992 and -1.997 v. There does not seem to be any trend with amalgam concentration, though a range of nearly a factor of ten was covered. This substantiates the assumption that $\gamma_{\text{Ca}} = 1$.

Drucker and Luft's third series (which they consider to be the most accurate) gives an average potential

$$E^0 = -1.996 \pm 0.001 \text{ v}$$

which agrees with the results from cells without liquid junction to within 1 mv.

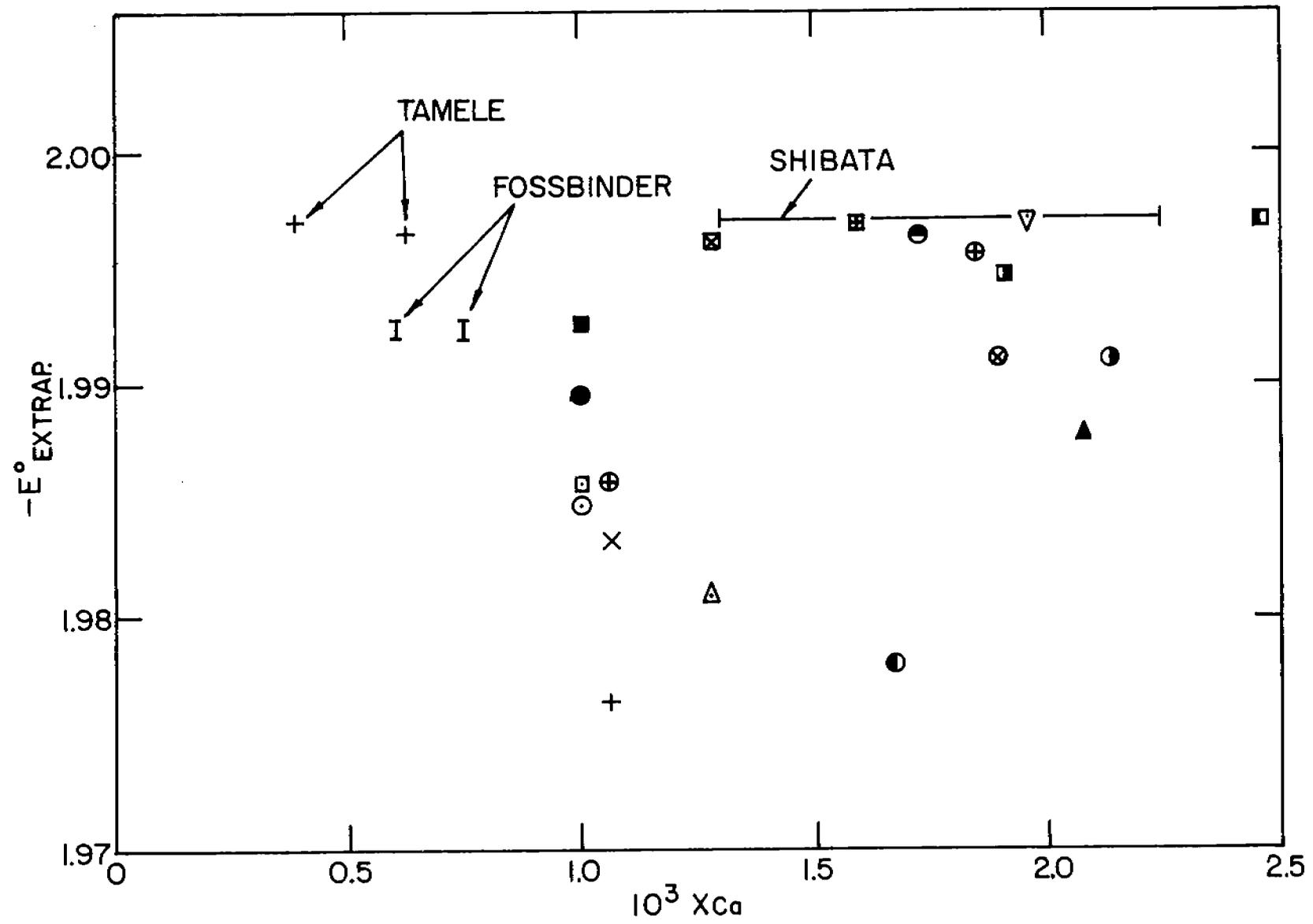


Fig. 10 Standard potential as a function of calcium amalgam concn. (all unmarked points: Drucker and Luft).

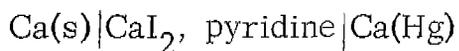
In conclusion, the most reliable value for the standard potential of calcium amalgam (reference state: infinite dilution, mole fraction units for amalgam concentration, moles/l for electrolyte concentration) is

$$E^0 = -1.996 \pm 0.002 \text{ v}$$

Non-Aqueous Cells. Although the thermodynamic potential of calcium amalgams apparently can be established in aqueous solutions with respect to standard reference electrodes, the potential of pure calcium is much too negative for any kind of electrochemical equilibrium to be established with an aqueous solution. The rapid corrosion and passivation problems cause entirely spurious potentials (much too positive) to be developed.

The standard potentials of the alkali metals have been measured by Lewis and co-workers using the standard potential of the amalgam in aqueous solutions, and combining this information with the potential of a non-aqueous cell which has the amalgam as the positive electrode and the pure metal as the negative electrode. Such an approach should also work for calcium, and has been attempted on a number of occasions. However, the results obtained in this way for the standard potential of Ca have been discarded by the compilers of most tables of oxidation-reduction potentials^(56, 68, 84, 85). The value given is -2.87 v, which was calculated by Latimer⁽⁹³⁾ from the heat of dissolution of Ca in acid and the entropies of the hydrogen and calcium ions.

A much more important difficulty with the experimental measurements is the passivation of the calcium electrode. All the workers who have attempted measurements with the cell:



or similar non-aqueous cells, have remarked on the necessity for scraping the surface of the calcium electrode continuously in order to obtain a

reproducible potential value. Tamele⁽⁸²⁾ says: "The EMF of the non-aqueous cell was less constant. If not scratched, the value was about 0.6 volt and indistinct. During scraping the value rose to 0.88-0.90 volts and remained constant, varying slightly with the concentration of the calcium amalgam. After prolonged, very intensive scratching, the EMF fluctuated towards still greater values, which was most probably due to the warming of the rubbed surface. Owing to the instability of the calcium amalgam, the final determinations had to be obtained from the couple (aqueous and non-aqueous cells measured simultaneously) to ensure the same concentration of amalgam in both amalgam electrodes."

Drucker and Luft⁽⁸¹⁾ said: "First we tried to make the measurement in a closed container but a remarkable case of passivity occurred, which has already been described by Tamele. A voltage of only 0.4 volts or less is observed when the calcium is completely immersed, but nevertheless no surface reaction is visible on the completely shiny metal. If one grinds the surface with a roughened glass or with carborundum, approximately 0.8 volts are obtained. Even a slight vibration of the electrode already dispenses with the passivity — for instance, hitting it against the glass wall. During the measurements, stirring was introduced, and the metal rod was always vibrating slightly against the glass wall. Under these circumstances, the voltage dropped only very slowly, and reached its highest value immediately after renewal of the amalgam surface. Stopping the stirring caused the voltage to drop immediately to 0.4 volts, after which it decreased slowly. Stirring again caused the original value to appear once more."

It appears from Drucker and Luft's illustration that their measurements were carried out in an open beaker. No mention was made of using a drybox or other inert-atmosphere facility. The fact that these measurements gave a lower potential difference may be explained by atmospheric contamination with oxygen or water or both.

Shibata⁽⁸³⁾ said: "The difficulty lies in the following points:

(1) When the calcium amalgam is brought into contact with water, decomposition begins, which lowers the concentration of calcium in the amalgam. (2) in the process of measuring the EMF between calcium and calcium amalgam, the surface of the calcium is oxidized, even though it is immersed in the organic solvent, so that the EMF is noticeably lowered. The vessel is made out of thick glass and is polished with rough sand. The reason for this is to keep a new surface of calcium continually exposed by rubbing the calcium electrode on a rough surface. When rubbing stops, the potential falls (from 0.895 volts) to 0.84 or lower. If the calcium electrode is not covered with de-Khotinsky cement, an unpolished spot is exposed to the solution, and in this case the observed value falls to 0.4 volts. If the diameter of the end is too large (i. e. 7 mm), then the potential also falls because of the unpolished parts; but an end which is too small also gives an unstable value. "

Again, the apparatus diagram implies that the experiments were done in an open beaker, and no indication of an inert-atmosphere facility is given.

It is clear from these experiments that passivation of the calcium surface is an important problem, but the fact that no real attempt was made to exclude oxygen or water-vapor from the system may have made the errors much larger than they need to be.

In Table IX, we have summarized all the experiments performed to date, including some early measurements by Cambi⁽⁹⁴⁾, some measurements by Smyrl⁽⁹⁵⁾ and our own preliminary measurements⁽⁹⁶⁾. (See Section VI.) The quantity, ΔE^0 , listed in the last column of the table, was calculated from the equation

$$\Delta E^0 = E_{\text{Ca(Hg)}}^0 - E_{\text{Ca}}^0 = E + (RT/2F) \ln X_{\text{Ca}} \gamma_{\text{Ca}}$$

As before, we have assumed that the activity coefficient of calcium in the amalgam is unity. The concentration of calcium ion in the electrolyte does not enter the calculation, but in most cases, the non-aqueous solution was saturated with the calcium salt.

TABLE IX

Potential between Calcium Amalgam and Solid Calcium
 $\text{Ca(s)}|\text{Ca}^{2+}$, Non-Aqueous Solution|Ca(Hg)

<u>Workers</u>	<u>Year</u>	<u>Salt</u>	<u>Concn.</u> <u>(M)</u>	<u>Solvent</u>	X_{Ca} <u>in Amalgam</u>	<u>T</u> <u>(°C)</u>	<u>E</u>	<u>ΔE^0</u>
Cambi ⁽⁹⁴⁾	1914	CaCl ₂	0.25	MeOH	0.0148(satd)	-80	0.502	0.467
		CaCl ₂	0.25	MeOH	0.01	-80	0.811	0.773
Cambi ⁽⁹⁴⁾	1915	CaCl ₂	0.35	MeOH	0.01	-80	0.829	0.791
		CaI ₂	0.0093	pyridine	0.01	+25	0.149	0.089
Tamele ⁽⁸²⁾	1924	CaI ₂	satd.?	pyridine	0.000385	17.5	0.88	0.782
							0.90	0.802
Drucker and Luft ⁽⁸¹⁾	1926	CaI ₂	satd.	pyridine	0.00126	17	0.843	0.759
Shibata ⁽⁸³⁾	1931	CaI ₂	satd.	pyridine	0.00133	15	0.895	0.813
		CaI ₂	satd.?	EtOH	0.00133	16	0.885	0.803
Smyrl ⁽⁹⁵⁾	1966	CaCl ₂	0.0288	DMSO	0.0051	25	0.310	0.242
			0.0551	DMSO	0.0051	25	0.316	0.248
Huston and Butler ⁽⁹⁶⁾	1967	CaCl ₂	0.010	propylene	0.000148	25	0.802	0.789
				carbonate	0.000136		0.876	0.762

From the observations quoted above, we expect that the highest values obtained for ΔE^0 are probably most nearly correct, since both factors introducing systematic error (corrosion and passivation of the solid calcium) tend to decrease the measured potential below its thermodynamic value. Thus we choose $\Delta E^0 = 0.813$ (Shibata's highest value) to be the best of the presently available experimental values. Several other measurements tend to confirm this, but are slightly lower: Cambi (0.791), Tamele (0.782), Shibata (0.803), and our own measurements (0.789). We believe now, in the light of all these studies, that it may be possible to obtain a more nearly thermodynamic value for ΔE^0 by being extremely careful to eliminate oxygen and water from our non-aqueous electrolyte, and by introducing freshly-prepared amalgam and freshly-polished solid Ca simultaneously into the electrolyte. If the potential is read as a function of time during the first few minutes of cell operation, it may be possible to extrapolate to zero time and obtain a better measurement than has formerly been possible.

Let us now compare the value of the standard potential of calcium obtained by Latimer with the value calculated from the best available experimental data. Since the amalgam concentrations used in both the aqueous and non-aqueous studies were roughly the same, the assumption of unit activity coefficient for calcium in the amalgam should not introduce appreciable error. The standard potential of the amalgam in aqueous solution we have already established as:

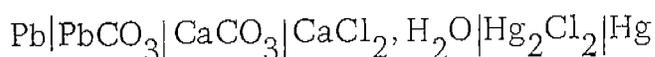
$$E_{\text{Ca(Hg)}}^0 = -1.996 \pm 0.002 \text{ v}$$

and in our discussion above, we proposed that the difference in standard potentials between the amalgam and solid calcium was greater than 0.813 v. This implies that

$$E_{\text{Ca}}^0 = -2.809 \text{ v}$$

or some more negative value. Latimer's calculated value is -2.87 v, and to obtain this experimentally, ΔE^0 would have to be larger than 0.87 v. A value this high has not yet been obtained, but might be possible to obtain with extreme care.

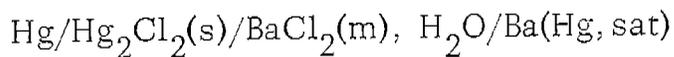
As a final note, we must report that recent measurements⁽⁹⁷⁾ of the cell:



when combined with other thermodynamic data, have yielded the value $E_{\text{Ca}}^0 = -2.868$ v, which supports Latimer's calculated value.

C. Standard Potential of the Barium Amalgam Electrode*

The most reliable results in the literature on the potential of a barium amalgam electrode are those of Tippetts and Newton⁽⁷³⁾, who measured the potential of the cell



at temperatures from 0 to 45°C. The potential of this cell is given by

$$E = E_{\text{Ba}(\text{Hg})}^0 - E_{\text{Hg}_2\text{Cl}_2}^0 + \frac{RT}{2F} \ln 4 m^3 \gamma_{\pm}^3 - \frac{RT}{2F} \ln X_{\text{Ba}} \gamma_{\text{Ba}} \quad (1)$$

where γ_{\pm} is the mean activity coefficient of aqueous BaCl_2 at molal concentration m , X_{Ba} is the mole fraction of barium in the amalgam, and γ_{Ba} is the activity coefficient of barium in the amalgam (reference state: infinite dilution, mole fraction scale). The activity coefficient γ_{\pm} of BaCl_2 in aqueous solutions was obtained from the tables of Robinson and Stokes⁽⁴¹⁾. For concentrations below 0.1 m, the extended Debye-Huckel equation with $a = 5$ was used.

Since the exact concentration of the barium amalgam was not measured by Tippetts and Newton, we calculated the values of the combination

* To be published.

$$E^{0'} = E_{\text{Ba(Hg)}}^0 - E_{\text{Hg}_2\text{Cl}_2}^0 - \frac{RT}{2F} \ln X_{\text{Ba}} \gamma_{\text{Ba}} \quad (2)$$

which are plotted in Fig. 11. This quantity should be independent of m ; except that γ_{\pm} for 25° was used for all temperatures. Therefore, these values are extrapolated to $m = 0$ to obtain the best value of $E^{0'}$ for each temperature.

The quantity $E^{0'}$ was extrapolated to $m = 0$ by fitting a least squares straight line to the plots of Fig. 11; and the results are given in Table X, with 95% confidence limits based on the statistics of this calculation.

TABLE X

Standard Potential of The Barium Amalgam Electrode

<u>Temp.</u> <u>°C</u>	<u>X_{Ba}</u>	<u>E^{0'}</u>	<u>E_{Ba(Hg)}⁰</u>
0	0.0024	-2.0302 ± .0006	-1.6841 ± .0008
15	0.0041	-2.0490 ± .0003	-1.7154 ± .0004
25	0.0055	-2.0620 ± .0002	-1.7271 ± .0003
35	0.0069	-2.0739 ± .0013	-1.7432 ± .0013
45	0.0084	-2.0875 ± .0008	-1.7613 ± .0008

Notes:

- X_{Ba} taken from the phase diagram of Ref. 70.
- $E^{0'}$ obtained by a least-squares linear extrapolation (Fig. 11)
Errors are 95% Confidence Limits.
- $E_{\text{Ba(Hg)}}^0$ calculated from Eq. 2 assuming $\gamma_{\text{Ba}} = 1$. The confidence limits include an estimate of the error due to uncertainties in X_{Ba} .

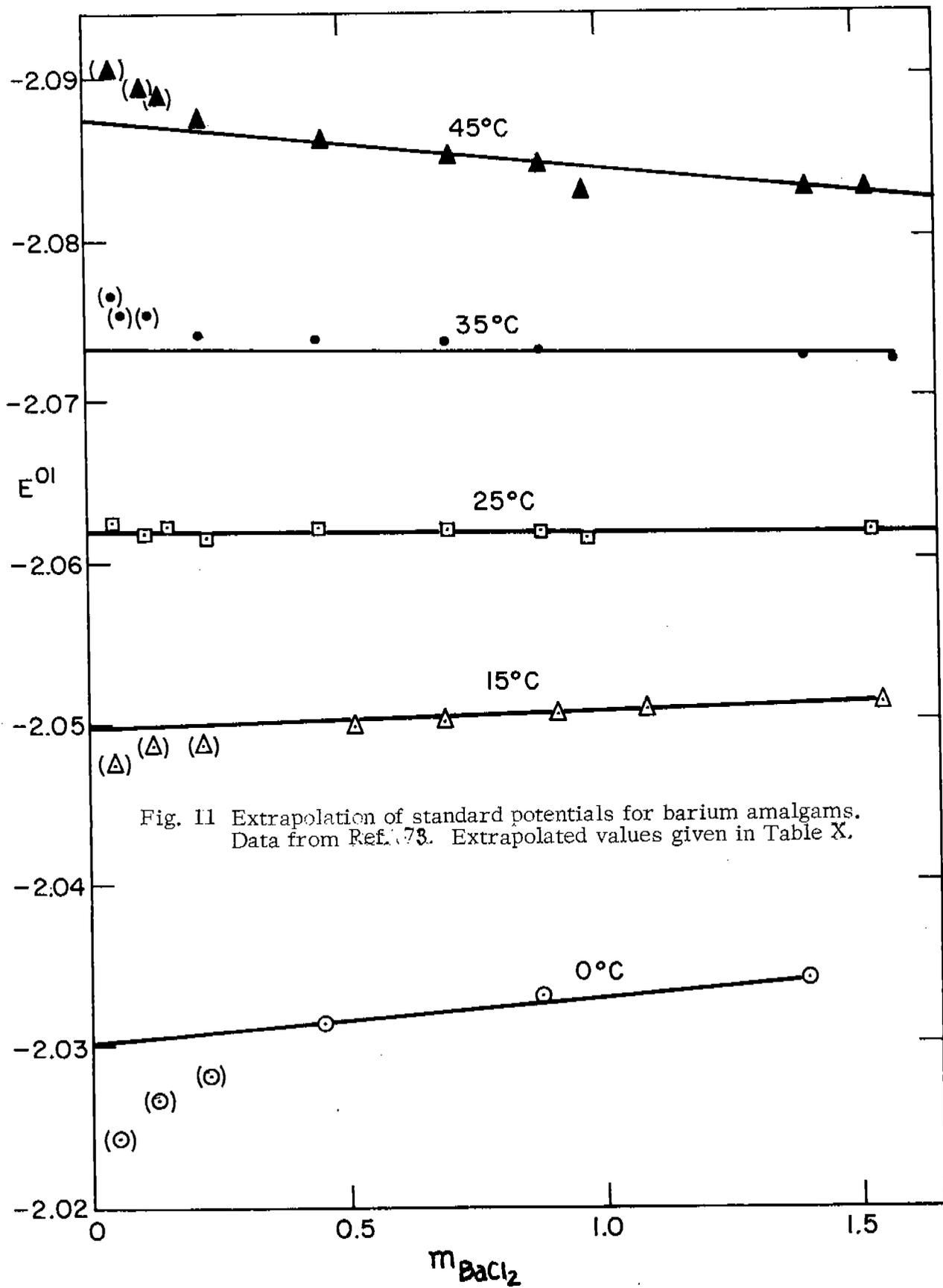


Fig. 11 Extrapolation of standard potentials for barium amalgams. Data from Ref. 73. Extrapolated values given in Table X.

The standard potential $E_{\text{Ba(Hg)}}^0$ was calculated using equation (2) from the $E^{0'}$ values. The standard potential of the calomel electrode $E_{\text{Hg}_2\text{Cl}_2}^0$ was taken to be $+0.2682 \pm 0.0001$ volts⁽⁴⁷⁾. The saturation concentrations of the amalgam X_{Ba} at different temperatures were obtained from the phase diagram⁽⁷⁰⁾ for barium-mercury alloys. The activity coefficient of barium in the amalgam was assumed to be unity in the absence of any other data, by analogy with calcium amalgams⁽⁷¹⁾. The saturation concentrations X_{Ba} used in these calculations, and the resultant values of $E_{\text{Ba(Hg)}}^0$ are given in Table X. The saturation concentration X_{Ba} is assumed to be in error by about 0.0001 mole fraction units. This introduces an error which was combined with the 95% confidence limits of $E^{0'}$ to obtain 95% confidence limits on $E_{\text{Ba(Hg)}}^0$ quoted in Table X along with the values of $E_{\text{Ba(Hg)}}^0$. We have used these values in the analysis of our kinetic data in the next section.

During the course of our kinetic measurements (see Section VI-F), we also had occasion to measure some potential values which were constant over a considerable time interval. These correspond to the equilibrium values measured by Tippetts and Newton. These measurements are summarized in Table XI. During the time interval given, the potential was constant to within the limits given. In general, these measurements support the accuracy of the standard potentials calculated from the data of Tippetts and Newton.

When the barium amalgams were analyzed by reaction with acid and back-titration with base, the concentrations were found to be higher than the saturation concentration ($X_{\text{Ba}} = 0.0055$) for 25°C. The analyzed concentrations were $X_{\text{Ba}} = 0.0064$ for runs 4 and 5, and $X_{\text{Ba}} = 0.01084$ for runs 6, 7 and 8*. The potentials calculated using these concentrations are considerably more negative than the observed potentials. If X_{Ba} is taken to be 0.0055, the calculated potentials are

* We believe the samples taken for analysis contained some solid amalgam, and hence do not reflect the true concentration at the dropping amalgam electrode.

TABLE XI

Equilibrium Potentials of Barium Amalgams

Run	m_{BaCl_2}	γ_{\pm}	X_{Ba} (Analyzed)	X_{Ba} (Satn)	E_{calc} (Analyzed)	E_{calc} (Satn)	E_{obs}	Drop Lifetime sec
4	0.3108	0.423	0.0064	0.0055	-1.6883	-1.6863	-1.685 ± .002	0.1
5	1.7053	0.4415	0.0064	0.0055	-1.6659	-1.6639	-1.663 ± .002	0.5
6	0.4787*	0.388	0.01084	0.0055	-1.6906	-1.6819	-1.6746 ± .0002	0.005
7	1.7053	0.4415	0.01084	0.0055	-1.6726	-1.6639	-1.6604 ± .0005	0.02
8	0.3108	0.423	0.01084	0.0055	-1.6950	-1.6863	-1.6834 ± .0005	0.1

* Contains also 0.5112 m CaCl_2

Notes:

- (1) Ba amalgam analysis by titration with acid. Sample analyzed may have contained some solid phase.
- (2) Saturation concentration from phase diagram of Ref. 70.
- (3) Calculated potentials assume $E_{\text{Ba(Hg)}}^0 = -1.7271$ volts (see Table X).
- (4) γ_{\pm} for no. 6 calculated from γ_{\pm} for BaCl_2 and Harned Rule Coefficient for CaCl_2 - MgCl_2 mixtures⁽²⁹⁾.

much closer to the observed potentials; within experimental error they agree for runs 4 and 5 (where observations were made at relatively long times; 0.1 and 0.5 seconds after the formation of the drop). For runs 7 and 8 the calculated potentials are about 3 mv more negative than the observed potentials.

Run 6 was an experiment in which the aqueous solution contained both BaCl_2 and CaCl_2 . The drop lifetime was too short (5 msec) to assure that true equilibrium had been reached, but the potential did not change by more than a few tenths of a millivolt over that period. If the activity coefficient of BaCl_2 is calculated using Harned Rule coefficients for the system MgCl_2 - CaCl_2 , as the closest analogous system, the calculated potential is 7.3 mv more negative than the observed potential. This could simply be a failure to reach equilibrium; it could reflect kinetic interference between the Ca and Ba reactions; but it could also reflect the fact that the activity coefficients for BaCl_2 in BaCl_2 - CaCl_2 mixtures is greater than that for MgCl_2 in MgCl_2 - CaCl_2 mixtures. Depending on the results we obtain in the future on the kinetics of the calcium amalgam electrode, it may turn out to be feasible to use the barium amalgam electrode to determine the activity coefficients of BaCl_2 in BaCl_2 - CaCl_2 mixtures.

V. EXPERIMENTAL METHODS

A. Solutions

Solutions were prepared from reagent grade salts and triple-distilled conductivity water. Typical analyses of the salts used are given in Table XII. Because it was not always possible to remove the last traces of water from these salts, stock solutions prepared by weighing definite amounts of salt and water were always analyzed after preparation. The pH was adjusted to 11 or 12 by adding an accurately weighed amount of reagent grade NaOH, and the excess Na^+ concentration included in the calculations of activity coefficient.

Analysis for chloride by the Volhard Method was carried out as follows: Duplicate portions of the chloride solution, approximately 10 grams each, were weighed and acidified with a few drops of concentrated nitric acid. One milliliter of nitrobenzene was added to assist in coagulating the silver chloride precipitate and to decrease the rate of reaction of AgCl with the thiocyanate solution during the back-titration. Standard (0.3000 N) silver nitrate solution was prepared by weighing the theoretical amount of silver nitrate which had been dried for several hours at 100°C. A 10% excess of this standard silver nitrate solution was added to the chloride samples. The precipitated silver chloride was shaken vigorously for a few minutes until it settled out in large, spongy flakes. The supernatant liquid was then titrated quickly with potassium thiocyanate solution (0.3N) (standardized against the silver nitrate) using one ml of ferric alum as the indicator. The end point was taken at the first appearance of a pink coloration.

The reproducibility of chloride analyses by this method was typically $\pm 0.1\%$ to $\pm 0.2\%$. However, the analyzed concentration of chloride was usually 0.2 to 0.4% smaller than that calculated by weighing out the required amounts of dried salt and water. This small discrepancy reflects the residual water in the salts.

TABLE XII

Manufacturer's Analyses of Salts Used

<u>NaCl (Fisher Certified Reagent)</u>		<u>NaOH (Fisher)</u>		<u>LiCl (Fisher Certified Reagent)</u>	
Iodide (I)	0.002%	Chloride (Cl)	0.005%	Sulfate (SO ₄)	0.004%
Bromide (Br)	0.01%	Iron (Fe)	0.0005%	Barium (Ba)	0.003%
Insoluble matter	0.002%	NaOH	98.9%	Calcium (Ca)	0.00%
Chlorate and nitrate as (NO ₃)	0.003%	Sodium carbonate	0.3%	Iron (Fe)	0.0002%
Nitrogen compounds as (N)	0.0003%	Sulfate	0.000%	Insoluble matter	0.007%
Phosphate (PO ₄)	0.0001%	Phosphate (PO ₄)	0.0005%	Acidity	none
Sulfate (SO ₄)	0.001%	Ammonium hydroxide ppt	0.009%	Alkalinity as (Li ₂ CO ₃)	0.03%
Barium (Ba)	0.001%	Heavy metals as (Ag)	0.0005%	Nitrate (NO ₃)	0.005%
Calcium, magnesium and R ₂ O ₃ ppt	0.003%	Potassium (K)	0.00%	Phosphate (PO ₄)	0.0002%
Heavy metals as (Pb)	0.00003%	Nitrogen compounds as (N)	0.001%	Ammonia (NH ₃)	0.001%
Iron (Fe)	0.0002%	Nickel (Ni)	0.000%	Heavy metals as (Pb)	0.0005%
Potassium (K)	0.001%			Magnesium (Mg)	0.0025%
pH of 5% solution at 25°C	6.14			Other alkalies as (Cl)	0.09%

TABLE XII (Cont.)

<u>CaCl₂ · 2H₂O (Fisher Certified Reagent)</u>		<u>Na₂SO₄ (Baker Analyzed Reagent)</u>	
Sulfate (SO ₄)	0.002%	Assay (Na ₂ SO ₄)	99.7%
Assay (CaCl ₂)	78%	Insoluble matter	0.008%
Insoluble matter and NH ₄ OH ppt	0.005%	Loss on ignition	0.25%
Oxidizing substances (NO ₃)	0.002%	pH of 5% solution at 25° C	6.2
Ammonium (NH ₄)	0.001%	Chloride (Cl)	0.002%
Barium (Ba)	0.001%	Nitrogen compounds as (N)	0.0003%
Heavy metals as (Pb)	0.0004%	Arsenic (As)	0.00003%
Iron (Fe)	0.0001%	Calcium, Magnesium and R ₂ O ₃ ppt	0.005%
Magnesium (Mg)	0.005%	Heavy metals as (Pb)	0.0003%
Strontium (Sr)	0.0%	Iron (Fe)	0.0003%
Potassium (K)	0.00%	Potassium (K)	0.004%
Sodium (Na)	0.01%		
pH of 5% solution at 25° C	6.0		

TABLE XII (Cont.)

<u>MgCl₂ · 6H₂O (Fisher Certified Reagent)</u>		<u>BaCl₂ · 2H₂O (Fisher Certified Reagent)</u>	
Insoluble matter	0.005%	Insoluble Matter	0.095%
Nitrate (NO ₃)	0.001%	Subs. not ppt. by H ₂ SO ₄	0.050%
Phosphate (PO ₄)	0.0005%	Calcium (Ca)	0.05%
Sulfate (SO ₄)	0.002%	Strontium (Sr)	Pass test (abt. 0.1%)
Potassium (K)	0.005%	Heavy metals (as Pb)	0.0005%
Sodium (Na)	0.005%	Iron (Fe)	0.0002%
Manganese (Mn)	0.0005%	Oxidizing subs. (as NO ₃)	0.005%
Ammonium (NH ₄)	0.002%	pH of a 5% sol'n. at 25°C	5.2-8.2
Barium (Ba)	0.005%	Loss on drying	14.6-14.9%
Calcium (Ca)	0.01%		
Heavy metals (as Pb)	0.0005%		
Iron (Fe)	0.0005%		
Strontium (Sr)	0.005%		

Later analyses for chloride were made by potentiometric titration with standard silver nitrate. Approximately 10g of solution was weighed into an Erlenmyer flask to which had been attached a side arm containing a porous frit salt bridge, and a reference electrode compartment. The solution was stirred magnetically as the AgNO_3 was added from a burette. The potential of a silver wire in the solution being titrated was measured with respect to a saturated calomel reference electrode. To prevent the diffusion of small amounts of chloride from the reference electrode into the titration cell, a 1M KNO_3 salt bridge was used, and the solution in this salt bridge changed frequently. Potentials were stable to ± 0.1 mv and were measured over a range of several ml either side of the end point. To avoid errors in volume reading from residual drops, the tip of the burette was rinsed after each addition.

