

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

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UNITED STATES DEPARTMENT OF THE INTERIOR • Walter J. Hickel, Secretary
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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 relevance of activity coefficient measurements to the development and engineering of desalination processes is discussed, and the scope of this research program is delineated. Short abstracts of ten published papers resulting from work done under this program are given, and unpublished work carried out during the past year is described in detail. This includes measurements of the activity coefficient of NaCl in electrolytes containing NaHCO₃ and Na₂CO₃ (the first work of this type), studies of acid-base equilibria of carbonate systems in the presence of NaCl, and a theoretical analysis of the above data in terms of an ion-pairing model. The amalgam electrode method is shown to be much more accurate than glass electrode measurements in solutions containing HCO₃⁻. The first measurements of activity coefficients in the system NaCl-NaF-H₂O, making use of a fluoride-reversible LaF₃ membrane electrode, are also reported, and again the amalgam electrode method gives more accurate results than measurements with a glass electrode, which deteriorates rapidly in the presence of fluoride. In contrast, sodium selective glass electrodes are shown to give quite accurate measurements of activity coefficients for NaCl in mixtures with KCl and to retain this selectivity at high ionic strengths. Some experiments with a new liquid ion exchange electrode system selective for Ca²⁺ are described. These results are much more accurate than those obtained using previously available ion exchangers.

Some brief studies of the kinetics of the barium and calcium amalgam electrodes are summarized, and the computer programs used for calculations described in this report are given in full.

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I. INTRODUCTION

Many different physical and chemical phenomena are involved in desalination processes, but their quantitative description almost invariably involves the chemical potentials of the various components of a saline solution. Accurate evaluation of chemical potentials, in turn, requires knowledge of activity coefficients which express the deviations (as much as a factor of ten) from ideal concentration dependence. Because of this wide ranging applicability, studies of activity coefficients in multicomponent salt solutions are of basic importance to all desalination methods.

Until recently, there were virtually no data available on the activity coefficients of solutions containing more than one salt component. In the past 4 years, however, a number of systems containing two salt components have been studied, and a useful body of data is beginning to be built up. Before we present the result of our research, let us first examine a few cases to see where knowledge of activity coefficients in multicomponent solutions could improve the quantitative understanding and design of desalination processes.

A. Distillation

Distillation is conceptually the simplest and technically the most advanced of desalination processes. Thermodynamically, it depends on the vapor pressure of the saline solution at the temperature of distillation and, hence, on the activity of water in the solution. It is possible to calculate the activity of water by knowing the activity coefficients of all the various salt components (using the Gibbs-Duhem relation), but in practice a fairly accurate approximation of the vapor pressure can be obtained simply from activity coefficient and heat of dilution data for NaCl solutions, with small modifications to account for the presence of divalent ions.¹

However, other properties of saline solutions which are equally important for the design and operation of distillation plants cannot be predicted from such a simple model. Scale formation, for example,

involves specific ionic equilibria which depend, of course, on the activities of minor components (Ca^{2+} , Mg^{2+} , SO_4^{2-} , CO_3^{2-}) of the saline solution. Nucleation and growth phenomena are also important, and these depend on chemical potential gradients in the boundary layer at the wall there the scale deposits.

Activity coefficients have rarely been used in the analysis of data on scale formation because of their limited availability, particularly in concentrated solutions of many components. Activity, not concentration, is well known to be the important parameter. This is clear, for example, from the increase in solubility of calcium sulfate as the total salt content is increased, but the effects of specific salts are quite complex and difficult to predict.² An understanding of such interactions is necessary to explain, and thus predict, the wide variability in the quantity and thermal resistance of scale formed in different waters. For example, the thermal resistance of scale formed during the boiling of water from the Donets Basin is considerably larger than that formed during the boiling of water from the Caspian Sea, although the concentration of scale forming agents in Caspian Sea water is three to four times larger.³ The origin of this difference is to be found in the much larger total salt content of the Donets Basin water, and the specific effects of these higher ionic concentrations on the activity of scale forming materials.

B. Reverse Osmosis and Electrodialysis

The effect of the chemical potentials, and hence of activity coefficients of individual components, in multicomponent solutions become quite obvious when we examine the basic equations governing transport of solutions through membranes. The economically important processes of reverse osmosis and electrodialysis depend on these principles, and all engineering design of such systems is ultimately based on the same transport equations. The driving force, X_i , for the separation process of each component, i , is the sum of a chemical potential gradient $\nabla\mu_i$, an electrical potential gradient, $\nabla\phi$, and the external hydrodynamic or mechanical forces, Y , imposed on the system:

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

Here z_i is the charge on species i . (By convention, the Faraday constant, F , is explicitly included, but not the conversion factors between thermal and mechanical energy units.)

In reverse osmosis, the mechanical force (pressure) opposes the chemical and potential gradient due to salt concentration (each of these is typically 10^5 J/mol cm), and the electrical potential term is small except in the interfacial regions where some space charge may develop. In electro dialysis, the mechanical forces are small and the chemical potential gradient is opposed by an electrical potential gradient (typically 10^5 J/mol cm) supplied by an external power source. In either case, 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 now the sum is taken over all the components of a multicomponent electrolyte (with suitable concentration restrictions to make the electrolyte as a whole neutrally charged), v_i is the partial molar volume of component i , p is the pressure, and ∇c_k is the gradient in concentration of each of the various components.

For a concentration ratio of 2 across a membrane of thickness 0.01 cm, the chemical potential gradient is approximately $1.7 \times 10^5 \text{ J/mol cm}$, if we approximate activities by concentrations. Let us now assume that the activity coefficient, γ_i , of component i changes from 0.6 to 0.8 as we go from the more concentrated to the more dilute solution. Then, $\nabla \mu$ is reduced to $1.0 \times 10^5 \text{ J/mol cm}$, and the driving force for the desalination process changes by about 70%.

This example makes an obvious point, but it must be emphasized that the kinetics as well as the thermodynamics of the overall process are affected. The flux of component k is, in the first approximation, a linear function of the forces, X_i :

$$J_k = \sum_i L_{ki} X_i \quad (3)$$

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.

In multicomponent solutions, the diagonal coefficients of 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, these become

$$\left(\frac{\partial \mu_i}{\partial c_i} \right) = \frac{RT}{c_i} + \frac{RT}{\gamma_i} \left(\frac{\partial \gamma_i}{\partial c_i} \right) \quad (4)$$

$$\left(\frac{\partial \mu_i}{\partial c_k} \right) = \frac{RT}{\gamma_i} \left(\frac{\partial \gamma_i}{\partial c_k} \right) \quad i \neq k \quad (5)$$

In these expressions, the term RT/c_i is typically positive, of magnitude 0.5 to 5 kJ-l/mol. The terms involving activity coefficients usually tend to become larger as the concentrations increase, and may reach magnitudes equal to that of the main term. In solutions of concentration near 1m, the activity coefficient terms are typically 10 to 20% of the main term. The cumulative effect of several such terms can thus exceed the magnitude of the term RT/c_i , but the activity coefficient terms are generally ignored at present in the analysis of membrane processes.

Thus, unless we have determined the activity coefficients of the various components in the multicomponent solutions we are dealing with, we may make errors of as much as 100% in analysis or prediction of the behavior of specific practical systems.

Another aspect of the membrane based processes is the description and proper evaluation of the effects of a concentrated boundary layer formed near the membrane. In equations of hydrodynamic flow, which are based on the forces and fluxes outlined above, it is conventional to replace gradients of activity (which arise from chemical potential gradients) by gra-

dients of concentration. The result is to introduce errors of the type discussed above. These show up as additional concentration dependence of parameters such as diffusion coefficients and ionic mobilities, and their consequence is to limit the usefulness of measurements made under particular circumstances for application to more general situations.

C. Other Processes

The activity of individual components is also of significance in other desalination processes. For example, the ultimate efficiency of a freezing process depends on the activity of water and salts in both the liquid phase and the solid phase, and only if there is a high degree of salt rejection from the solid phase can the process be effective. Solvent extraction processes depend on the activity of salt components both in the aqueous phase and the organic phase, and to predict the solubility of organic material in the aqueous phase, the effect of ionic components on the activity of neutral molecules must be known. In adsorption processes the essential factors are quite specific chemical and physical equilibria between the aqueous phase and the surface of the adsorbent, and again, these depend on the activity of ionic components in the aqueous phase. The use of total concentration instead of ionic activity makes the phenomena seem even more complicated than they really are. Electrosorption, in the same way, depends on the activity of dissolved species, and the structure of the electrical double layer at the electrode-solution interface involves chemical potential gradients and space charge layers of the same type as we discussed in connection with membrane processes.

Thus, we can see that virtually all desalination processes involve the activity of ionic species, and the use of concentration as a substitute is often quite a poor approximation. Accurate knowledge of activity coefficients in multicomponent solutions would make it possible to describe these processes in terms of true chemical potentials, and hence to avoid many errors of interpretation and extrapolation.

D. The Scope of Activity Coefficient Measurements

How close are we to reaching the stage where multicomponent activity coefficient data can be used with confidence in engineering de-

sign? For some simple situations we already have at our disposal the required data, and the problem is largely one of making them available in a form which can be readily used. Useful bibliographic and numerical tables of activity coefficient data for solutions containing more than one salt component have been partially compiled.^{4,5,6} Some measurements are available on nearly 100 systems, but a comprehensive and critical survey has not yet appeared in a single volume, and most engineering handbooks have no such data at all.

The difficulty with making such data available for a usefully wide variety of systems is the lack of a simple and general theoretical framework in which to present experimental results. For relatively dilute aqueous solutions there is no problem at all, since the Debye-Hückel theory and its simple extensions^{7,8} can provide an accurate estimation of activity coefficients in quite complex electrolyte mixtures, provided the total ionic strength is below 0.1m. If the ionic strength exceeds this limit, errors greater than 3% are encountered for univalent electrolytes, and at ionic strengths exceeding 1.0, the theoretical expressions lose all predictive value because of the complex and specific association phenomena between ions.⁹ This is precisely the range which is of most interest for desalination. The situation is even worse with polyvalent ions, where a whole series of stable ion pairs^{8,10} and coordination complexes^{9,11} may be present in the solution.

Activity coefficients for electrolytes containing a single salt component have invariably been presented in tabular form for all concentrations higher than about 0.1m, because of the difficulty of finding a simple algebraic form for the function.^{12,13,14} For the same reason, accurate presentation of data for solutions containing two or more salt components becomes exponentially more cumbersome. The major components of sea water are the ions Na^+ , Cl^- , Mg^{2+} , and SO_4^{2-} . These concentrations are restricted by the electroneutrality condition, so that there are only three independently variable components in a solution containing these four ions. If we include the temperature as an additional variable, and consider all accessible ranges of concentration, a compilation of activity coefficient

data to cover in reasonable detail the solutions containing these four ions would require thousands of measurements. Of this hypothetical compilation, we can at present supply about 1% of the data, and some of this is not as accurate as we would like.

Although we know the activity coefficients of solutions containing each possible salt component (i. e., NaCl, Na₂SO₄, MgCl₂, or MgSO₄) alone in water, only for NaCl has a substantial temperature range been covered. Furthermore, we know the data for most solutions with two salt components only at 25 °C. Since some heat of mixing data are also available, this might be extended 10 or 20° in either direction without the loss of too much accuracy, but predictions for much higher temperatures could be quite uncertain. We have only scattered data on mixtures containing three salt components, mostly at compositions close to that of sea water. No systematic study has been made over a wide range of concentrations, and virtually no temperature dependence data are available at all.

If we now consider the other components present in sea water, brackish water, and various inland saline waters, the possible number of combinations become staggering. Additional species which are relevant include Ca²⁺, K⁺, Sr²⁺, H⁺, HCO₃⁻, CO₃²⁻, Br⁻, BO₂⁻, F⁻, OH⁻, H₃BO₃, dissolved CO₂, dissolved O₂, as well as numerous trace metal ions and organic materials. Only an infinitesimal fraction of the required data is presently available.

Certainly, the immensity of this required body of data could be greatly reduced by means of adequate theories of ionic interactions. Even empirical relations which are orders of magnitude more complex than the Debye-Hückel theory⁶ are a help. But before further theories and empirical relations can be evolved and tested, we must have considerably more accurate and complete data than we do now.

At present, the most useful simplification that can be made in expressing data for multicomponent concentrations greater than 0.1m is Harned's rule, an approximate empirical relationship:^{12,13}

$$\log \gamma_{12} = \log \gamma_{10} - \alpha_{12} X_2 I \quad (6)$$

where I is the ionic strength of the solution under consideration, γ_{12} is the mean activity coefficient of salt 1 in the mixed electrolyte, X_2 is the ionic strength fraction of salt component 2, and γ_{10} is the mean activity coefficient of 1 in a solution containing only that salt, but at the same ionic strength, I . Thus, by using data obtained in a solution with only a single salt component (γ_{10}) together with the composition of the solution with two salt components (I and X_2), one can calculate γ_{12} from α_{12} , or vice versa.

The advantage of this transformation is that α_{12} is a much less complicated function of composition. For most systems studied thus far, the Harned rule coefficient, α_{12} or α_{21} , has been found to be virtually independent of X_2 , and in some cases, e. g., NaCl-Na₂SO₄ or NaCl-KCl, nearly independent of I as well. A comprehensive table of γ values would require about 800 numerical entries for each pair of salt components. Using Harned's rule, this table can be reduced (in these latter cases) to two numerical values (α_{12} and α_{21}) with little loss in accuracy. Clearly, this is desirable if it can be done.

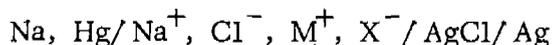
Still more desirable would be the possibility of calculating γ_{12} entirely from data for solutions containing each of the two components separately (i. e., from γ_{10} and γ_{20}), but this has not proved sufficiently accurate. In some cases, however, a theory of this type (Bronsted-Guggenheim, for example)^{4, 5, 11, 12} can provide a better estimate of γ_{12} than simply neglecting the specific interactions entirely ($\alpha_{12} = \alpha_{21} = 0$). The obvious extension of these ideas is the possibility of calculating activity coefficients in solutions containing three salt components from data obtained in simpler solutions. Thus far, not enough data have been collected to assess the possibility of doing this, although some progress has been made in correlating free energies^{15, 16} and heats of mixing.¹⁷

What does this mean for the designer of practical desalination systems? Certainly he will not wait until we have compiled libraries full of activity coefficient data. But neither should he be forced to carry out his calculations with the meager amount of badly scattered data that we presently have available. If no theoretical framework for treating thermodynamic data for multicomponent systems is developed, then engineering

design data must be measured under actual operating conditions, and optimizing the many variables involved becomes an enormously difficult task. Indeed, one may reasonably expect that libraries full of engineering data of less theoretical value, covering a considerably more restricted range of compositions, temperatures, and pressures, will eventually be accumulated.

E. The Scope of this Research

The study of activity coefficients in multicomponent salt solutions being carried out under this program is aimed at providing the required body of data related to saline water conversion systems. The primary experimental technique used is to measure the emf of the cell



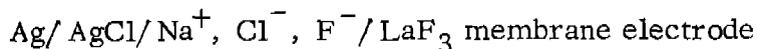
which is determined by the activity of NaCl in the multicomponent electrolyte, provided that the metal ion, M^+ , is not reducible by the sodium amalgam and that the silver salt of the anion, X^- , is more soluble than AgCl. Two such cells, using dropping amalgam electrodes fed from the same reservoir, are measured simultaneously, providing a direct comparison of the activity coefficient of NaCl in the multicomponent salt solution with aqueous NaCl at the same ionic strength. The electrolyte must be rigorously purified from dissolved oxygen and organic material, and the amalgam must contact the solution for the shortest time required to make the measurement. Accurate measurements of the activity coefficients of NaCl in mixtures with lithium, calcium, or magnesium ions, as well as a variety of nonreducible anions, can be made because these do not interfere with the operation of the sodium amalgam electrode.

Thus far, activity coefficient measurements using the above cell have been made in aqueous NaCl- Na_2SO_4 ,⁽¹⁸⁾ NaCl-KCl,⁽¹⁹⁾ NaCl-LiCl,⁽¹⁹⁾ NaCl- CaCl_2 ,⁽²⁰⁾ NaCl- MgCl_2 ,⁽²⁰⁾ NaCl- BaCl_2 ,⁽⁵⁾ NaCl- NaHCO_3 , NaCl- Na_2CO_3 , and NaCl-NaF electrolytes at ionic strengths between 0.1 and 6m. In the first five cases, where isopiestic data have also been obtained, agreement was within experimental error. Measurements with other electrochemical

cells have also been made to compare with the amalgam electrode results. Sodium selective glass electrodes agree well for the systems NaCl-Na₂SO₄,^(15, 16, 21) NaCl-CaCl₂,^(15, 20) NaCl-MgCl₂,^(15, 20) and NaCl-KCl.⁽²²⁾ A lead amalgam-lead sulfate electrode (reversible to sulfate ion) has been used to measure the activity of Na₂SO₄ electrolytes,²¹ and good agreement has been obtained with isopiestic data^{6, 16, 23} as well as with values calculated from NaCl activity using the Gibbs-Duhem equation.¹⁸

Because two components (CO₂ and H₂O) are volatile in carbonate or bicarbonate-containing electrolytes, conventional isopiestic methods cannot be applied to these important systems, and the amalgam electrode method is the most direct approach to obtain thermodynamic data. Measurements made under the present program are the first of this type.

In NaCl-NaF electrolytes, measurements have been made using a sodium amalgam electrode cell, and also a fluoride reversible LaF₃ solid state membrane electrode, from which the activity coefficient of NaF in electrolytes can be obtained directly. These data have been confirmed by measurements with the cell



which gives the ratio of activity coefficients for the two components.

In addition to the work discussed above, thermodynamic and kinetic data have been obtained for the calcium and barium amalgam electrodes^{5, 24} as well as the lithium amalgam electrode.²⁵ Attempts have been made to measure the activity of CaCl₂ directly using liquid ion exchange electrodes,^{26, 27} and a critical review of thermodynamic studies using ion selective electrodes²⁸ has been prepared.

In this report, we shall first present brief summaries of all published work resulting from this program since its inception, and then present in detail the unpublished work carried out during the period 1 August 1968 to 18 July 1969.

The amalgam electrode method, when it can be used, is the primary standard for electrochemical activity measurements. It complements re-

sults obtained by the isopiestic and other methods, and results can be combined with heats of solution to calculate thermodynamic properties of multicomponent solutions related to sea water and brackish inland waters. Future work will concentrate on solutions of three salt components and systems containing volatile components (e. g., carbonates) which are not readily accessible to isopiestic techniques.

II. PUBLISHED WORK

In this part, we present brief summaries of published results obtained under this program. A relatively complete discussion of this work has already been presented in the previous Interim Report,* with the exception of the studies of NaCl-KCl electrolytes using glass electrodes, paper no. 4, below. This latter paper, in press at the time this report is being prepared, is based on data which are presented in full in Section III.

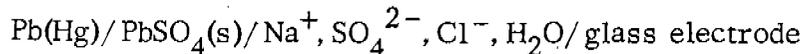
NaCl-Na₂SO₄ Electrolytes

1. Activity Coefficient Measurements in Aqueous NaCl-Na₂SO₄ Electrolytes Using Sodium Amalgam Electrodes, by J. N. Butler, P. T. Hsu, and J. C. Synnott, J. Phys. Chem. 71, 910 (1967).

Measurements of the activity coefficient of NaCl in NaCl-Na₂SO₄ electrolytes have been made using the cell Na(Hg)/Na⁺, Cl⁻, SO₄²⁻/AgCl/Ag, and have been compared with literature values obtained using cation sensitive glass electrodes. Harned's rule is shown to be obeyed for both components within experimental errors over the ionic strength range from 1 to 6m. A good approximation to the data can be obtained by taking $\alpha_{12} = +0.048$ and $\alpha_{21} = -0.034$, independent of ionic strength. The resulting activity coefficient values agree with experimental results within ± 0.01 in $\log \gamma$.

2. The Mean Activity Coefficient of Na₂SO₄ in Aqueous Na₂SO₄-NaCl Electrolytes, by J. C. Synnott and J. N. Butler, J. Phys. Chem. 72, 2474 (1968).

The activity coefficient of Na₂SO₄ in aqueous Na₂SO₄-NaCl electrolytes at 25° and total ionic strength 1.0 has been measured using the cell



where the glass electrode is reversible to Na⁺. If care is taken to exclude oxygen from

* James N. Butler, The Use of Amalgam Electrodes to Measure Activity Coefficients of Metal Salts in Multicomponent Salt Solutions, Office of Saline Water Research and Development Progress Report No. 388 (1968).

the cell during preparation and measurements, reproducibility of the order of + 0.05 mV is obtained. Harned's rule was found to be obeyed within experimental error for Na₂SO₄ (component 2) in these mixtures, and the coefficient α_{21} at I = 1 was calculated by a least-squares method to be -0.035 ± 0.005 . This agrees with the value of α_{21} calculated from published osmotic coefficients and activity coefficients of NaCl (component 1) in the corresponding mixtures.

NaCl-LiCl and NaCl-KCl Electrolytes

3. Activity Coefficient Measurements in Aqueous NaCl-LiCl and NaCl-KCl Electrolytes Using Sodium Amalgam Electrodes, by J. N. Butler, R. Huston, and P. T. Hsu. J. Phys. Chem. 71, 3294 (1967).

Measurements have been made of the potential of the cell Na, (Hg)/Na⁺, M⁺, Cl⁻/AgCl/Ag where M⁺ is either Li⁺ or K⁺. In the case of LiCl-NaCl electrolytes, activity coefficients can be calculated from these measurements, which agree with results obtained by the isopiestic method. Attempts to measure activity coefficients in KCl-NaCl electrolytes using the same cell were unsuccessful because of the reaction Na(Hg) + K⁺ = K(Hg) + Na⁺. This interference mechanism is discussed and the potentials observed in KCl electrolytes are explained quantitatively.

4. Activity Measurements in Concentrated Aqueous NaCl-KCl Electrolytes Using Cation-Sensitive Glass Electrodes, by R. Huston and J. N. Butler. Anal. Chem. 41, 0000 (1969).

Measurements of the cell

Ag/AgCl/Na⁺, K⁺, Cl⁻/glass electrode

using two commercial sodium selective glass electrodes (NAS-11-18 and LAS-10-23) have been made at 25.0 °C and constant ionic strengths from 0.5 to 4.0m, to obtain the mean activity coefficient of NaCl in the mixed electrolyte. These values are found to obey Harned's rule, and are consistent with isopiestic measurements of activity coefficients in the same system. The Harned rule coefficient, α_{12} , is 0.023 ± 0.002 at I = 3.0 and 4.0, and less precise at lower ionic strengths. The response of these

two types of glass electrodes to sodium ion activity in concentrated solutions has been shown to have the same high selectivity (1000:1 for Na^+ over K^+) as in dilute solutions.

NaCl-CaCl₂ and NaCl-MgCl₂ Electrolytes

5. Activity Coefficient Measurements in Aqueous NaCl-CaCl₂ and NaCl-MgCl₂ Electrolytes Using Sodium Amalgam Electrodes, by J. N. Butler and R. Huston, *J. Phys. Chem.* 71, 4479 (1967).