The end point in this potentiometric titrations was determined in three ways. The simplest method was to read from the titration curve the volume at which the potential reached the theoretical value for the equivalence point, in this case, 240 ml. The second method was to measure the potential increment as small amounts of AgNO_3 were added and to find the point where dE/dV was maximum. To do this, the finite difference ratio $\Delta E/\Delta V$ was plotted as a function of the average volume in the interval, and a symmetrical cusp-shaped curve fitted to the points. The line of symmetry of this curve was taken to be the end point. A third method, (Gran's method) was to plot the function

$$y = 10^{-(E/0.059)}$$

which should be proportional to the concentration of silver ion added after the equivalence point. A linear extrapolation of this function to the axis $y = 0$ gave the end point volume.

Figure 12 shows all three of these methods applied to the titration of 10.182 g of approximately 0.57M NaCl with 0.3002N AgNO₃. Both the direct potential method and Gran's method give the same result, 18.98 ± .005 ml. The volume at which dE/dV reaches a maximum is less certain but was estimated to be 18.97 ± .02 ml. The precision of these potentiometric titrations is much better than the Volhard method, approximately ± 0.02% to ± 0.05%; and with a simple computer program to perform the calculations, the time required is comparable to that for the Volhard method. An important advantage over the Volhard method is the elimination of systematic errors due to the slow reaction of solid AgCl with the KSCN titrant, which can cause the measured value of chloride concentration to be too low.

Analysis for sulfate was performed gravimetrically. Sulfate was precipitated with reagent grade BaCl₂. The precipitate of BaSO₄ was allowed to digest overnight, collected on sintered crucibles (previously brought to constant weight (± 0.1 mg) by heating in a muffle furnace at 750°C) and dried in a desiccator. The precipitate was dried at 150°C for several hours, ignited at 750°C for 30 minutes, weighed, re-ignited, and weighed again. A subsequent ignition and weighing changed the weight by less than 0.1 mg. The Na₂SO₄ stock solution which was prepared to have a concentration of 0.3323 M was found by this analysis to have a concentration of 0.3275 ± 0.0010 M. This 1.5% discrepancy resulted from the unknown water content of the Na₂SO₄ used.

Even if the concentration of the stock solutions is uncertain by 0.1% or more, the error in activity coefficient measurements need not be this large, provided that the same stock solutions are used to prepare all the solutions measured. The dilutions, performed by weighing the required quantities of stock solutions into a dry glass vessel, can be made with an error of ± 0.02g in 200g, or ± 0.01%. Provided the same stock solutions are used, the errors in the concentration ratios, which are the primary quantities which enter the calculations of the activity coefficient ratios, will be approximately equal to the errors in making the

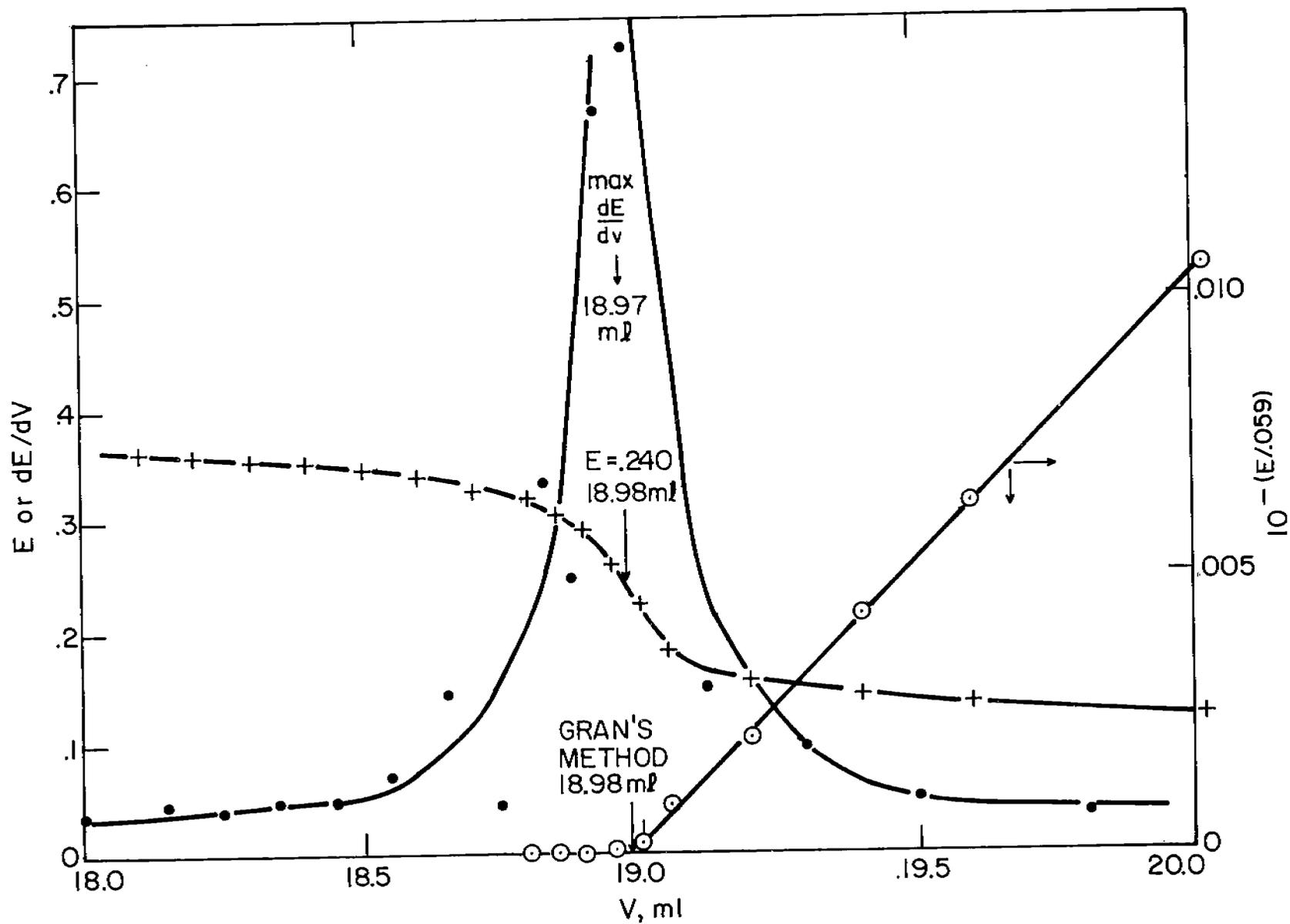


Fig. 12 End point determination in potentiometric chloride titration.

dilutions. An error of 0.01% in the concentration ratios corresponds to an error of only about 0.005 mv in the potential measurement, which is quite negligible.

As we pointed out in Section III-B, accurate measurements with amalgam electrodes can only be made in solutions free of even small traces of oxygen, organic materials, or reducible metal ions. Organic materials are minimized by using apparatus constructed entirely of glass and Teflon, without any grease on ground joints or stopcocks. To remove dissolved oxygen we have pre-electrolyzed the solutions with a platinum black electrode while saturating the solutions with hydrogen⁽⁵⁴⁾. No external current source is needed — the platinum black electrode acts as both anode (oxidizing hydrogen gas to water) and cathode (reducing oxygen and metal ions). The platinum black electrode also removes the last traces of organic materials by adsorption. The purification cell is shown in Fig. 13.

To prevent addition of impurities from the gas bubbling through the solution, hydrogen was generated by electrolysis of concentrated alkali at a silver-palladium cathode. Only hydrogen gas diffused through the metal membrane into the gas system, which was constructed entirely of glass and Teflon. The manufacturer of the hydrogen generator (Matheson Co.) reports that the impurity content of the hydrogen is less than one part in 10^8 .

Changes in concentration can be produced during the purification of solutions if large volumes of dry gas are passed through the solution or if extensive pre-electrolysis is carried out. We have studied the effect of bubbling hydrogen through the solutions for periods of time corresponding to our purification procedure.

A solution containing 0.5 molal KCl and 0.5 molal NaCl was prepared. The total chloride content, determined immediately after preparation, was 0.9971 ± 0.0005 molal. After bubbling hydrogen gas through 500 ml of the solution for twenty hours at a rate of 2-5 ml/min, the total chloride content was found to be 0.9996 ± 0.0002 molal, an increase in concentration of 0.25%.

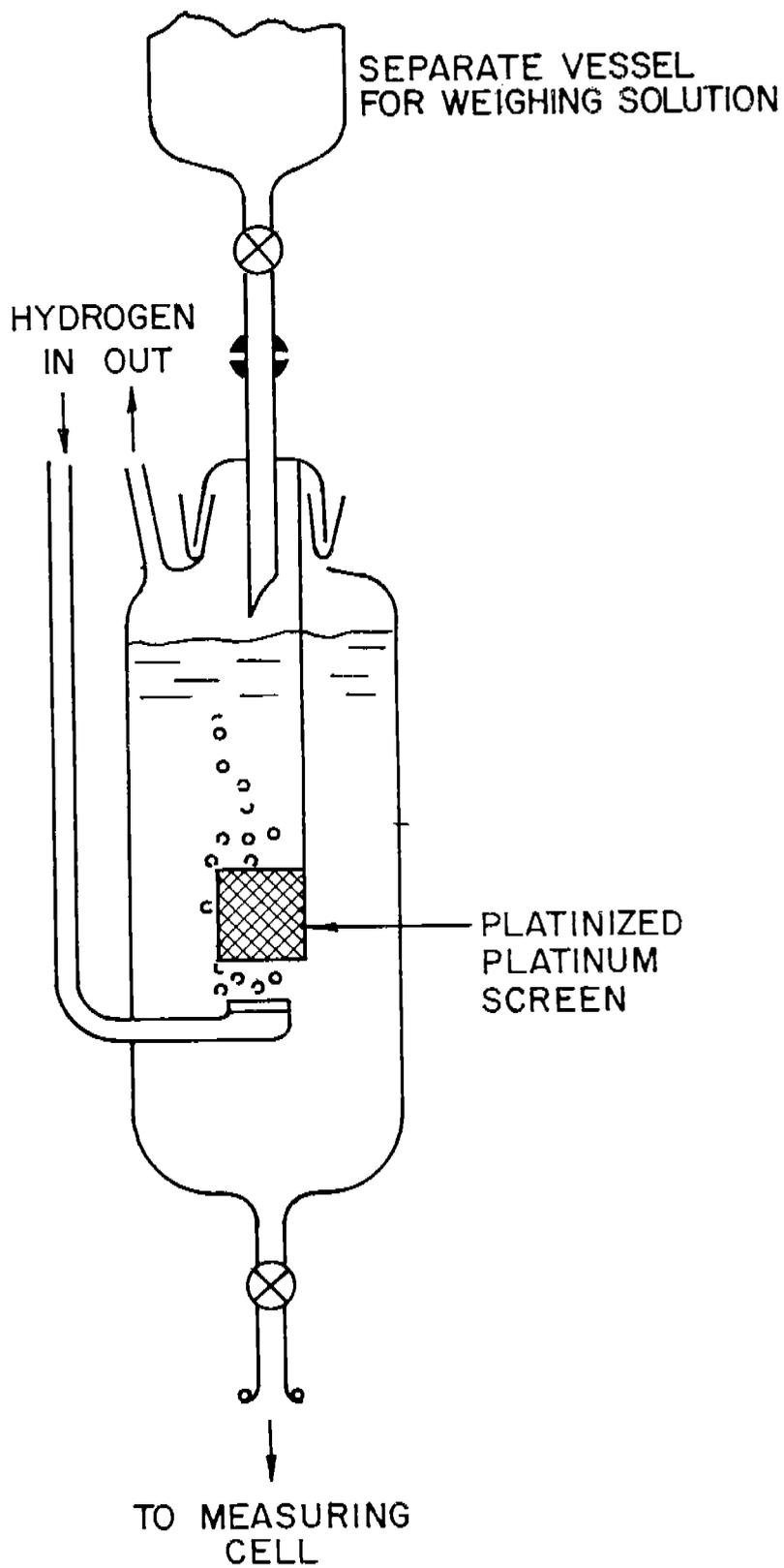


Fig. 13 Cell for purification of solutions.

This experiment indicates that even without presaturation, the changes in concentration due to gas bubbling in the solutions are small. By presaturating the gas with a solution of the same concentration, and by shortening bubbling times to one or two hours, the changes in concentration can be made less than 0.01%, which is entirely negligible.

Pre-electrolysis for the periods of time involved in our experiments also produces negligible change in concentration. At a current of 1 ma with 1% current efficiency for decomposition, electrolysis for six days would be required to produce a change in concentration of 0.01%. For alkali or alkaline earth halides and sulfates in a solution saturated with hydrogen, the current efficiency for decomposition at platinum electrodes is considerably less than 1%, and thus this effect is entirely negligible.

B. Amalgam

In our studies (Section VI-A), sodium amalgam was used, but the preparation and handling of other amalgams is similar. The optimum concentration^(3, 7, 9, 45) of sodium in the amalgam is between 0.01 and 0.05 weight percent. Thus electrolysis of NaOH at a mercury cathode is the most convenient method of preparation. The alternate method, direct combination of the elements, is less convenient. Because only a tenth of a gram of sodium is required to make 200g of amalgam, the atmosphere in which the sodium is weighed and combined with the mercury must be extremely dry and free from oxygen or the sodium will have oxidized before the amalgam can be prepared.

To prepare the amalgam by electrolysis, the cell shown in Fig. 14 was constructed. A mercury cathode pool (500 g) was covered with 40 ml of 6M NaOH, reagent grade. A platinum screen anode (approximately 5 cm² area) was used, and the solution was saturated with hydrogen during the electrolysis (0.5 amp for 4 hours). At the completion of the electrolysis, the amalgam was drained through a stopcock at the bottom of the cell into the previously evacuated reservoir for the dropping amalgam

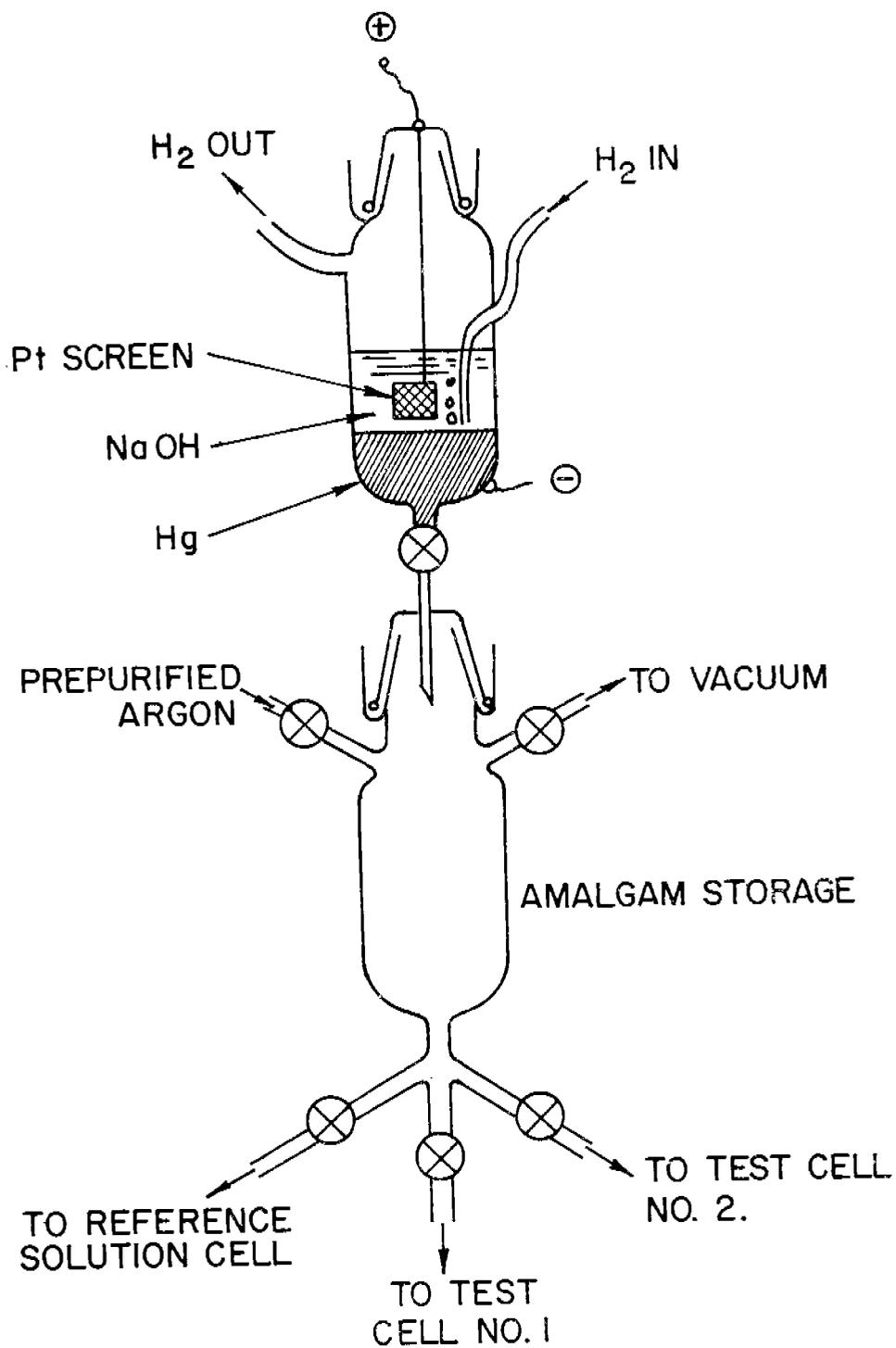


Fig. 14 Amalgam preparation and storage.

electrodes. The silicone grease in the stopcock acted as an effective barrier to water, and no difficulty was experienced from traces of water causing decomposition of the amalgam in the reservoir. So long as the amalgam was kept in vacuo or under an atmosphere of purified argon (< 0.5 ppm O_2), it retained the bright surface characteristic of mercury, although the contact angle with glass seemed to be smaller than that of mercury. Traces of water and oxygen, such as are present in unpurified nitrogen or argon, caused the surface to tarnish almost immediately.

The analysis of the amalgam for its sodium content was carried out as follows: Duplicate samples of amalgam, approximately 150g each, were weighed accurately into beakers. An excess of standardized H_2SO_4 was added, and the amalgam was stirred until evolution of hydrogen gas ceased. The excess acid was titrated with standardized NaOH solution using phenolphthalein as the indicator. Duplicate analyses of the amalgam prepared as described above gave 0.0462 and 0.0455 weight percent Na.

C. Reference Electrodes

The silver-silver chloride electrodes were prepared by the thermal-electrolytic method⁽⁴⁷⁾. Platinum wire (20-gauge) was formed into a spiral of 5 or 6 turns approximately 2 mm in diameter, washed with boiling concentrated nitric acid, and held in a flame until the spectrum due to metallic impurities disappeared. The spirals were then rinsed with triple-distilled water and dipped into a paste made by stirring silver oxide (Fisher purified grade) with triple-distilled water. A ball of the paste at least 2 mm diameter was formed on the spiral, which was then supported in an electric furnace. To avoid sputtering of the paste by the rapid formation of steam, the electrode was maintained at $70^\circ C$ for about one hour; then the temperature was raised slowly to approximately $450^\circ C$, where it was held for half an hour. The electrode was cooled slowly in the furnace to avoid cracking due to thermal shock. This coating process was repeated five times in all to give a porous ball of silver approximately 5 mm in diameter.

The silver electrode was then chloridized by making it the anode in a U-tube containing 1% HCl solution. A platinum wire served as the cathode, and a current of 10 ma was passed through this cell for 6 minutes, resulting in the conversion of approximately 5% of the silver to silver chloride.

Eight such electrodes were prepared and aged for three days in 1m NaCl solution. Intercomparison of the potentials of these eight electrodes gave differences which were in all cases less than 0.02 mv. Several pairs of electrodes showed differences less than 0.005 mv. After aging for 36 days, the differences had changed less than 0.005 mv.

Electrodes were used in pairs from the same batch, and equilibrated for several hours with the solution to be measured. The observed potentials of the amalgam cells were corrected by using the bias potentials measured in 1m NaCl. After several months, the electrodes began to drift in potential (probably because of the accumulation of AgBr from the traces of bromide in the salts or because the AgCl dissolved in the electrolytes of high chloride concentration) and were discarded.

Lead amalgam-lead sulfate electrodes were prepared as follows: Approximately 1% (by weight) of lead metal (Mallinkrodt Analytical Reagent) was dissolved in mercury (Doe and Ingalls, triple distilled) at 100°C, with stirring, under an argon atmosphere in a glove box. The (saturated) amalgam was cooled to room temperature in a sealed flask with a stopcock and long tube for filling the cells (see Fig. 15, p. 82). The long tube was filled with argon and sealed during transfer from the drybox to the cell.

The amalgam flask was removed from the drybox and the amalgam introduced through the filling tube into each of the pool reservoirs of the two cells (which had been previously freed with argon). To avoid systematic differences in amalgam composition, first one reservoir in one cell, then one reservoir in the other cell, were filled, and the process repeated. Dry lead sulfate was sprinkled over the top of the amalgam pools. The

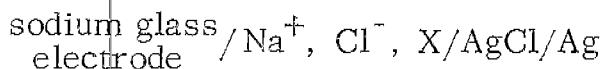
cells were then filled with solution, from which oxygen had been removed by bubbling prepurified argon gas (< 1 ppm oxygen) through a separate reservoir. The whole system was allowed to equilibrate under argon until the bias potential between the two pools was less than 0.05 mv. The glass electrode (see Section V-D) was then introduced through the top of the cell and its potential measured as a function of time. A steady value was usually reached within 1 or 2 minutes. The glass electrode was then transferred to the other cell and the potential read again. The potential of the glass electrode is extremely reproducible, and the precision of ΔE is better than ± 0.05 mv. However, only by careful deoxygenation of the solutions, and by preventing any access of oxygen to the PbSO_4 electrode, could results of this precision be obtained.

The pH of the solutions was between 4 and 6. All measurements were made at $25.00 \pm .05^\circ\text{C}$.

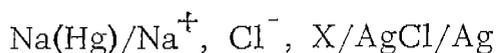
D. Glass Electrodes

Although glass electrodes have long been used in quantitative measurements of hydrogen ion activity, and form the basis for virtually all practical pH measurements, the development of special-purpose cation-sensitive glass electrodes is relatively recent. The most important of these are the monovalent cation-sensitive (sodium-aluminum silicate) and sodium-sensitive (lithium aluminum silicate) glasses. The latter has a much greater selectivity for sodium ion over other monovalent cations. Interference from hydrogen ion can be essentially eliminated by adjusting the pH to a range near neutrality. A number of commercially-available electrodes (e. g. Beckman 39137 "cationic glass electrode" and 39278 "sodium ion glass electrode") have excellent stability and selectivity, and can be used for thermodynamic measurements.

The agreement of activity coefficients measured by means of the cell⁽²⁷⁾



with the amalgam electrode cell^(32,34)



(here X stands for any set of non-interfering anions or cations) as well as with measurements by the isopiestic method, has established the accuracy of glass electrode activity coefficient measurements. Similar measurements have been made in solutions of a single salt component⁽⁹⁸⁻¹⁰¹⁾, and these agree with measurements made by a number of other methods.

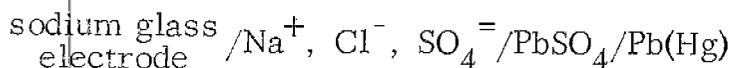
The important precaution to be taken in making accurate thermodynamic measurements with a glass electrode system is continuous calibration against a solution of known activity⁽¹⁰²⁾. In practice, the glass electrode is transferred from a cell containing a reference solution to a cell containing a test solution, and back again, several times, while the potential of the cell is recorded continuously. With a noise-free electrometer and proper shielding, measurements accurate to a few hundredths of a millivolt, comparable in accuracy to those obtained with the amalgam electrode cells, can be obtained. Experimentally simpler, because the elaborate precautions for eliminating oxygen are not necessary, the glass electrode method can provide detailed activity coefficient data much more rapidly than the amalgam electrode method.

Continuous recording of the potential and repetitive calibration is essential because of both short-term and long-term changes in the response of the glass electrode. Short-term changes in the potential (10 to 20 mv) as the solution is changed in composition result both from the establishment of phase-boundary equilibria (e. g. ion-exchange reaction) at the glass surface, and diffusion processes both in the boundary layer of the solution and within the glass itself⁽¹⁰³⁾. Although transients in the concentration of Ag^+ , Li^+ , and Na^+ can be followed by both the cation-sensitive and sodium-sensitive glass electrodes with a time constant of less than 20 msec, a transient in K^+ or NH_4^+ requires as long as

30 seconds for establishment of equilibrium in the case of the sodium-sensitive electrode. The cation-sensitive electrode responds rapidly (< 20 msec) to changes in K^+ or NH_4^+ , but both electrodes showed much longer-time transients (100 msec) in response to changes in the concentration of divalent cations. The time-dependence shows diffusion control, and suggests that the foreign ions decrease the mobility of Na^+ in the hydrated layer of the glass electrode⁽¹⁰³⁾. In general, then, it appears that changes in concentration of an ion to which the electrode is not sensitive may produce observable transients in the potential of the electrode, before equilibrium is reached.

In addition to these short-time transients, glass electrodes undergo longer-time drifts in potential (1 mv/hr or less) which apparently arise from structural modifications of the glass. To obtain accuracy of ± 0.02 mv in potential measurements, it is clearly necessary to measure the rate of drift and to extrapolate the pseudo-equilibrium potentials in the two solutions to the same point in time.

In practice, using a small cell without stirring (Fig. 15), and rinsing the glass electrode with the solution to be measured as it is transferred between the test and reference cells, approximately one minute is required to reach equilibrium; transfer between cells is made about once every five or ten minutes, and the transfer takes approximately fifteen to thirty seconds. Figure 16 shows an actual trace obtained during our measurements of the cell⁽³⁶⁾



which were used to obtain the activity coefficients of Na_2SO_4 in its mixtures with aqueous NaCl solutions.

The glass electrode we used was a Corning "Sodium Ion Electrode," type NAS 11-18. It was connected to an Instrumentation Laboratories Model 135-A electrometer, which operated a Sargent Model SR recorder. Calibration was made with bias boxes differing in potential by a few

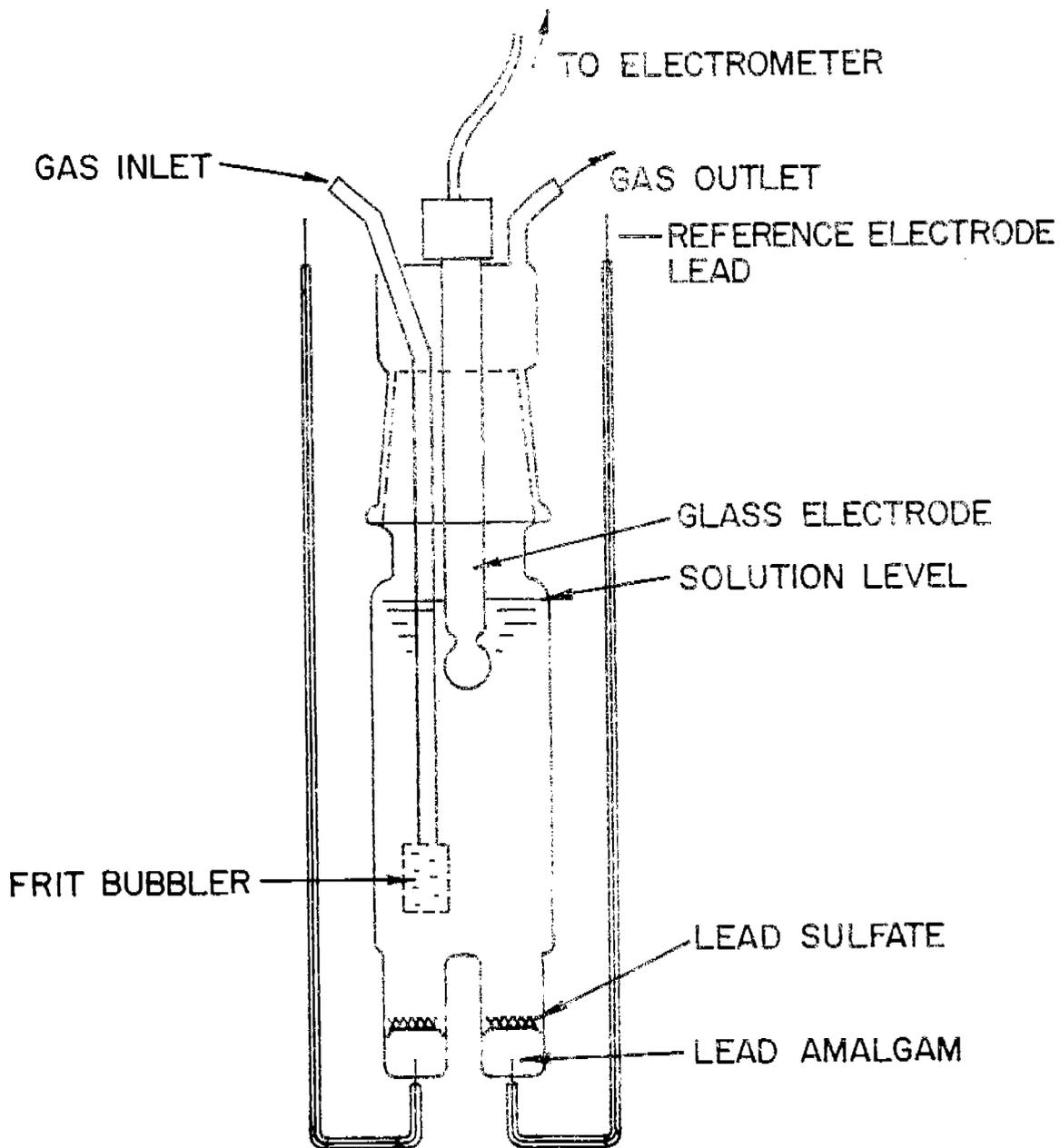
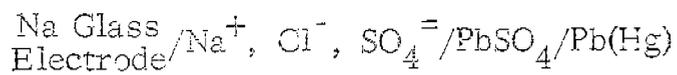


Fig. 15 The cell



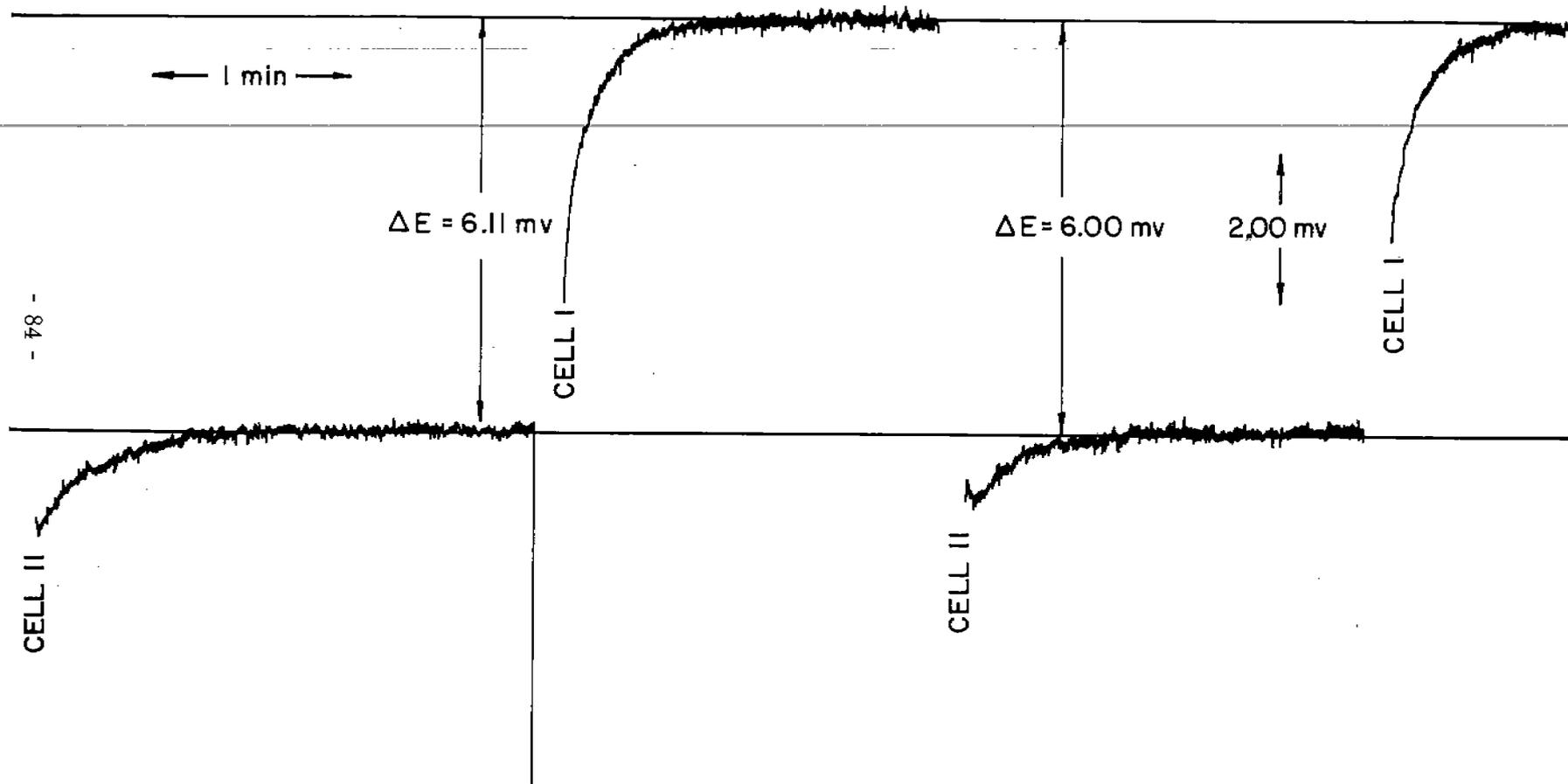


Fig. 16 Potential of the cell $\text{Pb(Hg)/PbSO}_4/\text{Na}_2\text{SO}_4, \text{NaCl}, \text{H}_2\text{O/Na}$ glass electrode with two different electrolytes in Cell I and Cell II.

millivolts. These were connected in place of the cell, and the change in deflection of the recorder noted. The true potential difference was read from the bias boxes to ± 0.005 mv on a Leeds and Northrup Model K-3 potentiometer. Another bias box was introduced in the recorder circuit so that the recorder zero could be offset by potentials large compared to its span. A switch allowed rapid comparison of the two sulfate-reversible electrodes incorporated in each cell (Fig. 15).

So long as the mixed electrolytes contain only a single cation, problems of selectivity do not arise; but when mixtures involving two or more cations are involved, the glass electrode potential may depend on the concentrations of more than one cation. Typically⁽¹⁰⁴⁾, this dependence is described in terms of a selectivity ratio K_i : For example, a sodium-sensitive glass electrode may have a potential given formally by

$$E = E^0 + \frac{RT}{F} \ln [a_{\text{Na}^+} + \sum K_i a_i]$$

where a_i is the activity of the interfering cation i . If a cell without liquid junction is used (as we have done in all our experiments), the reference electrode responds to anion (e. g. chloride) activity, and the above equation can be modified to contain only thermodynamic quantities. The activity of each ion a_i is replaced by $m_i m_{\text{Cl}^-} \gamma_i^2$, where γ_i is the mean activity coefficient of the metal chloride. If polyvalent ions are to be included, their activity is raised to the power $(1/z_i)$ where z_i is the charge on the ion.

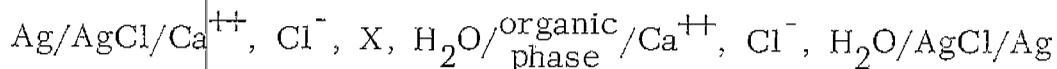
Selectivity ratios defined in this way are more or less characteristic of the glass composition, and in dilute solutions are relatively independent of the composition of the solution. In concentrated solutions, however, the interactions of ions in the hydrated glass layer leads to quite complicated dependences of K_i on solution composition. Unfortunately, the theory of the glass electrode is not sufficiently advanced to predict the composition dependence of selectivity ratio quantitatively,

and it is necessary to verify activity coefficient measurements made with glass electrodes by other independent methods, such as the amalgam electrode or isopiestic method. This verification has been made in a number of cases and the glass electrode method can be used with increasing confidence as more checks are made.

E. Liquid Ion Exchange Electrodes

In the last two years, considerable interest has been aroused by the commercial availability (Orion Research, Cambridge, Mass.) of specific-ion electrodes based on the liquid-liquid ion exchange principle. These electrodes consist of three liquid phases, an aqueous test solution, an aqueous reference solution, and an organic phase which physically separates the test and reference solutions. The structure of the electrode is shown in Fig. 17. The organic phase is immobilized in a membrane which is supported across the bottom of the electrode body. The reference solution is contained within the electrode body and the internal reference electrode is a silver chloride-coated silver wire.

Consider, for example, the cell



where the organic phase consists of 0.1M calcium didecylphosphate dissolved in di-n-octylphenylphosphonate⁽¹¹⁵⁾. X represents any ion which neither reacts with AgCl nor dissolves in the organic phase. The right-hand aqueous solution is within the electrode body, along with the right-hand reference electrode. The simplest situation occurs when there are no foreign ions present and the only difference between the two aqueous phases is the concentration of calcium chloride.

We have made a number of measurements (see Section VI-B) on this system using different concentrations of calcium chloride in the reference solution. The dependence of cell emf on the activity of calcium chloride in the test solution and internal reference solution is consistent, over a

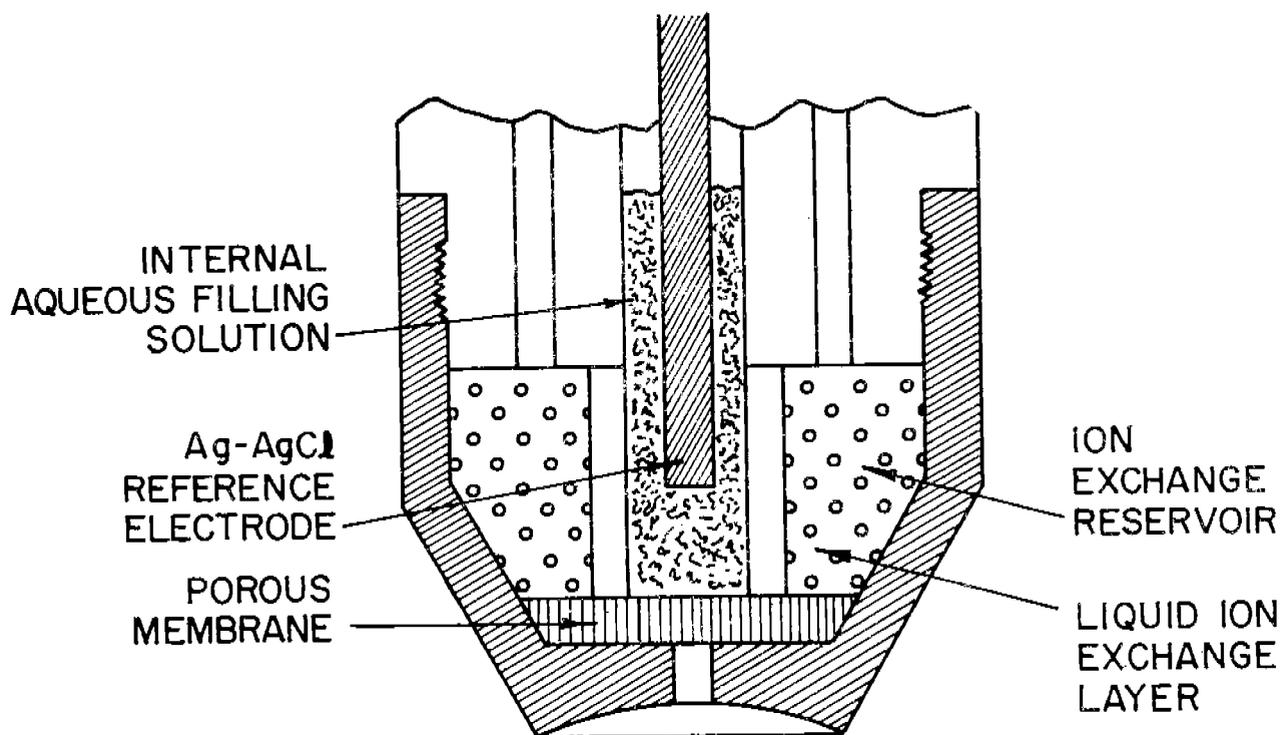


Fig. 17 Liquid ion exchange calcium-sensitive electrode structure.
The electrode dips into the test solution.

wide range, with the formal description of the organic phase as a membrane permeable only to calcium ion. The emf may be thought of as arising because the counter-ions, Cl^- , are unable to penetrate the membrane; but the actual mechanism involves ion-exchange equilibria at both interfaces between the organic and aqueous phases. The potential is generally given by a Nernst relation:

$$E = E^{\circ} + \frac{3 RT}{2 F} \ln (m \gamma)$$

where m is (for example) the molal concentration of CaCl_2 and γ is the mean activity coefficient of CaCl_2 in the test solution. E° contains a similar term for the reference solution, which is constant in composition over a series of measurements; as well as any assymetry potentials resulting from the interfacial charge distribution being different at the two interfaces.

The crucial factor in obtaining thermodynamic measurements with a system such as this is the stability of the charge distribution at the interfaces as the test solution is changed in composition; and this is determined both by the nature of the membrane used to contain the organic phase and the mechanical design of the electrode body. For example, the potential is affected by the hydrostatic pressure on the lower interface (i. e. depth of immersion), and by stirring in the test solution⁽²⁷⁾. With unstirred solutions and constant depth of immersion, typical reproducibility was ± 0.1 mv, which is adequate for the determination of thermodynamic quantities such as activity coefficients and equilibrium constants.

Liquid-ion-exchange systems have advantages which neither the glass-electrode nor amalgam electrode systems can claim, even though at the present state of the art their reproducibility is less. The most important advantage is versatility. There are potentially thousands of possible organic ion-exchange systems which could be used, and small structural changes in the solute of the organic phase may make large changes in the selectivity of the 'membrane' for particular ions. Orion

Research, Inc. presently markets liquid ion exchangers which have particular selectivity for Ca^{++} , Mg^{++} , Cu^{++} , Cl^- , ClO_4^- , and NO_3^- . New ion-exchange systems are being tested and will be available on an experimental basis to research laboratories carrying out fundamental work on these systems⁽²⁸⁾.

F. Other Apparatus

Cell Construction. The primary difficulty to be overcome in the design of the apparatus is to maintain pure, oxygen-free solutions and amalgam while permitting the solution and the amalgam to be changed rapidly. The general plan of the apparatus is shown in Fig. 18. Purification of solutions and preparation of the amalgam have already been discussed.

Two separate test cell systems and a reference cell system are all fed from the same reservoir of amalgam, thus insuring that the composition of the amalgam is identical in both the cells in which measurements are being made. While one solution is being purified, the other solution can be measured; in this way the time required to change the composition of the solution is minimized. Both the solution and the amalgam can be flowed continuously through the measuring cell, without opening the cell to the air.

The electrodes were prepared by attaching 1-cm lengths of polarographic capillary to a 1-mm i. d. capillary stem using thin-walled Teflon tubing (Fig. 19). In this way the capillary could easily be changed when it became plugged with solid material from the amalgam. Drops with a maximum diameter of 1 mm were formed at a rate of approximately one per second. The cell (Fig. 20) was constructed so the drops of amalgam from the capillary fell through a 4 mm diameter hole in the bottom of the cell, through a gas space, and into a waste compartment. Solution was prevented from flowing through this hole by a slight back-pressure of hydrogen. The amalgam was thus in contact with the solutions only during through the hole in the bottom of the cell. Fresh deoxygenated solution was then added from a solution reservoir without opening the cell to the air.

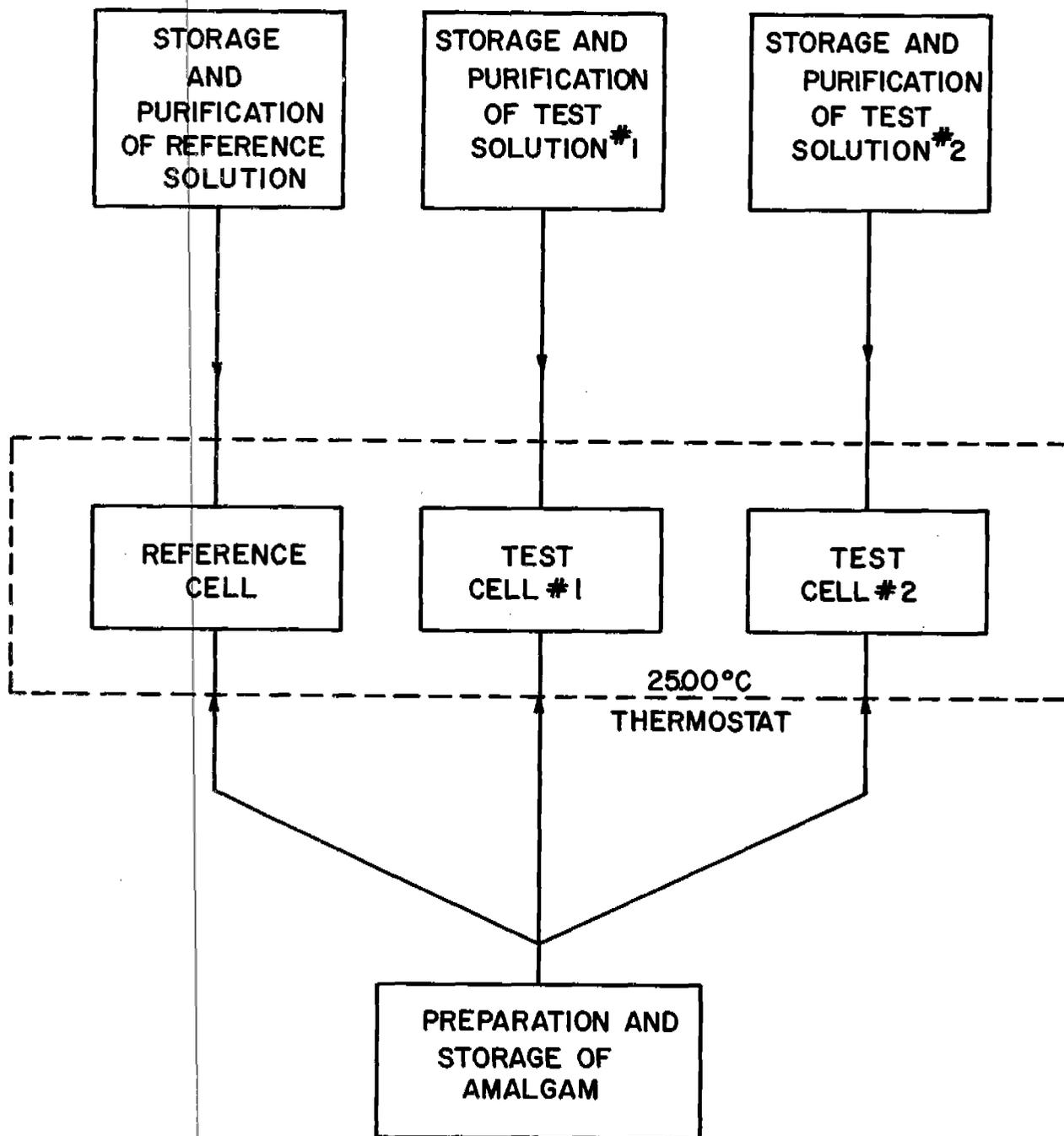


Fig. 18 General plan of apparatus.

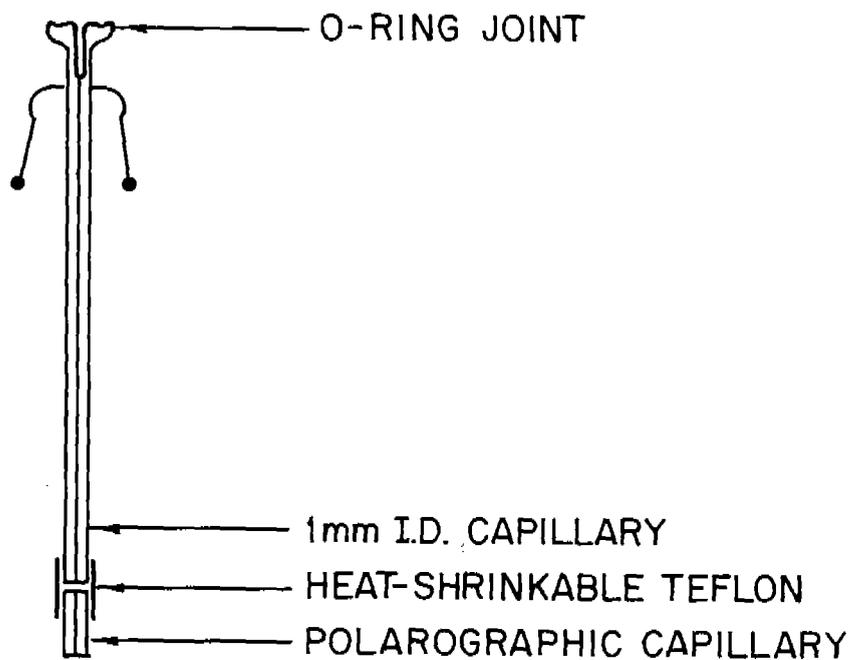


Fig. 19 Construction of dropping capillary.

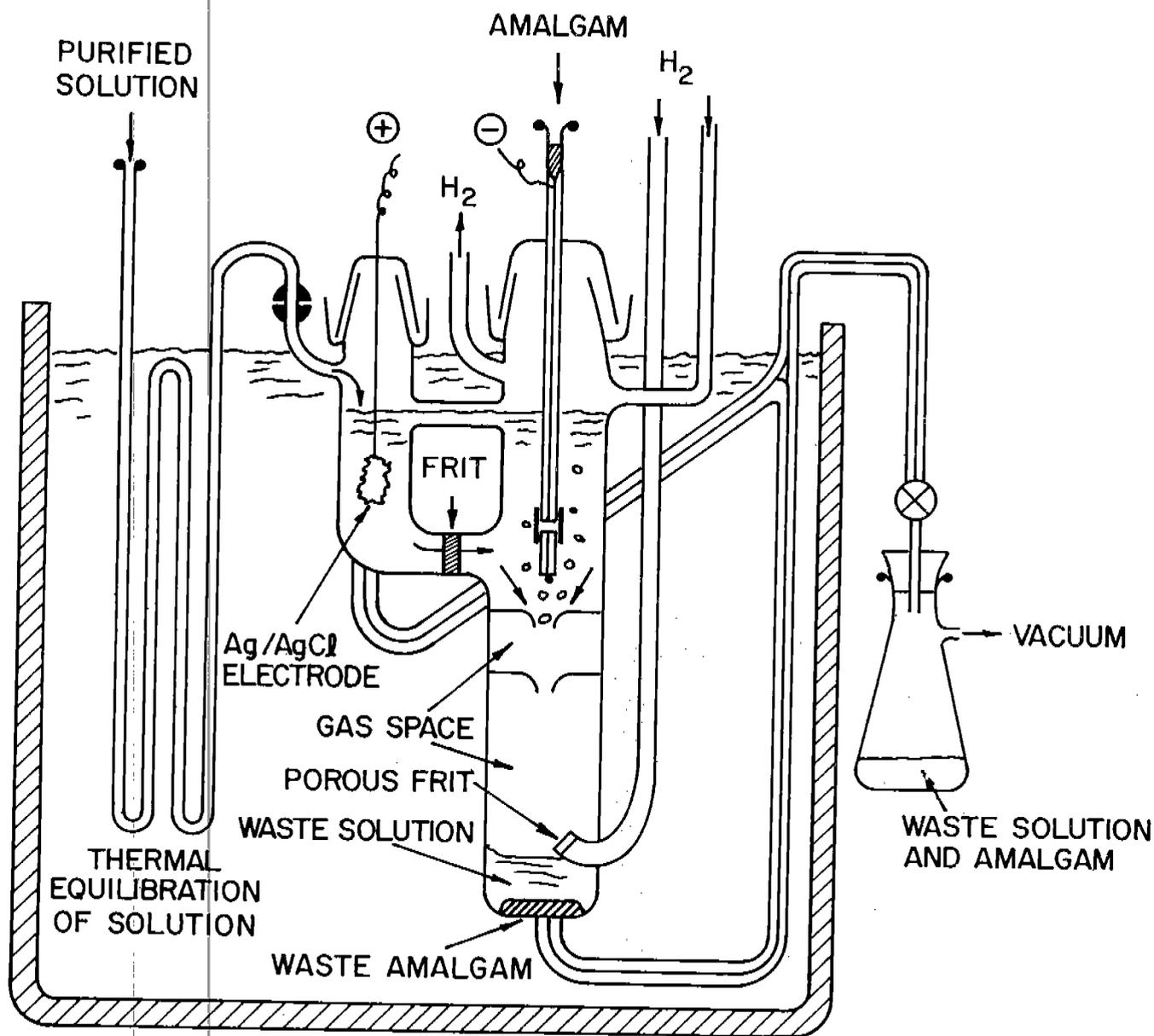


Fig. 20 Details of measuring cell. (The system contains three cells of identical design.)

The polarographic capillaries of the dropping sodium amalgam electrode eventually became plugged with small amounts of solid material, often after operation for only a few minutes. They could sometimes be cleared by tapping the cell or by applying a vacuum to the top of the amalgam column and sucking a small amount of electrolyte back into the capillary. After the latter treatment, however, the electrodes occasionally gave large and irreproducible potentials, which implied that internal cells of variable potential were being set up within the capillary. The most precise measurements and the longest operating time were obtained if the capillaries were kept scrupulously dry until after the amalgam was flowing.

Other designs of dropping capillary were tried. A larger diameter capillary with a tungsten or amalgamated copper wire plunger extending nearly to its tip gave a good control of the flow of mercury in pure water, but when used with sodium amalgam gave poorly regulated flowrate, because of the strong potential dependence of interfacial tension. Solution crept along the inside of the capillary, causing the amalgam to react within the capillary, and introduced large errors because of the increased sodium ion concentration in this small region. A design where the electrode was an amalgam pool in a Teflon cup, instead of a hanging drop, was also unsatisfactory.

Thermostat. All measurements were conducted in a thermostat at $25.00 \pm 0.02^\circ\text{C}$. The thermostat was assembled from a glass battery-jar approximately 40 cm in diameter and 30 cm high, and contained approximately 35 liters of distilled water. A uniform temperature throughout the bath was obtained by using a variable-speed stirrer (Gerald K. Heller Co., Model 2T60-100). A Bronwill Contact Thermometer (0-100°C range) was adjusted to close the control circuit of a Fisher Unitized Bath Control (Model 50) at exactly 25.00°C . The relay of the Bath Control operated an immersion heater of approximately 250 watt capacity. The temperature was measured by an ASTM calibrated thermometer accurate to $\pm 0.01^\circ\text{C}$ at 25°C .

This thermostat system can maintain the temperature of the water-bath constant at $25.00 \pm 0.02^\circ\text{C}$ for an indefinite period of time. The fluctuations observed were generally less than 0.01°C in a five-minute period. To test the response of the system to sudden temperature variations, several hundred grams of ice were introduced into the bath-water, causing the temperature to drop to approximately 24°C . Within 3 minutes, the temperature had risen to 24.97°C , and in 7 minutes to 25.03°C . Within 10 minutes after the ice had been introduced, the temperature was again constant at 25.00°C and deviated less than 0.01° during the next hour. If the stirring was stopped for a period of up to 20 minutes, the temperature of the bath drifted by less than 0.02°C . The differences in temperature between the two cells being measured are certainly be smaller than this if the bath is well-stirred.

The temperature control we have achieved is more than adequate. Since the two cells are being measured at the same time, constancy of temperature over a long period is not necessary, but the electrode surfaces in both cells should be at the same temperature. Since E is directly proportional to the absolute temperature, a difference in temperature of 0.1°C will introduce an error in E of $0.1/300$ or 0.03% . This corresponds to an error of 0.02 mv if the activity ratio is ten and will be smaller if the activity ratio is near unity. The error due to the change in E° and γ_{\pm} with temperature is an order of magnitude smaller, of the order of 0.002 mv. Thus the effects of temperature fluctuations are entirely negligible.

Electrical Measurements. Potentials were measured with a Leeds and Northrup Model K-3 potentiometer, using a Honeywell Model 104W1-G galvanometer with a sensitivity of 0.001 microamp/mm and a response time of approximately 0.2 seconds for full-scale deflection (40 mm). The standard cell (Eppley Laboratory Type 100) was calibrated against a U. S. National Bureau of Standard cell and guaranteed to have the value $1.01922 \pm .00005$ volts.

This combination can measure one volt to 0.005% accuracy, which means that the error in the potential measurement (on the 0.01 scale) may be made as small as the readability of the slide wire, 0.001 mv. This is smaller than the sensitivity of the galvanometer normally used with the potentiometer, or the stray potentials resulting from circuit contact rectification, and certainly is negligible compared to the observed precision of 0.02 - 0.05 mv.

The variation of potential during the lifetime of the drops is of considerable interest. To measure this, the galvanometer was replaced by a Tektronix oscilloscope, and the unbalance signal from the potentiometer was displayed as a function of time. A typical potential-time curve is shown in Fig. 21. The large transients occur immediately after the drop falls, when a large portion of the current passing is used to charge the electrical double layer. Within a few milliseconds, however, the potential is nearly constant. (This phenomenon was used to study the kinetics of the barium amalgam electrode. The results are described in Section VI-F.) The potential measured with a galvanometer, balancing at the moment when the needle paused in its oscillation, was $12.28 \pm .02$ mv, which agreed with the value read from a photograph of the oscilloscope screen.

The potential of the combined cell

$\text{Ag/AgCl/NaCl, H}_2\text{O/Na, Hg---Na, Hg/NaCl, MX, H}_2\text{O/AgCl/Ag}$

or (where MX represents Na_2SO_4 , LiCl , MgCl_2 , or CaCl_2) was measured during the period when the drops of both amalgam electrodes were nearly fully formed: Such potentials were reproducible to ± 0.02 mv for periods of up to an hour under favorable conditions. Changes of solution sometimes had a negligible effect on the potential but at other times produced changes as large as 0.5 mv. These large changes were attributed to

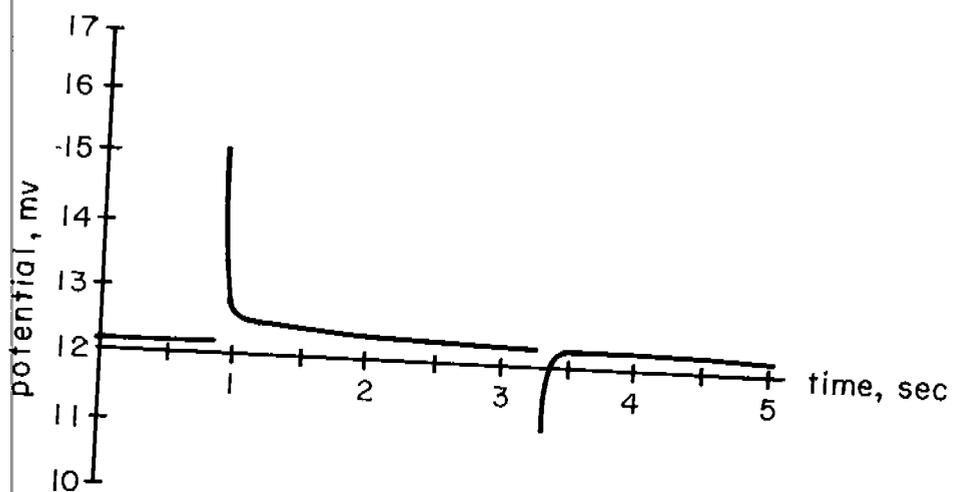


Fig. 21 Potential of the cell during the lifetime of a drop.

traces of oxygen being admitted to one of the cells, and whenever possible, the value taken to be correct was one which remained constant through several changes of solution as well as at least a half hour of amalgam flow.