The potential of the cell $\text{Na}(\text{Hg})/\text{Na}^+, \text{M}^{2+}, \text{Cl}^-, \text{H}_2\text{O}/\text{AgCl}/\text{Ag}$, where M^{2+} is either Ca^{2+} or Mg^{2+} , has been measured, and the activity coefficient of NaCl in the mixed electrolyte has been calculated. At ionic strengths from 0.2 to 6m, Harned's rule is obeyed within experimental error. The coefficient α_{12} is near zero at high ionic strength, but becomes more negative at ionic strengths below 2m; α_{12} is more negative for NaCl-MgCl₂ than for NaCl-CaCl₂ at all ionic strengths. The results obtained agree with published activity coefficient measurements made by the isopiestic method and with cation-sensitive glass electrodes.

6. The Standard Potential of the Calcium Amalgam Electrode, by J. N. Butler, *J. Electroanal. Chem.* 17, 309 (1968).

Experimental data in the literature on the potentials of calcium amalgam electrodes in aqueous solutions have been critically evaluated, and the standard potential of the amalgam in aqueous solutions found to be $-1.996 + 0.002$ V versus the standard hydrogen electrode. The standard state of calcium in the amalgam was infinite dilution, mole fraction scale, and, within experimental error, the activity coefficient of calcium in the amalgam was unity over the range from 0 to 0.25 mol %.

7. The Thermodynamic Activity of Calcium Ion in NaCl-CaCl₂ Electrolytes, by J. N. Butler, *Biophys. J.* 8, 1426 (1968).

Experimental data on the mean activity coefficient of CaCl₂ in NaCl-CaCl₂ mixtures at ionic strengths below 1m have been used to prepare a table of activity coefficients for Ca^{2+} in solutions of physiological interest. The establishment of an empirical

calcium ion activity scale is discussed, and a number of possible assumptions are examined. The assumption $\gamma_{++} = (\gamma_+)^2$ is suggested as being the simplest with a theoretical basis.

8. Calcium Activity Measurements Using a Liquid Ion Exchange Electrode in Concentrated Aqueous Solutions, by R. Huston and J. N. Butler, *Anal. Chem.* 41, 200 (1969).

A calcium selective liquid ion exchange electrode has been used in a cell without liquid junction to test the Nernstian behavior of the liquid ion exchange membrane. With solutions of CaCl_2 alone on both sides of the membrane, the potential was a linear function of the logarithm of the mean activity of CaCl_2 with the theoretical slope (88.7 mV at 25 °C), provided the concentration difference across the membrane was not too large. The allowable concentration difference decreased as the concentrations of the solutions increased. With solutions of approximately 3m CaCl_2 , deviations were observed for concentration differences as little as a factor of 3. With 0.1m CaCl_2 on one side, the activity on the other side could be as large as 2.0 or as small as 10^{-4} without substantial deviations. Although the calcium didecyl phosphate ion exchanger used is quite selective ($\sim 10^3$) for Ca^{2+} over Na^+ in solutions more dilute than 0.1m, this selectivity is much less (~ 10) in concentrated solutions, and varies in a complex way with both ionic strength and solution composition.

Other Work

9. The Standard Potential of the Lithium Electrode in Aqueous Solutions, by R. Huston and J. N. Butler, *J. Phys. Chem.* 72, 4263 (1968).

Measurements at 25° of the cell without liquid junctions $\text{Pt}/\text{H}_2(\text{g})/\text{Li}^+, \text{OH}^-, \text{H}_2\text{O}/\text{Li}(\text{Hg})$ lead to a value of -2.1963 ± 0.0016 V for the standard potential of the lithium amalgam electrode (reference state: infinite dilution, mole fraction scale for amalgam, and molal scale for aqueous solution). This is combined with the previously measured difference in standard potentials between the lithium amalgam electrode and solid lithium to obtain a value of -3.0401 ± 0.0016 V for the standard potential of the lithium electrode in aqueous solutions. Using the experimental heat

of dissolution of lithium in acid, the standard entropy of the lithium ion (relative to H^+) is calculated to be 3.0 ± 0.1 cal/mol deg.

10. Thermodynamic Studies, by J. N. Butler. Chapter 5 of "Ion-Selective Electrodes," edited by R. A. Durst, National Bureau of Standard Special Publication No. 314 (1969).

A critical review has been made of thermodynamic studies using ion selective electrodes, with emphasis on solid state membrane and liquid ion exchange membrane types. After a discussion of the principles involved, detailed reviews are presented concerning the lanthanum fluoride membrane electrode, the silver sulfide membrane electrode, calcium selective liquid and solid membrane electrodes, and other electrodes of this type.

III. UNPUBLISHED WORK

In this part, we present in full the results of research carried out during the period 1 August 1968 to 18 July 1969. Part of this material is in the process of being published, and the remainder of it will be the basis of additional papers to be submitted for publication during 1969.

The paper, "Activity Measurements in Concentrated NaCl-KCl Electrolytes" by Rima Huston and James N. Butler, based on results given in Section III. E, has been accepted for publication in Analytical Chemistry, and will appear in October 1969. A summary of that paper was given in Section II.

The review "Thermodynamic Studies," which was also summarized in Section II, included some material on the NaCl-NaF system (Section III. D) and some material on the CaCl_2 and CaCl_2 -NaCl systems (Section III. F).

A Brief extract of the material in Sections III. A, B, and C will be presented to the Division of Water, Air, and Waste Chemistry of the American Chemical Society in September 1969, under the title "Activity Coefficients and Ion-Pairs in the Systems NaCl-NaHCO₃-H₂O and NaCl-Na₂CO₃-H₂O" by James N. Butler and Rima Huston.

A. Activity Coefficients in NaCl-NaHCO₃ and NaCl-Na₂CO₃ Electrolytes

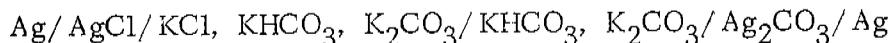
Next to sodium chloride, the bicarbonate ion is probably the most significant component of natural waters. The pH control of many ecological systems depends on carbonate buffering, and the deposition of carbonate salts on boiling is a very important problem in desalination by distillation. It is surprising, therefore, that such a limited amount of thermodynamic data are available on multicomponent systems containing bicarbonate and carbonate salts.

A brief historical summary of some relevant data will be presented first, and then we will give the results of our experimental investigations. In the next section, we will concern ourselves with the acid-base equilibria of carbonates, and following that will outline some possible interpretations of the existing experimental data in terms of ion pairing hypotheses.

The usual sources for activity coefficient data^{12,13,14} give no information at all concerning the activity coefficients of alkali carbonates or bicarbonates, but a considerable body of data exists on the protonation equilibria,¹¹ mostly in media where extrapolation to infinite dilution is possible. A significant piece of early work in this direction is that of Walker, Bray, and Johnston²⁹ who measured the carbonate-bicarbonate equilibrium in solutions of the carbonates of potassium, sodium, and lithium, over the concentration range from 0.01 to 2.5M, and also in solutions of potassium and sodium carbonate containing chloride concentrations up to 2.5M. The method used was to equilibrate the solution with a known pressure of carbon dioxide and then to analyze the equilibrium solution for total base, bicarbonate, and neutral salt (e. g., chloride). The original measurements are given for all experiments, and we intend in the near future to reanalyze these data in the light of our own experiments. Additional data were obtained with the cell:

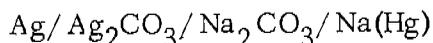


where the added KCl on the right-hand side was only 0.01M, and thus the liquid junction potential was kept to a nominal value (0.1 to 0.2 mV). These measurements give the pH of the solutions directly, and hence the protonation equilibrium constant for CO_3^{2-} (see the next section). In addition, measurements of the cell



were made, from which the solubility product of silver carbonate was obtained, as well as data which could be correlated with the original measurements of composition as a function of carbon dioxide pressure. By analysis of all these data, using the assumption $\gamma_{2-} = \gamma_{-}^2$ implied by the Debye-Hückel theory (but by no means as restrictive as any of the Debye-Hückel type equations), Walker, Bray, and Johnston were able to obtain activity coefficients for the alkali carbonates and bicarbonates.

However, the direct measurement of cells such as



was not done. We intend to carry out such measurements in the near future. These measurements will give the activity coefficients of the carbonate salts directly.

Garrels, Thompson, and Siever³⁰ have carried out an extensive series of measurements using pH-type glass electrodes in cells with liquid junctions (KCl salt bridge) in order to determine the activity of carbonate species in solutions resembling sea water. This work rests on a number of ad hoc assumptions which have not been thoroughly evaluated, and thus we cannot at this time offer an opinion on its accuracy. It is clear, that one of the critical variables—the liquid junction potential—need not have been included in these measurements. However, these authors did not make use of cation selective glass electrodes or amalgam electrodes, which would have made much of the complex analysis required to reduce pH measurements to activities of carbonate or bicarbonate species unnecessary. This work showed relatively strong association between Na^+ and CO_3^{2-} , which is not borne out by our work. We discuss this question in Section III. C.

Berner³¹ measured the pH of sea water samples equilibrated with known partial pressures of carbon dioxide, and with samples of calcium carbonate. From these data he has calculated the activity coefficients of bicarbonate, carbonate, and calcium ions in sea water. Again, cells with liquid junctions (saturated KCl) were used and a number of ad hoc, nonthermodynamic assumptions were made in order to determine individual ionic activity coefficients. These data should also be reevaluated.

Pytkowicz and coworkers have measured the dissociation constants of carbonic and boric acids in sea water and related solutions^{32,33} using a cell without liquid junction involving a glass pH electrode and an Ag/AgCl reference electrode. These results have been related to the solubility of calcium carbonate³⁴ and foraminifera³⁵ in sea water at high pressures.

In our work, we concentrated on measuring the activity coefficients of NaCl in mixtures with NaHCO_3 or Na_2CO_3 at constant ionic strength leaving the more difficult problem of direct measurement of the carbonate salt activity to subsequent work. The principal questions to be resolved were (1) whether Harned's rule was obeyed, and (2) the extent to which sodium ion associates with the bicarbonate or carbonate ion. Both these effects are

apparent in the mean activity coefficient of NaCl, as well as in the less reliable quantities looked at by the workers reviewed above.

The experiments were carried out as described previously.^{5,20,21} Na₂CO₃ was Fisher Certified reagent grade (S-263), and NaHCO₃ was of comparable purity (S-233). Chloride was less than 0.003%, potassium less than 0.005% and heavy metals less than 0.0005%. No analysis for Br⁻ or I⁻ was given, but these are almost certainly less than 0.01%.

Tables I to IV give the experimental data obtained in our work. These data have been treated by the method of least squares, after correction to round values of ionic strength, to obtain the Harned rule coefficient, α_{12} . In these least squares fits, the intercept was allowed to vary to give equal weight to all points. The values of the Harned rule coefficients obtained are summarized in Table V, together with their statistical 95% confidence limits. The data are displayed in Figs. 1 through 6, and the line representing the best fit of Harned's rule to the amalgam electrode data is drawn on each figure.

From these measurements, four observations are quite clear:

1. The glass electrode cell can give substantial systematic deviations from Harned's rule which are not supported by the amalgam data. In particular, NaCl-NaHCO₃ electrolytes at both 0.5 and 1.0m total ionic strength (Figs. 1 and 2) show this effect markedly. It is smaller but still detectable in the NaCl-Na₂CO₃ measurements (Figs. 3, 4, and 5).

2. The two glass electrodes (NAS-11-18, electrode C, and LAS-10-23, electrode B) disagree by as much as 2 mV in 0.5m NaCl-NaHCO₃, but agree more closely in NaCl-Na₂CO₃. In every case, the reproducibility of the glass electrode becomes poorer at smaller values of X₁ (larger fractions of bicarbonate or carbonate). This trend is reflected in the lower values of α_{12} obtained in the least squares fits for the glass electrode data (Table V). If points for X₁ < 0.5 are discarded, as we did in one case (1.0m NaHCO₃-NaCl), good agreement with the amalgam electrode data can be obtained. However, there is no clear theoretical basis for such a drastic limitation of the allowed composition range, and we thus must remain cautious in interpreting any precise data obtained with cation selective glass electrodes in solutions containing carbonate or bicarbonate, particularly in the pH range

near 8 or 9.

3. As we will see in Section III. C, the systematic deviations from Harned's rule observed for glass electrode data are in the wrong direction to be accounted for by ion pairing phenomena, implying that there is an excess of Na^+ at the glass electrode surface over the bulk of the solution. Because the amalgam electrode measurements give good agreement with Harned's rule, these deviations cannot be a result of solution equilibria or of reactions with the Ag/AgCl electrode. The pH of the solutions is sufficiently high that a contribution to the potential from hydrogen ions at the glass electrode is extremely unlikely. In fact, one expects deviations in this direction at low pH of the amalgam electrode measurements, rather than of the glass electrode measurements. Loss of CO_2 to the atmosphere may occur (see next section), but it has a negligible effect on these measurements. The hypothesis of some kind of specific adsorption of Na^+ does not seem too reasonable, since the Na_2CO_3 solutions do not show these deviations, and since two glasses (B and C) of quite different composition show roughly the same effect (although there are quantitative differences). Thus, there is no straightforward explanation of these systematic deviations in bicarbonate solutions at this time.

4. At constant total molality, the "Harned Rule" plot (Fig. 6) for $\text{NaCl}-\text{Na}_2\text{CO}_3$ is clearly nonlinear. This is to be expected from measurements on other mixed monovalent-polyvalent ion systems.⁴

5. All the amalgam electrode data obey Harned's rule, and the coefficient α_{12} is 0.047 ± 0.003 for all ionic strengths and for both NaHCO_3 and Na_2CO_3 as added electrolytes. This a particularly simple and elegant result.

Table I. Activity Coefficient Measurements in NaCl-NaHCO₃
Electrolytes at 25 °C

[Cell: Ag/AgCl/NaCl, NaHCO₃, H₂O/Na(Hg)]*

Total Ionic Strength I	X ₁	pH	ΔE, mV	-log γ ₁₂ (Experimental)	-log γ ₁₂ (Corrected) [†]
0.5031	1.0000	11.02	0	0.1672	0.1668
0.5073	0.7486	8.83	8.50 8.25	0.1791 0.1770	0.1784 0.1763
0.5133	0.5055	9.18	18.15 18.30	0.1782 0.1795	0.1767 0.1780
0.5215	0.1793	8.21	48.00 48.30	0.2092 0.2117	0.2064 ? 0.2089 ?
0.5240	0.0761	8.22	68.50 68.00	0.1974 0.1932	0.1941 0.1899
1.0981	1.0000	9.0	0	0.1838	0.1824
1.0400	0.4122	8.6	27.20 27.28	0.2102 0.2109	0.2087 0.2094
1.0115	0.1135	8.4	62.50 62.70	0.2225 0.2234	0.2219 0.2228
1.0049	0.0444	8.2	87.10 87.30	0.2255 0.2272	0.2252 0.2269

*Component 1 is NaCl, component 2 is NaHCO₃; $I = m_1 + m_2$,
 $X_1 = m_1/I$ (protonation equilibria not included in calculating ionic strength);
pH of 0.5m NaHCO₃ stock solution was 9.0; pH of 1.0m NaHCO₃ stock
solution was 8.12.

[†]γ₁₂ corrected to round ionic strength (0.50 or 1.00) in last column.

Table II. Activity Coefficients of NaCl in NaCl-NaHCO₃ Electrolytes at 25 °C

(Cell: Ag/AgCl/NaCl, NaHCO₃, H₂O/Na Glass)*

Total Ionic Strength	X ₁	pH	ΔE, mV	-log γ ₁₂ (Experimental)	-log γ ₁₂ (Corrected)
Electrode B					
0.4805	1.0000	7.0	0	0.1664	0.1668
0.4898	0.8252	8.10	5.40	0.1745	0.1740
			5.35	0.1740	0.1735
			5.33	0.1739	0.1734
0.5012	0.6087	8.24	13.25	0.1798	0.1798
			13.40	0.1810	0.1810
			13.38	0.1809	0.1809
			13.41	0.1811	0.1811
0.5108	0.4274	8.57	21.75	0.1789	0.1792
			21.90	0.1802	0.1805
			21.75	0.1789	0.1792
0.5186	0.2797	8.90	33.09	0.1860	0.1864
			33.14	0.1865	0.1869
			33.10	0.1861	0.1865
0.5251	0.1567	8.28	45.10	0.1645	0.1648
			45.62	0.1689	0.1692
			47.02	0.1808	0.1811
			47.05	0.1810	0.1813
			45.27	0.1659	0.1662
Electrode C					
0.4805	1.0000	7.0	0	0.1664	0.1668
0.4898	0.8252	8.10	6.45	0.1833	0.1828
			6.30	0.1821	0.1816
0.5012	0.6087	8.24	15.10	0.1954	0.1954
			15.05	0.1950	0.1950
			15.23	0.1965	0.1965

*pH of 0.5m NaHCO₃ stock solution was 9.0; electrode B is a Beckman (LAS-10-23 glass) electrode, no. 39278; electrode C is a Corning (NAS-11-18 glass) electrode, no. 476210.

Table II (Cont.)

Total Ionic Strength	X_1	pH	ΔE , mV	$-\log \gamma_{12}$ (Experimental)	$-\log \gamma_{12}$ (Corrected)
Electrode C (Cont.)					
0. 5108	0. 4274	8. 57	23. 16	0. 1909	0. 1912
			23. 12	0. 1905	0. 1908
			23. 45	0. 1933	0. 1936
0. 5186	0. 2797	8. 90	33. 88	0. 1927	0. 1931
			33. 87	0. 1926	0. 1930
0. 5251	0. 1567	8. 28	47. 83	0. 1876	0. 1879
			48. 22	0. 1909	0. 1912
			48. 18	0. 1905	0. 1908
0. 9323	1. 0000	7. 48	0	0. 1816	0. 1824
0. 9585	0. 8249	8. 58	5. 35	0. 1911	0. 1920
			5. 30	0. 1907	0. 1916
			5. 40	0. 1915	0. 1924
0. 9722	0. 7340	8. 72	8. 50	0. 1954	0. 1961
			8. 70	0. 1971	0. 1978
			8. 93	0. 1991	0. 1998
0. 9852	0. 6469	8. 66	11. 80	0. 1988	0. 1992
			11. 95	0. 2001	0. 2005
			11. 90	0. 1997	0. 2001
0. 9949	0. 5823	8. 64	14. 20	0. 1984	0. 1986
			14. 45	0. 2005	0. 2007
			14. 80	0. 2034	0. 2036
1. 0046	0. 5175	8. 47	18. 10	0. 2078	0. 2079
			18. 13	0. 2081	0. 2082
			18. 05	0. 2074	0. 2075
1. 0114	0. 4726	8. 33	18. 05	0. 1892	0. 1888
			18. 40	0. 1921	0. 1917
1. 0323	0. 3331	8. 34	27. 95	0. 2013	0. 2000
			28. 45	0. 2055	0. 2041
			28. 30	0. 2043	0. 2029
1. 0345	0. 3184	8. 47	29. 20	0. 2025	0. 2010
			29. 38	0. 2040	0. 2025
			30. 37	0. 2124	0. 2189
1. 0484	0. 2252	8. 44	37. 90	0. 2038	0. 2014
			38. 30	0. 2071	0. 2047
			38. 20	0. 2063	0. 2039
1. 0634	0. 1256	8. 35	49. 15	0. 1752	0. 1718
			49. 35	0. 1769	0. 1735
			49. 50	0. 1781	0. 1747

Table III. Activity Coefficient Measurements in NaCl-Na₂CO₃
Electrolytes at 25 °C

[Cell: Ag/AgCl/NaCl, Na₂CO₃, H₂O/Na(Hg)]

Total Ionic Strength*	X ₁	pH [†]	ΔE, mV	-log γ ₁₂ (Experimental)	-log γ ₁₂ (Corrected)
0.5685	1.0000	8.3	0	0.1707	0.1669
0.5575	0.9096	10.24	3.57 3.70	0.1707 0.1718	0.1671 0.1682
0.5062	0.4868	10.89	26.98 26.65	0.1817 0.1789	0.1812 0.1784
0.4699	0.1880	11.07	56.50 56.10	0.1794 0.1761	0.1821 0.1788
0.4585	0.0944	10.99	77.30 76.97	0.1893 0.1865	0.1932 0.1904
1.0315	1.0000	9.04	0	0.1832	0.1824
1.0092	0.5069	10.1	25.50 25.40	0.2085 0.2076	0.2081 0.2072
0.9923	0.1357	10.8	66.10 65.80	0.2265 0.2240	0.2269 0.2244
0.9883	0.0483	10.9	94.28 93.95	0.2301 0.2273	0.2308 0.2280
3.0487	1.0000	10.90	0	0.1448	0.1465
3.0247	0.7459	10.98	14.70 14.00	0.1845 0.1786	0.1851 0.1792
2.9973	0.4831	11.15	31.80 31.71	0.2112 0.2104	0.2112 0.2104
2.9762	0.2621	11.00	54.40 54.30	0.2475 0.2466	0.2475 0.2466
2.9523	0.0532	11.35	100.92 100.65	0.2715 0.2692	0.2719 0.2696

*I = m₁ + 3m₂, X₁ = m₁/I (protonation equilibria not included in calculating ionic strength).

[†]pH of 0.33m Na₂CO₃ = 11.06; pH of 1.0m Na₂CO₃ = 11.42.

Table III (Cont.)

Total Ionic Strength*	X_1	pH [†]	ΔE , mV	$-\log \gamma_{12}$ (Experimental)	$-\log \gamma_{12}$ (Corrected)
1.0315 [‡]	1.0000	9.04	0	0.1832	—
1.9883 [‡]	0.5051	10.3	15.15 14.90	0.2441 0.2420	— —
2.6857 [‡]	0.1444	11.0	45.64 45.88	0.2764 0.2744	— —
2.8762 [‡]	0.0458	11.2	74.50 74.34	0.2797 0.2784	— —

[‡]These four solutions were at constant total molality rather than constant ionic strength. See Fig. 6.

Table IV. Activity Coefficient Measurements in NaCl-Na₂CO₃ Electrolytes
(Cell: Ag/AgCl/NaCl, Na₂CO₃, H₂O/Na Glass Electrode)*

Total Ionic Strength, I	X ₁	pH	ΔE, mV	-log γ ₁₂ (Experimental)	-log γ ₁₂ (Corrected)
Electrode C'†					
0.5685	1.0000	8.3	0	0.1707	0.1669
0.5575	0.9096	10.24	3.66	0.1715	0.1679
			3.62	0.1712	0.1676
			3.73	0.1721	0.1685
0.5062	0.4868	10.89	26.19	0.1750	0.1745
			26.22	0.1752	0.1747
0.4699	0.1880	11.07	56.50	0.1794	0.1821
			56.47	0.1792	0.1819
			56.52	0.1796	0.1822
0.4585	0.0944	10.99	75.63	0.1751	0.1790
			75.65	0.1751	0.1792
			75.10	0.1707	0.1746
0.4559	0.0726	10.95	83.35	0.1795	0.1837
			83.25	0.1787	0.1829
Electrode B					
1.030	1.000	—	0	0.1828	0.1824
0.9487	0.8544	10.36	6.20	0.1929	0.1939
			6.26	0.1934	0.1944
			6.40	0.1946	0.1956
0.9691	0.6739	10.69	14.9	0.2044	0.2053
			14.75	0.2032	0.2041
			14.55	0.2014	0.2023
0.9876	0.5098	10.82	23.85	0.2094	0.2099
			23.8	0.2090	0.2095
			23.9	0.2099	0.2104

*Ionic strength and X₁ as in Table III; pH of 0.33m Na₂CO₃ = 11.06.