VI. EXPERIMENTAL RESULTS AND DISCUSSION

A. Summary of Activity Coefficient Data Obtained*

In this section, a summary and discussion of the results of our activity coefficient measurements will be given. These results have been published as they were obtained: Measurements of the activity coefficients of NaCl in NaCl-Na₂SO₄ mixtures⁽³²⁾, NaCl-KCl, and NaCl-LiCl mixtures⁽³³⁾, NaCl-CaCl₂ and NaCl-MgCl₂ mixtures⁽³⁴⁾ were made using the sodium amalgam-silver chloride cell. Measurements of the activity coefficients of Na₂SO₄ in NaCl-Na₂SO₄ mixtures were made using a glass electrode-lead amalgam-lead sulfate cell⁽³⁶⁾. Measurements of the activity coefficients of NaCl in NaCl-BaCl₂ mixtures were made using a glass electrode silver chloride cell. These latter measurements have not yet been published and are given for the first time in this report.

Measurements were made using the combined cell

Ag/AgCl/NaCl, H₂O/Na(Hg) -- Na(Hg)/NaCl, MX, H₂O/AgCl/Ag

* The results quoted in this section have been published in detail in the following four papers:

1. "Activity Coefficient Measurements in Aqueous Sodium Chloride-Sodium Sulfate Electrolytes Using Sodium Amalgam Electrodes," by James N. Butler, Philomena T. Hsu, and John C. Synnott. *J. Phys. Chem.* 71, 910-914 (1967). (Ref. 32)
2. "Activity Coefficient Measurements in Aqueous NaCl-LiCl and NaCl-KCl Electrolytes Using Sodium Amalgam Electrodes," by James N. Butler, Rima Huston, and Philomena T. Hsu. *J. Phys. Chem.* 71, 3294-3300 (1967). (Ref. 33)
3. "Activity Coefficient Measurements in Aqueous NaCl-CaCl₂ and NaCl-MgCl₂ Electrolytes Using Sodium Amalgam Electrodes," by James N. Butler and Rima Huston. *J. Phys. Chem.* 71, 4479-4485 (1967). (Ref. 34)
4. "The Mean Activity Coefficient of Sodium Sulfate in Aqueous Sodium Sulfate-Sodium Chloride Electrolytes," by John C. Synnott and James N. Butler. *J. Phys. Chem.* 72, 2474-2477 (1968). (Ref. 36)

and the mean activity coefficient γ_{12} of NaCl in the mixed electrolyte was calculated from the known emf and concentration values using the equation

$$E = - \frac{RT}{F} \ln \frac{(m_{\text{Na}^+}) (m_{\text{Cl}^-}) (\gamma_{12})^2}{(m_{\text{Na}^+}^\circ) (m_{\text{Cl}^-}^\circ) (\gamma_{10})^2} \quad (1)$$

where m_{Na^+} and m_{Cl^-} are the molalities of Na^+ and Cl^- in the mixed electrolyte, $m_{\text{Na}^+}^\circ$ and $m_{\text{Cl}^-}^\circ$ are the molalities in the reference solution, and γ_{10} is the mean activity coefficient of NaCl in the reference solution.

Using data⁽⁴¹⁾ for the concentration dependence of the activity coefficients of aqueous NaCl, together with an approximate value of the Harned Rule coefficient, the measured activity coefficients were corrected to round values of ionic strength. At constant ionic strength, I , the logarithm of the activity coefficient of NaCl in the mixed electrolyte (γ_{12}) was found to be linearly dependent on the ionic strength fraction of the second component X_2 , according to Harned's Rule^(40, 41)

$$\log \gamma_{12} = \log \gamma_{10} - \alpha_{12} X_2 I \quad (2)$$

where γ_{10} is the activity coefficient of a solution containing only NaCl at ionic strength I (our reference solution).

Except at very low ionic strength fractions of NaCl, Harned's Rule was found to be obeyed for all the systems studied. A typical Harned Rule plot is shown in Fig. 22, for the system NaCl- CaCl_2 , and in Fig. 23 for the system NaCl- Na_2SO_4 . The deviations at low fractions of NaCl observed by us⁽³²⁾ and by Lanier⁽²⁷⁾ in the case of NaCl- Na_2SO_4 mixtures, probably reflect a systematic error resulting from the effect of sulfate ions on the silver chloride electrode; not a true thermodynamic deviation from Harned's Rule. Similar deviations⁽³⁴⁾ were observed in the NaCl- CaCl_2 and NaCl- MgCl_2 systems (see Fig. 22), and were attributed to interference by the alkaline earth metal cations with the

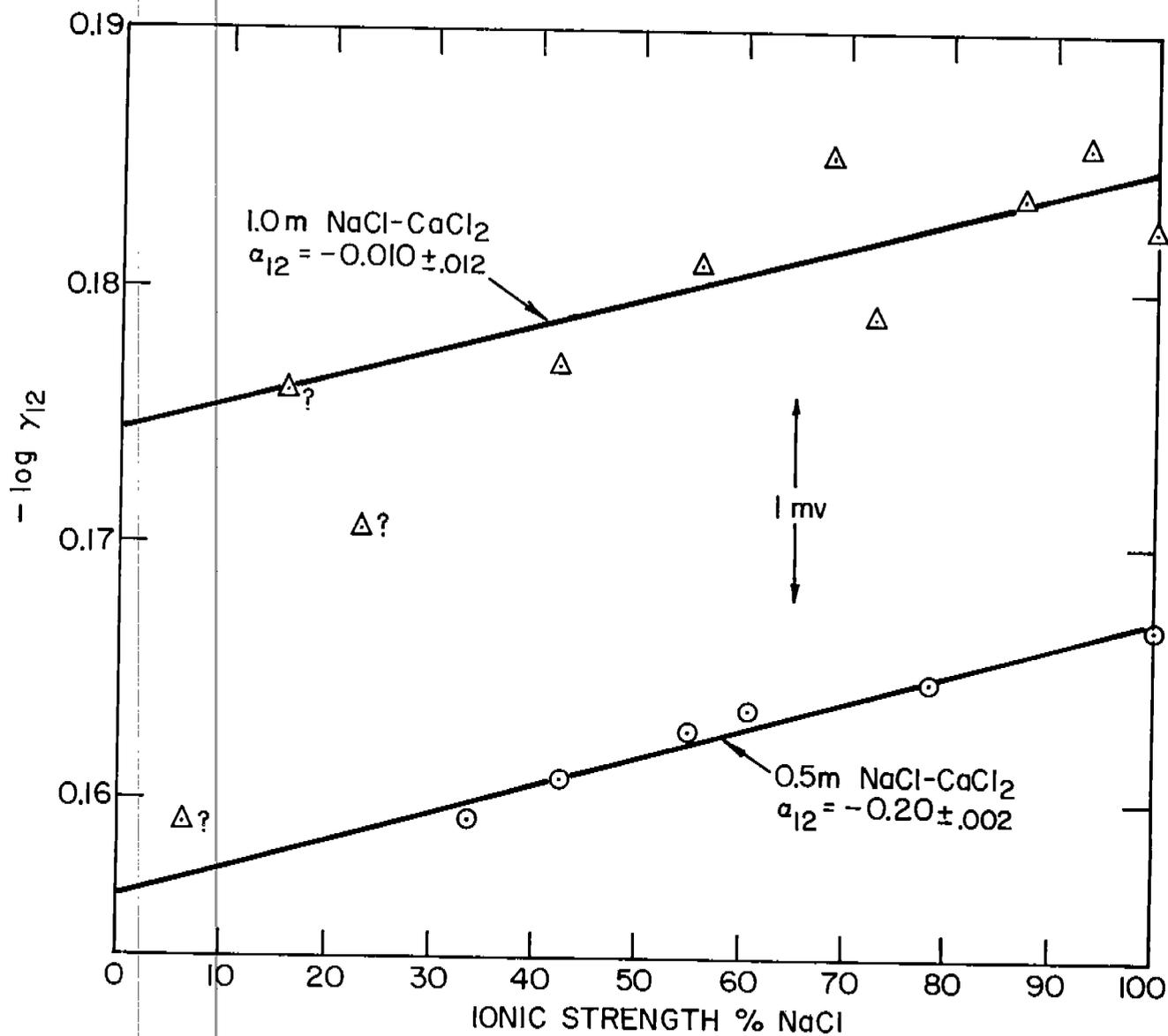


Fig. 22 Activity coefficient of NaCl in NaCl-CaCl₂ electrolytes, showing fit of experimental data to Harned's rule. The straight lines correspond to the least-squares values given in Table XIII.

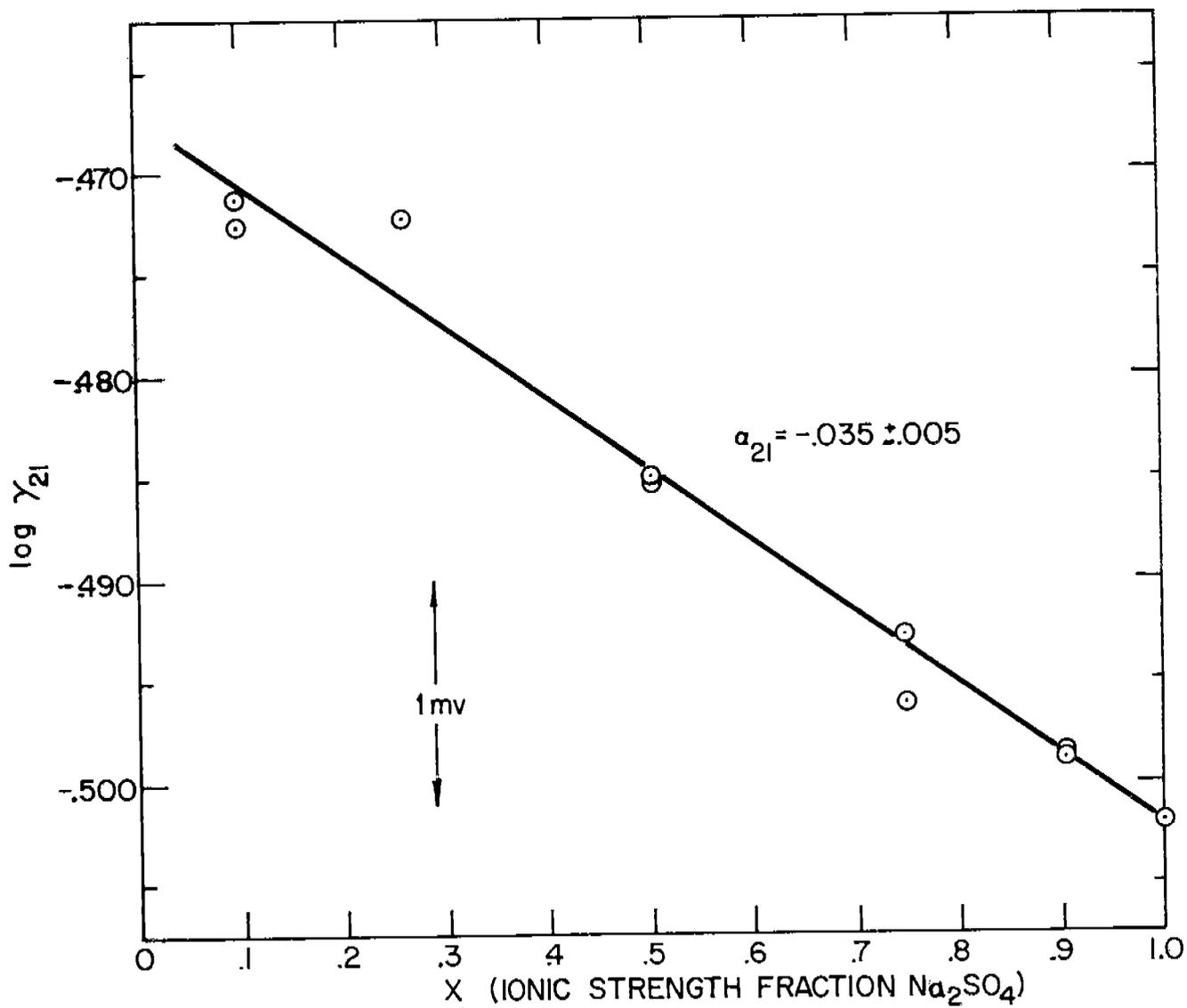


Fig. 23 Activity coefficient of Na_2SO_4 - NaCl electrolytes at $I = 1.000$ m. The straight line represents Harned's rule and was fitted by the method of least squares, allowing the intercept to vary.

sodium amalgam electrode. The detailed numerical data (except for NaCl-BaCl₂) are not reproduced here, but are given in our publications, as indicated by the reference numbers in Table XIII.

In Table XIII, the Harned Rule coefficients obtained for the various systems studied are summarized. The straight line corresponding to Harned's Rule was fit to the data by a least squares approach. Two methods were used; the results given in Table XIII are the values with the smallest limits of error.

In the first method, $\log \gamma_{10}$ was held constant at the literature^(9, 40, 41) value, and a value of α_{12} was calculated from Eq. 2 for each mixture. The mean of these values for each set, together with the 95% confidence intervals (obtained from Student's distribution) was taken to be the best value for α_{12} . This method gives heavier weight to points of higher MX/NaCl ratio.

In the second method, the experimental values of γ_{12} and X_2 were fitted to Eq. 2 by the least-squares method (assuming X_2 exact), and best values of α_{12} and γ_{10} were obtained from the slope and intercept of the straight line. These parameters, together with their 95% confidence limits (from Student's t distribution), were taken as alternate values. The least-squares value of γ_{10} obtained by our second method agrees with the literature value to better than 99% confidence for all data sets.

In Table XIII are also given the values of α_{21} , the Harned-rule coefficient for the second component MX. These were calculated from the values of α_{12} measured in this work by means of the Gibbs-Duhem relation, expressed as the equation^(40, 41) for Na₂SO₄, CaCl₂, and MgCl₂:

$$\alpha_{21} = 2\alpha_{12} - \frac{2}{2.3031} [2\phi_1^0 - \phi_2^0 - 1] \quad (3)$$

where ϕ_1^0 is the osmotic coefficient of a NaCl-H₂O solution and ϕ_2^0 is the osmotic coefficient of a MX-H₂O solution at ionic strength.

TABLE XIII

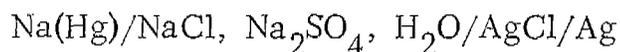
Harned Rule Coefficients Determined in this Work*

<u>MX</u>	<u>Ionic Strength</u>	<u>α_{12}</u>	<u>α_{21}</u>	<u>Ref.</u>
Na ₂ SO ₄	1.00	0.048 ± .005	(-0.034 ± .005)	32
	3.00	0.049 ± .002	(-0.032 ± .002)	
Na ₂ SO ₄	1.00	(0.048 ± .003)	-0.035 ± .005	36
LiCl	0.10	0.17 ± 0.16		33
	0.50	0.042 ± .018		
	1.00	0.045 ± .017		
	2.00	0.067 ± .016		
	3.00	0.019 ± .025		
CaCl ₂	0.20	-0.06 ± .10	(+0.2 ± 0.3)	34
	0.50	-0.020 ± .002	(-0.013 ± .010)	
	1.00	-0.010 ± .012	(-0.006 ± .010)	
	3.00	0.000 ± .006	(-0.013 ± .010)	
	6.00	+0.004 ± .003	(-0.020 ± .003)	
MgCl ₂	0.50	-0.065 ± .040	(-0.09 ± .12)	34
	1.00	-0.012 ± .006	(-0.006 ± .021)	
	2.00	-0.012 ± .006	(-0.014 ± .013)	
	3.00	-0.009 ± .009	(-0.016 ± .019)	
	5.00	-0.002 ± .002	(-0.005 ± .004)	
	6.00	0.000 ± .002	(-0.002 ± .002)	
BaCl ₂	0.1	-0.05 ± .02		(See Table XIV)
	0.2	-0.07 ± .02		
	0.5	+0.040 ± .005		
	1.0	+0.005 ± .002		

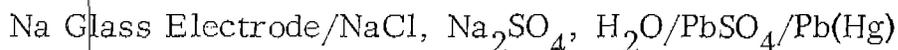
* Component 1 - NaCl, Component 2 - MX
 Values in parenthesis are calculated using osmotic coefficients (41)
 Errors are 95% confidence limits.

The osmotic coefficients used were those tabulated by Robinson and Stokes⁽⁴¹⁾. The values of α_{21} obtained for the NaCl-CaCl₂ system agree within experimental error with the corresponding values obtained from isopiestic data⁽³⁰⁾. Further comparison with other experimental data is made below.

NaCl-Na₂SO₄ Electrolytes. The results of five separate studies on the system NaCl-Na₂SO₄ are compared in Fig. 24. Our first measurements⁽³²⁾ were made using the cell



and gave the activity coefficients of NaCl in the mixed electrolyte directly. Our second set of measurements⁽³⁶⁾ was made using the cell



which gave directly the activity coefficients of Na₂SO₄ in the mixed electrolyte. The work of Lanier⁽²⁷⁾ and Gieskes⁽³¹⁾ was done with the cell



and presumably should give the same results as our first set of experiments. Platford's measurements^(35a) were made by the isopiestic method. Some more isopiestic measurements have been made recently by Rush⁽³⁸⁾ and in a private communication, he stated that his results agreed with our measurements; but detailed data were not available at the time this report was prepared.

At high ionic strengths, there is reasonably good agreement between the results of various workers, but at ionic strength 1.0 and below, the discrepancies seem to be outside the expected limits of error

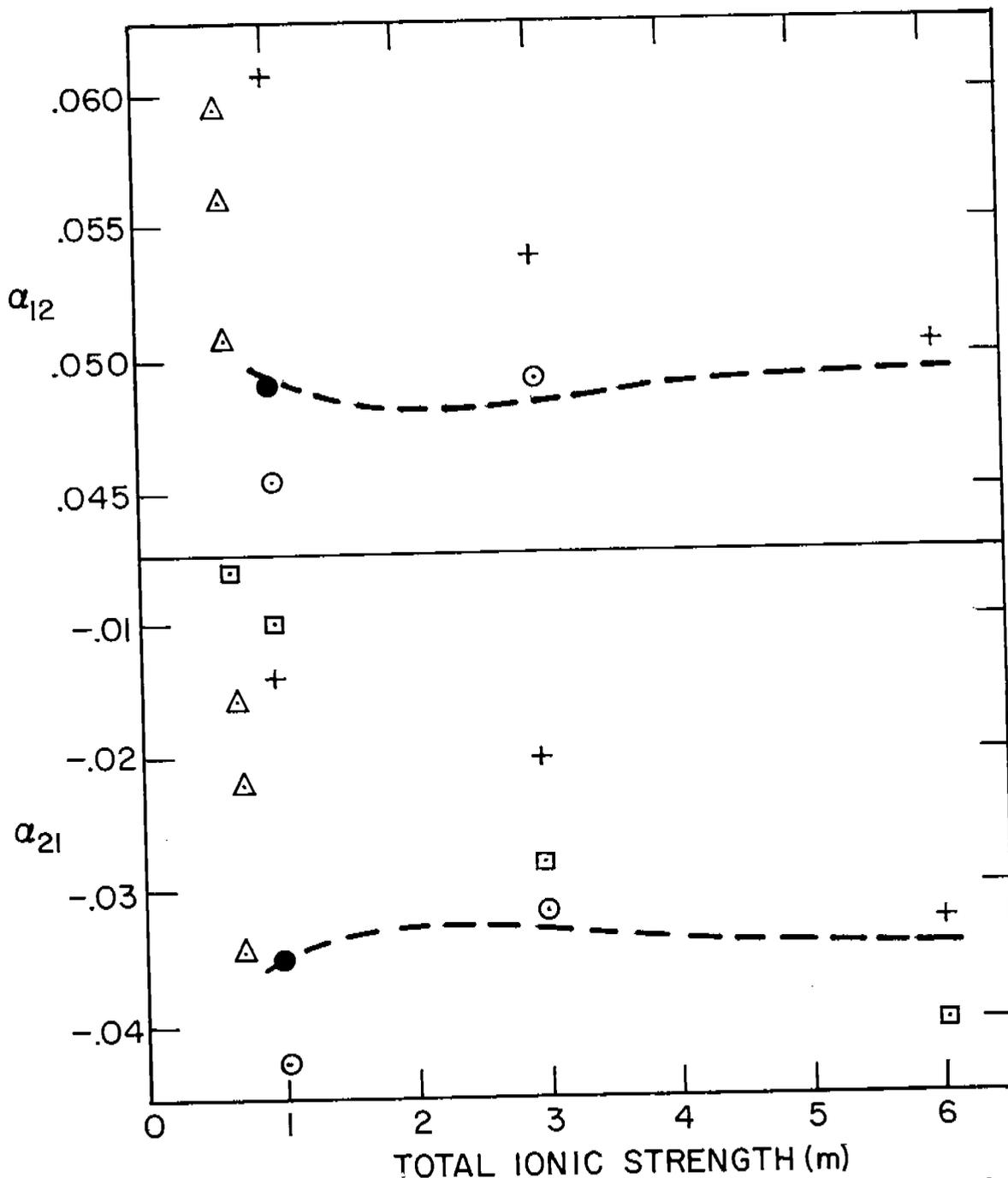


Fig. 24 Variation of the Harned rule coefficients with ionic strength for the system NaCl-Na₂SO₄.

- Calculated
- \circ This work (32)
- \bullet This work (36)
- $+$ Lanier (27)
- Δ Gieskes (31)
- \square Platford (35a)

for the experimental techniques employed (e. g. ± 0.005 in α_{12}). Furthermore, there appears to be a systematic decrease in both α_{12} and α_{21} according to the data of Lanier and Platford, a result which is inconsistent with Harned's Rule being obeyed for each component. The calculated curves in Fig. 24 were obtained as follows:

If both electrolytes obey Harned's rule, then thermodynamic cross-differentiation relations require that a further test of thermodynamic consistency be satisfied^(40, 41). The quantity

$$S' = 6 \alpha_{12} + 3 \alpha_{21} \quad (4)$$

should be independent of ionic strength. Lanier⁽²⁷⁾ found that S' varied with ionic strength and from this concluded that the activity coefficients of Na_2SO_4 did not necessarily obey Harned's rule. Our data show that S' is 0.14 at $I = 1.0$ and 0.20 at $I = 3.0$, compared with 0.32 and 0.26, reported by Lanier.

If S' is assumed to be independent of ionic strength, then the precise dependence of α_{12} and α_{21} on ionic strength can be calculated. Combining Eq. 3 and 4, we obtain

$$\alpha_{12} = (S' + 3B)/12 \quad (5)$$

$$\alpha_{21} = (S' - 3B)/6 \quad (6)$$

where B is defined by

$$B = \frac{2}{2.303I} [2 \phi_1^0 - \phi_2^0 - 1] \quad (7)$$

Using tabulated values⁽⁴¹⁾ for the osmotic coefficients of NaCl and Na_2SO_4 , B can be calculated as a function of ionic strength and a value for S' can be chosen which best fits the experimental data

at high values of ionic strength. In Fig. 24, the broken lines are calculated values of α_{12} and α_{21} based on the assumption $S' = 0.190$. Increasing the assumed value of S' makes both α_{12} and α_{21} more positive, but does not change the shape of the curves.

On the other hand Platford^(35a) has stated that Harned's rule is not obeyed for NaCl in NaCl-Na₂SO₄ electrolytes and thus he did not calculate values of α_{12} from his data. All the EMF data indicates that Harned's rule is obeyed for NaCl; and our studies⁽³⁶⁾ have shown directly that Harned's rule is obeyed for Na₂SO₄. Furthermore, the unpublished work of Rush⁽³⁸⁾ apparently has verified the validity of Harned's rule for both components.

Thus, at the present time, having analyzed critically all the available data, we may conclude regarding the system NaCl-Na₂SO₄:

(a) Harned's rule is obeyed for both components of NaCl-Na₂SO₄ electrolyte mixtures.

(b) The published value of osmotic coefficients⁽⁴¹⁾ can be used to predict the variation of α_{12} and α_{21} with ionic strength if $S' = 0.190$ (obtained at $I \geq 3$) is assumed to be independent of ionic strength.

(c) The best values of the Harned rule coefficients in the ionic strength range from 1 to 6 are $\alpha_{12} = 0.048 \pm 0.003$ and $\alpha_{21} = -0.035 \pm 0.005$, essentially independent of ionic strength.

There is no clear reason for the discrepancy between our measurements and those of Lanier and Platford, but we believe our values of Harned rule coefficients are more likely to be correct, since they have been obtained by two independent experiments using both chloride-reversible and sulfate-reversible electrodes, and are also consistent with a thermodynamically based extrapolation from higher ionic strengths, where all results are in agreement.

The behavior of the Harned rule coefficients for this system at ionic strengths below 0.5 is not yet established. This is of theoretical rather than practical interest, since in this range even large deviations

from the above values will not introduce appreciable error in calculated activity coefficients.

NaCl-KCl Electrolytes. Although we attempted to measure activity coefficients in NaCl-KCl electrolytes using sodium amalgam electrodes⁽³³⁾, the kinetic interference of the sodium and potassium ion reactions was so great that results of sufficient accuracy could not be attained. Nevertheless, we obtained a general confirmation of the theory of amalgam electrodes in systems with more than one cation, as described in Section III-E; and our results were consistent with the isopiestic data^(13, 14, 17) of Robinson on this system.

NaCl-LiCl Electrolytes. Our measurements⁽³³⁾ were made using the cell Na(Hg)/NaCl, LiCl, H₂O/AgCl/Ag. The only other data on this system are the isopiestic measurements of Robinson and Lim⁽¹⁵⁾, which give $\alpha_{12} = 0.037$ at 2.00 m and 0.035 at 3.00 m. Within the confidence limits, our data (Table XIII) agree with $\alpha_{12} = 0.035$ for all points except 2.00 m. The least-squares value of γ_{10} obtained agrees with the literature value to better than 99% confidence.

Although our experiments have shown general agreement, we have not been able to attain the precision afforded by the isopiestic method. At higher ionic strengths, the potential measurements were irreproducible. At lower ionic strengths, although the measurements were reproducible, α_{12} is uncertain because the error in α_{12} for a given error in slope varies inversely with the ionic strength. Nevertheless, these results are useful because they provide a completely independent check on the isopiestic method. A good approximation for NaCl-LiCl electrolytes appears to be to use $\alpha_{12} = -0.035$ independent of ionic strength below 4 m, decreasing to -0.033 at 6 m.

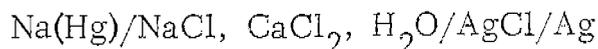
From the osmotic coefficients⁽⁴¹⁾ of NaCl and LiCl solutions, we can obtain a value of α_{21} , which will give the activity coefficients of LiCl in the mixed electrolytes. For 1-1 electrolytes, if Harned's rule is obeyed by both components, the Gibbs-Duhem relation becomes^(40, 41)

$$\alpha_{21} = \alpha_{12} + \frac{2}{2.303I} (\phi_2^0 - \phi_1^0) \quad (8)$$

The second term in this equation is 0.070 for ionic strengths between 1 and 3 m, increases to 0.073 at 0.5 m, and increases to 0.075 at 6 m. Taking $\alpha_{12} = -0.035$ as a representative value, we obtain $\alpha_{21} = +0.035$ for ionic strengths below 3 m, increasing to +0.040 at ionic strength 6 m. Since α_{12} and α_{21} are both virtually independent of ionic strength, their sum is also independent of ionic strength and the thermodynamic cross-differentiation consistency test^(41,41) is satisfied. The isopiestic data⁽¹⁵⁾ show small deviations from Harned's rule at high ionic strengths, but these are negligible below 4 m.

Thus, as we saw for the NaCl-Na₂SO₄ system, a single value for α_{12} and a single value of α_{21} suffice to calculate the activity coefficients of NaCl-LiCl electrolytes, at all ionic strengths, for any requirements but the most exacting.

NaCl-CaCl₂ Electrolytes. The experimental results of five separate studies are summarized in Fig. 25. Our measurements⁽³⁴⁾ were made with the cell



and gave the activity coefficient of NaCl in the mixed electrolyte directly. Lanier⁽²⁷⁾, Fitzgerald and Mangelsdorf⁽²¹⁾, and Moore and Ross⁽²⁶⁾ all used a similar cell with the sodium amalgam electrode replaced by a cation-sensitive glass electrode. Robinson and Bower⁽³⁰⁾ used the isopiestic method.

In general, the agreement is excellent, with the exception of the two values of α_{12} marked with a question mark, which are apparently in error because of errors in values obtained close to 100% NaCl. With our first least-squares method of calculating α_{12} , these points are given exceptionally high weight, but when the second method is used, the same data give Harned rule coefficients with much smaller confidence limits, in agreement with those of other workers.