†Electrode C' is a new Corning NAS 11-18 sodium ion electrode; electrodes B and C as in Table II.

Table IV (Cont.)

Total Ionic Strength I	X_1	pH	ΔE , mV	$-\log \gamma_{12}$ (Experimental)	$-\log \gamma_{12}$ (Corrected)
Electrode B (Cont.)					
1. 0087	0. 3227	10. 84	37. 2 37. 6 37. 4	0. 2109 0. 2143 0. 2126	0. 2105 0. 2139 0. 2122
1. 0229	0. 1972	10. 94	51. 3 51. 16 51. 2	0. 2147 0. 2135 0. 2139	0. 2135 0. 2123 0. 2127
Electrode C					
1. 030	1. 000	—	0	0. 1828	0. 1824
0. 9487	0. 8544	10. 36	6. 2 6. 1 6. 6	0. 1929 0. 1921 0. 1963	0. 1939 0. 1931 0. 1973
0. 9691	0. 6739	10. 69	14. 9 14. 75 14. 57	0. 2044 0. 2032 0. 2016	0. 2053 0. 2041 0. 2025
0. 9876	0. 5098	10. 82	23. 7 23. 9 23. 7	0. 2082 0. 2099 0. 2082	0. 2087 0. 2104 0. 2087
1. 0087	0. 3227	10. 84	37. 9 37. 65 37. 6	0. 2168 0. 2147 0. 2143	0. 2164 0. 2143 0. 2139
1. 0229	0. 1972	10. 94	51. 9 52. 1 52. 0	0. 2198 0. 2215 0. 2206	0. 2186 0. 2203 0. 2194
3. 1134	1. 0000	—	0	0. 1424	0. 1465
3. 1001	0. 8075	10. 48	9. 30 9. 06 8. 55	0. 1595 0. 1575 0. 1532	0. 1621 0. 1601 0. 1558

Table IV (Cont.)

Total Ionic Strength, I	X ₁	pH	ΔE , mV	$-\log \gamma_{12}$ (Experimental)	$-\log \gamma_{12}$ (Corrected)
Electrode C (Cont.)					
3.0931	0.7070	10.40	16.30	0.1815	0.1835
			16.40	0.1823	0.1843
			16.54	0.1835	0.1855
3.0779	0.4872	10.50	32.40	0.2174	0.2184
			32.48	0.2181	0.2191
			31.80	0.2123	0.2133
			32.30 [‡]	0.2166 [‡]	0.2176 [‡]
			32.50 [‡]	0.2182 [‡]	0.2192 [‡]
3.0640	0.2874	11.01	50.85	0.2395	0.2397
			50.86	0.2396	0.2398
			50.65	0.2379	0.2381
3.0544	0.1498	11.05	71.15	0.2553	0.2551
			71.07	0.2546	0.2544
			71.40	0.2574	0.2572
			71.67 [‡]	0.2597 [‡]	0.2595 [‡]
			71.78 [‡]	0.2606 [‡]	0.2604 [‡]
			71.85 [‡]	0.2612 [‡]	0.2610 [‡]

[‡]Electrode B. All others electrode C.

Table V. Harned Rule Coefficients

Component 1	Component 2	Na ⁺ Sensor	I [*]	pH [†]	α_{12} [‡]
NaCl	NaHCO ₃	Na(Hg)	0.50	8.2-9.2	0.050 \pm 0.009
		Na(Hg)	1.00	8.2-8.6	0.045 \pm 0.003
		Glass (B)	0.50	8.1-8.9	0.02 \pm 0.03
		Glass (C)	0.50	8.1-8.9	0.03 \pm 0.03
		Glass (C)	1.00	8.3-8.7	0.047 \pm 0.016 [§]
NaCl	Na ₂ CO ₃	Na(Hg)	0.50	10.2-11.1	0.048 \pm 0.016
		Na(Hg)	1.00	10.5-10.9	0.049 \pm 0.003
		Na(Hg)	3.00	10.9-11.4	0.044 \pm 0.003
		Glass (C')	0.50	10.2-11.1	0.031 \pm 0.009
		Glass (B)	1.00	10.4-10.9	0.032 \pm 0.008
		Glass (C)	1.00	10.4-10.9	0.040 \pm 0.005
		Glass (C)	3.00	10.4-11.0	0.046 \pm 0.003

* Formal ionic strength held constant. For NaCl-NaHCO₃ mixtures, $I = m_1 + m_2$; for NaCl-Na₂CO₃ mixtures, $I = m_1 + 3m_2$.

† Range of pH for which either HCO₃⁻ (pH = 8 to 9) or CO₃²⁻ (pH > 10.5) is predominant. Effect of protonation equilibria on ionic strength not included.

‡ Least squares fit to Harned's rule including all points, except where noted. Errors are 95% confidence limits.

§ Using only points for $X_1 > 0.5$. Systematic deviations corresponding to $X_1 < 0.5$ result in $\alpha_{12} = 0.02 \pm 0.02$ for the entire set.

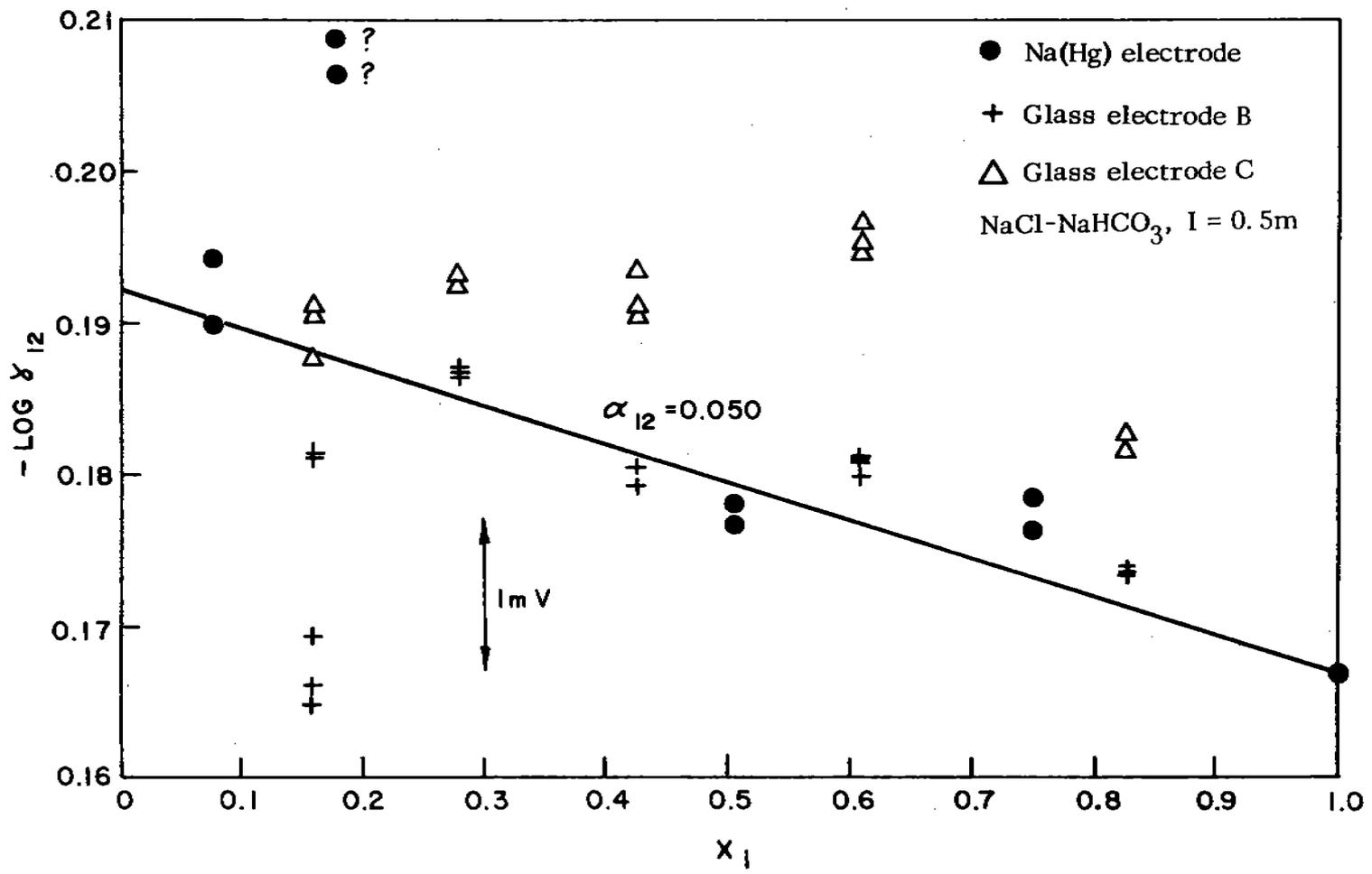


Fig. 1. Activity coefficients of NaCl in NaCl-NaHCO₃ electrolytes at ionic strength 0.5m (the straight line is Harned's rule)

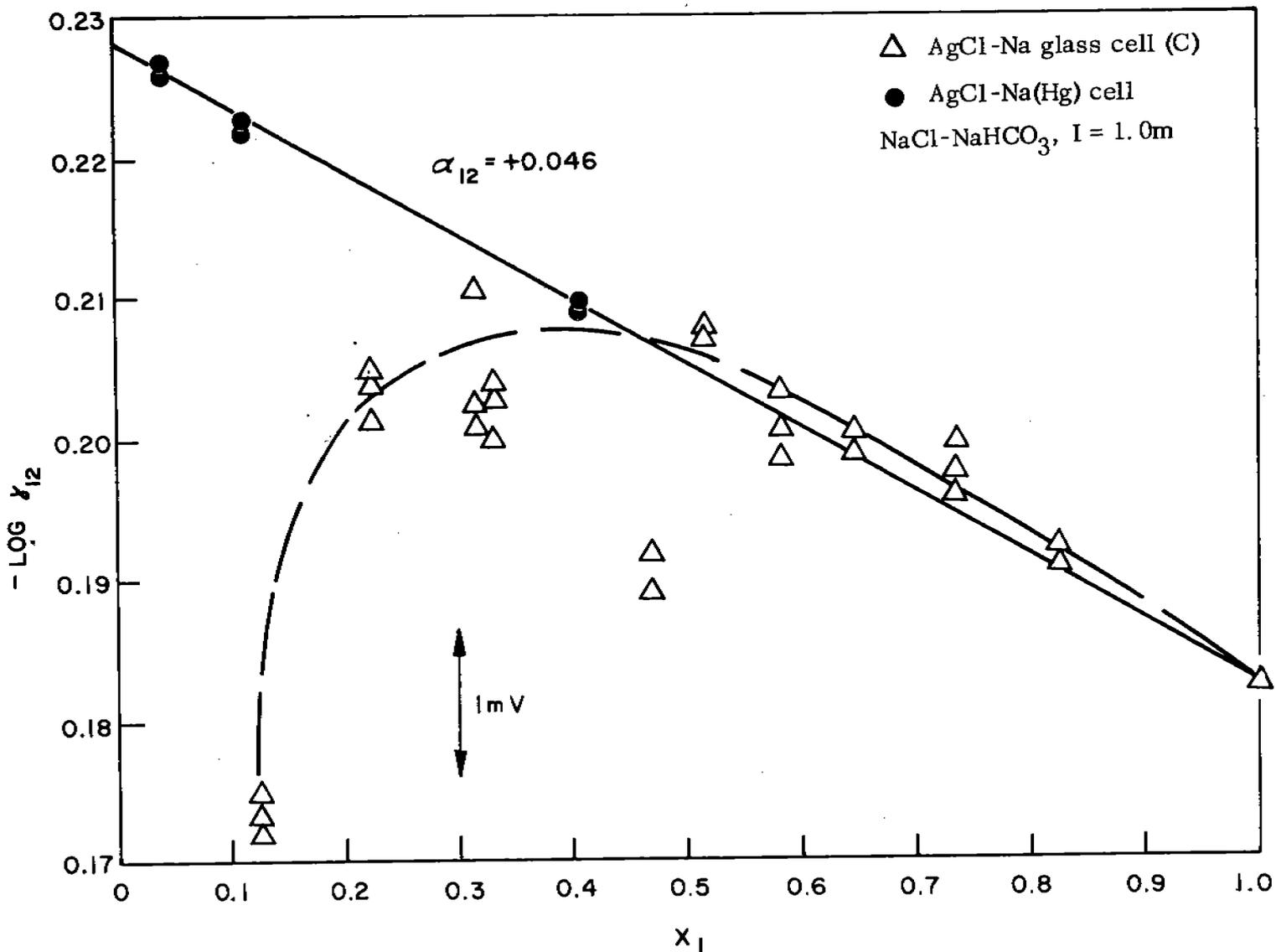


Fig. 2. Activity coefficients of NaCl in NaCl-NaHCO₃ electrolytes at ionic strength 1.0m (note deviations of glass electrode data)

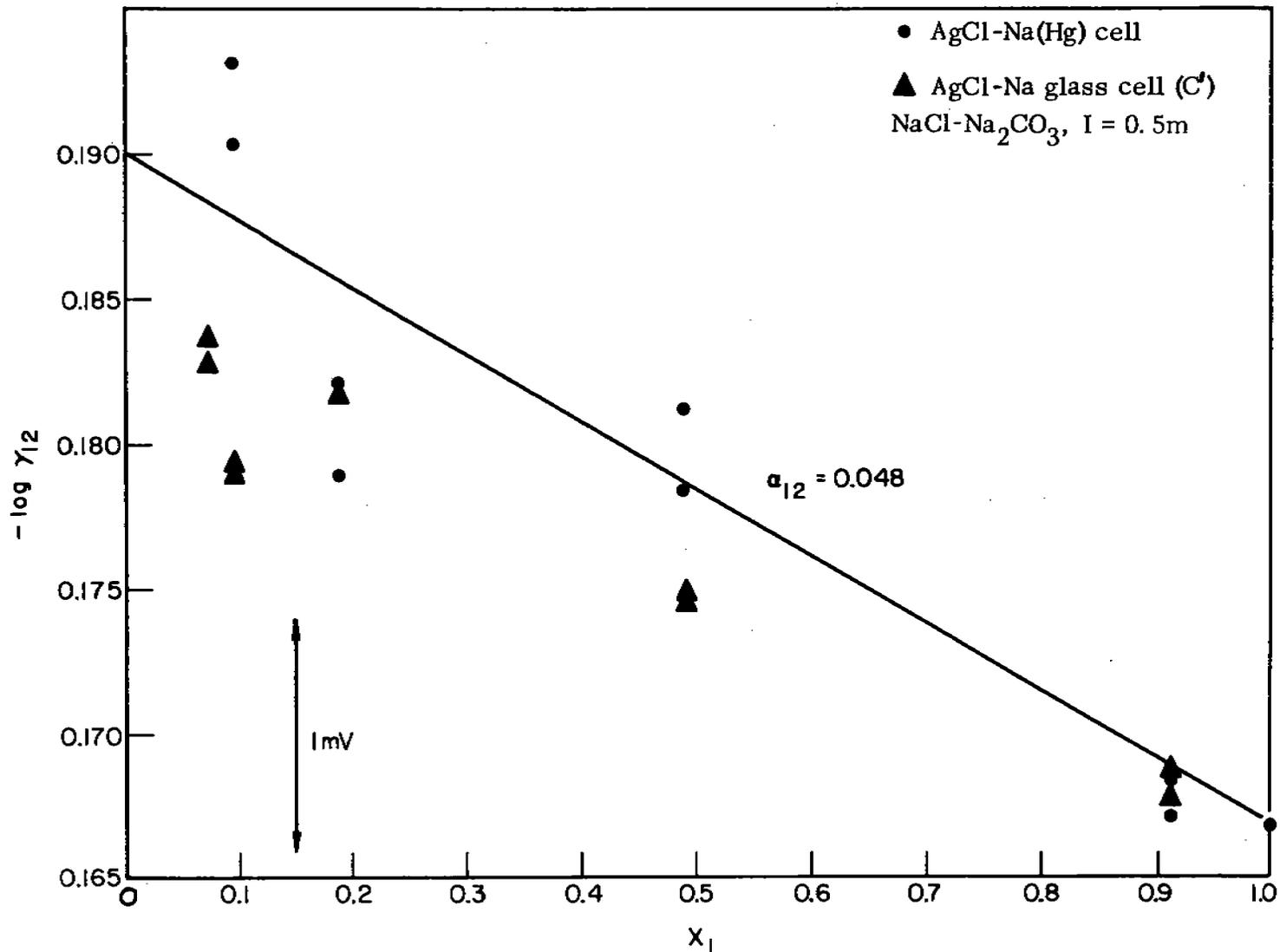


Fig. 3. Activity coefficients of NaCl in NaCl-Na₂CO₃ electrolytes at ionic strength 0.5m

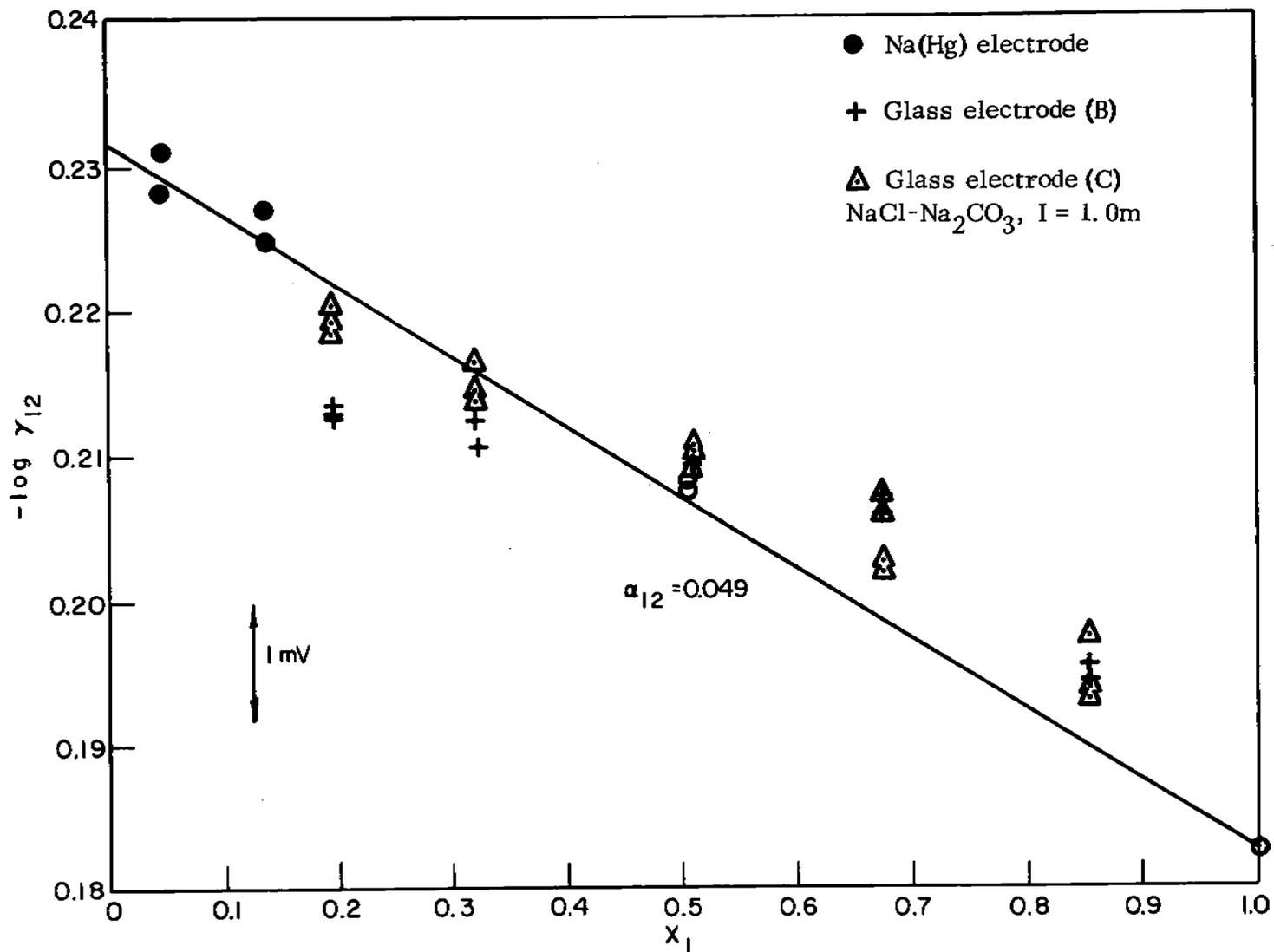


Fig. 4. Activity coefficients of NaCl in NaCl-Na₂CO₃ electrolytes at ionic strength 1.0m