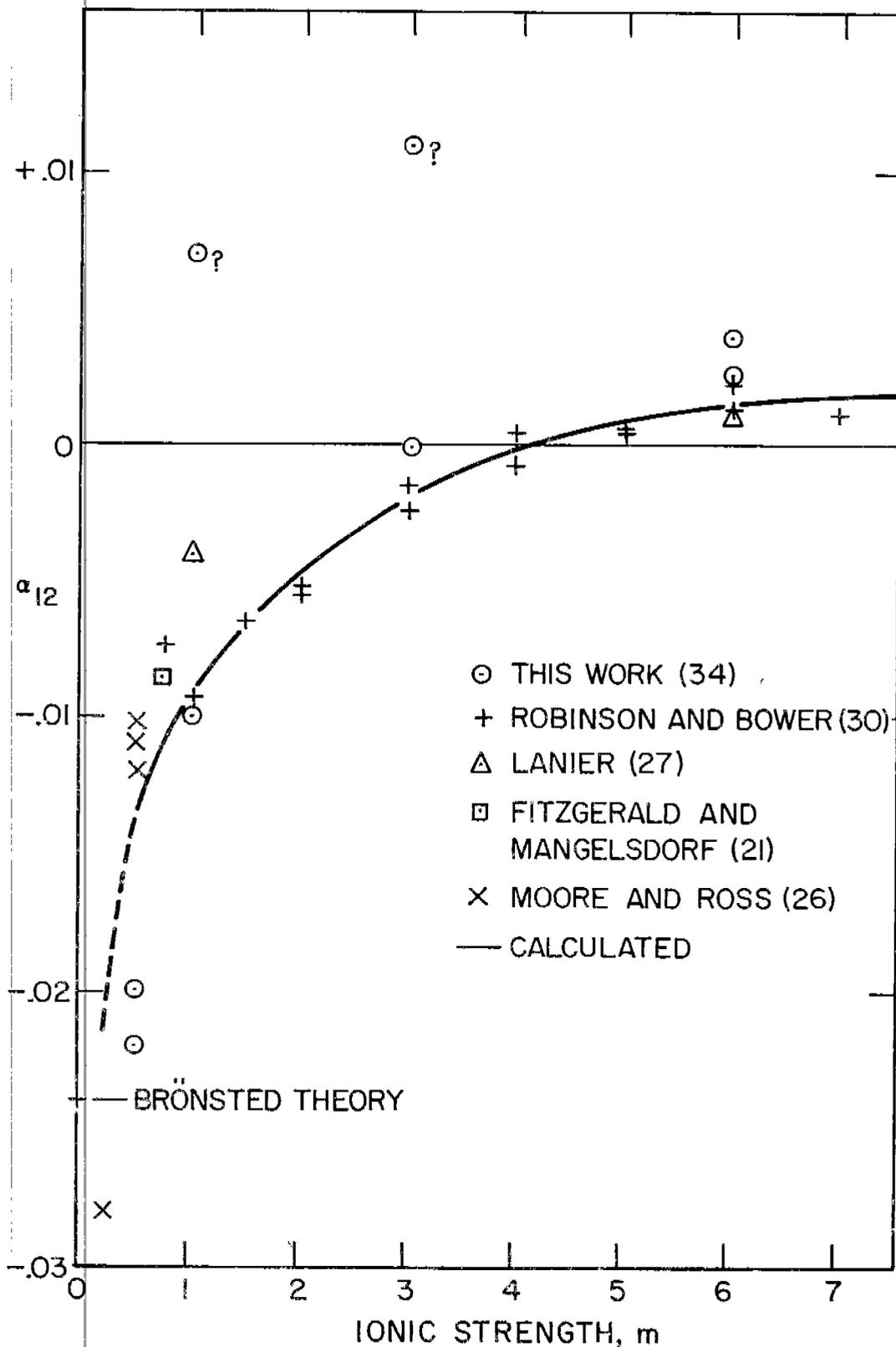


Fig. 25 Dependence of the Harned-rule coefficient α_{12} on ionic strength for NaCl-CaCl₂ electrolytes. The curve was calculated from osmotic coefficients as described in the text.

The range of ionic strengths below 1.0 is discussed in more detail in Section VI-C of this report, and we will only point out here that both our results and those of Moore and Ross indicate that α_{12} tends to much more negative values than is predicted by the Bronsted theory⁽³⁰⁾. There appears to be evidence from Friedman's ionic solution theory, as well as from experiments on other solution parameters such as density and viscosity^(97a) that the Harned rule coefficients may tend toward infinite values at zero ionic strength. The Bronsted theory gives an excellent prediction of the experimental results in the region around 0.5 m. At ionic strengths below 0.2 m, the deviations of γ_{12} from the extended Debye Huckel theory are in any case quite small so that this apparently sharp trend is not very significant for most purposes.

Bagg and Gregor⁽²⁰⁾ measured potentials across calcium stearate membranes separating aqueous solutions containing both NaCl and CaCl₂ at ionic strengths from 0.01 to 0.8 m. They did not calculate Harned-rule coefficients from their data, but stated that specific interaction effects were small compared to the errors in their measurements. This observation is consistent with the small magnitude of α_{21} for the NaCl-CaCl₂ system in the range between 0.5 and 1.0 m.

NaCl-MgCl₂ Electrolytes. Our results for the system NaCl-MgCl₂ are compared in Fig. 26 with those obtained by other investigators and the theoretical curve calculated from osmotic coefficients as described above.

Our measurements⁽³⁴⁾ were made with the cell



and those of Lanier⁽²⁷⁾, and Fitzgerald and Mangelsdorf⁽²¹⁾ were made with the corresponding cell using a cation-sensitive glass electrode. Platford has sent us the results of his isopiestic measurements⁽³⁷⁾, and has also quoted some unpublished work of Wu, Rush and Scatchard⁽³⁷⁾. All these data are included on Fig. 26.

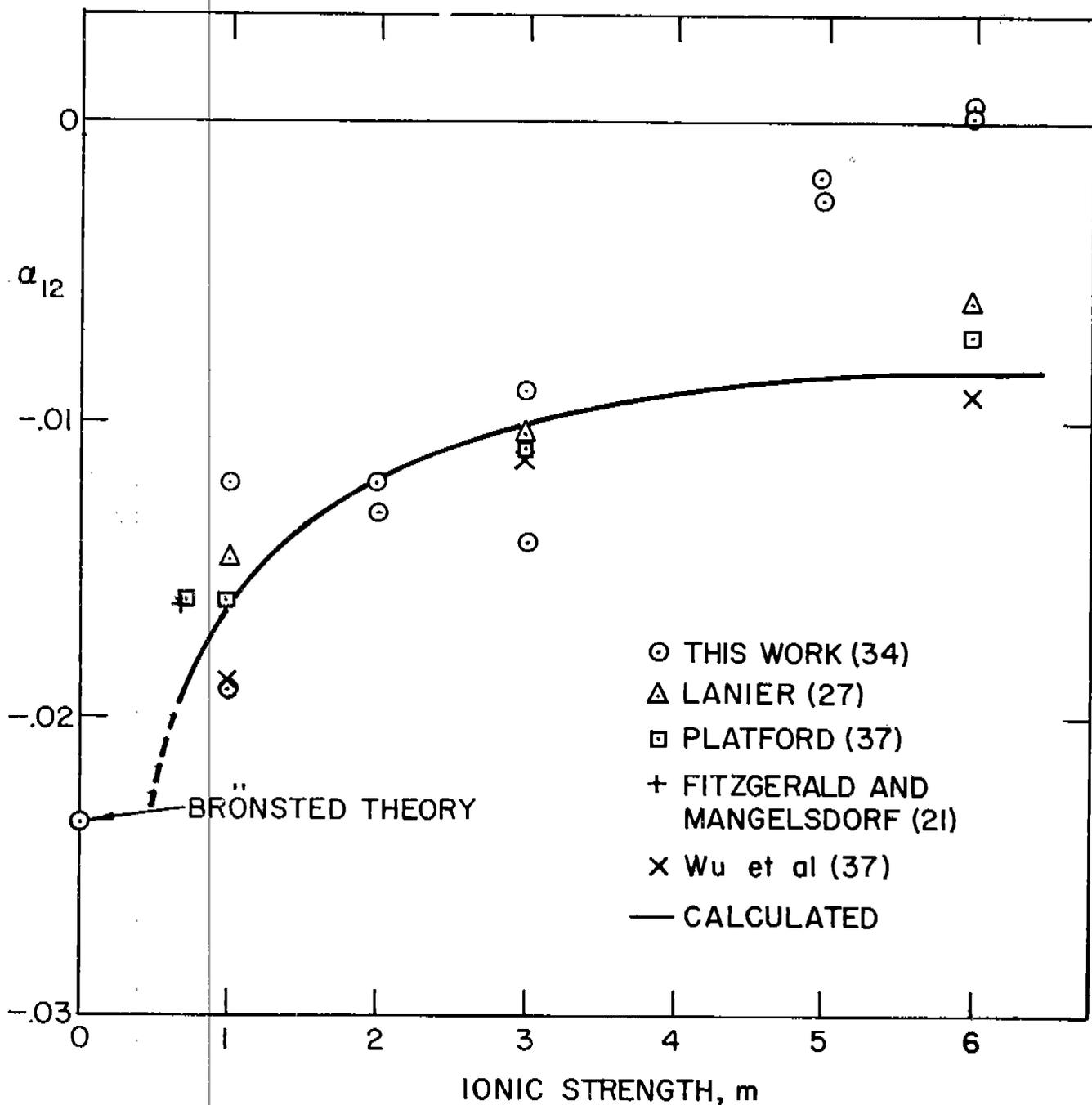


Fig. 26 Dependence of Harned rule coefficient on ionic strength for the system NaCl-MgCl₂.

Our data obtained at ionic strengths 5.0 and 6.0 differ substantially from the results of the theoretical calculation, the isopiestic results and Lanier's glass electrode measurements, all of which agree with each other. This discrepancy is not readily explainable. Our data at these ionic strengths were the most precise we have obtained, and thus it is unlikely that a random error of this magnitude could be present. On the other hand, there is no obvious systematic error which would cause deviations of this magnitude and direction without also causing apparent deviations from Harned's rule. We did not observe such deviations. Nevertheless, the overwhelming weight of evidence is that α_{12} is -0.009 to -0.010 at $I = 6.00$, and not near zero as our data have indicated.

Up to the present time, no attempt has been made to measure α_{21} directly in NaCl-MgCl₂ solutions, which would provide an unambiguous confirmation of the results at high ionic strengths. The reason for lack of information in this case is that an electrode directly responsive to magnesium ion in the presence of sodium ion has not been available. Although magnesium amalgam electrodes cannot be used in this situation (see Section IV-A) because of their irreversibility, it may be possible to obtain some results using liquid ion exchange electrodes, as discussed in Section VI-B. This has not yet been done.

We have computed a value of α_{12} for the NaCl-MgCl₂ system at zero ionic strength using the Brønsted theory, following the scheme described by Robinson and Bower⁽³⁰⁾ for NaCl-CaCl₂. To obtain a value for the constant B_c , which describes the deviation (due to specific ionic interactions) of the activity coefficients of pure MgCl₂ in water from the Debye-Hückel theory, we calculated values of B_c from tabulated activity coefficients of MgCl₂ in water⁽⁴¹⁾ using Eq. 21 of ref. (30)

$$\log \gamma_c = 2 \log \gamma^{st} + 4/9 I B_c$$

where

$$\log \gamma^{\text{st}} = \frac{-A I^{\frac{1}{2}}}{1 + 1.5 I^{\frac{1}{2}}}$$

A is the Debye-Hückel constant, and I is the ionic strength.

Thus each value of the activity coefficient for pure MgCl_2 yields a value for B_C . At ionic strengths greater than 2 ($m = 0.7$), B_C was found to be a linear function of I and, when extrapolated to zero ionic strength, gave $B_C = 0.170$. (This is comparable to the value obtained by Robinson and Bower for CaCl_2 , $B_C = 0.176$.)

The Harned-rule coefficients were then calculated from Eq. 24 and 25 of ref (30)

$$\alpha_{12} = \alpha_B = 2/3 B_B - 1/6 B_C$$

$$\alpha_{21} = \alpha_C = 1/9 B_C - 2/3 B_B$$

at $I = 0$. Using Robinson and Bower's value (which they calculated from the activity coefficients of pure aqueous NaCl solutions) $B_B = 0.007$, we obtain for our NaCl- MgCl_2 solutions at zero ionic strength, the limiting values

$$\alpha_{12} = -0.0236$$

$$\alpha_{21} = +0.0142$$

at $I = 0$, which are close to the value obtained by Robinson and Bower⁽³⁰⁾ for NaCl- CaCl_2 solutions. The calculated value of α_{12} at zero ionic strength is shown on Fig. 26.

Thus we see that the dependence of α_{12} on ionic strength is similar for the systems NaCl- MgCl_2 and NaCl- CaCl_2 , but α_{12} is more positive for the latter system. Our experiments have provided additional confirmation of the values for the Harned-rule coefficients which were obtained by other methods.

NaCl-BaCl₂ Electrolytes. Activity coefficient measurements of NaCl in NaCl-BaCl₂ electrolytes were attempted using barium amalgam electrodes (see section VI-F) but were not sufficiently accurate due to kinetic interference between the sodium ion and the barium ion reactions. However, we have made some measurements at low ionic strengths using a sodium ion-selective glass electrode.

The experimental technique was the same as we used in our studies of Na₂SO₄-NaCl electrolytes⁽³⁶⁾ (see Section V-D), except that an Ag/AgCl reference electrode was used. Lanier⁽²⁷⁾ made measurements of this type at ionic strengths of 1, 3 and 5 m; and the isopiestic results of Robinson and Bower⁽²³⁾ at ionic strengths from 0.75 to 5 m were consistent with the results of Lanier.

Our results are summarized in Table XIV, and some data are plotted in Fig. 27. The Harned rule coefficient α_{12} appears to go through a maximum positive value at an ionic strength of 0.2 m, and then become negative, at lower ionic strengths. From the present data, this trend appears to be outside experimental error, but when corrections to round values of ionic strength are made, it may change. Further measurements at ionic strengths below 0.2 m will be made to verify this trend. At 1 m, our results agree with those of Lanier⁽²⁷⁾ and those of Robinson and Bower⁽²³⁾. By analogy with the CaCl₂-NaCl system, and the MgCl₂-NaCl system, we might expect that α_{12} would tend toward large negative values at low ionic strengths. The maximum positive value is an unusual effect, and is not predicted by any theoretical model.

B. Calcium Activity Measurements Using a Liquid Ion Exchange Electrode*

During the past two years, a considerable amount of work has been published which involves the use of the calcium-selective liquid ion exchange electrode system⁽¹⁰⁵⁻¹¹⁵⁾. All of these studies, however, have been limited to relatively low concentrations of calcium ion (< 0.1 m) because the commercial calcium-selective electrode systems use an internal reference solution of approximately this concentration. In this report

* Submitted for publication in Science.

TABLE XIV

Activity Coefficient of NaCl in NaCl-BaCl₂ Electrolytes

I = 0.1 m

<u>% I NaCl</u>	<u>Total Ionic Strength</u>	<u>ΔE_{obs} (mv)</u>	<u>$-\log \gamma_{12}^*$</u>
100	0.1012	0	0.1096
88.14	0.1007	3.9	0.1060
70.78	0.0999	11.3	0.1054
49.88	0.0990	23.0	0.1096
29.07	0.0982	38.9	0.1055
15.58	0.0976	56.8	0.1095

$$\alpha_{12} = -0.05 \pm 0.02$$

I = 0.2 m

100	0.1960	0	0.1331
81.76	0.1966	7.45	0.1365
68.08	0.1970	13.75	0.1422
45.63	0.1977	25.9	0.1398
34.29	0.1980	35.0	0.1448
13.89	0.1986	60.5	0.1451

$$\alpha_{12} = +0.07 \pm 0.02$$

* Not corrected to round values of ionic strength.

TABLE XIV (Cont.)

I = 0.5 m

<u>% I NaCl</u>	<u>Total Ionic Strength</u>	<u>ΔE_{obs} (mv)</u>	<u>$-\log \gamma_{12}^*$</u>
100	0.5187	0	0.1669
85.64	0.5191	5.75	0.1712
65.69	0.5197	15.13	0.1774
52.29	0.5201	21.44	0.1701
28.58	0.5208	40.86	0.1819
12.22	0.5214	55.02	0.1867

$$\alpha_{12} = +0.040 \pm 0.005$$

I = 1.0 m

100	1.0738	0	0.1832
79.55	1.0433	8.0	0.1818
73.06	1.0342	11.5	0.1867
51.02	1.0034	24.0	0.1901
34.07	0.9798	36.1	0.1840
17.23	0.9563	56.3	0.1849

$$\alpha_{12} = +0.005 \pm 0.002$$

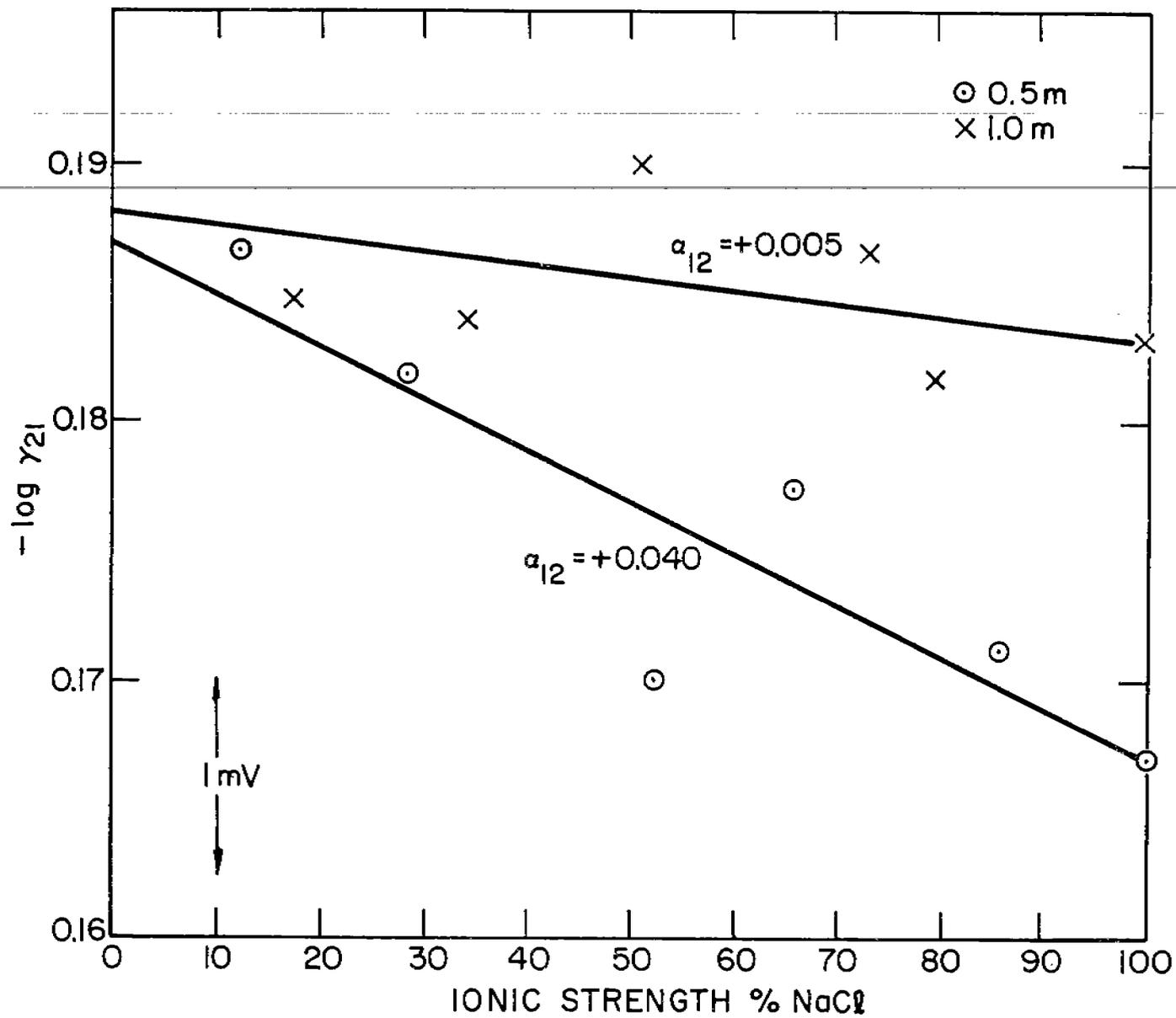


Fig. 27 Harned rule plot for activity coefficient of NaCl in NaCl-BaCl₂ electrolytes.

we give the results of experiments carried out to see whether the activity of calcium salts could be measured at concentrations above 1.0 m.

We have made a number of measurements of the potential of the cell



where the organic phase consists of 0.1 m calcium didecylphosphate dissolved in di-n-octylphenylphosphonate⁽¹⁰⁵⁾. X represents any ion which neither reacts with AgCl nor dissolves in the organic phase. The right-hand aqueous solution is within the electrode body, along with the right-hand reference electrode. The simplest situation occurs when there are no foreign ions present and the only difference between the two aqueous phases is the concentration of calcium chloride.

In our first set of measurements, both test and reference solutions consisted of CaCl_2 (pH 6-8) solutions of various concentrations. In order to eliminate any bias potential arising from asymmetry in charge on the membrane, two identical cells with matched Ag/AgCl reference electrodes were used, one containing the reference solution, which was also the internal filling solution, and the other containing the test solution (concentration m). The calcium ion-exchange electrode body and the ion exchanger were those marketed commercially by Orion Research Inc. This electrode body was transferred back and forth between the two cells, and the potential recorded as a function of time, by means of an expanded-scale pH meter and potentiometric recorder, as described in Section V-E.

Instability and deviations from Nernstian behavior, which were observed at high concentration of both internal and external solutions, were partly due to deterioration of the silver-silver chloride reference electrodes. Even though all solutions were saturated with AgCl, this apparently did not completely prevent the deterioration. However, by

repeatedly replacing an unstable reference electrode with a stable one and making the measurements as quickly as possible, we were able to obtain reproducible measurements up to 5.5 m.

The dependence of cell potential on the activity of CaCl_2 in the test solution and reference solution (Fig. 28) is consistent, over a wide range, with the formal description of the organic phase as a membrane permeable only to calcium ion. The potential may be thought of as arising because the counter-ions (Cl^-) are unable to penetrate the membrane, but the actual mechanism involves ion-exchange equilibria at both organic-aqueous interfaces. From Fig. 28, the potential is seen to be given by the expected Nernst relation;

$$E = E^{\circ} + \frac{3 RT}{2 F} \ln (m \gamma) \quad (1)$$

where m is the molal concentration of CaCl_2 and γ is the mean activity coefficient of CaCl_2 in the test solution. E° contains a similar term for the reference solution, which is constant in composition over a series of measurements; as well as any asymmetry potentials resulting from the interfacial charge distribution being different at the two interfaces. The higher is the concentration of the internal solution, the higher is the concentration of external test solution for which equation (1) is obeyed. On the other hand, with concentrated internal solutions, equation (1) is not obeyed for dilute test solutions. Thus the most accurate measure of calcium activity in a given solution is obtained if the internal solution is similar in concentration to the test solution. Even in 5 to 6 m CaCl_2 ($\log m \gamma = 1.0$), equation (1) is obeyed over a narrow range of activities if the internal solution and external solution are matched.

In a second set of experiments we attempted to measure the activity of calcium in mixed solutions containing sodium ion. The Orion electrode was used without any modification (internal solution 0.1 m CaCl_2) and the test solution consisted of NaCl-CaCl_2 mixtures at total ionic strengths of

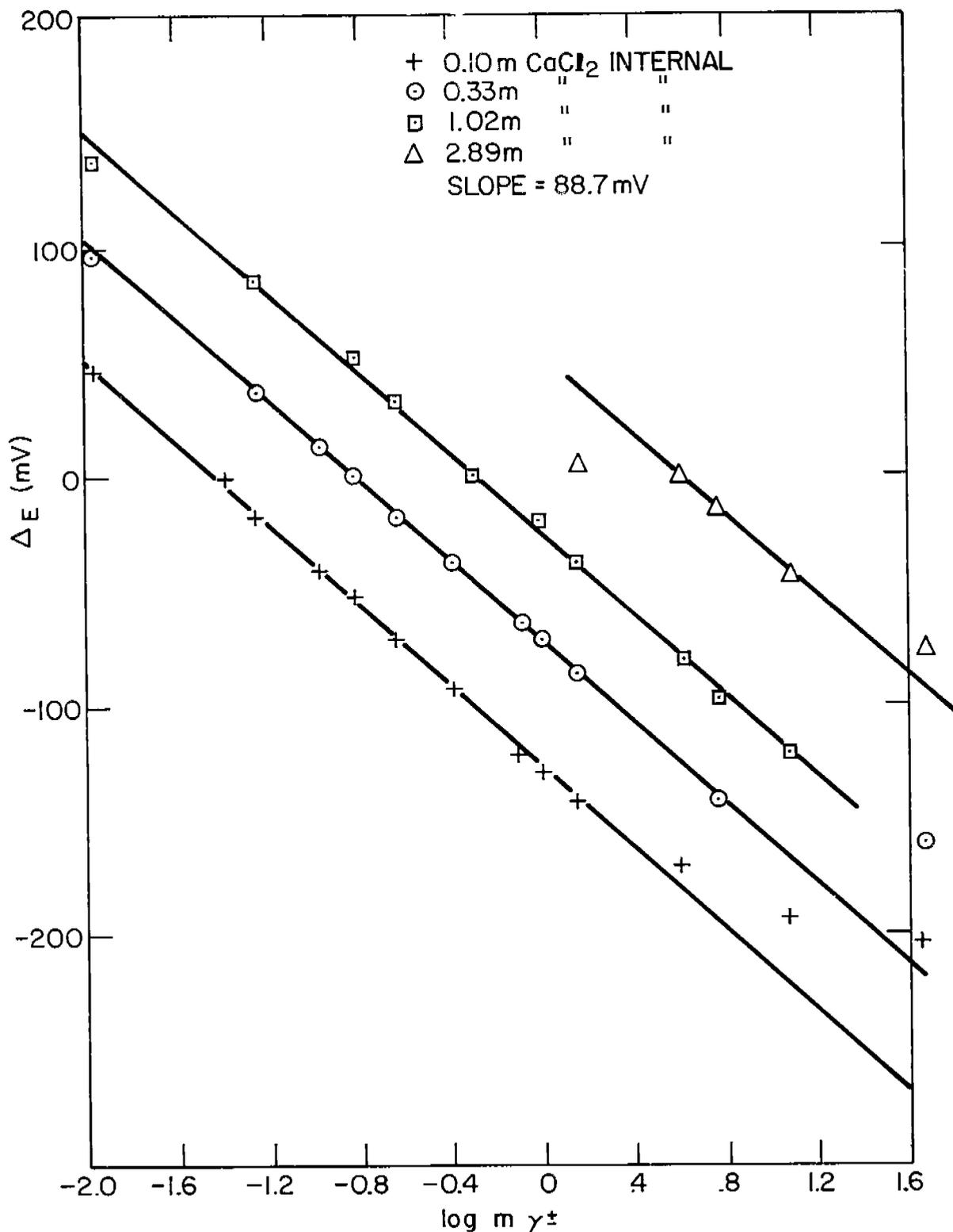


Fig. 28 Response of the calcium-sensitive liquid ion exchange electrode with different concentrations of CaCl_2 as internal reference solution. The abscissa values (m) refer to the molal concentration and mean activity coefficient of CaCl_2 in the test solution. Through each set of data, a line of theoretical slope (88.7 mv) has been drawn, as predicted by Equation (1).

1, 3, and 6 m. In such mixtures the potential of the cell depends on the concentration of both NaCl (m_1) and CaCl₂ (m_2).

$$E = E^{\circ} = \frac{RT}{2F} \ln [m_2 (m_1 + 2 m_2)^2 \gamma_{21}^3 + K m_1^2 (m_1 + 2 m_2)^2 \gamma_{12}^4] \quad (2)$$

where γ_{12} is the mean activity coefficient of NaCl and γ_{21} is the mean activity coefficient of CaCl₂ in the mixed electrolytes and K is the selectivity ratio. Although the selectivity ratio for the calcium-sensitive liquid ion exchange electrode in the presence of Na⁺ is approximately 10⁻⁴ in dilute solutions⁽¹⁰⁵⁾, its behavior in the presence of interfering ions is much more complicated in concentrated solutions. Figure 29 shows the selectivity ratios calculated from our measurements. The activity coefficients γ_{12} and γ_{21} were taken from measurements made by the isopiestic and amalgam electrode methods^(30, 34).

A relatively simple explanation can be made both of the deviation from Nernstian behavior when a CaCl₂ test solution differs widely in concentration from the reference solution, and the complex variations of the selectivity ratio in the presence of sodium ion⁽¹⁰⁷⁾. If species such as CaClR (where R is the decylphosphate group in the ion exchanger) are transported through the organic phase instead of CaR₂ at high chloride ion concentrations, this would have the effect of making the liquid ion exchange membrane permeable to chloride ion and would destroy the simple Nernstian behavior in CaCl₂ solutions. The observed deviations from ideal behavior are in the predicted direction (Fig. 28). Furthermore, the species CaClR would be expected to be more easily interchangeable with the species NaR, and the selectivity of the electrode for Ca⁺⁺ over Na⁺, which depends on the formation of CaR₂, decreases (K increases) at high chloride concentrations, as we have observed.

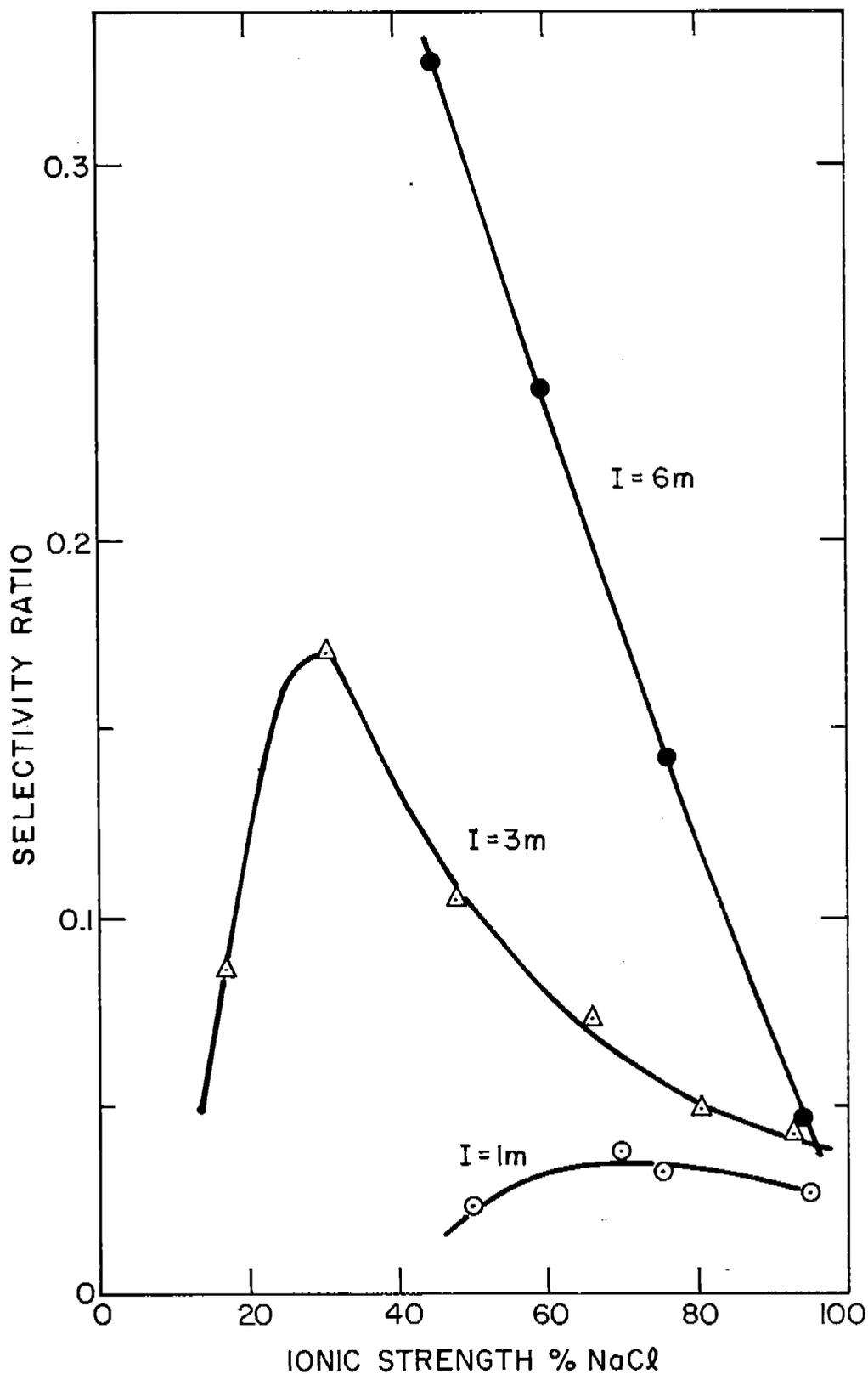


Fig. 29 Selectivity ratio (defined by Equation (2)) for calcium-sensitive liquid ion exchange electrode in NaCl-CaCl₂ solutions of constant ionic strength.

C. The Activity of Calcium Ion*

Introduction. The activity of calcium ion in blood serum, urine, and other extra-cellular fluids is well known to be an important physiological parameter^(26, 112). Direct measurement of this quantity until recently has been experimentally difficult, and also depends on non-thermodynamic assumptions to split experimentally accessible chemical potentials into parts attributable to single ions. Calcium ion concentration, a quantity directly measurable by ion exchange⁽¹¹⁶⁾ titration⁽¹¹⁹⁾, spectrophotometry^(117, 118) or flame photometry^(120, 121), has often been used as a measure of calcium ion activity, but the activity coefficient of calcium ion in physiological fluids is certainly not unity, and may vary considerably with the composition of the solution.

Recent interest in the measurement of calcium ion activity using specific ion electrodes^(105, 112, 113, 114) has raised the question⁽¹¹⁵⁾ of establishing an unambiguous calcium ion activity scale in a manner analogous to the establishment of the hydrogen ion activity (pH) scale. Quite apart from experimental difficulties, there are two important problems associated with establishing such a scale. The first is a choice of the method by which the chemical potential of a calcium salt in a mixed electrolyte shall be divided into contributions from its individual ions. The second is the establishment of standard solutions of known activity against which the specific-ion electrode system may be calibrated in practice⁽¹²²⁾.

The activity coefficients of the salts in $\text{NaCl-CaCl}_2\text{-H}_2\text{O}$ mixtures have been the subject of a number of studies^(26, 27, 30, 34) during the last three years, and sufficient data is now available to provide an accurate measure of the thermodynamic activity of calcium ion in solutions consisting primarily of NaCl. These solutions can be taken as calibration mixtures for direct measurements of calcium activity in serum and related solutions.

* Papers based on this section were submitted to Analytical Chemistry and the Biophysical Journal.

This paper presents a summary of experimental data on the NaCl-CaCl₂ electrolyte mixtures, discusses the possible calcium ion activity scales, and gives a table of activity coefficients for solutions of physiological interest.

Experimental Data. All available experimental measurements of the activity coefficients of CaCl₂ in NaCl-CaCl₂ mixtures are indirect, and depend on the use of thermodynamic relations to obtain the desired quantity. Cation-sensitive glass electrodes^(26, 27) and sodium amalgam electrodes⁽³⁴⁾ measure the activity of NaCl in mixtures with CaCl₂. From the osmotic coefficients of the pure components^(40, 41) the activity coefficients of CaCl₂ in the same mixtures can be calculated (see Section VI-A). An independent measurement has been made by the isopiestic method⁽³⁰⁾, which essentially measures the vapor pressure or activity of water in the mixed electrolyte by comparison with an electrolyte of known vapor pressure. Again, by using the osmotic coefficients of the pure components, the activity coefficients of NaCl or CaCl₂ in the mixture can be calculated.

In Fig. 30, the various experimental data are summarized in terms of the Harned Rule coefficient α_{21} , defined by the equation^(40, 41)

$$\log \gamma_{21} = \log \gamma_{20} - \alpha_{21} m_1 \quad (1)$$

where γ_{21} is the mean activity coefficient of CaCl₂ in the mixed electrolyte, γ_{20} is the mean activity coefficient of CaCl₂⁽⁴¹⁾ in a solution of the same ionic strength but containing only CaCl₂, and m_1 is the molal concentration of NaCl in the mixed electrolyte. The available data extend to ionic strength 7.0⁽³⁰⁾, but we have presented data only for the range of ionic strength ($I < 1.0$) which is of physiological interest. The line on Fig. 30 represents our appraisal of the "best values" for α_{21} .

For the convenience of those wishing to avoid the graphical interpolation and subsequent calculations required to evaluate γ_{21} in a solution of interest, we have prepared a summary, presented in Table XV, of the

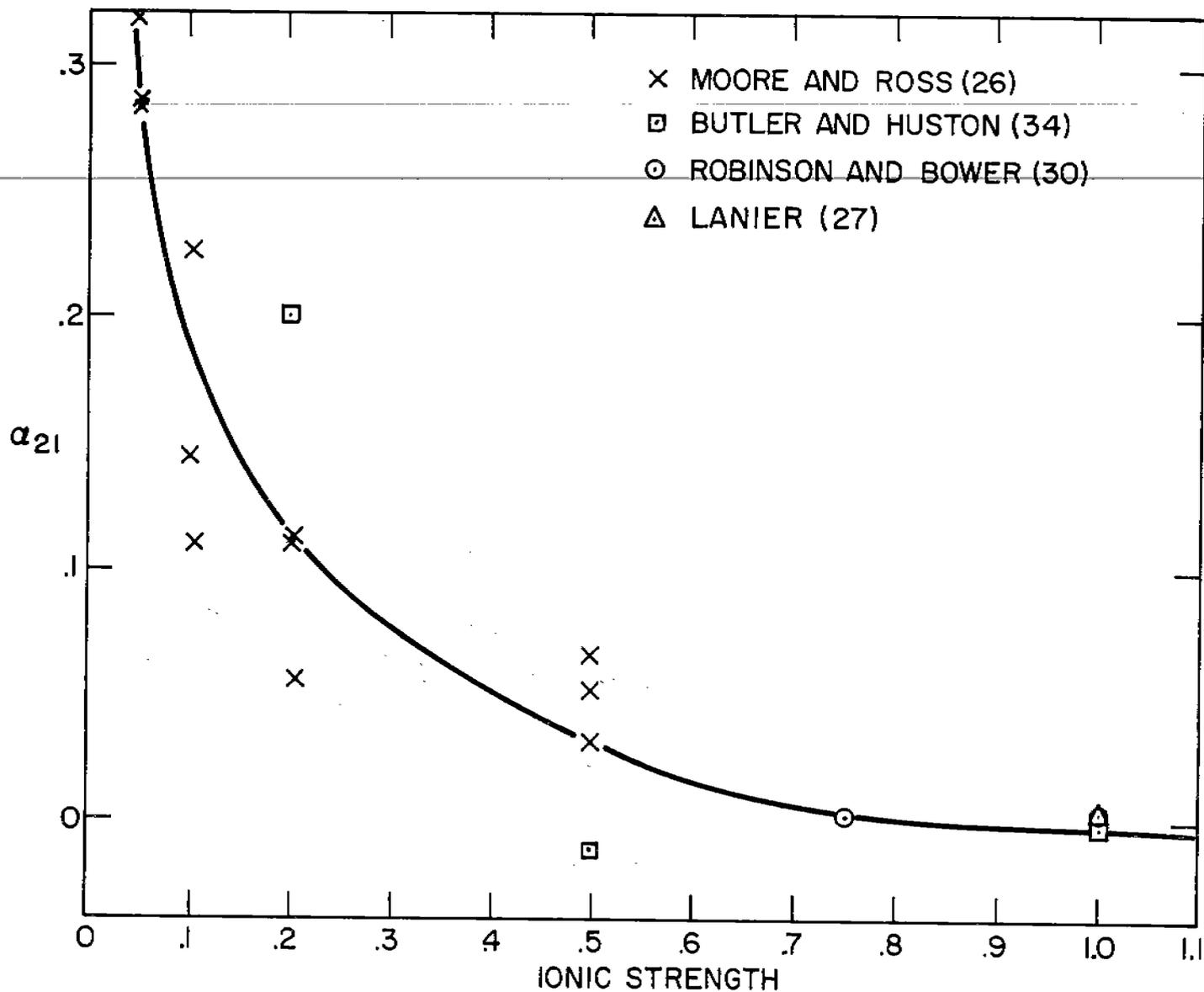


Fig. 30 Harned rule coefficient for calcium ion in NaCl-CaCl₂ mixtures at 25°C. Points are experimental results of various workers, and the line represents the values used in preparing Table I.

TABLE XV

Mean Activity Coefficient of CaCl_2 in NaCl-CaCl_2 Mixtures at 25°C^*

m_2 m_1	0	.05	.1	.2	.5	1.0
0	1.000	.650	.577	.521	.463	.456
.001	.881	.645	.575	.520	.463	.456
.002	.843	.641	.573	.519	.463	.456
.005	.775	.628	.568	.517	.463	.455
.01	.718	.609	.559	.514	.463	.455
.02	.654	.582	.545	.507	.464	.455
.05	.567	.538	.520	.490	.462	.454

* m_1 = molal concentration of NaCl , m_2 = molal concentration of CaCl_2

activity coefficients of CaCl_2 in solutions containing various molal concentrations of NaCl (m_1) and CaCl_2 (m_2). To calculate this table, we used our "best values" of α_{21} from Fig. 30, together with activity coefficients for pure CaCl_2 solutions γ_{20} obtained from the tables of Robinson and Stokes⁽⁴¹⁾. These tables cover only the range of ionic strength above 0.3. For the range below 0.3, we used the Guggenheim modification of the Debye-Hückel equation⁽⁴⁰⁾

$$\log \gamma_{20} = - \frac{2 A \sqrt{I}}{1 + \sqrt{I}} + BI \quad (2)$$

with $A = 0.509$, $B = 0.2486$, and the total ionic strength given by

$$I = m_1 + 3 m_2 \quad (3)$$

The value of B was obtained by making $\gamma_{20} = 0.518$ at $I = 0.3$, to correspond to the Robinson and Stokes tables. This resulted in a discontinuity in slope at $I = 0.3$, which was smoothed graphically, resulting in activity coefficient values slightly higher than those obtained by the Guggenheim equation in the range $I = 0.1$ to 0.3 . The largest discrepancy (0.004 in γ_{20}) was at $I = 0.2$.

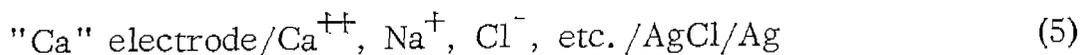
All the activity coefficient values presented were obtained at 25°C instead of 37 to 38°C , the normal human body temperature. The effect of a 13 degree temperature change is not inordinately large. The predominant effect may be calculated from the temperature dependence of the coefficient A in the Debye-Hückel theory. At 38°C , $A = 0.475$, and at ionic strength 1.0, this results in a value of γ_{20} which is higher than the 25°C value by approximately 0.025. This discrepancy is relatively constant down to $I = 0.1$, but decreases to zero at $I = 0$, and may be calculated from Equation 2, assuming B is independent of temperature:

$$\gamma_{20}^{(38^\circ)} = \gamma_{20}^{(25^\circ)} \text{antilog} [0.050 \sqrt{I}/(1 + \sqrt{I})] \quad (4)$$

Corrections calculated from this equation may be applied to the data in Table XV. For intermediate temperatures, note that A varies inversely with the $3/2$ power of the absolute temperature^(40, 41).

The influence of other ionic components of physiological fluids on the activity of calcium ion is probably small. Certainly potassium and magnesium ion, which comprise less than 6% of the total ionic strength of serum, have a negligible effect on the activity coefficient of Ca^{++} at ionic strengths less than 1. Calcium forms complexes with protein and other organic materials^(116, 118) but complexed calcium species are not normally measured by a specific ion electrode, and because of their low charge density and low concentration probably do not affect the activity coefficient of free calcium ion. Because of the unavailability of complexed calcium for precipitation and membrane transport processes, it is best to consider the free ionic calcium as a separate species and to work out the equilibrium with protein and other organic materials separately. These equilibria may, however, introduce substantial discrepancies between ionic calcium as measured with a specific ion electrode and total calcium as determined by other methods such as flame photometry^(120, 121). Provisionally, then, we may suggest that NaCl-CaCl_2 solutions, of the same ionic strength (or less precisely, NaCl concentration) as the serum samples to be measured, be used as standards for calibration of specific ion electrodes.

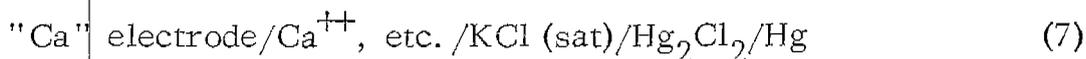
The Calcium Ion Activity Scale. There are two important types of cells which can be used to measure calcium ion activity directly using a calcium-selective specific ion electrode. The first type is a cell without liquid junction:



where the reference electrode is reversible to chloride ion, and the potential is given by

$$E = E_5^0 + \frac{RT}{2F} \ln (m_{Ca^{++}}) + \frac{RT}{F} \ln (m_{Cl^-}) + \frac{3 RT}{2 F} \ln (\gamma_{\pm}) \quad (6)$$

where γ_{\pm} is the mean activity of $CaCl_2$ in the mixed electrolyte, given approximately by values in Table XV. The second type is more common, and employs a salt bridge and reference electrode of fixed potential:



The right-hand electrode, including the KCl salt bridge, is embodied in commercial saturated calomel reference electrodes. The potential of this cell is given by

$$E = E_7^0 + \frac{RT}{2F} \ln (m_{Ca^{++}}) + \frac{RT}{2F} \ln (\gamma_{++}) + E_j \quad (8)$$

where γ_{++} is the "single ion activity coefficient" of Ca^{++} , and E_j is the diffusion potential resulting from the liquid junction between the salt bridge and the test solution. The standard potentials E_5^0 and E_7^0 are independent of the composition of the test solution, provided the specific ion electrode does not respond to any ions in the solution besides Ca^{++} .

The first cell is thermodynamically well-defined, and the mean activity coefficient of $CaCl_2$ in a mixture of extreme complexity can in principle be obtained by any of the various methods used for simpler mixtures. The second cell is not at equilibrium because of the liquid junction between solutions, where mixing is taking place continuously. The diffusion potential is small if the transport numbers of cation and anion in the salt bridge are small, and the salt bridge concentration is large compared to the test solution concentrations (e. g. saturated KCl). In practice this condition is obtained with good commercial reference electrodes, and E_j may vary by less than 5 millivolts over a considerable range of test solution compositions. Unfortunately, there is no unambiguous way to separate γ_{++} and E_j either thermodynamically or theoretically,

without making certain ad-hoc assumptions; and an uncertainty in E_j of 5 millivolts corresponds to an uncertainty in γ_{++} of 50%. For this reason, various methods of eliminating the uncertainty in E_j have been proposed.

These methods are based on the same principle as the "operational" definitions of pH⁽¹²²⁾. Cell 7 is measured with a known solution whose composition approximates that of the unknown solution as closely as possible, but the known solution is prepared so that the thermodynamic activity coefficient γ_{\pm} is known from measurements in Cell 5 or by other measurements. The single ion activity coefficient γ_{++} is either calculated theoretically or taken to be some function of the quantity γ_{\pm} . Three simple choices of this function have been made, each of which has some validity.

Shatkay^(113, 114) chose to set $\gamma_{++} = \gamma_{\pm}$, and justified this choice by comparison of experimental potential measurements made on Cell 7 with a theoretical curve calculated assuming $E_j = 0$. Garrels⁽¹²⁴⁾ assumed that the activity coefficient of chloride ion can be approximated by the mean activity coefficient of KCl in aqueous KCl solutions of the same ionic strength. This leads to the relation

$$\gamma_{++}(\text{Ca}) = [\gamma_{\pm}(\text{CaCl}_2)]^3 / [\gamma_{\pm}(\text{KCl})]^2. \quad (9)$$

Still another assumption is suggested by the various equations based on Debye-Hückel theory^(40, 41). For a 1-2 electrolyte like CaCl_2 , the value of γ_{++} is given by

$$\log \gamma_{++} = -4A \sqrt{I} / (1 + \sqrt{I}) + \text{extended terms} \quad (10)$$

whereas the mean activity coefficient γ_{\pm} is given by

$$\log \gamma_{\pm} = -2A \sqrt{I} / (1 + \sqrt{I}) + \text{extended terms} \quad (11)$$

If the extended terms are similar in both equations 10 and 11, the relationship

$$\gamma_{++} = (\gamma_{\pm})^2 \quad (12)$$

is obtained. Although this cannot be tested experimentally any more than the other two assumptions can, it has a stronger theoretical basis than Shatkay's assumption, and is simpler to calculate than Garrels' assumption. In addition to these assumptions, we have also included two curves calculated by means of theoretical expressions; the Debye-Hückel equation for a divalent ion⁽⁴⁰⁾

$$\log \gamma_{++} = - \frac{(0.509)(4) \sqrt{I}}{1 + 0.328 a \sqrt{I}} \quad (13)$$

with the ion-size parameter $a = 6$; and the Davies⁽¹²³⁾ equation for a divalent ion

$$\log \gamma_{++} = - (0.509)(4) \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2 I \quad (14)$$

The Davies equation has been shown to give a good fit to the mean activity coefficients of a large number of 1-1 and 1-2 electrolytes. In both of these equations I is the ionic strength, $m_1 + 3 m_2$.

The discrepancy between these four estimates is shown in Fig. 31 and corresponds to less than 2 mv in the potential of a specific ion electrode for m_1 less than 1.0. In contrast, $\gamma_{++} = \gamma_{\pm}$ (Shatkay's assumption) gives values between .45 and .55, which are off scale at the top of Fig. 27, and the difference from the group of four other estimates on Fig. 27 corresponds to as much as 10 mv in the potential of a specific ion electrode. A similar set of curves is shown in Fig. 32 for CaCl_2 alone.

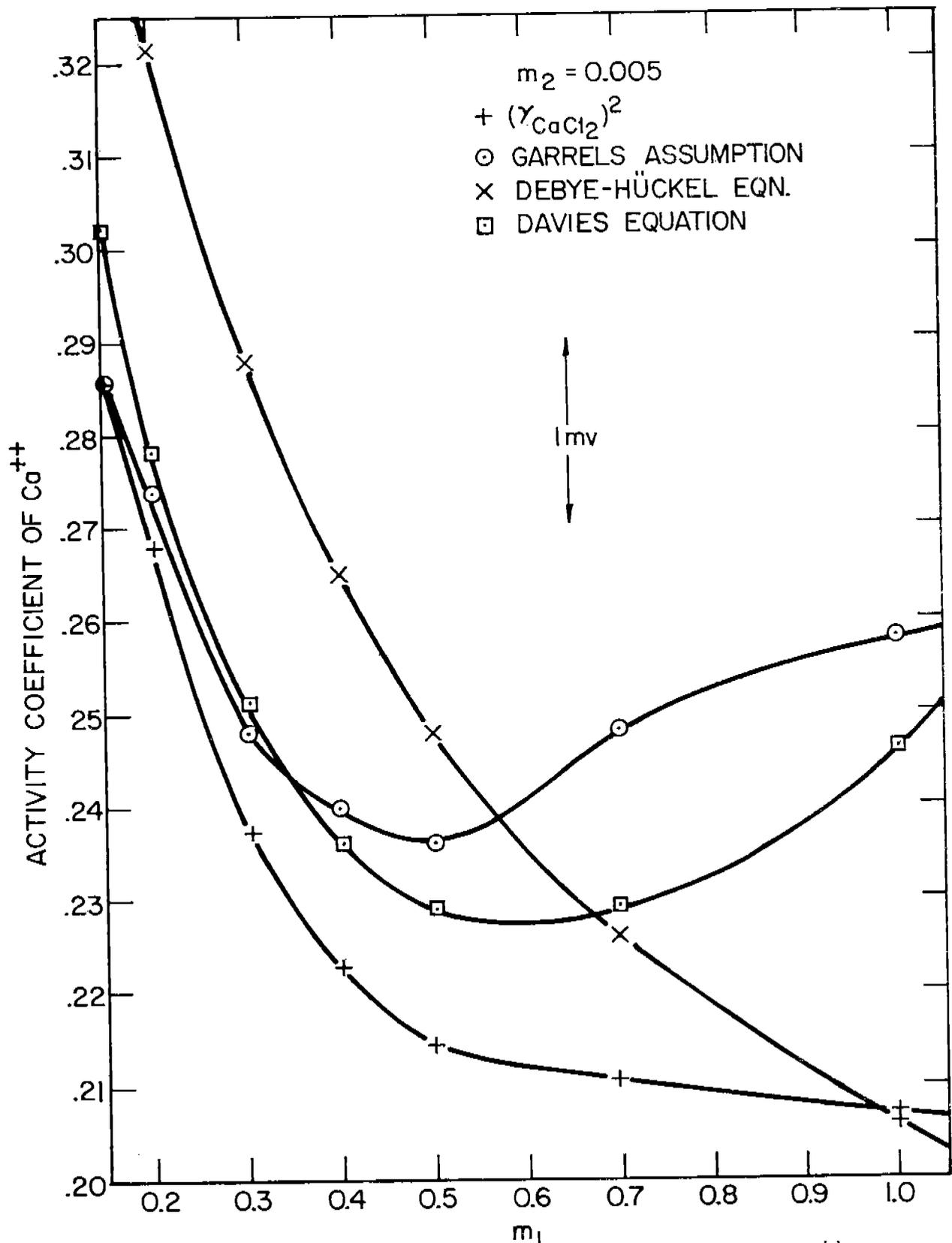


Fig. 31 Estimates of the single-ion activity coefficient for Ca^{++} (at concentration $m_2 = .005$) in NaCl solutions of concentration m_1 . The various methods of calculation are described in the text.

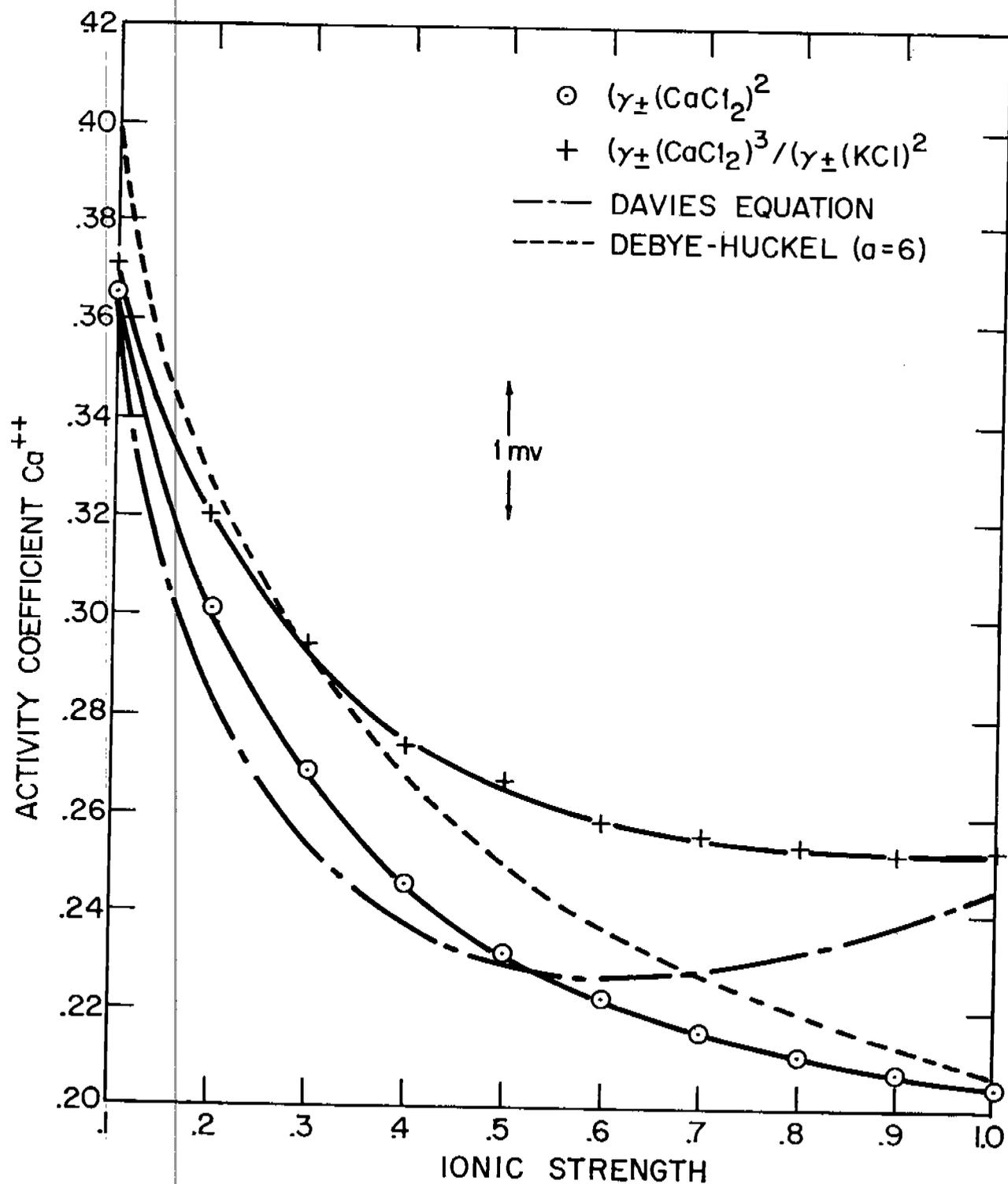
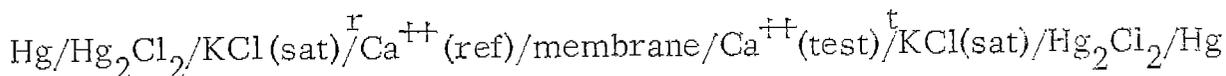


Fig. 32 Single ion activity coefficients of Ca^{++} in aqueous CaCl_2 solutions.

Frant⁽¹¹⁵⁾ was correct in pointing out that in CaCl_2 solutions the ratio γ_{\pm}/γ_{++} is larger than unity (1.2 to 1.6), but he did not point out that these particular ratios result because γ_{\pm} varies between 0.8 and 0.6 over the range of ionic strength 0.01 to 0.15. The ratio $(\gamma_{\pm})^2/\gamma_{++}$ over this same range is $0.95 \pm .05$; the exact values depending on how γ_{++} is calculated. Certainly $(\gamma_{\pm})^2$ is just as simple and convenient to use as is γ_{\pm} itself, and has the additional advantage of a sound theoretical basis.

One further point should be made regarding Shatkay's choice of reference electrode system. He has explicitly excluded the possibility of potential differences arising from the liquid junctions in his cell:



at points \underline{r} and \underline{t} . The over-all potential of the above cell, assuming the membrane is permeable only to Ca^{++} is

$$E = \frac{RT}{2F} \ln \frac{m_{\text{Ca}^{++}}(\text{test})}{m_{\text{Ca}^{++}}(\text{ref})} + \frac{RT}{2F} \ln \frac{\gamma_{++}(\text{test})}{\gamma_{++}(\text{ref})} + E_t - E_r$$

In the simplest of Shatkay's experiments⁽¹¹⁴⁾ the concentration of Ca^{++} was kept constant, and only the concentration of added NaCl was varied. Shatkay attributed all the changes in observed potential to variations in the activity coefficient of the test solution, and assumed that E_r was equal to E_t regardless of the composition of the test solution. The difference $E_r - E_t$ could have been as large as 10 mv for the concentrated test solutions, but need not have been included at all if chloride-reversible reference electrodes had been used in both compartments without salt bridges.

Because of the agreement with theoretical values for γ_{++} , we recommend that either the assumption $\gamma_{++} = (\gamma_{\pm})^2$ or the Garrels⁽¹²⁴⁾ assumption be used to estimate single-ion activity coefficients for calcium

ion in standard mixtures. Either of these would result in a calcium ion activity scale with an uncertainty of less than 0.05 pCa units at ionic strengths less than 0.5. Although this is not as well-defined as the pH scale⁽¹²²⁾, it may form an interim basis for calcium ion activity measurements until international agreement is reached on activity standards.

D. Prediction of Multicomponent Activity Coefficients Using the Bronsted Theory*

In a paper published recently⁽³⁴⁾ we have used the Bronsted-Guggenheim theory of specific ionic interaction to estimate the Harned rule coefficients of NaCl-CaCl₂ and NaCl-MgCl₂ mixtures at zero ionic strength. This theory assumes that the deviation of the logarithm of the activity coefficient from the Debye-Hückel theory is a linear function of the products of molalities of ions of opposite sign. The coefficients are evaluated from data for the pure salts. Although the Harned rule coefficients predicted were not as accurate as the measured values, they were of the correct magnitude and sign, and thus the Bronsted-Guggenheim theory is useful for estimating deviations from the Debye-Hückel theory at moderate concentrations.

Since data now exists for the three systems NaCl-CaCl₂, NaCl-MgCl₂^(30, 34), and CaCl₂-MgCl₂⁽²⁹⁾, it was of interest to see how closely one could predict the activity coefficients of one pair from the data for the other two pairs. Following the formalism set out by Robinson and Bower,⁽³⁰⁾ which we used to calculate α_{12} for MgCl₂ in Section VI-A, we have

$$\alpha_{12} = \frac{2}{3} B_{\text{NaCl}} - \frac{1}{6} B_{\text{CaCl}_2} \text{ for NaCl-CaCl}_2 \text{ mixtures}$$

$$\alpha'_{12} = \frac{2}{3} B_{\text{NaCl}} - \frac{1}{6} B_{\text{MgCl}_2} \text{ for NaCl-MgCl}_2 \text{ mixtures}$$

$$\alpha''_{12} = \frac{4}{9} (B_{\text{CaCl}_2} - B_{\text{MgCl}_2}) \text{ for CaCl}_2\text{-MgCl}_2 \text{ mixtures}$$

* Unpublished

In each of the mixtures, the first compound quoted is component 1 and the second is component 2. From the above relations it immediately follows that

$$\alpha''_{12} = \frac{8}{3} (\alpha'_{12} - \alpha_{12})$$

In Fig. 33, these two quantities are compared as a function of ionic strength. To obtain these curves, we used experimental data for the three multicomponent mixtures obtained by ourselves and by Robinson and Bower. Note that although the curves are approximately parallel, the Bronsted-Guggenheim theory predicts values for the Harned rule coefficient α''_{12} which are 0.007 more positive than the experimental values obtained by Robinson and Bower. Nevertheless, such a prediction is more accurate than could be obtained from data on solutions containing a single salt.