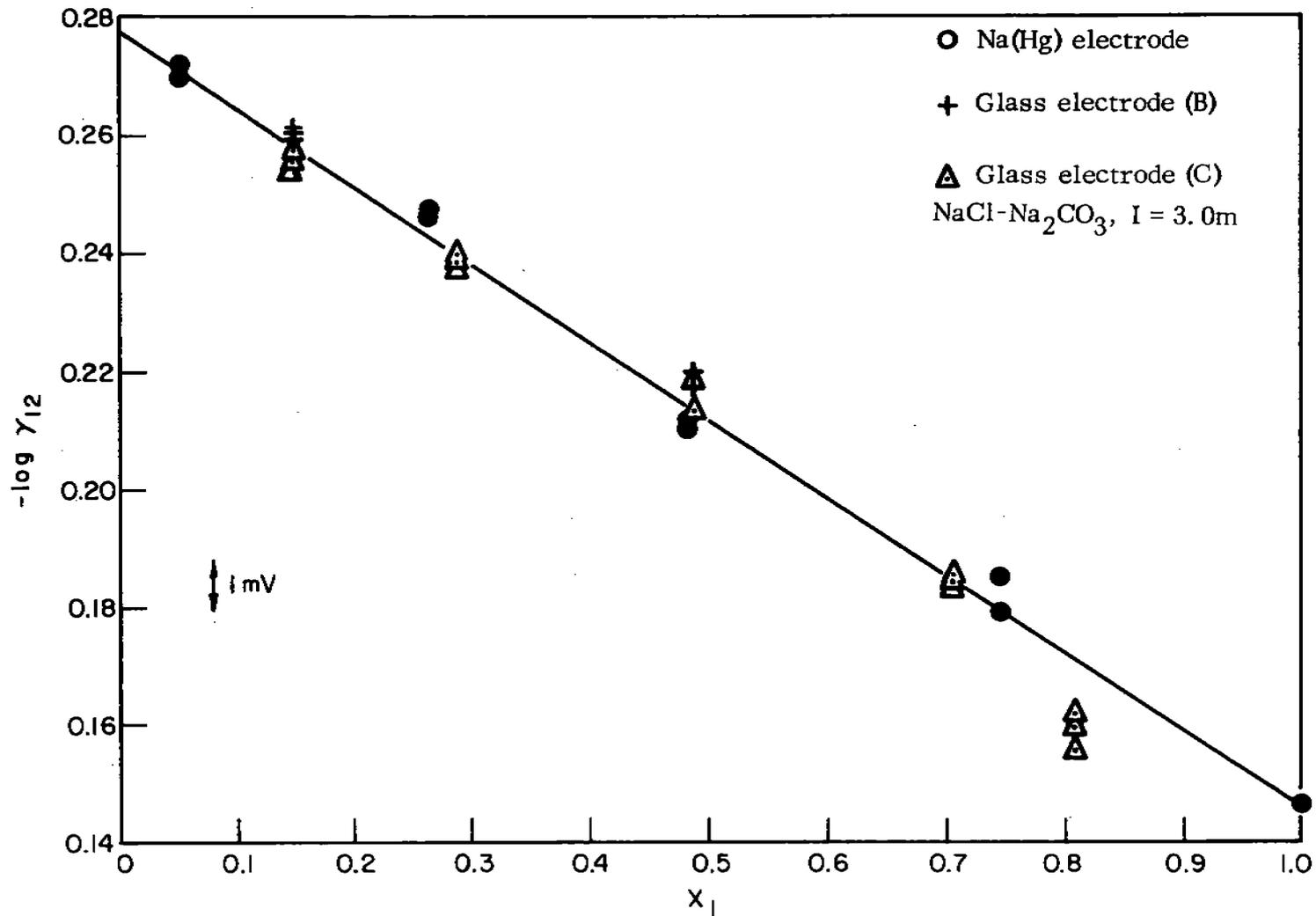


Fig. 5. Activity coefficients of NaCl in NaCl-Na₂CO₃ electrolytes at ionic strength 3.0m

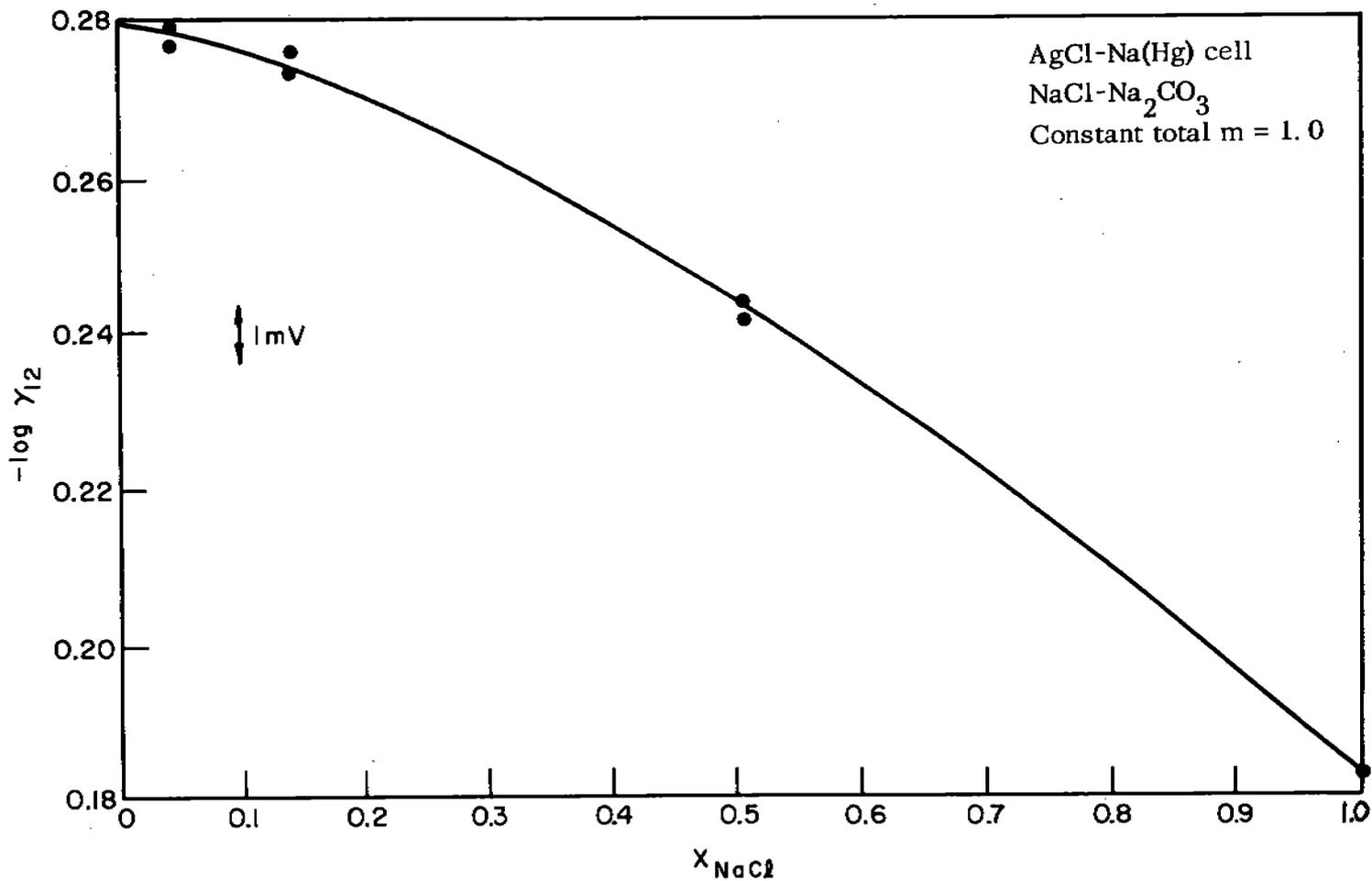


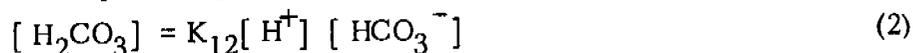
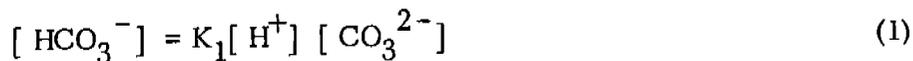
Fig. 6. Activity coefficients of NaCl in NaCl-Na₂CO₃ electrolytes at constant total molality m = 1.0 (note the nonlinearity compared to Figs. 4 or 5)

B. Acid-Base Equilibria in NaCl-NaHCO₃-Na₂CO₃ Electrolytes

The pH values we observed for our solutions in the previous section varied with NaCl content, and this suggested some specific interactions which might be revealed by studying the bicarbonate-carbonate equilibrium in the presence of NaCl. Most studies of this acid-base equilibrium have been made in dilute solutions and extrapolated to zero ionic strength. Previous work^{29, 30, 31} in the presence of NaCl had been done either in cells with liquid junctions or at varying ionic strengths, and the only literature value for the equilibrium constant K_1 (see Eq. 1 below) in NaCl of constant ionic strength ($\sim 1m$) was measured by an indicator technique³⁶ which gave $\log K_1 = +9.37$. The medium was 1.0M NaCl at 25 ± 2 °C. We shall review some other related equilibrium constant measurements at the end of this section.

We have made a number of titration experiments to determine two important factors: (1) to establish whether there is excess free acid or base in the salts (NaHCO₃ and Na₂CO₃) used in our activity coefficient experiments, and (2) to evaluate the constant for acid-base equilibria. Such excess acid or base would change the relative amounts of HCO₃⁻ and CO₃²⁻, and hence the ionic strength. The simplest way to see this is to titrate the salt with both acid and base and plot the potential of a glass electrode versus a reference electrode according to the linearized titration curve methods first devised by Gran,³⁷ and recently popularized by Dyrssen and coworkers.^{38, 39} These plots are nearly linear and should intersect at or above the equivalence point where there is no excess acid or base. Presence of excess acid or base causes the intersection to shift to the right or left of the zero volume axis.

The Gran plots³⁷ are based on the equations of the titration curve for the carbonate system. To derive these functions, we must consider four separate cases, but all involve some of the same basic equations.⁹ The equilibria (with activity coefficients included in the equilibrium constants) are



If we define the following variables:

$$\begin{aligned} V_o' &= \text{volume of NaHCO}_3 \text{ or Na}_2\text{CO}_3 \text{ of concentration } C_o \\ V_o'' &= \text{volume of NaCl of concentration } C_o'' \\ V_o &= V_o' + V_o'' = \text{total volume at start of titration} \\ V &= \text{volume of HCl or NaOH of concentration } C \text{ added} \end{aligned}$$

then we can write the mass balance on carbonate as

$$\frac{C_o' V_o'}{V + V_o} = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (3)$$

As the pH increases, terms to the far right become relatively larger. Normally, only two terms will be significant. This is shown on the logarithmic concentration diagram of Fig. 7 (which is only schematic, having been constructed using equilibrium constants applying at zero ionic strength).

The proton balance is different for each of the four possible titrations. Terms on the right of the following equations are listed in decreasing order of importance. Normally, only the first term need be taken into consideration:

NaHCO₃ - HCl (pH 8 → 5)

$$\frac{CV}{V + V_o} = [\text{H}_2\text{CO}_3] - [\text{CO}_3^{2-}] + [\text{H}^+] - [\text{OH}^-] \quad (4)$$

NaHCO₃ - NaOH (pH 8 → 11)

$$\frac{CV}{V + V_o} = [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}_2\text{CO}_3] - [\text{H}^+] \quad (5)$$

Na₂CO₃ - HCl (pH 11 → 8)

$$\frac{CV}{V + V_o} = [\text{HCO}_3^-] - [\text{OH}^-] + 2 [\text{H}_2\text{CO}_3] + [\text{H}^+] \quad (6)$$

Na₂CO₃ - NaOH (pH 11 → 13)

$$\frac{CV}{V + V_o} = [\text{OH}^-] - [\text{HCO}_3^-] - 2 [\text{H}_2\text{CO}_3] - [\text{H}^+] \quad (7)$$

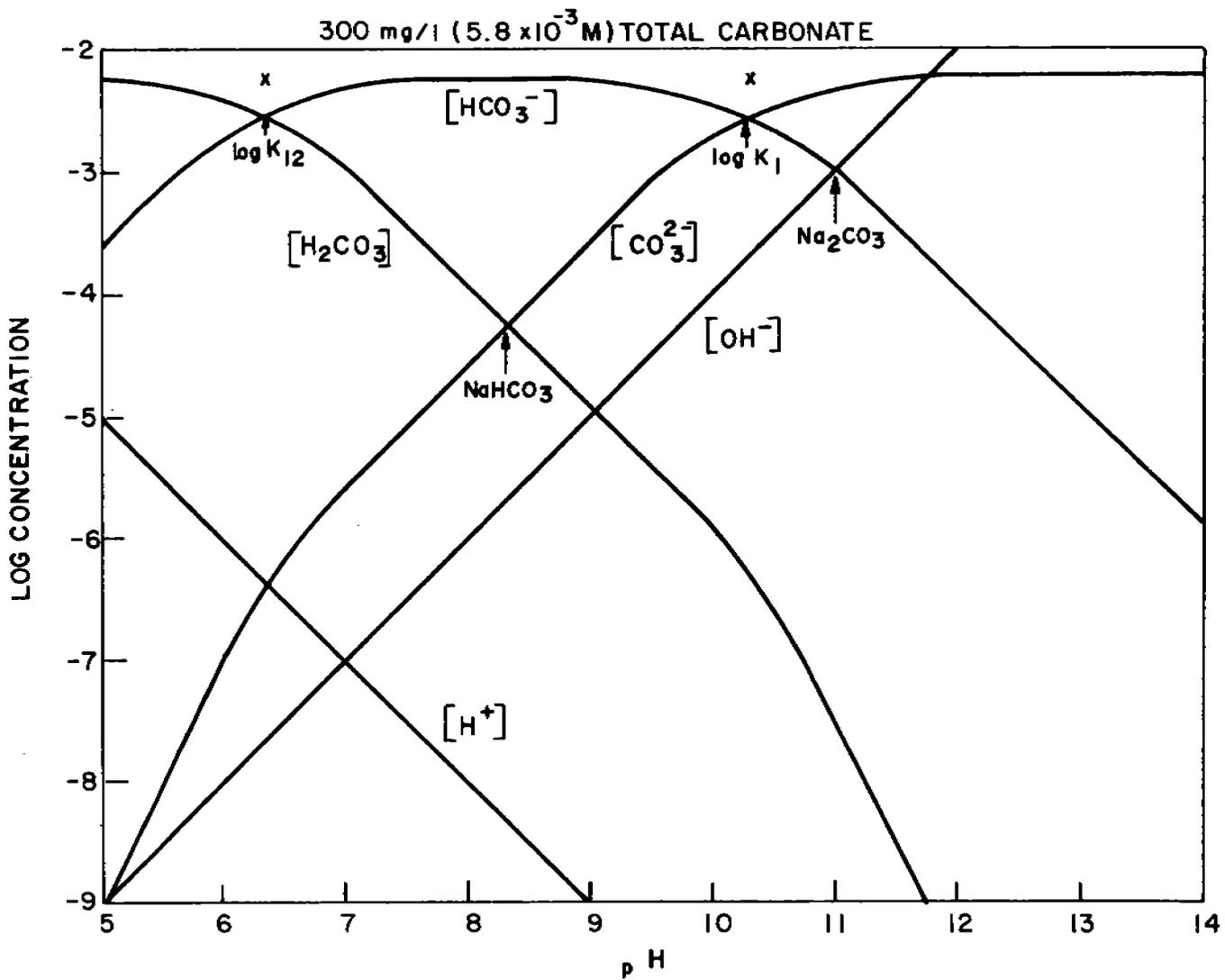


Fig. 7. Logarithmic concentration diagram for the carbonate-bicarbonate system at total carbon content of 5.8×10^{-3} M (increasing total concentration moves the $[H_2CO_3]$, $[HCO_3^-]$, and $[CO_3^{2-}]$ lines upward by the same amount, but does not shift the $[H^+]$ and $[OH^-]$ lines: the equilibrium constants used are for zero ionic strength; adding neutral salt shifts the equilibrium constants (crosses) to the right; see Fig. 16 for details)

In our titrations, we used a glass pH electrode versus a silver-silver chloride electrode in the same solution. Titrants were added with an RGI micrometer burette. If the activity coefficients of H^+ and Cl^- , and the total concentration of Cl^- are assumed constant (since a large excess of NaCl is present and ionic strength is constant) and included in E^0 , the potential is easily related to $[H^+]$.

$$\begin{aligned} E &= E^Z + \frac{RT}{F} \ln \left([H^+] [Cl^-] \gamma_{H^+} \gamma_{Cl^-} \right) \\ &= E^0 + \frac{RT}{F} \ln [H^+] \end{aligned} \quad (8)$$

E^0 was determined (see below), but need not be known for the Gran plots.

We may thus express $[H^+]$ as a function of E, and $[OH^-]$ as a function of $[H^+]$ ($K_w = 10^{-14}$):

$$[H^+] = 10^{(E - E^0)/59} \quad (9)$$

$$[OH^-] = K_w / [H^+] \quad (10)$$

where E is in mV and the temperature is 25 °C.

The Gran functions are best considered by taking one case at a time.

1. NaHCO₃ - HCl

In Eq. 3, the predominant terms are $[H_2CO_3]$ and $[HCO_3^-]$. Substituting for $[H_2CO_3]$ from Eq. 2 gives

$$\frac{C_o' V_o'}{V + V_o} = [HCO_3^-] (1 + K_{12} [H^+]) \quad (11)$$

If Eq. 2 is substituted in Eq. 4, and only the first term is retained, we have

$$[HCO_3^-] = \frac{CV}{V + V_o} \left(\frac{1}{K_{12} [H^+]} \right) \quad (12)$$

and this may be substituted in Eq. 11 to give

$$C_o' V_o' = CV \left(1 + \frac{1}{K_{12} [H^+]} \right) \quad (13)$$

If we use Eq. 9, we can express this in terms of E:

$$F_1 = (V_1 - V) 10^{(E - E_s)/59} = V \left(\frac{10^{(E^0 - E_s)/59}}{K_{12}} \right) \quad (14)$$

Here we have defined

$$V_1 = \frac{C_o' V_o'}{C} \quad (15)$$

which is the equivalence point of the titration (for the titration plotted in Fig. 8, $V_1 = 0.660$ ml). Note that the function F_2 (for any arbitrary value of E_s) is proportional to V , since the terms in parentheses on the right-hand side of Eq. 14 are all constant, and E^0 need not be known. E_s is thus a scale factor which can be used to expand or compress the value of F_2 to a convenient size (in Fig. 8, $E_s = 215.2$ mV). Because we neglected the $[\text{CO}_3^{2-}]$ term in Eq. 4, the plot curves sharply at small values of F_1 . Furthermore, this is the least reliable pH range, because gaseous CO_2 escapes from the solution during the titration. This is discussed further below.

2. NaHCO₃ - NaOH

In Eq. 3, the predominant terms are $[\text{HCO}_3^-]$ and $[\text{CO}_3^{2-}]$. Substituting for $[\text{HCO}_3^-]$ from Eq. 1 gives

$$\frac{C_o' V_o'}{V + V_o'} = [\text{CO}_3^{2-}] (1 + K_1 [\text{H}^+]) \quad (16)$$

Substituting from Eq. 5, with only the first term retained, we have

$$C_o' V_o' = CV (1 + K_1 [\text{H}^+]) \quad (17)$$

Making use of Eq. 9, we have

$$F_2 = (V_1 - V) 10^{(E_s - E)/59} = V \left(K_1 10^{(E_s - E^0)/59} \right) \quad (18)$$

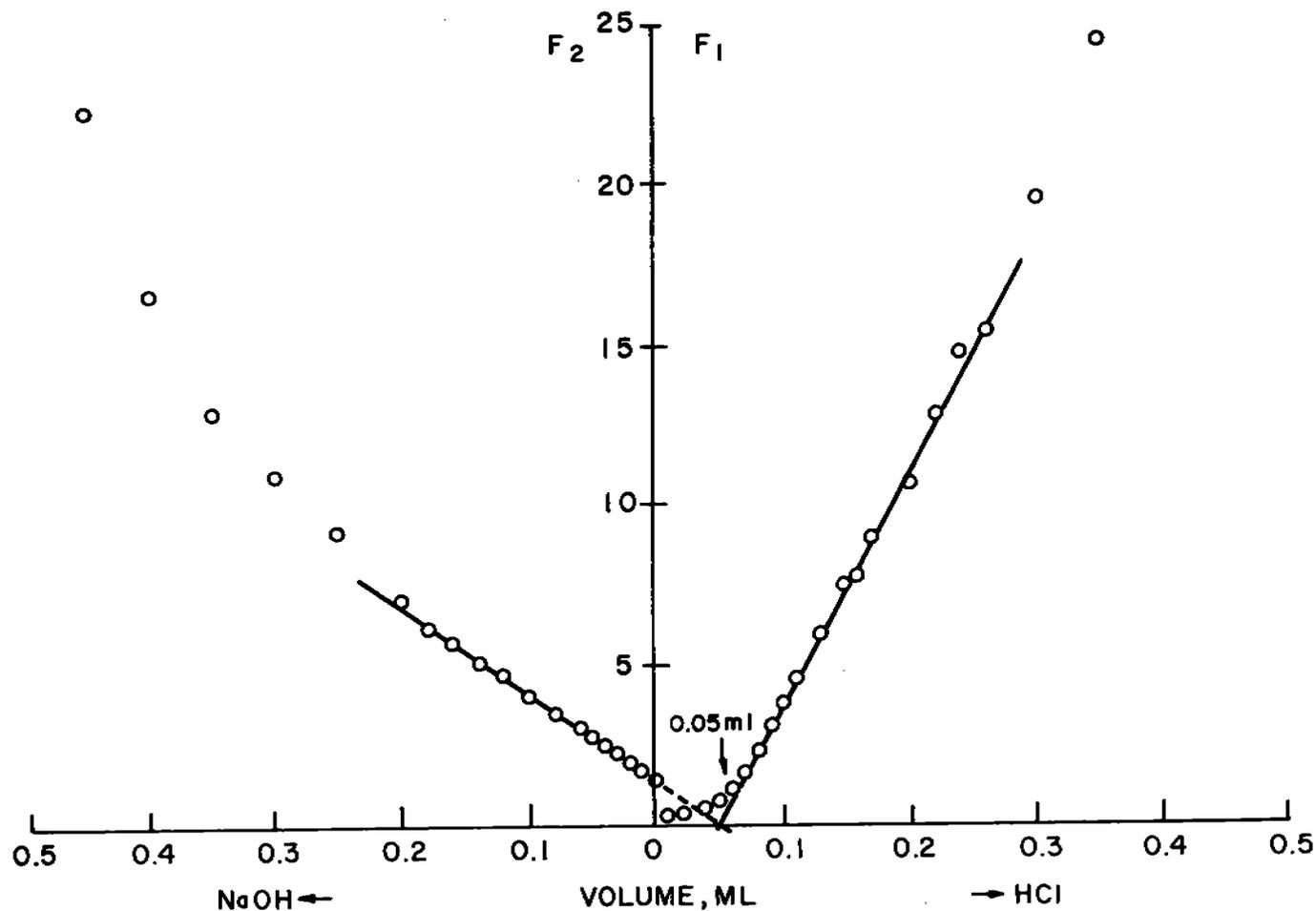
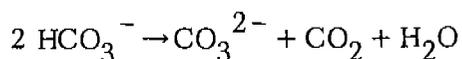


Fig. 8. Titration of 25.00ml of 0.02639m NaHCO_3 (containing NaCl to make $I = 1.0540$ m) with 1.00N NaOH and 1.00N HCl (the Gran functions F_1 and F_2 are defined by Eqs. 14 and 18 in the text; the equivalence point is $V_1 = 0.660$ ml)

where V_1 is defined by Eq. 15 as before, but V_1 and E_s will in general have values different from the HCl titration. Fig. 8 shows a plot of this Gran function. Note again that there is curvature due to failure of the approximations in Eq. 5. In this titration, V_1 is 0.660, the same as the HCl titration of the same solution only because both the HCl and NaOH titrants were the same concentration, 1.00M. For the HCl titration, $E_s = -215.2$, and for the NaOH titration, $E_s = -69.0$. These values were arbitrarily chosen to make the Gran functions both 4.0 at $V = 0.1$ ml, so that both plots would have approximately 45° slope.