In a similar manner, we can predict that the Harned rule coefficient for the second component is given by

$$\alpha''_{21} = 4 (\alpha'_{21} - \alpha_{21})$$

where the notation is the same as before. These two quantities are compared on Fig. 34. Again the Bronsted-Guggenheim theory predicts a more positive value for α''_{12} , but the discrepancy is so large in this case that it is of little predictive use.

Thus we observe that the Bronsted-Guggenheim theory is of limited use in predicting the Harned rule coefficients of unknown mixtures. If we may generalize from only a single case, we may say that α_{12} is predicted more accurately than is α_{21} .

E. Studies on the Calcium Amalgam Electrode*

Preliminary Experiments. We have made some preliminary experiments using calcium amalgam electrodes, which are summarized here.

* Unpublished

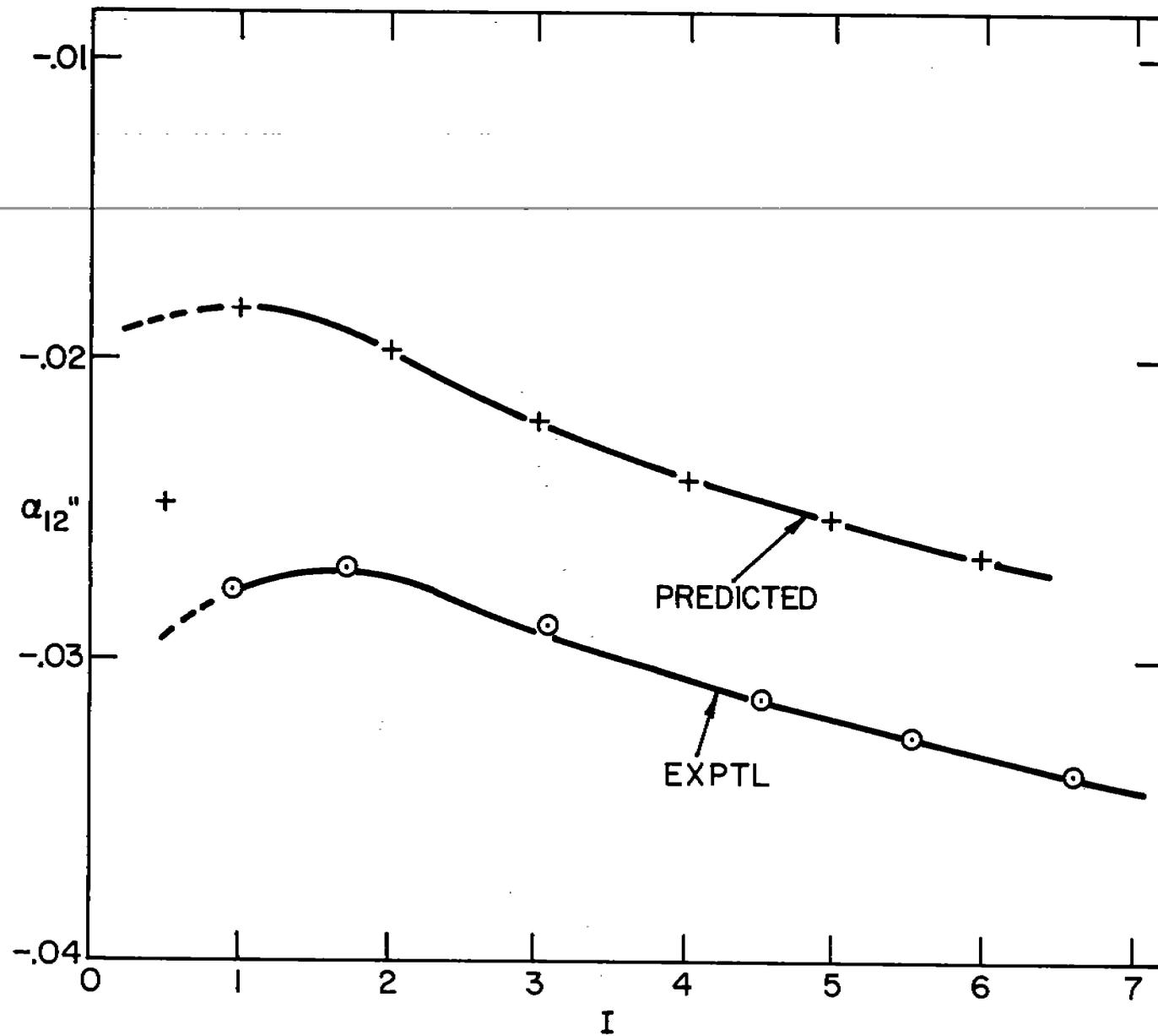


Fig. 33 Prediction of α_{12}'' for the $\text{CaCl}_2\text{-MgCl}_2$ system by the Bronsted theory.

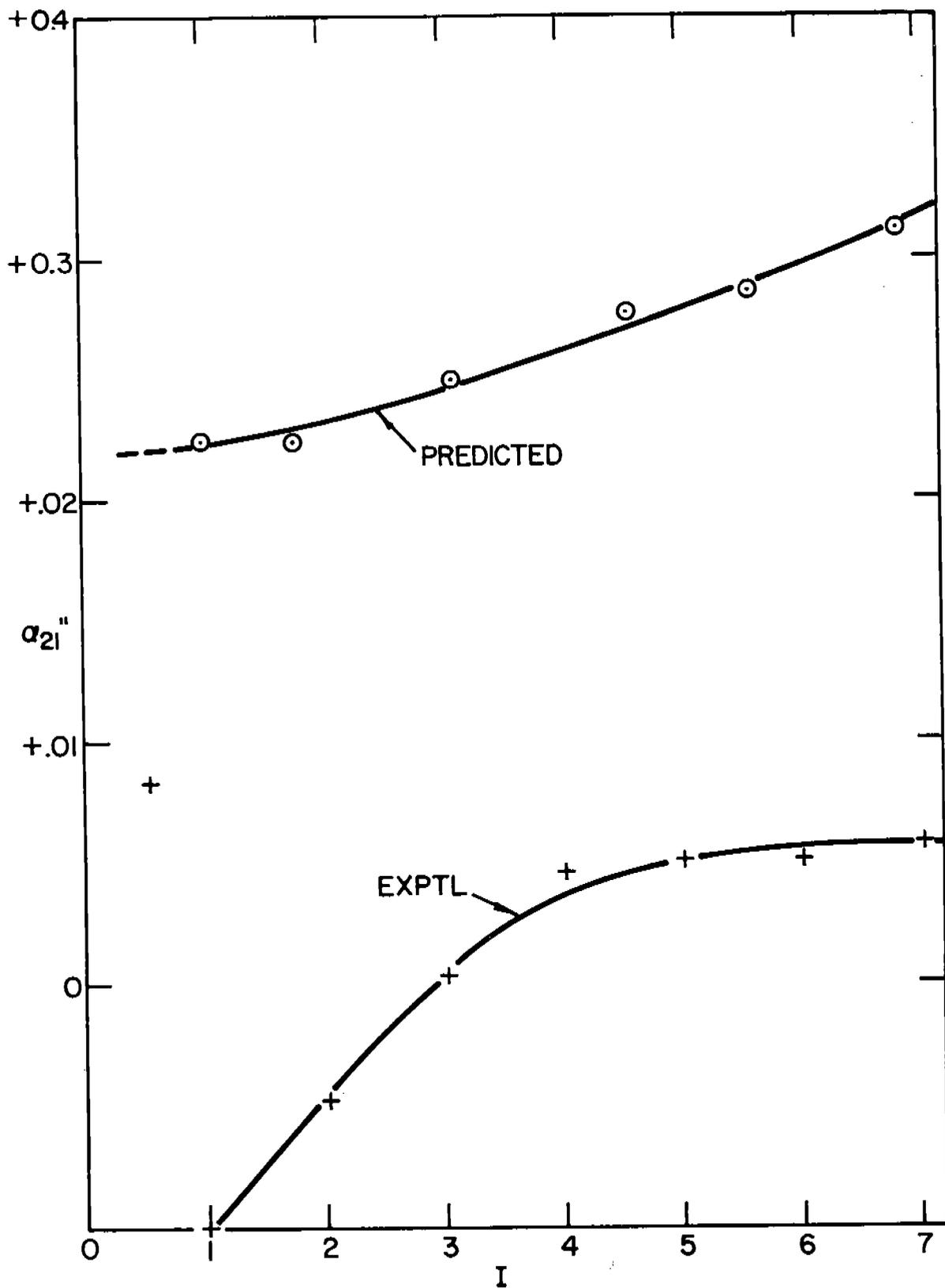


Fig. 34 Prediction of the Harned rule coefficient α_{21}'' for the CaCl_2 - MgCl_2 system by the Bronsted theory.

1. Calcium amalgams may be easily prepared by direct combination of the elements, but preparation by electrolysis is more difficult than for sodium amalgams, because of concurrent hydrogen evolution.

2. The calcium amalgam electrode is not as reversible as the sodium amalgam electrode, and a study of its electrode kinetics probably ought to precede any attempt to use it for thermodynamic measurements. This is confirmed by the literature data (Section IV-B).

3. Because calcium hydroxide is relatively insoluble, calcium-containing solutions cannot be made basic enough to inhibit the hydrogen evolution reaction on calcium amalgam electrodes and thus errors result both from the kinetic imbalance effects and from concentration polarization effects. The kinetic effects are much greater than for sodium amalgams because of the lower exchange current of the calcium amalgam electrode.

4. The presence of one or two percent sodium ion in the electrolyte changes the potential of the calcium amalgam electrode as much as 200 mv more positive, which indicates that reliable thermodynamic measurements cannot be made using a calcium amalgam electrode in solutions containing both sodium and calcium ions.

Studies in Nonaqueous Solutions. Although investigators have successfully made measurements in aqueous solutions using calcium amalgam electrodes, it is of interest to establish what the thermodynamic potential of such an electrode is in nonaqueous solutions. From calculations based on absolute entropies and heats of reaction, the standard potential of pure calcium in aqueous solution is found to be -2.87 volts⁽⁵⁶⁾. If measurements are made of the potential difference between pure calcium and calcium amalgams of various concentrations in a nonaqueous electrolyte containing calcium ions, where no other reactions (such as corrosion of the electrodes by the solvent) can take place,

then the thermodynamic potential of the calcium electrode in aqueous solution can be established experimentally, as discussed in Section IV-B.

During this program we have carried out some preliminary experiments in an attempt to measure the potential difference between a pure calcium electrode and a calcium amalgam electrode. We have chosen propylene carbonate (4-methyl dioxolone-2, abbreviated PC) as the solvent, since it is known⁽¹²⁵⁻¹²⁷⁾ to be a good solvent for ionic salts and to be stable in the presence of lithium metal.

Propylene carbonate, obtained from Matheson, Coleman, and Bell, was distilled at approximately 1 mm pressure in a packed fractionating column (Podbielniak Semi-Cal) of approximately 50 theoretical plates and the distilled material analyzed by gas chromatography. A two-meter column of Porapak Q (a hydrophobic polystyrene resin) was used, with an injector port temperature of approximately 140°C, a column temperature of approximately 75°C, a detector temperature of approximately 120°C, and a thermal conductivity detector current of 220 ma. The flow rate of helium through the column was approximately 50 ml/min. The distilled propylene carbonate contained 31 ppm (0.0031%) of water and less than 60 ppm of organic impurities, which were mostly propylene oxide and propylene glycol.

Working in a glove-box with an argon atmosphere we prepared a solution of 0.0100 M anhydrous CaCl_2 in this solvent, which was analyzed and found to contain 118 ppm water. Calcium amalgam was prepared by dissolving clean calcium metal (A. D. Mackay, Inc.) in mercury. The pure calcium electrodes were polished mechanically before measurements were made and appeared shiny and metallic (like stainless steel) throughout the experiments. Potentials of the cell

Ca(s)/CaCl₂ (0.01 M in PC)/Ca(Hg)

were measured for amalgams of four concentrations, as well as for an amalgam pool which contained a piece of solid calcium in contact with it, and was presumably saturated. The results are listed in Table XVI. If the Nernst relation were obeyed, the quantity listed in the third column should be independent of the amalgam concentrations; by analogy with other amalgams⁽¹²⁸⁾, the effect of changes in the activity coefficient of Ca in the amalgam over the concentration range covered should be less than 10 mv. The observed variation of nearly 300 mv must be attributed to the irreversibility of the cell. Even so, the observed differences indicate that the potential of a calcium amalgam of this concentration range in aqueous solutions would be approximately 0.8 volts more positive than the potential of pure calcium, or approximately -2.1 volts. This is somewhat more negative than the standard potential which we calculated from literature data obtained in aqueous solutions (Section IV-B).

We believe that the precision of these measurements can be greatly improved by some modifications in the experiment. The most significant thing we observed was that although the amalgam pool developed a substantial number of gas bubbles in a rather short time, the pure calcium rod remained shiny in the propylene carbonate electrolyte and showed no signs of gas evolution. Furthermore, the water content (measured by gas chromatographic analysis) of the electrolyte removed from the cells was substantially lower than that of the original electrolyte, demonstrating that some of the water in the electrolyte had reacted with the electrode materials. These observations indicate two possibilities: The mercury used to prepare the amalgams may have contained either water or oxygen which caused the amalgam electrodes to corrode in the propylene carbonate electrolyte; or the calcium electrode passivated in the presence of the small amounts of water in the electrolyte, and therefore did not achieve its equilibrium potential.

TABLE XVI

Calcium Amalgam Electrode Measurements

Ca(s)/CaCl₂ (0.0100 M in PC*)/Ca(Hg)

X_{Ca} (mole % Ca in Hg)	E volts	$E + \frac{RT}{2F} \ln X_{Ca}$	H ₂ O content of electrolyte
0.0878	0.74	0.71	27 ppm
0.0410	0.65	0.61	
0.0148	0.82	0.77	
0.0136	0.96	0.91	32 ppm
sat'd	1.8-3.9	(very unstable)	< 11 ppm

* Propylene carbonate as distilled contained 31 ppm H₂O and < 60 ppm organic impurities. The CaCl₂ solution when first prepared contained 118 ppm H₂O.

A number of improvements in this experiment can be made, with the expectation of obtaining a more accurate value of the potential difference between solid calcium and calcium amalgam. First of all, the amalgam potential can be measured with respect to an independent non-aqueous reference electrode reversible to chloride ion, such as the TlCl/Tl(Hg) electrode. To avoid the possible introduction of oxygen or water with the mercury, the mercury can be distilled in an atmosphere of dry argon before preparing the amalgam, and the electrolyte can be pretreated with calcium amalgam before making up the cell. By following

the water, organic impurity, and calcium ion content, of the electrolyte during this prepurification process, errors due to corrosion of the amalgam can possibly be avoided.

Errors due to passivation of the solid calcium surface are more difficult to avoid, as we have explained in Section IV-B. Here it seems to be necessary to scrape the surface exposed to the solution actively during the measurement. Again, an external reference electrode (instead of a calcium amalgam electrode) in the cell would enable us to separate errors due to the amalgam electrode from errors due to the solid calcium electrode.

These experiments would result in an experimental value for the standard potential of the calcium electrode in aqueous solutions which would provide an independent experimental verification of the presently accepted value⁽⁵⁶⁾, which is based on entropy calculations⁽⁹³⁾ and not on a direct experimental measurement.

F. Studies on the Barium Amalgam Electrode*

NaCl-BaCl₂ Electrolytes. On the basis of the literature values for the standard potential of barium amalgams, we suggested in Section IV-C that accurate measurements of the activity coefficients of barium salts in combination with alkali metal ions and various anions such as chloride or hydroxide might be made using barium amalgam electrodes. In our preliminary measurements on BaCl₂-Ba(OH)₂ electrolytes, difficulties were encountered with the precipitation of material from these solutions. At first this was assumed to be BaCO₃, formed from traces of CO₂ in the solutions, but later analysis showed that it is more likely to be Ba(OH)₂, precipitated because of the common ion effect by addition of excess BaCl₂. The maximum ionic strength which can be reached in such systems is thus less than 0.1 m, and we decided to attempt measurements on a system which would not suffer from such drastic limitations on concentration.

* Unpublished

During this program, successful measurements were made with a barium amalgam electrode in BaCl_2 -NaCl electrolytes, using the cell



The apparatus was the same as we have used for our previous measurements with sodium amalgam electrodes (section V). The barium amalgam was approximately 0.06 atomic percent Ba, and measurements were made at ionic strengths of 1.0 m and 3.0 m, with various NaCl-BaCl₂ compositions in the right-hand cell. All solutions were prepared by weight from reagent grade salts (Fisher Scientific Co.) and were analyzed for chloride by titrating with standard AgNO₃ solution. The chloride concentration of the NaCl stock solution was 0.7% less than predicted, and the chloride concentration of the BaCl₂ stock solution was 3.4% less than predicted. These discrepancies resulted from the water content of the salt as obtained from the manufacturer. The manufacturer's lot analysis of BaCl₂ (Table XII) showed no impurities which would be expected to give a significant error in the EMF measurements, and so further purification of this salt was not carried out. The pH of 0.34 m BaCl₂ was 5.0 and that of 1.005 m, 5.2.

Barium amalgam was prepared by combination of the elements. Approximately 0.8 grams of reagent grade Ba metal (Fisher) was brought into contact with triple-distilled mercury (Doe and Ingalls) in a pre-purified argon atmosphere (< 1 ppm oxygen) in a glove-box. This mixture was allowed to stand overnight to achieve equilibrium, and the liquid phase (~ 0.5 atom percent Ba) was diluted to achieve the desired concentration of amalgam. Initially, 0.25 atom percent Ba amalgam was used, but this was much too viscous to flow through the capillaries at a uniform rate. For the successful experiments, a more dilute amalgam of 0.065 atom percent Ba was used. The concentration of the amalgam was confirmed

by analysis of the actual sample used in the experiment, by reacting with excess HCl and back-titration with standard NaOH.

In general, the barium amalgam electrode is much more troublesome than the sodium amalgam electrode. The capillaries of the dropping amalgam electrode system became plugged quite frequently, and extreme care had to be taken to keep even small traces of oxygen out of the system. The best results were obtained when the capillaries were kept under dry argon overnight while the solutions were being degassed. Measurements could then be made for up to 5 hours before the capillaries became plugged. Attempts to free the plugged capillaries were rarely successful, and the system had to be dismantled and cleaned after each experiment.

In spite of the efforts to keep the amalgam out of contact with oxygen, a layer of solid material appeared to form on the surface, and to become visibly thicker with time. Whether this is a slowly-formed stable solid compound of barium with mercury, or an oxide-containing film, was not firmly established. The liquid phase of the amalgam was analyzed and was not appreciably depleted of its barium content, so that the actual amount of solid may have been very small.

The stability of potential measurements was good (± 0.05 mv) as long as the dropping rate was high (> 2 drop/sec), but when the drop was slower in one electrode than the other, the potential fluctuated by as much as ± 1 mv and readings became very inaccurate. When solutions were changed every 15-20 minutes, the potentials were affected by only ± 0.1 to ± 0.4 mv, except at the very beginning of the measurement. The best value of EMF was taken to be the average of at least four readings which showed no systematic trend, and is estimated to be accurate to ± 0.1 mv.

The results of the two series of experiments carried out during this program are summarized in Table XVII. The activity coefficients (γ_{21}) were calculated using the equation

$$E = \frac{RT}{2F} \ln \left\{ \frac{m_{\text{Ba}^{++}}^{(0)} (m_{\text{Cl}^-}^{(0)})^2 (\gamma_{20})^3}{m_{\text{Ba}^{++}}^{(1)} (m_{\text{Cl}^-}^{(1)})^2 (\gamma_{21})^2} \right\}$$

The reference solution for each set (superscript zero in above equation) was the first entry, labeled "100% ionic strength BaCl₂", and the activity coefficient of this solution was taken from the tables of Robinson and Stokes⁽⁴¹⁾, as were the correction factors used to obtain the values of log γ_{\pm} at round ionic strength (listed in the last column of Table XVII).

TABLE XVII

Activity Coefficients of BaCl₂ in BaCl₂-NaCl Electrolytes at 25°C

<u>Total Ionic Strength</u>	<u>% Ionic Strength BaCl₂</u>	<u>E (mv)^(a)</u>	<u>-log γ_{\pm}</u>	<u>-log $\gamma_{\pm}(\text{corr})$^(b)</u>
1.019	100	0	.3782	.3778
1.029	81.28	0.60	.3848	.3862
1.036	68.42	0.44	.3763	.3783
1.046	49.71	-2.30	.3247	.3272
1.065	14.89	-12.00	.0827	.0861
3.015	100	0	.3965	.3969
3.009	92.72	-0.35	.3911	.3917
2.992	73.62	1.22	.3988	.3983
2.971	48.60	-0.35	.3493	.3474
2.954	28.09	-2.90	.2662	.2637
2.944	17.89	-6.35	.1679	.1654

(a) Reference solution "100% Ionic Strength BaCl₂"

(b) Corrected to 1.000 m and 3.000 m Ionic strength using data from Robinson and Stokes⁽⁴¹⁾.

The corrected values are plotted in Fig. 35. On the same graph we have drawn lines corresponding to the Harned rule coefficients obtained by Lanier⁽²⁷⁾ using a cation-sensitive glass electrode, calculating α_{21} by means of the Gibbs-Duhem relation using the known osmotic coefficients of the pure electrolytes⁽⁴¹⁾. Although the experimental points at greater than 60% BaCl₂ deviate by less than 1 mv from the theoretical lines based on Lanier's data, the deviations at low BaCl₂ percentages are quite large, systematic, and reproducible. These deviations are almost certainly due to interference by sodium ion with the electrode reaction, and can be explained in terms of kinetic effects.

Although the potential difference between a barium amalgam and sodium amalgam electrode is 300 mv when the concentrations are the same, the sodium exchange current is so rapid compared to the barium exchange current that interference can be obtained on a kinetic basis even when essentially no conversion of barium amalgam to sodium amalgam occurs. The quantitative evaluation of this effect can be made by a method similar to that described elsewhere⁽³³⁾ for the interference of alkali metal cations (Section III-E), and it may be possible to obtain an approximate numerical value for the exchange current of the barium reaction from the data listed in Table XVII.

A qualitative picture is given in Fig. 36. Reaction of Na⁺ with barium amalgam gives a small concentration of sodium in the amalgam, and even though the equilibrium potential of the sodium couple is more negative than the equilibrium potential of the barium couple, the high exchange current of the sodium reaction produces a large contribution to the anodic current. This kinetic imbalance shifts the zero-current potential (which we measure experimentally) to values more negative than the equilibrium potential which the barium amalgam electrode would attain if there was no interference from sodium ion. This shift is in the same direction as the systematic deviations from Harned's rule shown on Fig. 35. We plan to carry out a detailed numerical analysis of this system.

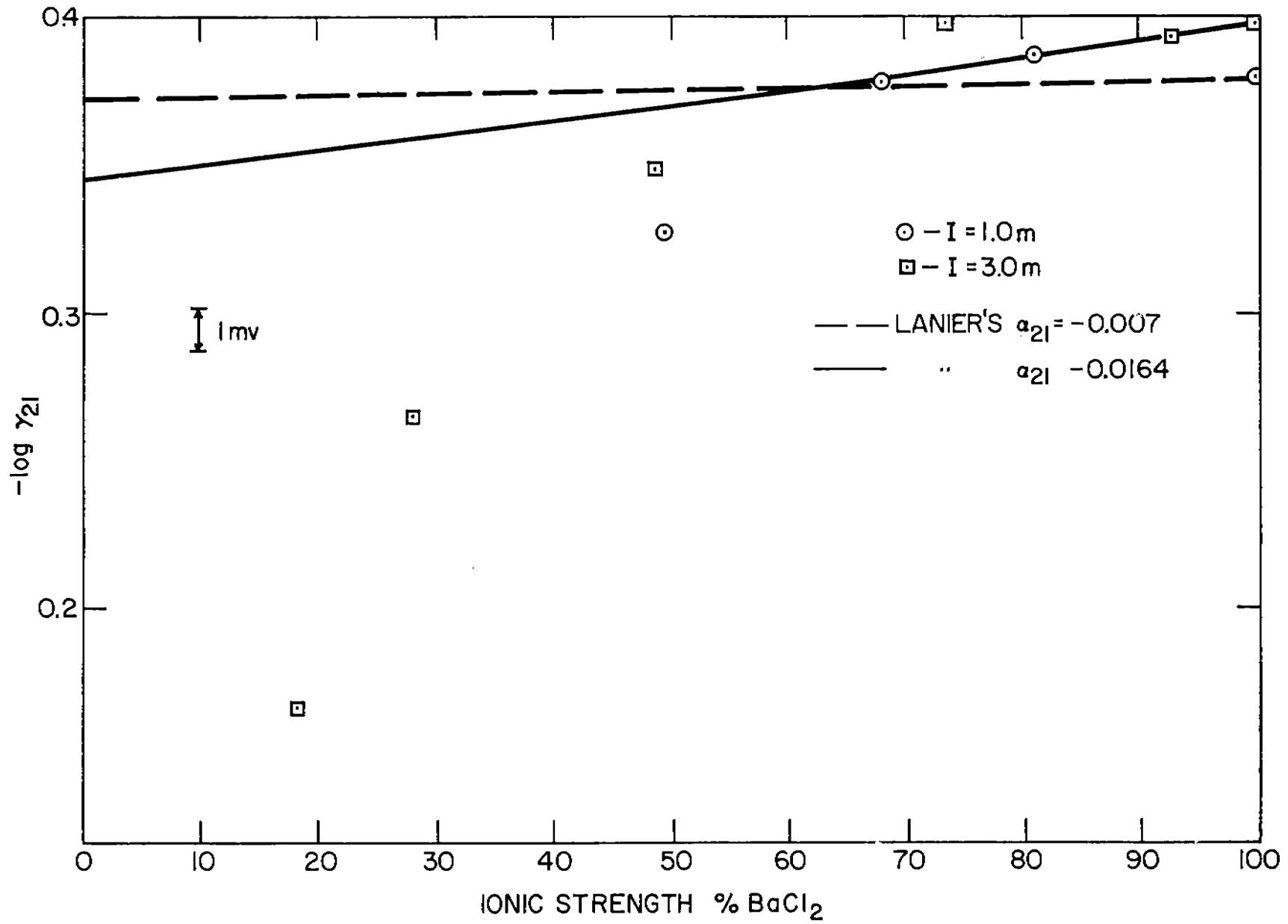


Fig. 35 Activity coefficient of BaCl_2 in NaCl-BaCl_2 electrolytes determined with the cell $\text{Ba(Hg)/BaCl}_2, \text{NaCl}, \text{H}_2\text{O/AgCl/Ag}$

From these experiments, it is clear that measurements of activity coefficients using barium amalgam electrodes in mixtures of barium salts with alkali metal salts are not as accurate as those obtained with cation-sensitive glass electrodes. The potential of potassium amalgam and the exchange current for the potassium reaction are almost the same as for sodium, so that the behavior of barium amalgam electrodes in BaCl_2 -KCl would be similar to BaCl_2 -NaCl. Better results would be expected for BaCl_2 -LiCl mixtures because of the more negative potential and smaller exchange current of the lithium couple.

The optimum system for the next study with barium amalgam electrodes appears to be the BaCl_2 - CaCl_2 or BaCl_2 - MgCl_2 system. There are several reasons for this. First, the potentials of calcium and magnesium amalgams are considerably more negative than that of sodium, and the little kinetic evidence available indicates that the exchange current for these amalgams is quite small. Thus both on thermodynamic grounds and on kinetic grounds, we would expect Ca^{++} or Mg^{++} to interfere far less than Na^+ with the operation of the barium amalgam electrode. Furthermore, measurements of activity coefficients in mixtures of two divalent cations cannot presently be made by any 'specific ion' electrode method. The barium amalgam experiment thus remains the only practical alternative to isopiestic measurements, and would be a valuable check on such measurements whenever they are done.

Kinetics of the Barium Amalgam Electrode. We have used a method suggested by Delahay^(129, 130) where the charge required by an electrode reaction is fed by the charging of the electrical double layer at open circuit, as the area of the amalgam drop increases. This method is particularly suited for studies of the kinetics of the alkaline earth metal amalgams, since the surface charge on the amalgam is quite negative, and the capacitance of the double layer is relatively constant.

In the case of a barium amalgam drop expanding into a solution containing a relatively large concentration of Ba^{++} , the expansion of the double layer (which is negatively charged) produces a cathodic current density

$$i_c = q \frac{1}{A} \frac{dA}{dt} \quad (1)$$

where t is the time (seconds) A is electrode area (cm^2), q is surface charge density, a thermodynamic property of the interface, given by

$$q = C_{int} (E - E_z) \quad (2)$$

where C_{int} is the integral capacity of the double layer at potential E , ($20 \mu f/cm^2$) and E_z is the zero-charge potential of the interfacial system (-0.16 v).

If the electrode is at open circuit, a situation which may be approximated experimentally by the use of a high-impedance oscilloscope amplifier, the cathodic charging current is balanced by a net anodic current from the dissolution of the amalgam:

$$i_a = i_o \exp \left[\frac{\beta F}{RT} (E - E_{eq}) \right] \quad (3)$$

In this equation, i_o is the exchange current and β is the anodic transfer coefficient, F is the Faraday constant, R is the gas constant, and T is the absolute temperature. The equilibrium potential E_{eq} is given by the Nernst equation:

$$E_{eq} = E_{Ba(Hg)}^O + \frac{RT}{2F} \ln \left(\frac{m_{Ba^{++}} \gamma_{\pm}}{X_{Ba} \gamma_{Ba(Hg)}} \right) \quad (4)$$

We have already calculated (Section IV-C) the standard potential of the barium amalgam electrode (molal scale for Ba^{++} activity, mole fraction scale for Ba amalgam activity) to be

$$E_{\text{Ba(Hg)}}^{\circ} = -1.7271 \pm .0003 \text{ volts vs. NHE} \quad (5)$$

from the data of Tippetts and Newton⁽⁷³⁾.