Note that the two Gran functions do not intersect at $V = 0$. Instead, the straight line extrapolations of the two functions intersect the zero ordinate at $V = 0.050$ on the HCl side. This implies that there is the equivalent of 0.050 ml of base (7.6% of the equivalence point volume) present in the NaHCO_3 solution being titrated. The most likely explanation for this is loss of CO_2 from the NaHCO_3 solution by escape into the atmosphere. Such loss of CO_2 affects the ionic strength of the medium slightly, because of the reaction



in which two monovalent ions are replaced by a divalent ion, and thus the new ionic strength is higher by the concentration of CO_2 lost:

Pure NaHCO_3 :

$$I = 1/2 ([\text{Na}^+] + [\text{HCO}_3^-]) = m$$

NaHCO_3 with CO_2 lost:

$$\begin{aligned} I &= 1/2 ([\text{Na}^+] + [\text{HCO}_3^-] + 4 [\text{CO}_3^{2-}]) \\ &= m + [\text{CO}_3^{2-}] \end{aligned}$$

On the other hand, addition of excess CO_2 does not affect the ionic strength of NaHCO_3 appreciably, except inasmuch as it represses the small dissociation to form CO_3^{2-} . In freshly prepared solutions, this

effect should be negligible. Corrections of this type can be applied to the activity coefficient measurements of Tables I through V, but this has not been done. Estimates of the required correction are of the order of 0.001 in α_{12} .

3. Na₂CO₃ - HCl

This covers the same pH range as the NaHCO₃ - NaOH titration, but in the reverse direction. In Eq. 3, the predominant terms are [HCO₃⁻] and [CO₃²⁻], and Eq. 16 still holds, but Eq. 3 may be more usefully employed in the form (substituting Eq. 1)

$$\frac{C_o' V_o'}{V + V_o} = [\text{HCO}_3^-] \left(1 + \frac{1}{K_1 [\text{H}^+]} \right) \quad (19)$$

If we approximate Eq. 6 by its first term, and substitute it in Eq. 19, we have

$$C_o' V_o' = CV \left(1 + \frac{1}{K_1 [\text{H}^+]} \right) \quad (20)$$

Note that Eq. 20 is of exactly the same form as Eq. 13, so that the Gran function, F_1 , given by Eq. 14 may be applied to this case as well. A typical plot is given in Fig. 9. Note again that the plot is curved.

4. Na₂CO₃ - NaOH

For this range, we can make use of Eq. 7 directly, dropping all but the first term and using Eq. 10 to obtain

$$\frac{CV}{V + V_o} = \frac{K_w}{[\text{H}^+]} \quad (21)$$

Using Eq. 9, we may cast this into the form

$$y = (V + V_o) 10^{(E_s - E)/59} = V \left[\frac{C}{K_w} 10^{(E_s - E^o)/59} \right] \quad (22)$$

where the quantities in the bracket on the right are all constant.

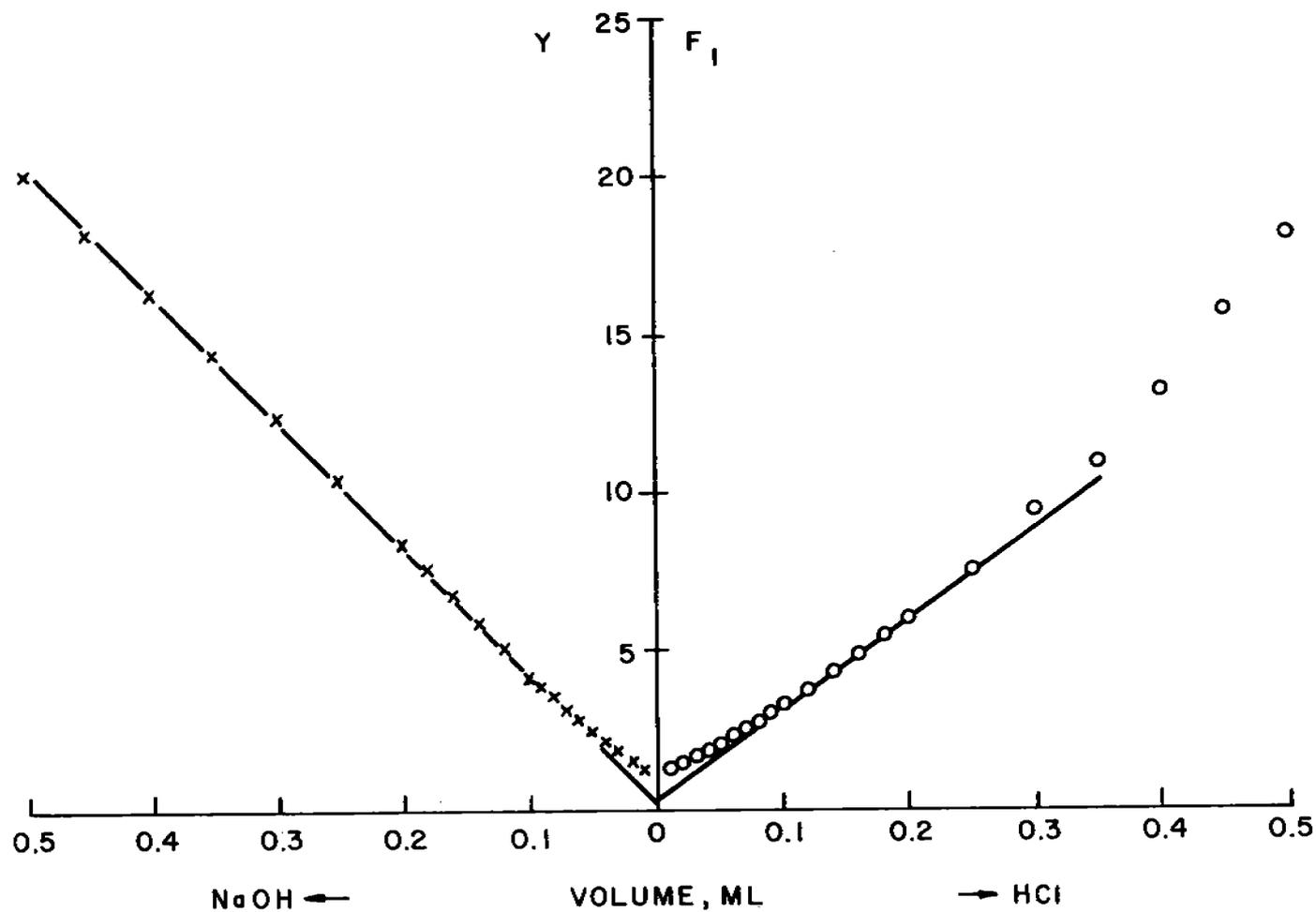
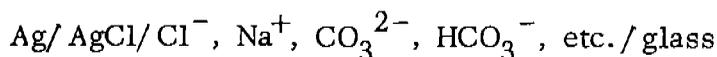


Fig. 9. Titration of 25.00 ml of 0.04745M Na_2CO_3 (containing NaCl to make $I = 3.098\text{ml}$ with 1.00N NaOH and 1.00N NaCl (the Gran functions F_1 and y are defined in the text by Eqs. 14 and 22 ; the equivalence point is $V_1 = 1.19\text{ml}$)

As can be seen from Fig. 9, y is a linear function of V except near $V = 0$, where the approximation of neglecting $[\text{HCO}_3^-]$ in Eq. 7 breaks down. Extrapolation of this straight line to the zero ordinate indicates less than 0.002 ml excess base. Since $V_1 = 1.19$ ml for this titration the Na_2CO_3 contains $<0.17\%$ excess base. Because of the curvature of the F_1 plot, not much may be concluded from the titration of Na_2CO_3 with HCl except that no gross errors were made in the NaOH titration.

5. Calculation of equilibrium constants

The equations already derived (13, 17, and 20) can be used to obtain the equilibrium constants for the acid-base reactions of carbonate in NaCl medium. In order to achieve some reasonable accuracy, we kept the NaCl concentration high compared to the total carbonate concentration, and used a cell without liquid junction. Since the solutions contain a fixed concentration of chloride already, the reference electrode was Ag/AgCl . The indicator electrode was a conventional glass pH electrode (Beckman 39301). The potential of the cell



may be written in the form

$$E = E^0 + \frac{RT}{F} \ln \left([\text{H}^+] [\text{Cl}^-] (\gamma_{21})^2 \right) \quad (23)$$

which is similar to Eq. 8 above, but now we have explicitly expressed the fact that the activity coefficient, γ_{21} , is the mean activity coefficient of HCl in the medium (NaCl) used.

These activity coefficient values in HCl - NaCl electrolytes have been measured by Harned and coworkers,⁴⁰ and may be represented by Harned's rule with coefficients

$$\begin{aligned} \alpha_{21} &= +0.0315 & \text{at } I = 1 \\ \alpha_{21} &= +0.0300 & \text{at } I = 3 \end{aligned} \quad (24)$$

(here component 1 is NaCl and component 2 is HCl). The mean activity coefficients of pure HCl (γ_{20}) used to obtain γ_{21} from these coefficients (α_{21}) were obtained from the tables of Robinson and Stokes.¹² The results were

$$\begin{aligned} (\gamma_{21})^2 &= 0.5624 && \text{at } I = 1.054\text{m} \\ (\gamma_{21})^2 &= 1.130 && \text{at } I = 3.098\text{m} \end{aligned} \quad (25)$$

Using these values together with the known chloride concentration ($[Cl^-] = I$), we could relate E and $[H^+]$ quantitatively.

Calibration of the glass electrode to obtain E^0 was made using values obtained by Bates and coworkers⁴¹ for a borax-NaCl buffer of pH ~ 9 . The exact buffer used consisted of 0.01038m $Na_2B_4O_7$ and 0.01925m NaCl. Its ionic strength was 0.030 and, from Bates' measurements, it was known to have

$$p(a_H\gamma_{Cl}) = -\log \left((\gamma_{21})^2 [H^+] \right) = 9.239 \quad \text{at } 25^\circ C \quad (26)$$

and $[Cl^-] = 0.01925$. E^0 was calculated from Eq. 23.

For the titration of $NaHCO_3$ with HCl, Eq. 13 gives a value of K_{12} for each point of the titration curve. Similarly, in the titration of $NaHCO_3$ with NaOH, Eq. 17 gives a value of K_1 for each point, and for the titration of Na_2CO_3 with HCl, Eq. 20 gives a value of K_1 for each point. The results of such calculations are summarized in Table VI. (No equilibrium constants can be obtained from the titration of Na_2CO_3 with NaOH.)

Deviations of the individual points from the average values are shown in Fig. 10. In no case were the points randomly distributed about an average value, and thus the confidence limits reported in Table VI are probably too small, since they do not take into account the systematic errors which are quite obvious in Fig. 10. The most reliable values are those obtained from titrating Na_2CO_3 with HCl, because these points fell within 10% of the average. Titrations of $NaHCO_3$ may have been misinterpreted because of the loss of CO_2 (Fig. 8), and we intend to repeat these measurements. Neglect of the excess base present in the $NaHCO_3$ could cause systematic deviations of the type shown in Fig. 10; if this is the case,

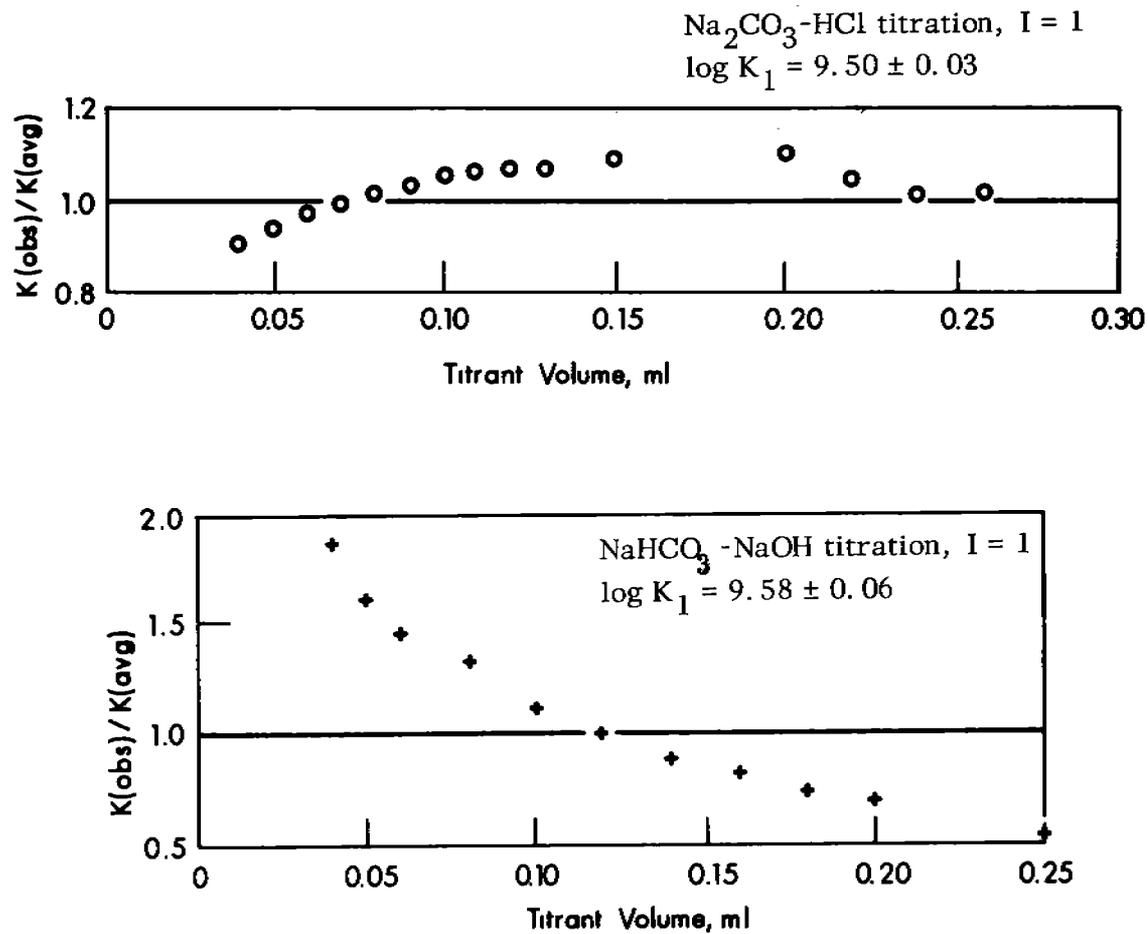


Fig. 10. Deviations of individual values of the equilibrium constants K₁ and K₁₂ from the average value (details are given on each plot; note that the systematic deviations far exceed the precision of the measurements)

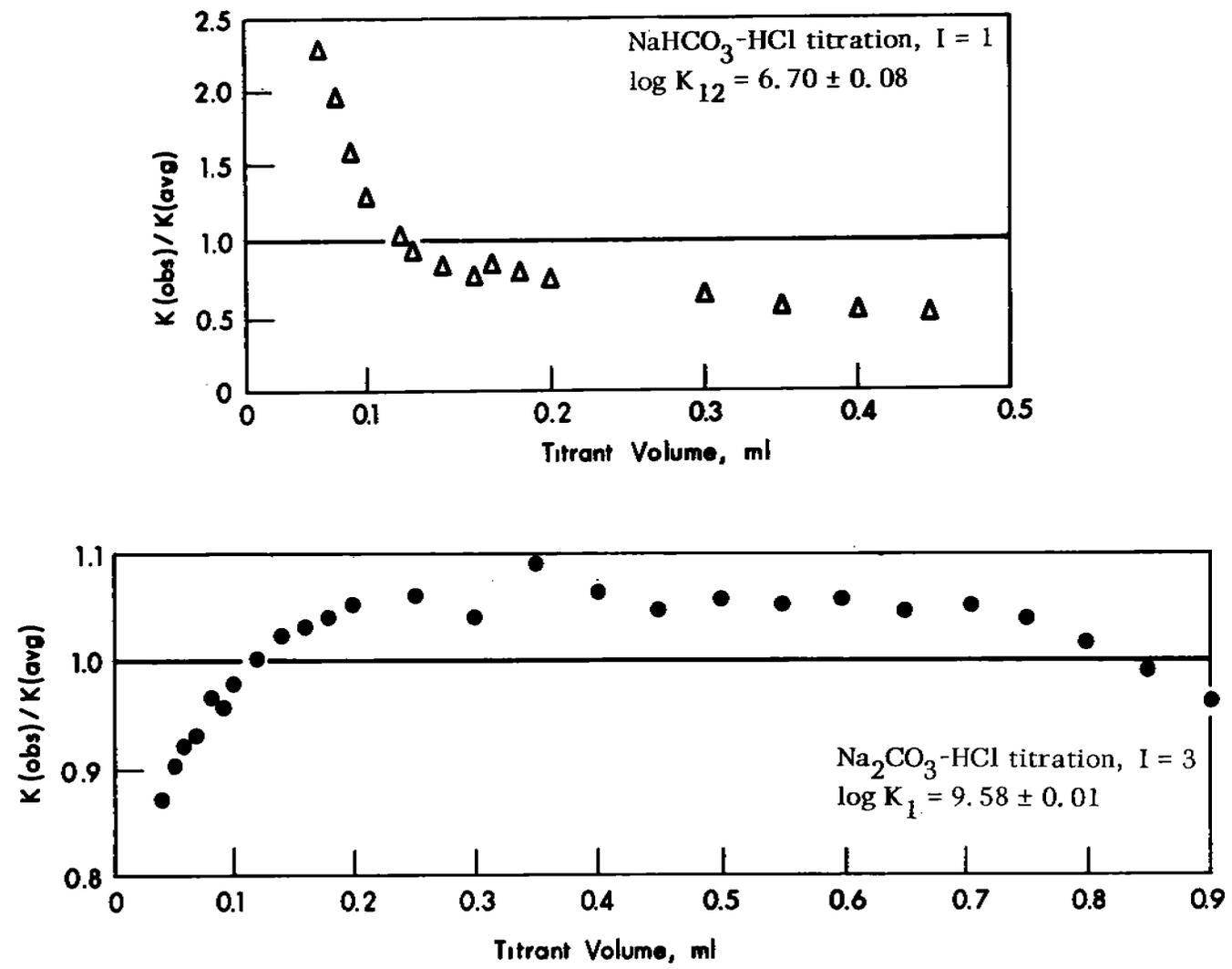


Fig. 10. Deviations of individual values of the equilibrium constants K_1 and K_{12} from the average value (Cont.)

then the most reliable value of the constants would not be the average, but the value obtained at large titrant volumes. This is certainly consistent with the observations: the data obtained at volume = 0.16 ml for the NaHCO_3 - NaOH titration at $I = 1$ gives $\log K_1 = 9.50$, in agreement with the average value obtained from the Na_2CO_3 - HCl titration.

In Table VI, we also compare our results with some representative values from the literature. Strict comparison is usually difficult because of the various pH scales employed, and because of the practice of using hydrogen ion activity corresponding to pH measurements, together with concentrations of the other species in "mixed" equilibrium constants. These are extrathermodynamic assumptions and need not be made if the experiment is designed correctly. First of all, one must note that the concentration equilibrium constants obtained in NaCl are quite different from those obtained at infinite dilution, particularly for K_1 . The direction of the deviations is qualitatively consistent with the formation of ion pairs such as NaCO_3^- and NaHCO_3 . Note that our values of K_1 obtained in 1m NaCl medium are quite close to those obtained spectrophotometrically in the same medium by Bruckenstein and Nelson,³⁶ and even better agreement with those obtained in 1m NaClO_4 by Frydman, et al.⁴² Note also that the negligible change in K_1 on going from $I = 1$ to $I = 3$ is verified by the results in NaClO_4 medium.⁴² Our value of K_{12} is probably too large because of escaping CO_2 ; this was not a factor in the experiments of the other workers quoted, who used closed vessels.

These data will be discussed further in the next section, when ion pairing is discussed. A detailed analysis will be made in the future when we have obtained data of our own which are free of systematic deviations. If adequate precautions are taken to prevent escape of CO_2 from the stock solution and the titrating solutions, and if titrations are made by weight (instead of with the plastic micrometer burettes which are subject to changes in calibration with temperature and time), it should be possible to obtain titration curves in NaCl medium yielding K_1 and K_{12} values with errors of as little as 0.002 logarithmic unit.

Table VI. Acid-Base Equilibria of Carbonates in NaCl

Solution Being Titrated	Concentration in 25.00ml	Titrant, 1.00 M	Total Ionic Strength	Initial pH	Equilibrium Constant*
Na ₂ CO ₃	0.01408	HCl	1.0549	10.86	Log K ₁ = 9.50 ± 0.03
NaHCO ₃	0.02639	HaOH	1.0540	8.85	Log K ₁ = 9.58 ± 0.06
NaHCO ₃	0.02639	HCl	1.0540	8.85	Log K ₁₂ = 6.70 ± 0.08 ?
Na ₂ CO ₃	0.04745	HCl	3.0981	11.07	Log K ₁ = 9.58 ± 0.01
	Reference 36		1.00		Log K ₁ = 9.37
	Reference 38		~0.54		Log K ₁₂ = 6.01 ± 0.01
	Reference 33		Sea water		Log K ₁₂ = 6.00 [†] Log K ₁ = 9.10 [†]
	Reference 42		1.00 (NaClO ₄)		Log K ₁ = 9.57 Log K ₁₂ = 6.04
			3.50 (NaClO ₄)		Log K ₁ = 9.56 Log K ₁₂ = 6.33
	Reference 11		0		Log K ₁ = 10.33 [†]
			0		Log K ₁₂ = 6.35 [†]

*Average value of constants with 95% confidence limits based on normal distribution. These limits may be too small because of systematic errors (Fig. 10).

[†]Mixed equilibrium constants, e.g., $K_1 = [\text{HCO}_3^-] / [\text{CO}_3^{2-}] a_{\text{H}^+}$, where a_{H^+} is obtained from the conventional (glass-calomel) pH measurements. We estimate $\log K_{12} = 6.13$ and $\log K_1 = 9.23$.

[‡]Representative values. Detailed bibliography in reference 11.

C. Ion Pairing Between Na^+ and HCO_3^- or CO_3^{2-}

The possibility of ion pairing between Na^+ and CO_3^{2-} or HCO_3^- has been suggested a number of times, and equilibrium constants for association have been calculated by Garrels and coworkers:^{30, 43}

$$[\text{NaCO}_3^-] = K_1' [\text{Na}^+] [\text{CO}_3^{2-}] \quad K_1' = 18.5 \quad (27)$$

$$[\text{NaHCO}_3] = K_1'' [\text{Na}^+] [\text{HCO}_3^-] \quad K_1'' = 0.55 \quad (28)$$

These values are derived from measurements made using a glass pH electrode-calomel cell with a saturated KCl salt bridge, and depend on various nonthermodynamic assumptions to obtain single ion activity coefficients, e. g., $\gamma_{\text{K}^+} = \gamma_{\text{Cl}^-} = \gamma_{\pm}$ for KCl at the ionic strength of interest. Activity coefficients of Na^+ , CO_3^{2-} , etc., are then obtained through a chain of relationships of this type. Bates⁴⁴ has shown that this type of calculation yields different values for single ion activity coefficients depending on the sequence of relationship assumed.

These considerations, together with the rather uncertain values²⁹ of activity coefficients for NaHCO_3 and Na_2CO_3 , led us to attempt to obtain ion pairing equilibrium constants from the activity coefficients of NaCl in mixtures with NaHCO_3 and Na_2CO_3 . In this analysis, we were guided by the type of calculations used for the $\text{NaCl-Na}_2\text{SO}_4$ system by Pytkowicz and Kester.⁴⁵ They showed that for weak association, a relationship approximating Harned's rule was obtained from a simple ion pairing model.

The assumptions of the ion pairing model for $\text{NaCl-Na}_2\text{CO}_3$ electrolytes were as follows:

1. The species present in the solution were Na^+ , Cl^- , CO_3^{2-} , and NaCO_3^- .
2. The mean activity of NaCl changes only as a result of ion pair formation, provided the total ionic strength is held constant. This assumption may be expressed by the equation

$$[\text{Na}^+] (\gamma_1')^2 = (m_1 + 2 m_2) (\gamma_{12})^2 \quad (29)$$

where $m_1 + 2 m_2$ is the total concentration of sodium ion and $[Na^+]$ is the equilibrium concentration of free sodium ion.

3. The activity coefficient of the free ion (γ_1') is assumed to be equal to the mean activity coefficient of NaCl at ionic strength I' . This ionic strength is calculated not on a formal basis, but on the basis of the equilibrium concentrations of the various ionic species:

$$[NaCO_3^-] = (m_1 + 2 m_2) - [Na^+] \quad (30)$$

$$[CO_3^{2-}] = m_2 - [NaCO_3^-] = [Na^+] - (m_1 + m_2) \quad (31)$$

$$I' = m_1 + m_2 + 2 [CO_3^{2-}] \quad (32)$$

The concentration equilibrium constant for ion pairing is defined by

$$[NaCO_3^-] = K_1' [Na^+] [CO_3^{2-}] \quad (33)$$

For NaCl-NaHCO₃ electrolytes, the species were assumed to be Na⁺, Cl⁻, HCO₃⁻, and NaHCO₃ (a neutral complex), and the equations are modified as follows:

$$[Na^+] (\gamma_1')^2 = (m_1 + m_2) (\gamma_{12})^2 \quad (34)$$

$$[NaHCO_3] = (m_1 + m_2) - [Na^+] \quad (35)$$

$$[HCO_3^-] = m_2 - [NaHCO_3] = [Na^+] - m_1 \quad (36)$$

$$I' = m_1 + \frac{m_2 + [HCO_3^-]}{2} \quad (37)$$

$$[NaHCO_3] = K_1'' [Na^+] [HCO_3^-] \quad (28)$$

The calculation procedure followed was the same in each case; we shall illustrate using NaCl-Na₂CO₃ as an example. The computer programs used are given in full in Section IV of this report.

An initial estimate of K_1' was obtained from α_{12} , which gave $[Na^+]$ from Eq. 29 under the assumption $I' = I$ (which allowed γ_1' to be obtained

from data for pure NaCl solution, γ_{10} at ionic strength I). Then, $[\text{NaCO}_3^-]$, $[\text{CO}_3^{2-}]$, and I' were calculated using Eqs. 30, 31, and 32. A new value of γ_1' was obtained (as γ_{10} at I'), which allowed us to calculate new values for $[\text{Na}^+]$, $[\text{NaCO}_3^-]$, $[\text{CO}_3^{2-}]$, and I'. This procedure was repeated until two successive values of I' agreed to ± 0.0001 , at which point K_1' was calculated from Eq. 27. In this way, a value of K_1' could in principle be obtained for each experimental value of γ_{12} . These detailed calculations will be performed at a later date.

Using the approximate value of K_1' , a curve of γ_{12} versus X_1 was calculated using the same equations. This was much simpler because no iteration was involved. Substituting in Eq. 27 from Eq. 31 for $[\text{Na}^+]$ and $[\text{NaCO}_3^-]$, we obtain a quadratic*

$$K_1' [\text{CO}_3^{2-}]^2 + \{1 + K_1' (m_1 + m_2)\} [\text{CO}_3^{2-}] - m_2 = 0 \quad (38)$$

This quadratic was solved using the quadratic formula, unless the quadratic term was very small, when a simple iterative procedure was used.⁹ Once a value was obtained for $[\text{CO}_3^{2-}]$, then $[\text{NaCO}_3^-]$, $[\text{Na}^+]$, and I' were calculated using Eqs. 31 and 27. Knowing I', γ_1' was obtained from the activity coefficients (γ_{10}) of NaCl solutions, and γ_{12} was then obtained from Eq. 29. As before, $X_1 = m_1 / (m_1 + 2 m_2)$. These plots are shown in Figs. 11, 12, and 13 for ionic strengths 0.5, 1.0, and 3.0.

The first thing to note is that the ion pairing model does not explain the deviations to smaller values of $-\log \gamma_{12}$ at low values of X_1 . The curvature is in the opposite direction and is relatively small for the values of K_1' used. The ion pairing model gives about as good a fit to the data as Harned's rule, although a quantitative analysis of the mean square errors has not yet been made.

* The corresponding equation for NaHCO_3 is:

$$K_1'' [\text{HCO}_3^-]^2 + (1 + K_1'' m_1) [\text{HCO}_3^-] - m_2 = 0, \quad (39)$$

which differs only in the coefficient of the linear term.

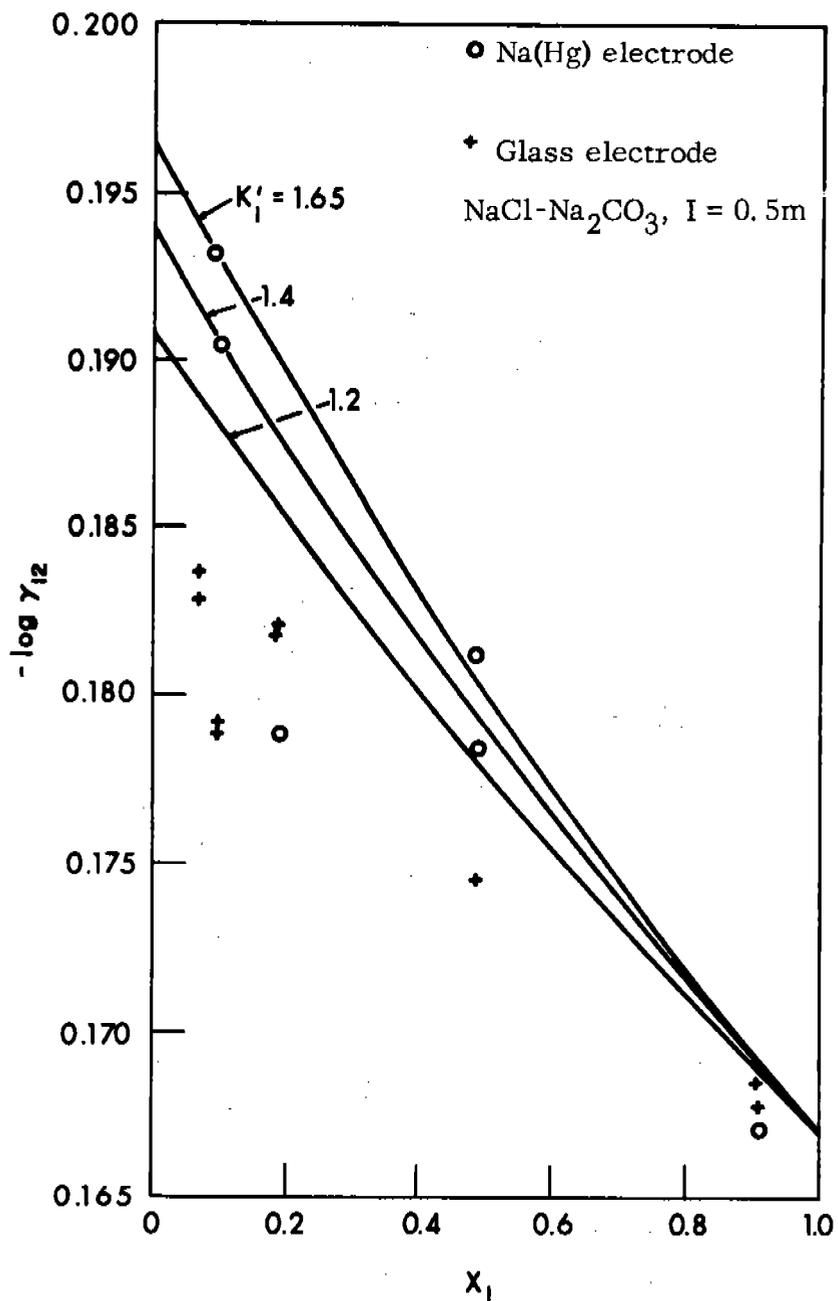


Fig. 11. Application of the ion pairing model to NaCl-Na₂CO₃ electrolytes at ionic strength 0.5m (curves were calculated as described in the text; points are the same experimental data given in Fig. 3)

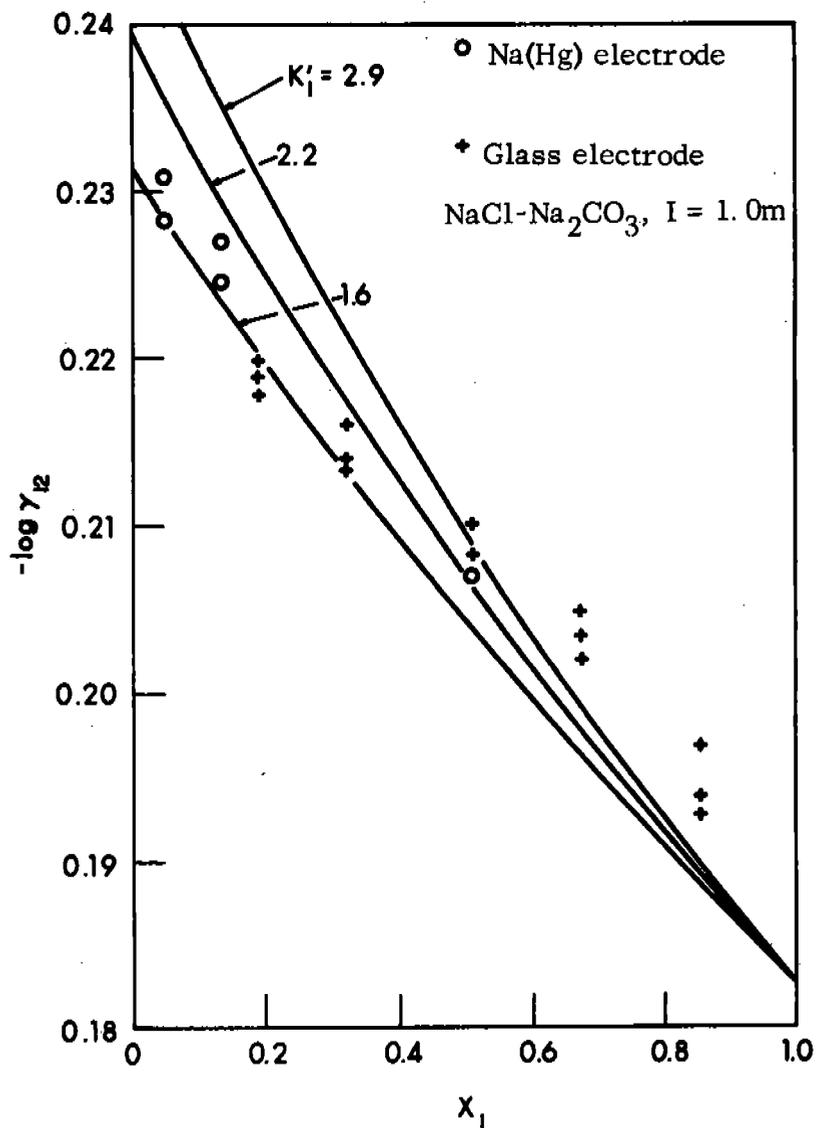


Fig. 12. Application of the ion pairing model to NaCl-Na₂CO₃ electrolytes at ionic strength 1.0m (points are the same experimental data as in Fig. 4)

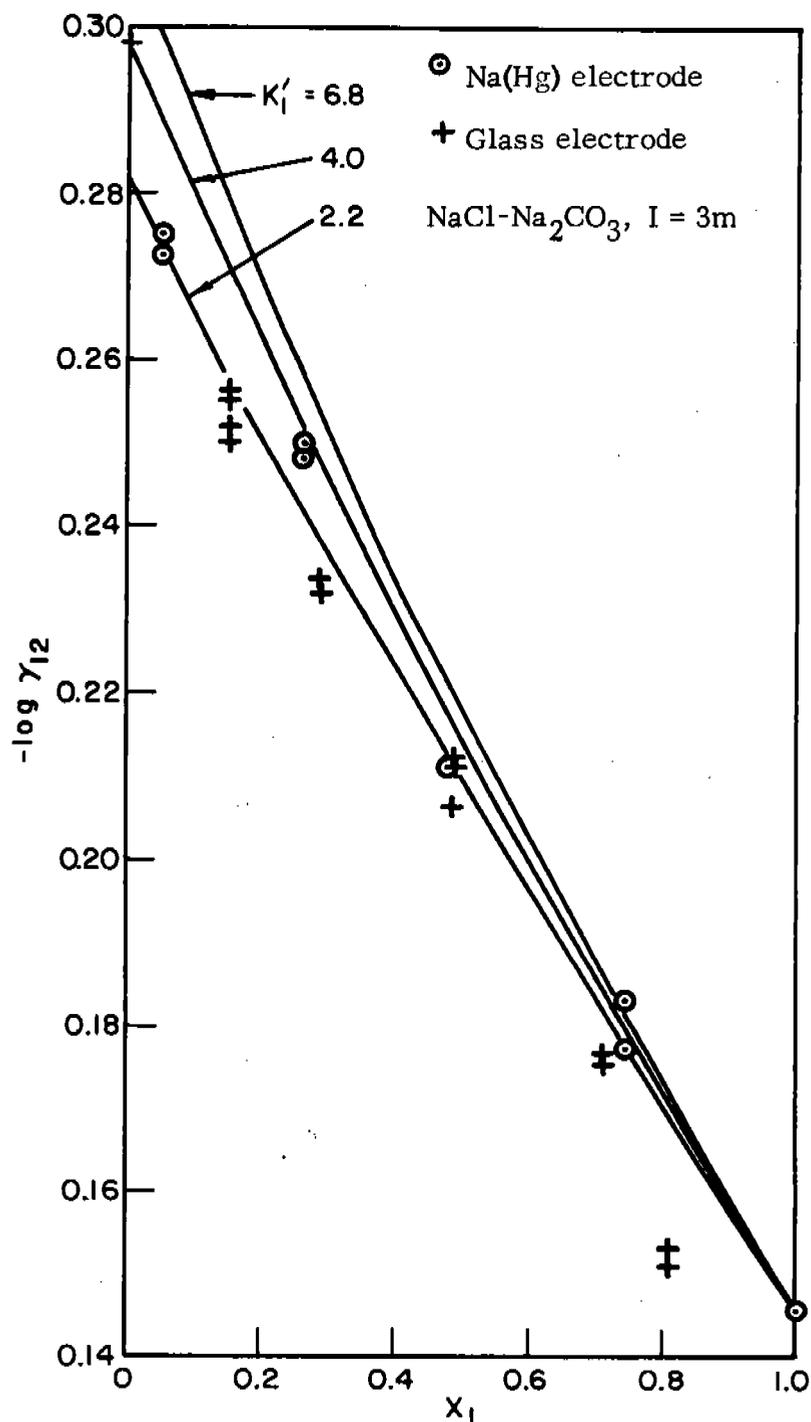


Fig. 13. Application of the ion pairing model to NaCl-Na₂CO₃ electrolytes at ionic strength 3.0m (curves were calculated as described in the text; points are the same experimental data given in Fig. 5)

A more significant point is the values of K_1' obtained. These are in the range of 1.5 to 2.5, and certainly are not as high as 18.5, the value obtained by Garrels.³⁰ This discrepancy is partly due to the fact that Garrels' constants were corrected to $I = 0$, but is also related to the different assumptions used in the calculations. These aspects will be explored further at a later date.

For the NaCl-NaHCO₃ electrolytes, the results are shown in Figs. 14 and 15. The best fit to the amalgam electrode data at both $I = 0.5$ and $I = 1.0$ is approximately $K_1'' = 0.30$, and this is only somewhat smaller than the value of 0.55 obtained by Garrels.⁴³ The calculated curves are almost straight and indistinguishable from Harned's rule.

Some further evidence for ion pairing between Na⁺ and CO₃²⁻ or HCO₃⁻ may be obtained from the variation of the acid-base equilibrium constants with ionic strength. Some representative values were given in Table VI, and these are plotted, along with some additional data⁴⁶⁻⁻⁴⁹ in Fig. 16. The ionic medium and reference is noted next to each point. Qualitatively, the association constant of HCO₃⁻ or CO₃²⁻ with H⁺ (K_{12} or K_1) decreases in the presence of added salt in the direction predicted, if the cation of the added salt was competing with H⁺ for the carbonate ligand. The differences are small for K_{12} , but much larger for K_1 .

Consider first the Na₂CO₃ case (K_1). The equilibria are

$$[\text{HCO}_3^-] \gamma_{\text{HCO}_3} = K_1^0 [\text{H}^+] [\text{CO}_3^{2-}] \gamma_{\text{H}} \gamma_{\text{CO}_3} \quad (40)$$

$$[\text{NaCO}_3^-] = K_1' [\text{Na}^+] [\text{CO}_3^{2-}] \quad (27)$$

$$[\text{NaHCO}_3] = K_1'' [\text{Na}^+] [\text{HCO}_3^-] \quad (28)$$

where K_1^0 is the acid-base equilibrium constant at zero ionic strength, and the activity coefficients are hypothetical single ion values for which only electrically neutral combinations (e. g., γ_{Na} , γ_{HCO_3}) can be empirically determined. K_1' and K_1'' are constants determined in the medium of interest, such as we have just obtained.

If the ionic medium (e. g., NaCl) is present in large excess, $[\text{Na}^+]$ will be determined by the total ionic strength and will be essentially fixed.

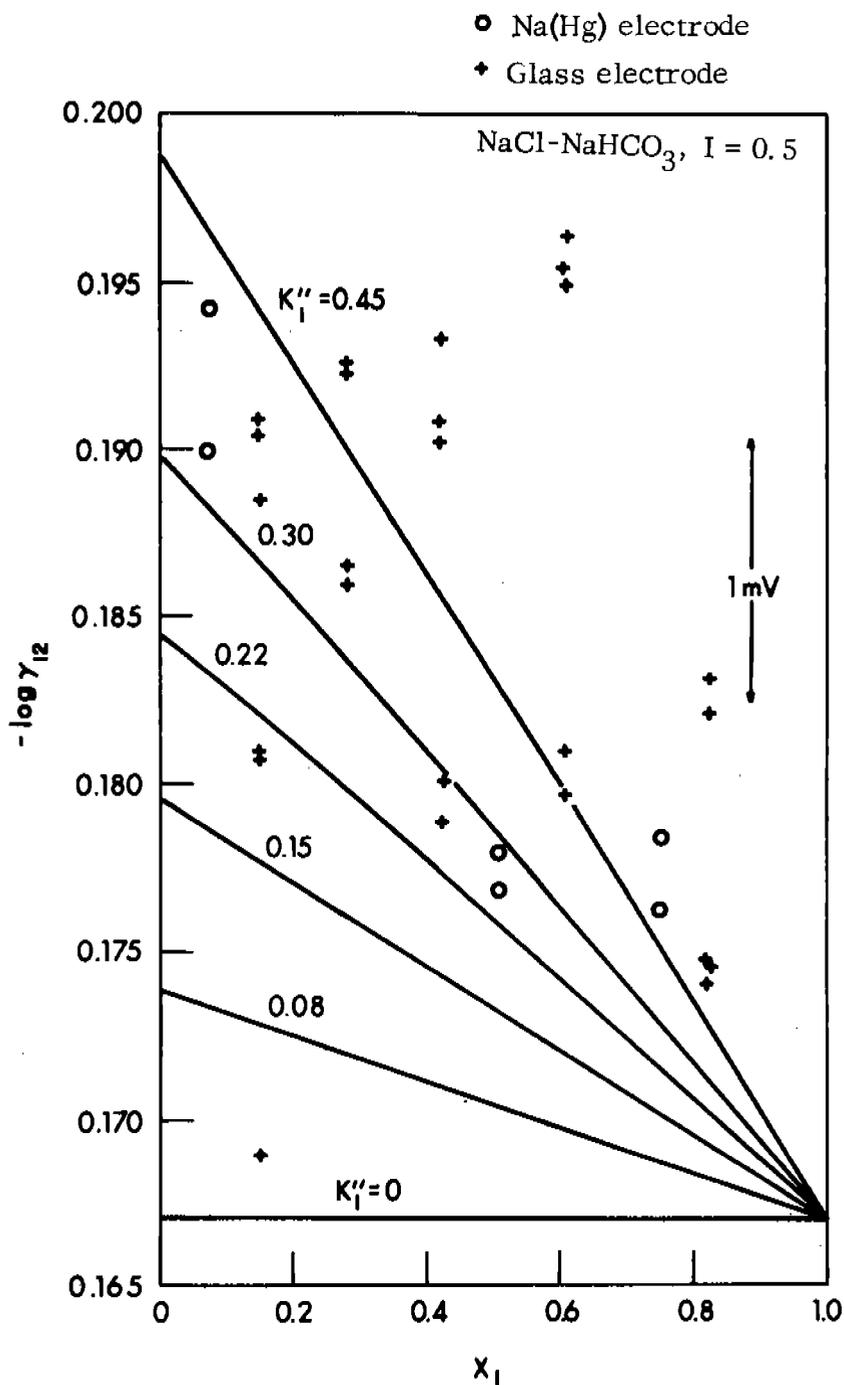


Fig. 14. Application of the ion pairing model to NaCl-NaHCO₃ electrolytes at ionic strength 0.5m (points are the same experimental data given in Fig. 1)

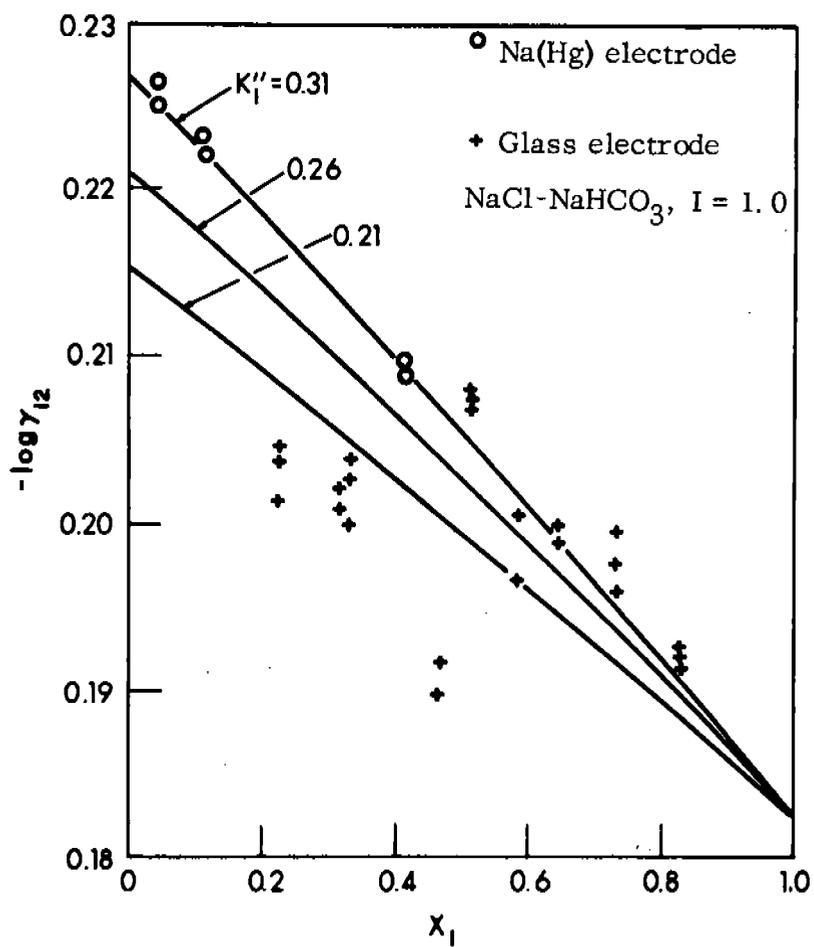


Fig. 15. Application of the ion pairing model to NaCl-NaHCO₃ electrolytes at ionic strength 1.0m (points are the same experimental data given in Fig. 2)