In our experiments, we used an Ag/AgCl reference electrode, whose potential varies with chloride activity; the potential which enters the equations above is on the Normal Hydrogen Electrode (NHE) scale, and is given by

$$E_{\text{NHE}} = E_{\text{exp}} + E_{\text{AgCl}}^{\circ} - \frac{RT}{F} \ln (m_{\text{Cl}} \gamma_{\pm}) \quad (6)$$

To evaluate the area of the electrode, we have assumed a spherical drop which grows at a constant mass-flow rate; an assumption which we have verified in our previous studies of hydrogen evolution on mercury and various amalgams⁽¹³¹⁾. This yields the simple relationship:

$$\frac{1}{A} \frac{dA}{dt} = \frac{2}{3t} \quad (7)$$

Combining Equations 1, 2, 3 and 7, we obtain an equation for the potential-time curve for a growing drop of amalgam:

$$i_0 t = \frac{2}{3} C_{\text{int}} (E_z - E) \exp \left[-\frac{\beta F}{RT} (E - E_{\text{eq}}) \right] \quad (8)$$

Since E (-1.1 to -1.4 volts) is much more negative than E_z (-0.16 volts) for the barium amalgam, this is an approximately logarithmic relationship:

$$E = a + b \log (i_0 t) \quad (9)$$

where the coefficients are

$$a = E_{eq} + b \log \left[\frac{2}{3} C_{int} (E_z - E) \right] \quad (10)$$

$$b = \frac{2.303 RT}{\beta F} \quad (11)$$

Note that the coefficient a depends slightly on E , but for a 20% change in $(E - E_z)$, a varies by only 1 mv, which is negligible on the scale of this experiment. Note also that the mass flow rate does not enter into the final expression.

Our experiment consisted of measuring the current-time curve of a single barium amalgam drop at open circuit, using a Tektronix Oscilloscope with a high-impedance differential amplifier. The oscilloscope trace was photographed and read with a scale.

The dropping amalgam electrode assembly and solution reservoirs were as described previously. A silver-silver chloride reference electrode was used in the $BaCl_2$ solution, and the potentials so observed were converted to the normal hydrogen electrode scale, as described in the previous report. All measurements were made using a Tektronix model 561A oscilloscope with a model 3A7 high-impedance differential amplifier containing a comparison voltage potentiometer with ± 0.0001 volt accuracy. The oscilloscope traces were photographed and read to ± 0.2 mm. Calibrations were made with the comparison potentiometer and a Tektronix model 180A time-mark generator.

The amalgam was prepared by bringing mercury and a piece of shiny barium metal in contact under an atmosphere of argon. This mixture was allowed to stand overnight, with occasional stirring, to insure complete saturation. The amalgam thus prepared was diluted to the desired concentration.

In runs 4, 5, 6, 7 and 8 (see Table XVIII), the saturated amalgam was used, and these resulted in potential readings which were essentially at equilibrium and did not change over a substantial period of time. A slight time-dependence of potential was observed in experiment 6, when the electrolyte contained both BaCl_2 and CaCl_2 , and an attempt was made to analyze this data for kinetic parameters (see below).

TABLE XVIII

Transfer Coefficients and Exchange Currents for
Barium Amalgams in BaCl_2 Solutions at 25°C

<u>Data Set</u>	<u>X_{Ba}</u>	<u>m_{BaCl_2}</u>	<u>E_{eq}</u>	<u>β</u>	<u>$\log i_0$</u>
3A	1.98×10^{-4}	.06635	-1.6435	$0.262 \pm .009$	$-3.71 \pm .02$
3B				$0.295 \pm .011$	$-3.70 \pm .03$
1	7×10^{-5}	.9642	-1.6459	$.343 \pm .018$	$-4.94 \pm .09$
10A	2.86×10^{-3}	1.7053	-1.6556	$1.23 \pm .06$	$-1.46 \pm .03$
10B				$1.267 \pm .029$	$-1.55 \pm .01$
2A	1.98×10^{-4}	.3108	-1.6600	$0.395 \pm .011$	$-3.70 \pm .02$
2B				$0.468 \pm .023$	$-3.75 \pm .05$
9A	2.86×10^{-3}	.3108	-1.6779	$1.69 \pm .03$	$-1.74 \pm .02$
9B				$3.1 \pm .3$	$-1.99 \pm .05$
6A	4.7×10^{-3}	.4787*	-1.6801	$12.6 \pm .3$	$-2.82 \pm .05$
6B				$15.6 \pm .3$	$-3.12 \pm .05$

* Solution also contained 0.5112 m CaCl_2

Note: Errors are standard deviations.

With the more dilute amalgams, reproducible current-time traces were obtained. These amalgams were analyzed to determine their concentrations, since the exact amount of barium in the saturated amalgam was not certain — some solid amalgam apparently was always transferred. The amalgams used in runs 1, 2, and 3 were analyzed by dissolving them in hydrochloric acid and analyzing the solution for barium with a Perkin-Elmer flame photometer. The amalgams used for runs 9 and 10 were analyzed by the flame photometer, and also by dissolving the amalgam in standard hydrochloric acid and back-titrating with standard NaOH. The concentration obtained by these two methods agreed to within 1%, which corresponds to an error of 0.1 mv in the potential, and is satisfactory.

A typical current-time curve obtained from the best measurements is given in Fig. 37. The notations A and B after the run numbers in Table XVIII signify duplicate measurements, sometimes with different time scales. For runs 6, 9, and 10, the drop times were only a few milliseconds, and the assumptions of spherical drops and uniform flow rates may not be as good as for runs 1, 2, and 3, where the drops had a lifetime of several tenths of a second.

There were several points about the results of the first calculations which concerned us. First, and most important, were the large values of β which were obtained consistently for runs 9 and 10. Whether these actually reflected a change in mechanism, or were due to some systematic error, was not clear. The other point was that while the iterative method appeared to converge adequately for the well-behaved runs no. 1, 2, and 3; the convergence was not so good for runs 9 and 10, and neither did the results of run 9A agree with the results of 9B.

Of the possible systematic errors, the most important were judged to be:

- (a) Failure of the assumption that the amalgam drops formed spherically at a uniform mass flow rate. This assumption is particularly likely to fail for the very short drop lifetimes of runs 9 and 10.

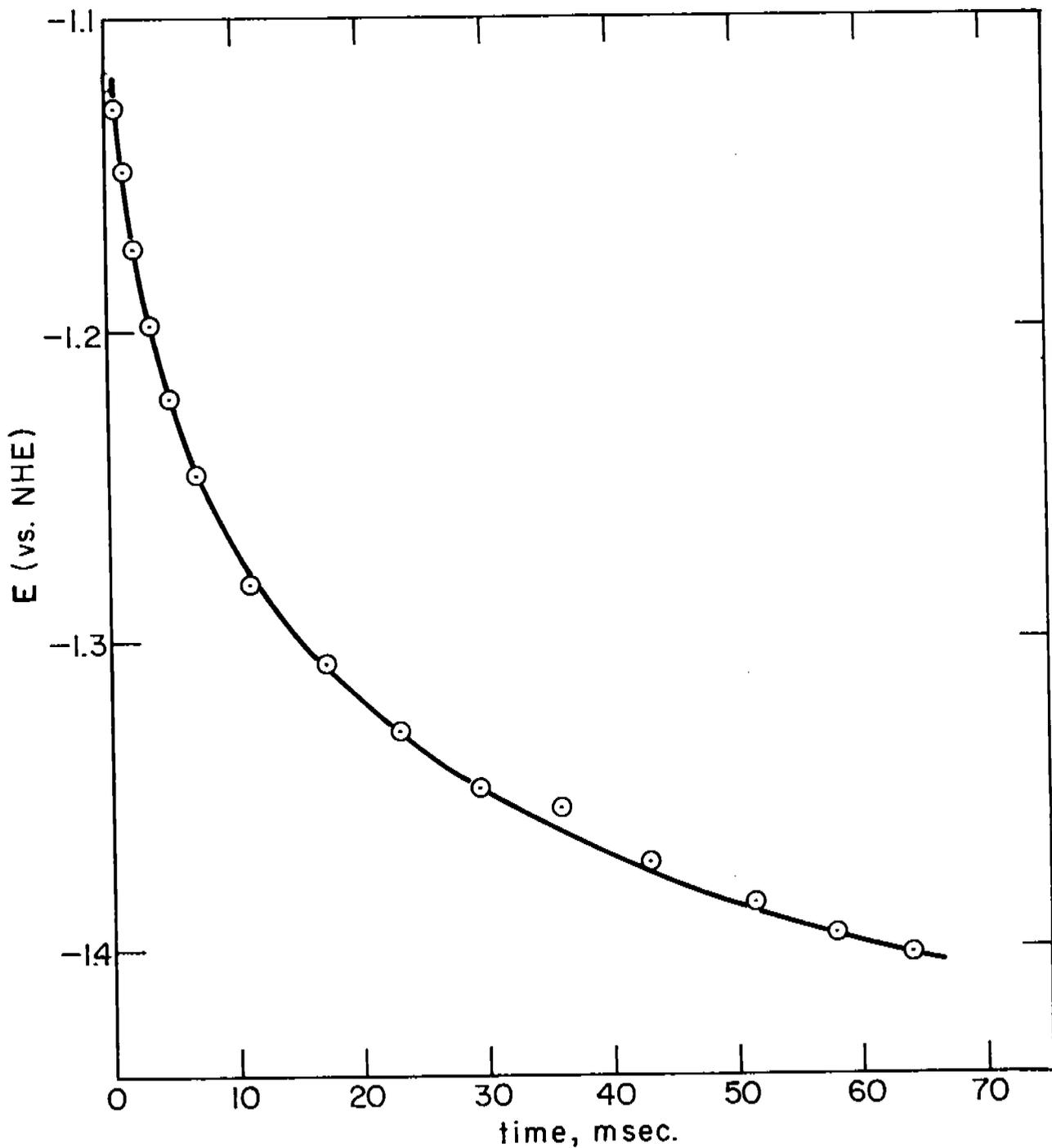


Fig. 37 Typical current-time curve for a barium amalgam electrode.
(Run 1, Table XVIII)

- (b) An additional cathodic contribution to the current from the deposition of barium on the amalgam (the back-reaction).
- (c) An additional cathodic contribution to the current from hydrogen evolution.

Although there is no simple way to assess the effect of the first of these errors, it is possible to correct for the second and third by the use of a more complex equation describing the current-time curve. The calculations based on this more sophisticated method are given next.

Correction for Cathodic Currents. In our original derivation, we assumed that the only cathodic contribution to the current came from double-layer charging and that the only anodic contribution came from dissolution of the amalgam. We can modify the basic equation to include cathodic contributions from deposition of Ba on the amalgam and from hydrogen evolution. At open circuit, we have:

$$i_a = i_{ch} + i_c + i_H \quad (12)$$

where

$$\left. \begin{aligned} i_a &= i_o \exp \left[\frac{\beta F}{RT} (E - E_{eq}) \right] \\ i_c &= i_o \exp \left[-\frac{\alpha F}{RT} (E - E_{eq}) \right] \end{aligned} \right\} \text{For Ba(Hg) = Ba}^{++} + 2e \quad (13)$$

$$i_H = i_o^H \exp \left[-\frac{\alpha_H F}{RT} (E + 0.059 \text{ pH}) \right] \quad (14)$$

$$i_{ch} = C_{int} (E_Z - E) \left(\frac{2}{3t} \right) \quad (15)$$

The pH of the solutions used was about 10. The transfer coefficient and exchange current for hydrogen evolution on mercury⁽¹⁵²⁾ are known to be: $i_o^H = 3 \times 10^{-13}$ amp/cm², $\alpha^H = 0.5$. The equilibrium potential of the barium amalgam (E_{eq}) was calculated as before, and C_{int} and E_z were the same as before. The problem is to determine the best values of the parameters β and i_o for a given set of E , t data.

To bring these equations into a form which is tractable for curve-fitting, we assumed that the cathodic transfer coefficient for the barium reaction was given by

$$\alpha = 2 - \beta. \quad (16)$$

Since the back reaction is a small contribution to the total current, this assumption does not have too much effect on the results. The equations then reduce to the form

$$y = \beta x + \log i_o \quad (17)$$

where

$$y = \log (i_{ch} + i_H) - \log \left\{ 1 - \exp - \frac{2F}{RT} (E - E_{eq}) \right\} \quad (18)$$

$$x = \frac{F}{2.303 RT} (E - E_{eq}) \quad (19)$$

from which β and i_o can be obtained by the method of least squares.

A computer program used to carry out these calculations was written in CAL, a conversational algebraic language used with the SDS-940 time-sharing system, marketed in this area by Dial-Data, Inc. The results of these calculations are given in Table XVIII.

Figures 38 and 39 show the deviations of the experimental data from the theoretical curve, expressed as $y(\text{calc}) - y(\text{obs})$. In all cases, the systematic (s-shaped) deviations far exceed the random error in

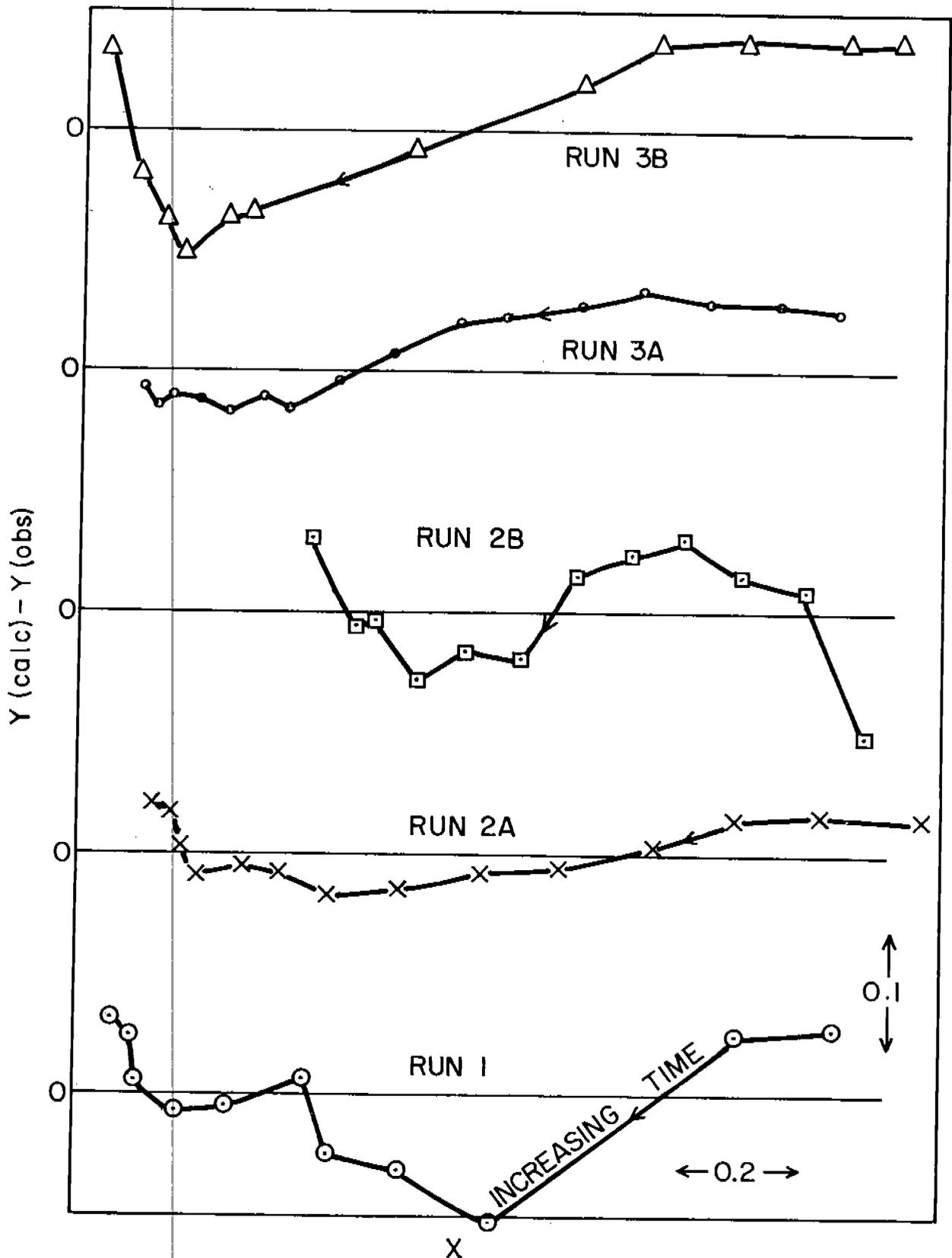


Fig. 38 Deviations of current-time curves from theoretical equations.

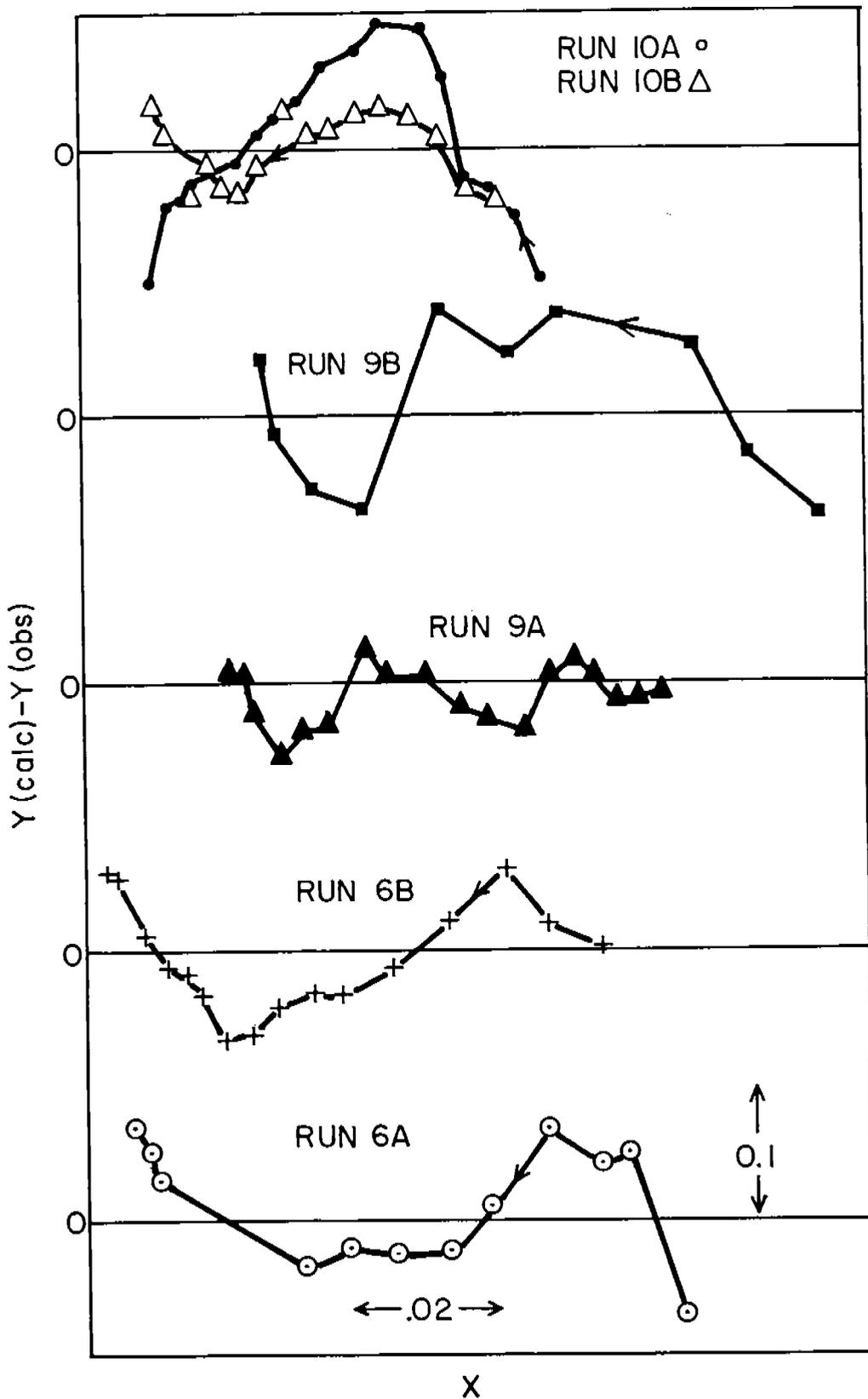
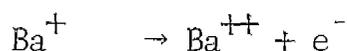
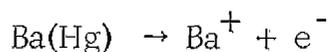


Fig. 39 Deviations of current-time curves from theoretical equations.

the measurements. Thus the equations do not describe the observed current-time curve exactly. However, in no case were the deviations greater than 10%, and some of these systematic deviations may be due to nonlinearity in the oscilloscope or in the method of reading the curves. On Figs. 38 and 39, potential becomes more negative and time increases as one proceeds from right to left. There are no obvious systematic deviations at the small time intervals, as one might expect if there were deviations from the spherical-uniform drop assumption.

Figure 40 shows the relative contribution of the hydrogen evolution current to runs 2 and 3. The arrows show increasing time. For all other runs the hydrogen evolution current was completely negligible: less than 4% for run 6, and less than 1% of the total for runs 1, 9, and 10. Similarly, the contribution of the back-reaction is also small, but not negligible at the high amalgam concentrations.

Discussion. Detailed analysis of the reaction mechanism must await studies of the concentration dependence of i_0 , but some speculations can be made at this early stage in the investigation. The anodic dissolution of barium amalgam may be represented formally by the two steps



and different expressions for the potential dependence of the over-all anodic reaction may be obtained depending on which of the two steps is assumed to be rate-controlling. In either case, an equation of the form of Equation 3 or Equation 13 results. If the first reaction is slow, β is the transfer coefficient for the first reaction, and should be between 0 and 1. If the second reaction is slow, $\beta = 1 + \beta'$, where β' is the transfer coefficient for the second reaction, and β should be between 1 and 2.

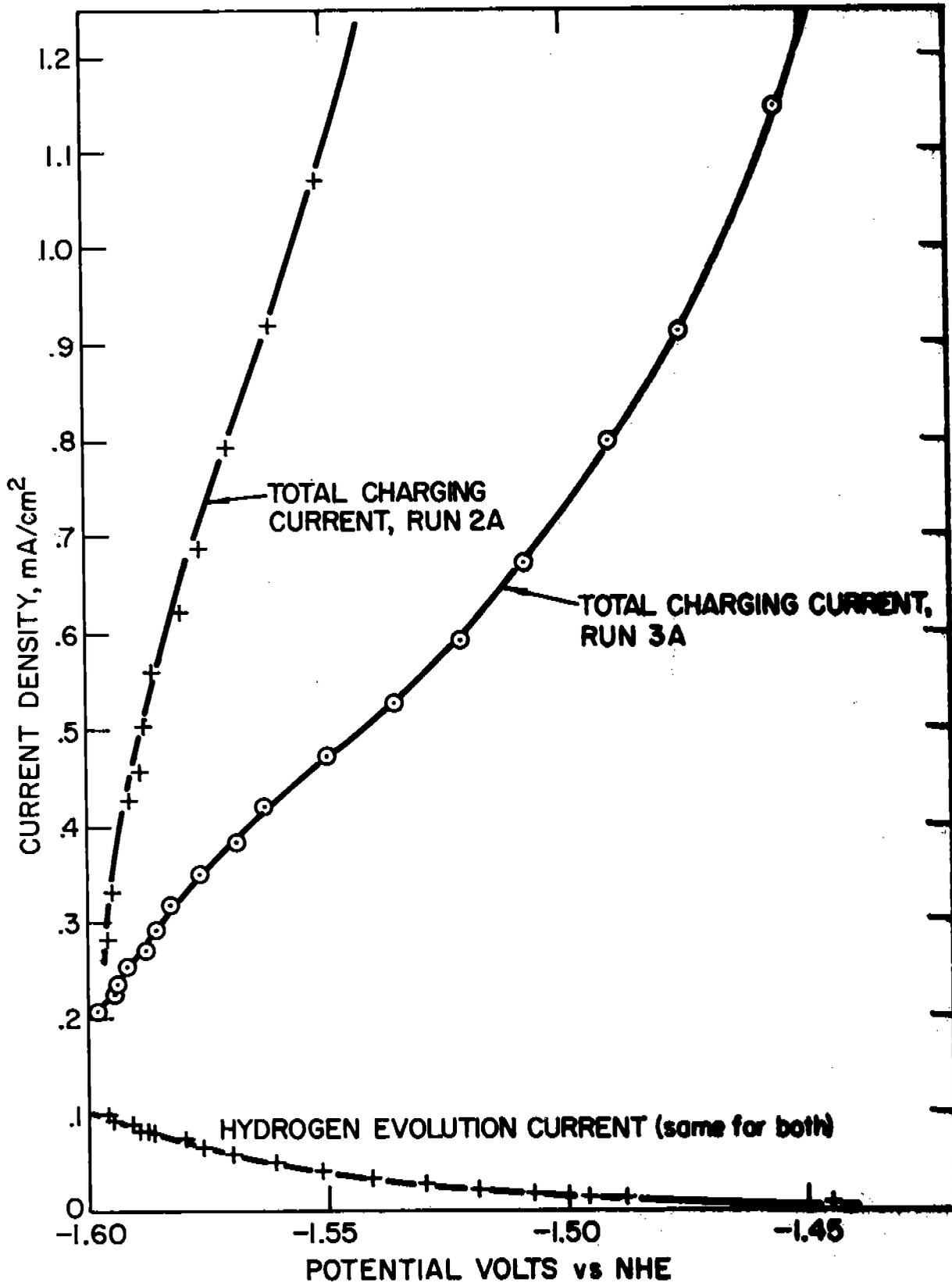


Fig. 40 Contribution of hydrogen evolution to total current.

If both electrons are transferred within the time of a collision with the electrode, the distinction is blurred, and β may have any value between 0 and 2. Unless β is approximately unity, however, this latter possibility is considered quite unlikely from a theoretical viewpoint^(132, 133).

Although there are differences from the results of the iterative method, runs 1, 2, and 3 still give values of β near 0.4; whereas runs 9 and 10 give large values of β . Run 6 does not fit the equations at all; it gives impossibly large values for β . It is interesting to note that runs 2 and 3 give essentially the same values of exchange current for the same amalgam concentration although the concentrations of BaCl_2 in the solution differ by a factor of 20. Run 1, with a lower amalgam concentration, gives a small i_0 .

Our experimental results at low amalgam concentration imply that the first step is rate controlling, and that the oxidation of Ba^+ to Ba^{++} occurs very rapidly. Thus a negligible concentration of Ba^+ will be present, and coulometric studies should reveal a rigorously constant two faradays barium ion produced. The most important criterion of mechanism is the concentration dependence of the exchange current i_0 . If the first electron-transfer step is rate-controlling, we expect that the exchange current will vary as the β power of the barium ion activity, and as the $1-\beta$ power of the barium amalgam activity. This is verified quantitatively. Further experiments with the effect of ligand concentration (such as pH effects) can identify the actual reacting species more definitely⁽¹³³⁾.

If the large values of β obtained for runs 9 and 10 (higher amalgam concentrations) are true estimates of the kinetic parameters and not the result of a systematic error due to the fast dropping rate, these results imply a dramatic change in mechanism over the concentration range from $X_{\text{Ba}} = 2 \times 10^{-4}$ to $X_{\text{Ba}} = 2 \times 10^{-3}$, whereby the second reaction becomes slower, and relatively high concentrations of Ba^+ can build up. Runs 9 and

10 have the same amalgam concentration, but the exchange current is significantly higher for run 10 (with the higher BaCl_2 concentration). This result indicates that the concentration of Ba^{++} (and hence Ba^+) influences the rate, which it apparently does not at lower amalgam concentrations.

A quantitative inconsistency in the results of runs 1, 2 and 3 is the very strong dependence of i_0 in amalgam concentration. If the reaction were a simple reversible electron-transfer, the coefficient $d(\log i_0)/d(\log X_{\text{Ba}})$ should be approximately equal to β . Evaluating this coefficient, from the results of runs 1, 2, and 3, we obtained approximately 2.7, instead of the expected 0.3 to 0.4. This may simply reflect the changing mechanism in this concentration region, and more dilute amalgams may give more consistent results.

The results of run 6 are ambiguous. It is not possible to tell whether the poor fit results from the short drop times, or from the interference of the calcium ion with the barium reaction. The low exchange currents obtained are meaningless because they result from the impossibly high values of β which are obtained. If the barium ion reaction is the only one taking place, β cannot be greater than 2. Interpretation of these results will have to wait until some kinetic data are obtained from the calcium amalgam electrode.

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VIII. PUBLICATIONS RESULTING FROM THIS WORK

The following publications have resulted from work done under this contract:

- (1) "Activity Coefficient Measurements in Aqueous Sodium Chloride-Sodium Sulfate Electrolytes Using Sodium Amalgam Electrodes" by James N. Butler, Philomena T. Hsu, and John C. Synnott, J. Phys. Chem. 71, 910 (1967).
- (2) "Activity Coefficient Measurements in Aqueous NaCl-LiCl and NaCl-KCl Electrolytes Using Sodium Amalgam Electrodes" by James N. Butler, Rima Huston, and Philomena T. Hsu, J. Phys. Chem. 71, 3294 (1967).
- (3) "Activity Coefficient Measurements in Aqueous NaCl-CaCl₂ and NaCl-MgCl₂ Electrolytes Using Sodium Amalgam Electrodes" by James N. Butler and Rima Huston, J. Phys. Chem. 71, 4479 (1967).
- (4) "The Standard Potential of the Calcium Amalgam Electrode" by James N. Butler, J. Electroanal. Chem. 17, 309 (1968).
- (5) "The Mean Activity Coefficient of Na₂SO₄ in Aqueous Na₂SO₄-NaCl Electrolytes" by John C. Synnott and James N. Butler, J. Phys. Chem. 72, 2474 (1968).
- (6) "The Activity Coefficient of Calcium Ion" by James N. Butler. Letter submitted to the editor of Anal. Chem.
- (7) "The Thermodynamic Activity of Calcium Ion in Sodium Chloride-Calcium Chloride Electrolytes" by James N. Butler. Biophysical Journal, in press.

- (8) "The Standard Potential of the Lithium Electrode in Aqueous Solutions" by R. Huston and J. N. Butler. J. Phys. Chem., in press.
- (9) "Calcium Activity Measurements Using a Liquid Ion Exchange Electrode in Concentrated Aqueous Solutions" by R. Huston and J. N. Butler. Submitted to Science.

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