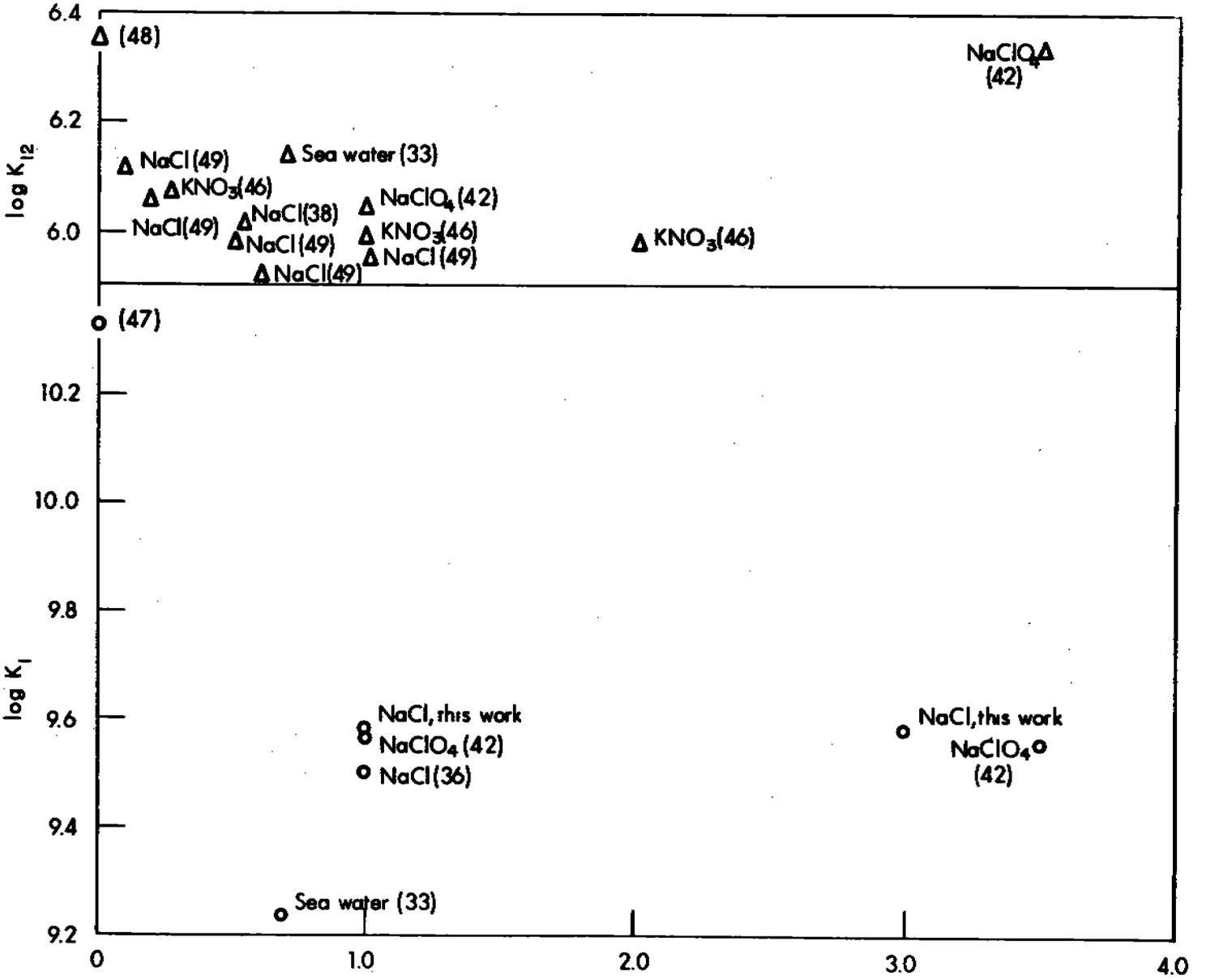


Fig. 16. Summary of values obtained from our experiments and from the literature (references in parentheses near points) for the protonation equilibrium constants of HCO_3^- (K_{12}) and CO_3^{2-} (K_1) in media of constant ionic strength (see text for discussion of the trends observed)

The mass balance will be (m_1 = concentration of Na_2CO_3):

$$m_1 + 2 m_2 = [\text{Na}^+] + [\text{NaCO}_3^-] + [\text{NaHCO}_3^-] \quad (41)$$

$$m_2 = [\text{CO}_3^{2-}] + [\text{NaCO}_3^-] + [\text{HCO}_3^-] + [\text{NaHCO}_3] \quad (42)$$

We may assume the pH is adjusted by adding HCl, so that the proton balance is irrelevant for these calculations.

Now let us evaluate the equilibrium constant, K_1 , in the NaCl medium. This is defined by

$$([\text{HCO}_3^-] + [\text{NaHCO}_3]) = K_1 [\text{H}^+] ([\text{CO}_3^{2-}] + [\text{NaCO}_3^-]), \quad (43)$$

Since, by the usual (pH) methods $[\text{NaCO}_3^-]$ and $[\text{CO}_3^{2-}]$ or $[\text{NaHCO}_3]$ and $[\text{HCO}_3^-]$ are indistinguishable in Eq. 42 and are calculated in toto. Substituting in Eq. 43 from Eqs. 27 and 28, we have

$$[\text{HCO}_3^-] (1 + K_1'' [\text{Na}^+]) = K_1 [\text{H}^+] [\text{CO}_3^{2-}] (1 + K_1' [\text{Na}^+]) \quad (44)$$

And making use of Eq. 40, we have

$$K_1 = K_1^o \left(\frac{\gamma_{\text{H}} \gamma_{\text{CO}_3}}{\gamma_{\text{HCO}_3}} \right) \left(\frac{1 + K_1'' [\text{Na}^+]}{1 + K_1' [\text{Na}^+]} \right) \quad (45)$$

This calculation separates the constant ionic medium equilibrium constant into three parts: (1) a zero ionic strength contribution, K_1^o , (2) an activity coefficient quotient, and (3) a term resulting from ion pairing with the medium ions $[\text{Na}^+]$. Note that the close agreement between data in NaCl and NaClO_4 medium in Fig. 16 indicates that the anion plays little part in these equilibria. The much lower value of K_1 in sea water can probably be attributed primarily to association with the Mg^{2+} ions present,⁴³ and further investigations of such phenomena will be made at a later date.

From a quantitative point of view, it is not trivial to separate the activity coefficient terms from the ion pairing terms, but some extrathermodynamic assumptions will allow this to be done for illustrative purposes. If we assume that the ion pairing constants are equal to the values ($K_1' = 2.0$, $K_1'' = 0.3$) we have calculated above, we arrive at a contribution from ion

pairing at $[Na^+] = 1$:

$$\frac{1 + K_1'' [Na^+]}{1 + K_1' [Na^+]} = 0.433 \quad (46)$$

which corresponds to a decrease in $\log K_1$ of 0.36 unit on going from $I = 0$ to $I = 1.0$.

Note that the actual values of K_1 obtained in 1.0M NaCl or NaClO₄ are approximately 0.75 logarithmic unit lower than at $I = 0$. The extra 0.4 logarithmic unit (a factor of 2.5) may be assumed to correspond to the activity coefficient term. How close is this to what we expect theoretically? If we assume that γ_H and γ_{HCO_3} are approximately equal (since the ions have the same charge and roughly the same size), and we take $\gamma_{CO_3} = \gamma_+^2$ for a typical 2 to 1 salt where ion association is probably small (e.g., $\gamma_+ = 0.53$ for 0.33m CaCl₂), then the activity coefficient term could contribute as much as $\log(0.23) = -0.64$ logarithmic unit to the decrease of K_1 . This is in excess of that needed to explain the observations. Use of the Davies equation or various extended Debye-Hückel equations gives only slightly larger values for the activity coefficient of a divalent ion,²⁶ and thus leads to the same conclusion.

In contrast, the constants reported by Garrels,^{30,43} ($K_1' = 18.5$, $K_1'' = 0.55$) lead to the prediction that $\log K_1$ will decrease by 1.1 units due simply to ion pairing alone. This is already in excess of the observed decrease (0.75), and although account has presumably been taken of changes in the activity coefficients, these could cause a still greater decrease of K_1 .

Thus provisionally, we may assign the change in K_1 as I varies from 0 to 1.0 as follows: (1) a decrease of 0.36 logarithmic unit due to ion pairing with Na^+ , (2) a decrease of 0.6 to 0.65 logarithmic unit due to changes in γ_{CO_3} , and (3) an increase of 0.2 to 0.25 logarithmic unit due to changes in the ratio $\gamma_H / \gamma_{HCO_3}$.

For the NaHCO₃ case (K_{12}), we can follow a similar course of reasoning to obtain

$$K_{12} = K_{12}^o \frac{\gamma_H \gamma_{HCO_3}}{\gamma_{CO_2}} \left[\frac{1}{1 + K_1'' [Na^+]} \right] \quad (47)$$

Here the ion pairing term (in brackets) is 0.77, and predicts a decrease of about 0.11 unit in $\log K_{12}$ on going from $I = 0$ to $I = 1.0$. * Since the observed change is a decrease of 0.35 unit, the activity coefficient ratio must correspond to approximately 0.24 logarithmic unit. This is not unreasonable. γ_{CO_2} is probably close to unity, since CO_2 (or H_2CO_3) is uncharged, and each of the singly charged ions would have activity coefficients of approximately 0.6 to 0.7 (e. g., typical values of γ_{\pm} for alkali halides). Thus, the activity coefficient term could cause a decrease of 0.3 to 0.45 logarithmic unit in K_{12} . This is in excess of what is observed, and could imply that γ_{CO_2} is less than unity or that γ_H or γ_{HCO_3} is greater than 0.7.

* Note that if Garrels' value of K_1'' is used, and one assumes that his calculations have taken account of the activity coefficient terms, one predicts a decrease in K_{12} of 0.17 logarithmic unit (only about half the observed change of 0.35 unit).

D. NaCl-NaF Electrolytes

Although the stability and high selectivity of the newly available lanthanum fluoride solid state membrane electrode²⁸ (manufactured by Orion Research, Inc.) make it eminently suitable for accurate measurements of activity coefficients in fluoride-containing electrolytes, no results have yet been published on such a use. We have now made such measurements, and these results are given here.

The most obvious experiment to perform is the measurement of the mean activity coefficients in solutions containing only NaF by means of the cell:

Na glass electrode/ Na^+ , F^- , $\text{H}_2\text{O}/\text{LaF}_3$ membrane electrode

Preliminary experiments of this type were carried out by Bates and his coworkers at the National Bureau of Standards. The potentials obtained were reported to be consistent with the activity coefficients of NaF in water as obtained by isopiestic measurements, but the reproducibility of the measurements (± 1 mV) was not as good as expected.^{44,50} At the time, it was not clear whether this irreproducibility resulted from instability in the sodium sensitive glass electrode or in the lanthanum fluoride electrode, but our subsequent experiments have provided evidence (including visible etching of the glass surface) that the glass electrode is probably responsible for the poor reproducibility of these measurements. Later in this section, we present some of our own measurements on this cell.

In our laboratory, we have been principally concerned with NaCl-NaF electrolytes, and have carried out measurements using the following cells:

$\text{Ag}/\text{AgCl}/\text{Na}^+$, Cl^- , F^- , $\text{H}_2\text{O}/\text{Na}(\text{Hg})$

$\text{Ag}/\text{AgCl}/\text{Na}^+$, Cl^- , F^- , $\text{H}_2\text{O}/\text{Na}$ glass (NAS 11-18)

$\text{Ag}/\text{AgCl}/\text{Na}^+$, Cl^- , F^- , $\text{H}_2\text{O}/\text{LaF}_3$ membrane

Na glass/ Na^+ , Cl^- , F^- , $\text{H}_2\text{O}/\text{LaF}_3$ membrane

The experiments were carried out as described previously.⁵ NaF was BDH reagent grade (92-584) and contained less than 0.002% chloride and less than 0.004% heavy metals. Potassium was approximately 0.01%. Stock solutions were analyzed by titration with standard $\text{La}(\text{NO}_3)_3$ using the LaF_3 electrode as an indicator.⁵¹

Let us first consider the AgCl-Na cells which measure the activity coefficients, γ_{12} , of NaCl in the mixed electrolytes. These experiments and calculations were carried out exactly as all our previous studies of this type, and the results are listed in Tables VII and VIII, and displayed in Figs. 17, 18, and 19 as Harned rule plots.

Probably the most obvious factor observed in these measurements is their lack of reproducibility compared to the other systems we have studied. This is most dramatically seen by comparing the glass electrode results plotted in Figs. 17 and 18. The data of Fig. 17 were obtained with a new Corning NAS-11-18 glass electrode (C), and these agree fairly well with amalgam electrode measurements. In contrast, an older electrode of the same type (C) which had been in use for about 1 yr, gave the results plotted in Fig. 18. Electrode C' gave an α_{12} of approximately zero; electrode C gave an α_{12} of approximately 0.10, and showed visible signs of etching after use. These results indicate the strong dependence of glass electrode measurements in fluoride-containing solutions on the history and surface characteristics of the glass electrode used. Similar (although not as extreme) irreproducibility is seen in the 1.0m solutions for which data are displayed in Fig. 19.

If we consider only the amalgam electrode results for the moment, there seems to be a trend to smaller values of $-\log \gamma_{12}$ at low values of X_1 (Figs. 17 and 19), which could indicate a true thermodynamic deviation from Harned's rule, particularly since it seems to be supported by the glass electrode measurements to some extent. However, it could also result from the effect of fluoride ion on the Ag/AgCl electrode. Since the effect is nearly within the apparent precision of the data, no firm conclusion can be reached at this time.

Table VII. Activity Coefficient Measurements in NaCl-NaF Electrolytes
 [Cell: Ag/AgCl/NaCl, NaF, H₂O/Na(Hg)]

Total Ionic Strength, I	pH*	X ₁	ΔE, mV	-log γ ₁₂ (Experimental)	-log γ ₁₂ (Corrected)
0.50307	11.02	1.0	0	0.1672	0.1668
0.4965	10.31	0.4919	18.90 18.65	0.1700 0.1679	0.1703 0.1682
0.4934	9.59	0.1531	48.78 48.30	0.1695 0.1654	0.1700 0.1659
0.4929	9.33	0.0901	61.20 60.80	0.1592 0.1558	0.1598 0.1564
1.0941	9.04	1.00	0	0.1838	0.1824
0.9815	10.07	0.4601	23.04 23.08	0.1868 0.1871	0.1874 0.1877
0.9044	10.9	0.0966	65.35 65.40	0.1883 0.1887	0.1923 0.1927
0.8973	11.0	0.0633	76.80 76.89	0.1918 0.1925	0.1962 0.1969
1.0801	11.14	1.0	0	0.1837	0.1824
1.0591	10.85	0.8347	4.50 4.31 5.00	0.1790 0.1774 0.1832	0.1780 0.1764 0.1822
1.0193	10.68	0.5207	19.03 19.08	0.1925 0.1929	0.1920 0.1924
0.9927	10.45	0.3109	33.44 33.31	0.1976 0.1965	0.1978 0.1967
0.9705	10.37	0.1353	55.59 55.49	0.2001 0.1993	0.2010 0.2002

*pH of 1m NaF = 11.10.

Table VIII. Activity Coefficient Measurements in NaCl-NaF Electrolytes
(Cell: Ag/AgCl/NaCl, NaF, H₂O/Na Glass)

Total Ionic Strength, I	pH	X ₁	ΔE, mV	-log γ _± (Experimental)	-log γ _± (Corrected)
Electrode C'					
0.5685	6.41	1.0	0	0.1707	0.1668
0.5629	7.49	0.9271	2.0	0.1690	0.1652
			2.1	0.1699	0.1661
			2.2	0.1707	0.1669
0.5421	7.73	0.6550	12.30	0.1725	0.1699
			12.35	0.1729	0.1703
0.4965	10.31	0.4919	24.95	0.1725	0.1727
			24.85	0.1717	0.1719
			24.80	0.1713	0.1715
0.5226	7.90	0.3991	25.65	0.1706	0.1691
			25.60	0.1698	0.1683
			25.75	0.1694	0.1679
0.4934	9.59	0.1531	54.10	0.1645	0.1649
			54.15	0.1649	0.1653
0.4929	9.33	0.0901	64.05	0.1338	0.1343
			64.60	0.1380	0.1385
Electrode C					
0.5482	—	1.00	0	0.1697	0.1669
0.5527	6.47	0.9430	1.75	0.1735	0.1700
			1.90	0.1748	0.1713
			2.10	0.1765	0.1730
			1.85	0.1744	0.1709
0.5635	6.71	0.8083	6.82	0.1871	0.1820
			6.73	0.1864	0.1813
			6.50	0.1844	0.1793
0.5894	7.01	0.4862	21.52	0.2108	0.2007
			22.45	0.2186	0.2085
			22.17	0.2163	0.2062

Table VIII. (Cont.)

Total Ionic Strength, I	pH	X_1	ΔE , mV	$-\log \gamma_{\pm}$ (Experimental)	$-\log \gamma_{\pm}$ (Corrected)
Electrode C (Cont.)					
0.6079	7.19	0.2558	38.94	0.2253	0.2106
			39.44	0.2295	0.2148
			39.03	0.2260	0.2113
			38.83	0.2243	0.2096
0.6172	7.23	0.1407	53.12	0.2186	0.2013
			53.27	0.2199	0.2026
			53.10	0.2184	0.2011
0.6239	7.31	0.0565	79.70	0.2473	0.2280
			79.50	0.2457	0.2264
			79.67	0.2471	0.2270
			79.87	0.2488	0.2295
1.0554	—	1.00	0	0.1839	0.1824
1.0494	7.60	0.9034	2.67	0.1827	0.1819
			3.12	0.1865	0.1857
			3.40	0.1889	0.1881
			3.50	0.1897	0.1889
1.0409	8.19	0.7672	8.48	0.1946	0.1937
			8.09	0.1913	0.1904
			8.30	0.1931	0.1913
			8.20	0.1922	0.1922
1.0225	8.01	0.4706	22.25	0.2010	0.2003
			22.49	0.2030	0.2023
			22.60	0.2039	0.2032
1.0182	8.17	0.4028	25.21	0.1913	0.1907
			25.73	0.1957	0.1951
			25.30	0.1921	0.1915
			25.83	0.1966	0.1960
1.0085	7.89	0.2463	40.11	0.2083	0.2080
			39.95	0.2070	0.2067
			40.07	0.2080	0.2077
1.0008	7.73	0.1235	56.52	0.1956	0.1956
			57.22	0.2015	0.2015
			57.00	0.1996	0.1996
0.9957	7.67	0.0407	84.09	0.1862	0.1864
			84.30	0.1880	0.1882
			84.18	0.1870	0.1872
			85.13	0.1950	0.1952

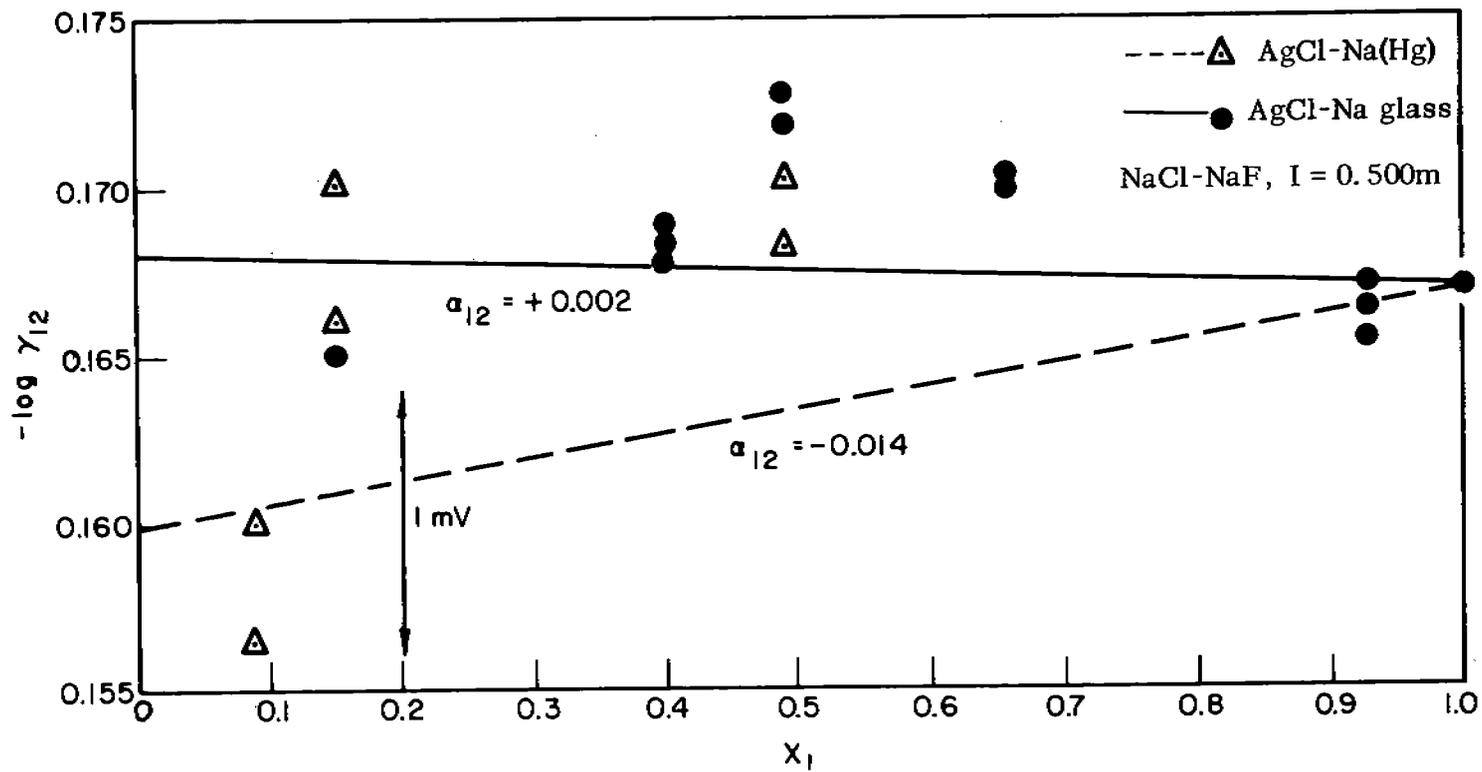


Fig. 17. Activity coefficients of NaCl in NaCl-NaF electrolytes at ionic strength 0.5m (the straight lines correspond to Harned's rule)

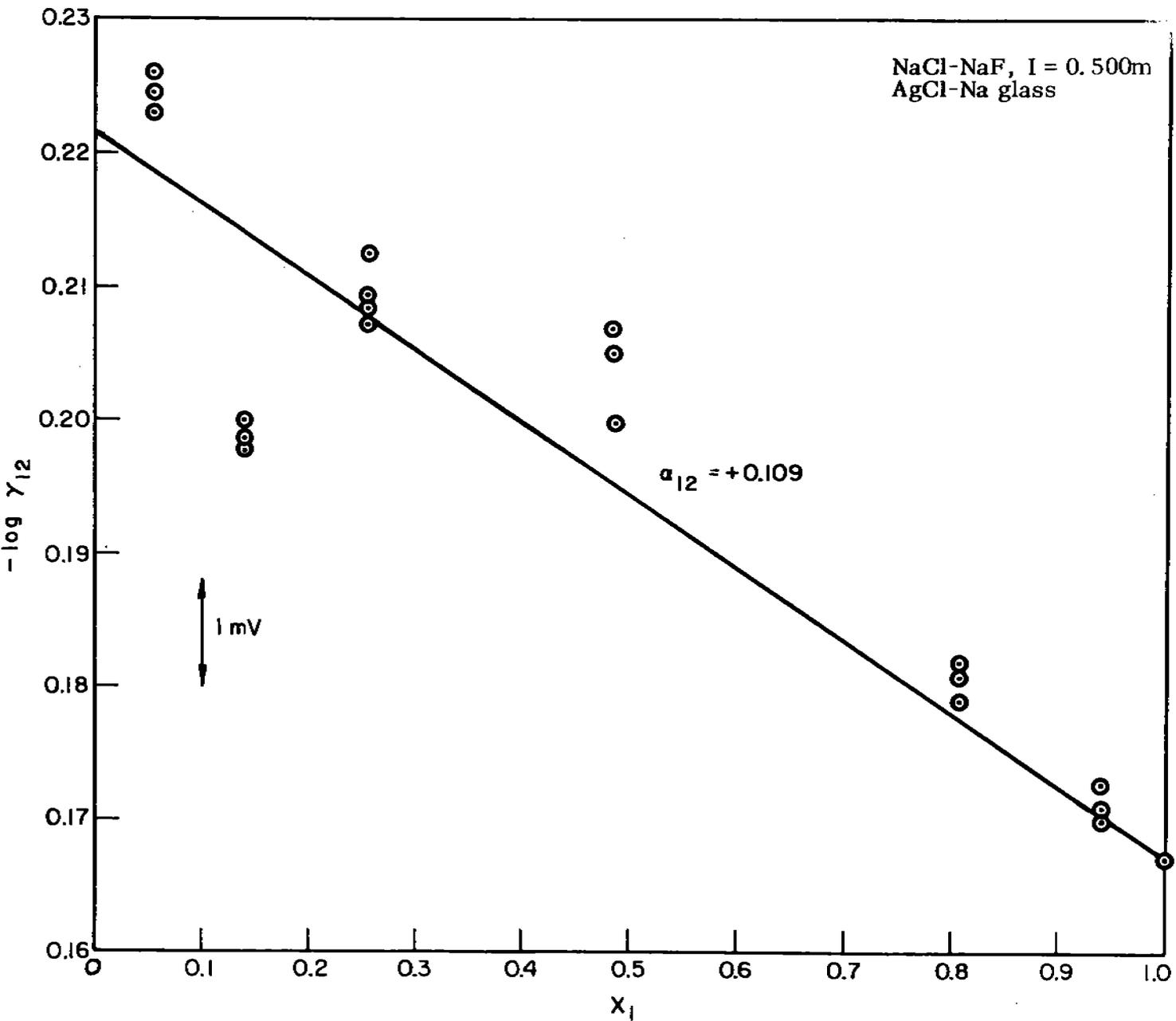


Fig. 18. Activity coefficients of NaCl in NaCl-NaF electrolytes at ionic strength 0.5m (note that the slope is much steeper than in Fig. 17; the glass electrode used was aged for some time and its surface appeared etched by the solutions; we do not consider these data reliable, in spite of their internal consistency)

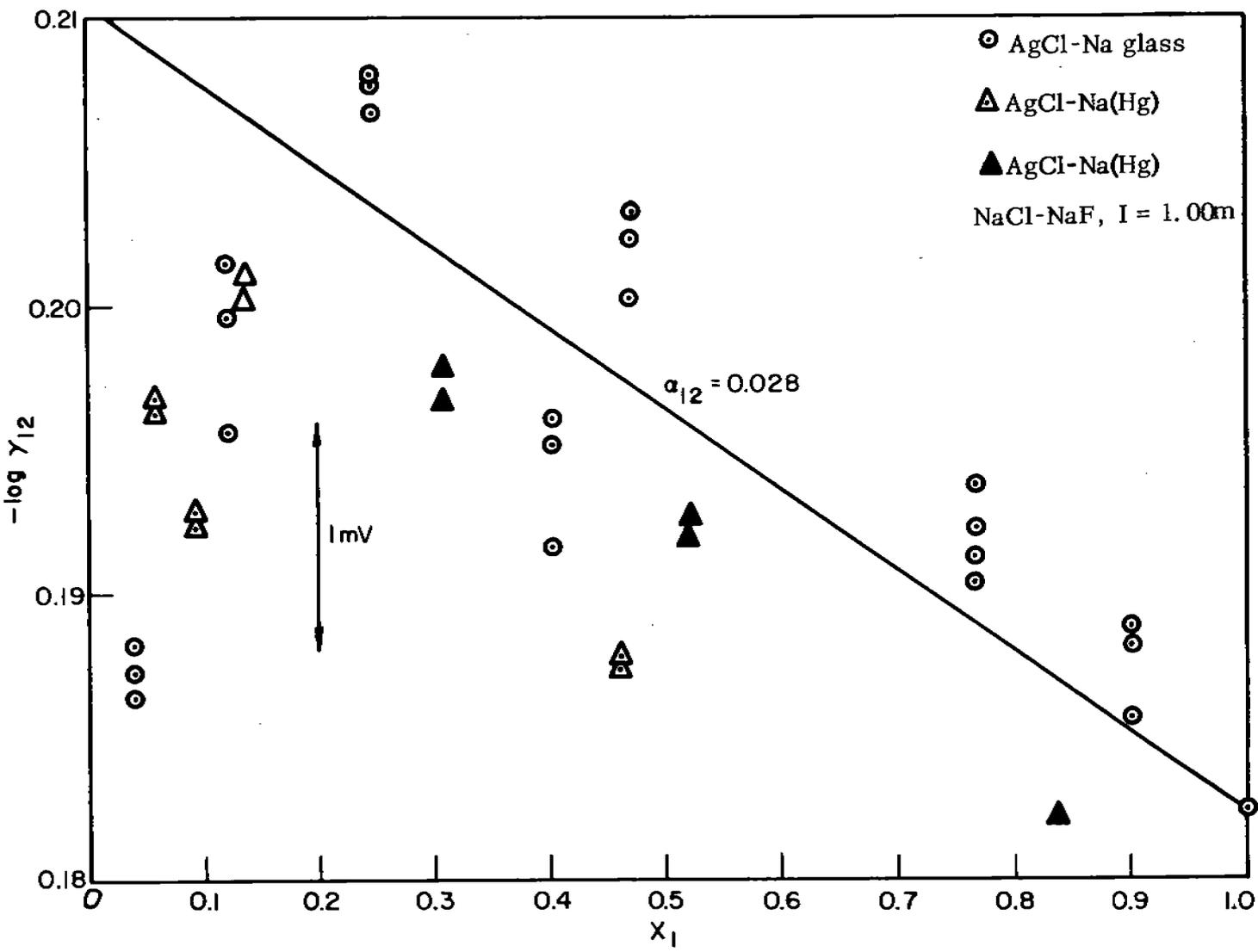
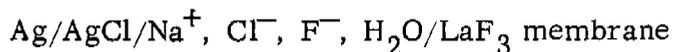


Fig. 19. Activity coefficients of NaCl in NaCl-NaF electrolytes at ionic strength 1.0m (note that the two separate series of measurements with the sodium amalgam electrode are in good agreement; the slope of the Harned rule line is obtained from the data in Table XI)

In spite of the systematic deviations from Harned's rule, we fitted the experimental data to a straight line by the method of least squares, and the results are summarized in Table IX. The inconsistency is not easily explicable, and further experiments seem warranted.

Consider next the measurements made with the cell



which gives directly the ratio of the mean activity coefficients γ_{12}/γ_{21} . This cell, although it does not give as direct an approach to the activity coefficients of the individual components, gave data which were more precise than any of our other measurements on the NaCl-NaF system, and provided independent information.

It is possible to obtain, by combining measurements of this cell with osmotic coefficients, the mean activity coefficients of γ_{12} and γ_{21} separately. The potential of this cell is given by

$$E = E^\circ + \frac{RT}{F} \ln \left(\frac{m_{\text{Cl}}}{m_{\text{F}}} \right) + \frac{2RT}{F} \ln \left(\frac{\gamma_{12}}{\gamma_{21}} \right) \quad (48)$$

where m_{Cl} and m_{F} are the molal concentrations of chloride and fluoride in the mixed electrolyte, respectively, γ_{12} is the mean activity coefficient of NaCl (component 1), and γ_{21} is the mean activity coefficient of NaF (component 2) in the mixed electrolyte. To eliminate long term uncertainties in E° , the test solutions are compared with a calibration solution with $m_{\text{Cl}} \approx m_{\text{F}}$:

$$E^\circ = E_{\text{ref}} - \frac{RT}{F} \ln \left(\frac{m_{\text{Cl}}}{m_{\text{F}}} \right)_{\text{ref}} - \frac{2RT}{F} \ln \left(\frac{\gamma_{12}}{\gamma_{21}} \right)_{\text{ref}} \quad (49)$$

To apply Harned's rule, solutions of a given set were approximately the same ionic strength (e. g. , 0.5 or 1.0m). Since the concentrations of chloride and fluoride in both the test and reference solutions and the temperature are known, the difference in potential between these solutions gives directly the quantity

Table IX. Harned Rule Coefficients for NaCl in Aqueous NaCl-NaF Electrolytes at 25 °C

Na ⁺ Sensor	I	pH	α_{12}
Na(Hg)	0.50	9.3 — 11.0	-0.014 ± 0.024
Na(Hg)	1.00	10.3 — 11.1	+0.028 ± 0.007
Glass (C')	0.50	6.4 — 10.3	+0.002 ± 0.016
Glass (C)	0.50	6.4 — 7.3	+0.109 ± 0.009
Glass (C)	1.00	7.6 — 8.2	+0.011 ± 0.009

$$R_{21} = \log \frac{\gamma_{21}^r \gamma_{12}^t}{\gamma_{12}^r \gamma_{21}^t} \quad (50)$$

where r stands for the reference solution and t stands for the test solution. Experimental values of this quantity are presented in Table X and plotted in Fig. 20.

If Harned's rule is assumed to be obeyed for both components, then the relations

$$\log \gamma_{12} = \log \gamma_{10} - \alpha_{12} X_2 I \quad (51)$$

$$\log \gamma_{21} = \log \gamma_{20} - \alpha_{21} X_1 I \quad (52)$$

where γ_{10} and γ_{20} are the activity coefficients of NaCl and NaF, respectively (in solutions containing only that salt at ionic strength, I, which is the same as the mixed solution) will hold. The ionic strength fraction of NaF, X_2 , is given simply by

$$X_2 = 1 - X_1 = \frac{m_F}{m_F + m_{Cl}} \quad (53)$$

Using these equations, one obtains

$$R_{21} = (\alpha_{12} + \alpha_{21}) (X_{ref} - X_2) \quad (54)$$

where $X_{ref} = X_2$ in the reference solution.

Independently, from the Gibbs-Duhem relation, one obtains the relation

$$\alpha_{21} - \alpha_{12} = \frac{2}{2.303I} (\phi_2^0 - \phi_1^0) = Q \quad (55)$$

where ϕ_2^0 and ϕ_1^0 are the osmotic coefficients of solutions containing only NaF and NaCl, respectively, at ionic strength I. Combining this with the above expression for R_{21} , we obtain two alternative expressions:

$$R_{21} = I (2 \alpha_{21} - Q) (X_{ref} - X_2) \quad (56)$$

$$R_{21} = I (2 \alpha_{12} + Q) (X_{ref} - X_2) \quad (57)$$

Table X. Activity Coefficient Measurements in NaCl-NaF Electrolytes
(Cell: Ag/AgCl/NaCl, NaF, H₂O/LaF₃ Membrane Electrode)

Total Ionic Strength, I	pH	Ionic Strength Fraction NaF, X ₂	ΔE, mV	R ₂₁ *
0.4929	9.33	0.9099	57.40	0.0099
			57.20	0.0116
			57.75	0.0069
0.4934	9.59	0.8469	41.75	0.0115
			42.05	0.0089
0.5226	7.90	0.6001	5.30	0.0084
			5.80	0.0042
			6.00	0.0025
0.4965	10.31	0.5081	0.00†	0.0000
0.5421	7.73	0.3450	-21.05	0.0034
			-20.80	0.0013
			-20.85	0.0017
0.5629	7.41	0.0729	-69.90	0.0033
			-70.00	0.0041
			-69.70	0.0016
			-69.60	0.0008
0.6239	7.31	0.9435	69.47	0.0121
			69.62	0.0109
			69.48	0.0120
0.6172	7.23	0.8593	45.32	-0.0022
			45.14	-0.0006
			45.30	-0.0020
0.6079	7.19	0.7442	28.20	-0.0185
			28.33	-0.0196
			28.40	-0.0202
			27.92	-0.0161
0.5894	7.01	0.5138	0.00†	0.0000
0.5635	6.71	0.1917	-38.47	0.0007
			-38.77	0.0033
			-38.73	0.0029

*R₂₁ is defined in text by Eq. 50.

†Reference solution.

Table X (Cont.)

Total Ionic Strength, I	pH	Ionic Strength Fraction NaF, X ₂	ΔE, mV	R ₂₁ *
0.5527	6.47	0.0570	-73.35	-0.0013
			-73.23	-0.0023
			-73.53	0.0002
			-73.50	0.0000
0.9957	7.67	0.9593	77.93	-0.0019
			77.94	-0.0018
			77.78	-0.0031
1.0003	7.69	0.8853	48.74	-0.0062
			49.18	-0.0025
			48.98	-0.0042
			49.07	-0.0034
1.0008	7.73	0.8765	47.70	0.0032
			47.35	0.0003
			48.05	0.0062
			48.02	0.0059
1.0085	7.89	0.7537	25.91	0.0017
			25.90	0.0016
			25.97	0.0022
1.0225	8.01	0.5294	0.00†	0.0000
1.0409	8.19	0.2328	-33.73	-0.0006
			-33.53	0.0011
			-33.52	0.0012
			-33.38	0.0028
1.0494	7.60	0.0966	-60.05	0.0034
			-60.03	0.0036
			-60.23	0.0019

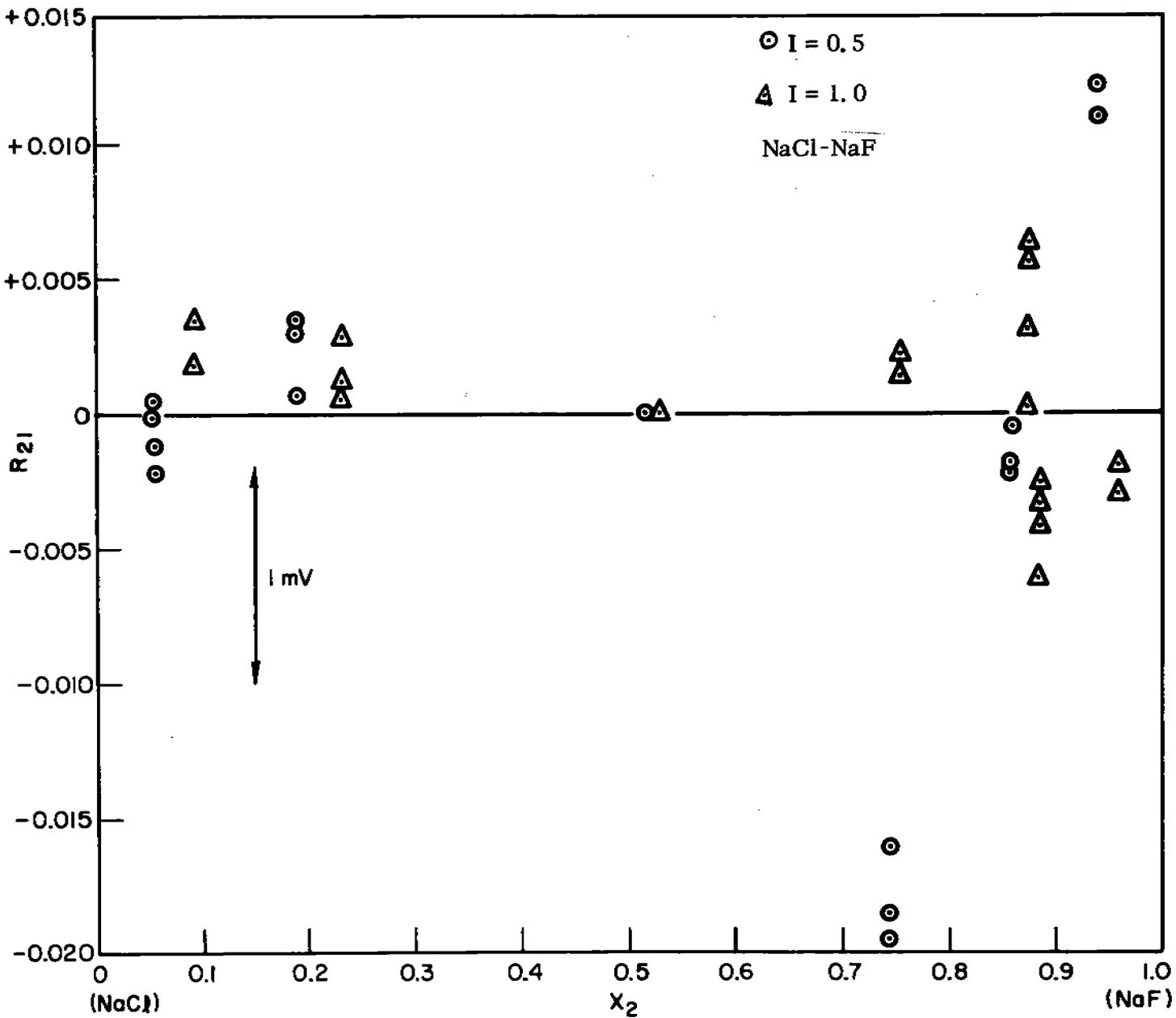
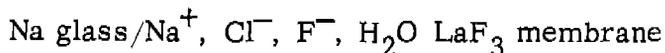


Fig. 20. Results showing the ratio of activity coefficients (γ_{12}/γ_{21}) in NaCl-NaF electrolytes at ionic strengths 0.5 and 1.0 (the function R_{21} is defined by Eqs. 50 and 54 in the text; the lack of any systematic trend indicates that $\alpha_{12} = -\alpha_{21}$ with good precision)

Thus, from each experimental point in Table X, one can obtain directly a value of α_{12} and a value of α_{21} . From osmotic coefficient values listed by Robinson and Stokes,¹² we obtained Q's corresponding to different I's, and these are listed in Table XI along with the resulting Harned rule coefficients. The mean values of these, together with their 95% confidence limits, are presented in Table XI at the top of each set.

We have also made experiments with a third kind of cell:



and a few preliminary results are given in Table XII and plotted in Fig. 21. These results are not very precise, both because of decay of the glass electrode and because of shielding problems in the LaF₃ electrode leads. The corresponding cell using the Na(Hg) electrode has not yet been measured, because the high impedance of the LaF₃ membrane electrode does not permit a short enough response time to follow the potential excursions of the dropping amalgam electrode. Some modifications of the electronics may eliminate this problem, and we hope to obtain such measurements in the near future.

If we compare the data obtained with the three different types of measurements, we may summarize our conclusions as follows:

1. The ratio of the activity coefficients, γ_{12}/γ_{21} , is essentially unity over the entire composition range from NaF to NaCl and at ionic strengths of 0.5 and 1.0m. There is more uncertainty in the measurements in solutions containing larger fractions of NaF, but no distinct trend. This is clear from the plot of Fig. 20. The Harned rule coefficients are thus approximately equal and opposite in sign (Eq. 54).

2. One may estimate the individual Harned rule coefficients (Table XI) by making use of osmotic coefficients, to be

$$\begin{aligned} \alpha_{12} &= +0.01 \pm 0.04 \\ \alpha_{21} &= -0.05 \pm 0.05 \end{aligned} \quad \text{at } I = 0.5\text{m} \quad (58)$$

Table XI. α_{12} and α_{21} Values From Osmotic Coefficient Data in NaCl-NaF Electrolytes

Total Ionic Strength, I	pH	Q	R_{21}	α_{12}	α_{21}
pH of reference solution (Table X) is 10.31; average $\alpha_{12} = -0.003 \pm 0.028$, average $\alpha_{21} = -0.064 \pm 0.030$.					
0.4929	9.33	-0.0610	0.0099	-0.0203	-0.0813
			0.0116	-0.0290	-0.0900
			0.0069	-0.0049	-0.0654
0.4934	9.59	-0.0614	0.0115	-0.0395	-0.1003
			0.0102	-0.0313	-0.0927
			0.0089	-0.0234	-0.0848
0.5226	7.90	-0.0605	0.0084	-0.0173	-0.2078
			0.0042	-0.0585	-0.1190
			0.0025	-0.0226	-0.0831
0.5421	7.73	-0.0602	0.0034	0.0692	0.0090
			0.0013	-0.0450	-0.0152
			0.0017	0.0496	-0.0106
0.5629	7.41	-0.0608	0.0041	0.0474	-0.0134
			0.0033	0.0441	-0.0167
			0.0016	0.0370	-0.0238
			0.0008	0.0337	-0.0271
pH of reference solution (Table X) is 7.01; average $\alpha_{12} = +0.044 \pm 0.018$, average $\alpha_{21} = -0.016 \pm 0.018$.					
0.6239	7.31	-0.0592	0.0121	0.007	-0.0522
			0.0109	0.0093	-0.0499
			0.0120	0.0072	-0.0520
0.6172	7.23	-0.0592	-0.0022	0.0348	-0.0244
			-0.0006	0.0310	-0.0282
0.6079	7.19	-0.0594	-0.0185	0.0957	0.0363
			-0.0196	0.0997	0.0403
			-0.0202	0.1018	0.0424
			-0.0161	0.0872	0.0278
0.5635	6.71	-0.0607	0.0033	0.0394	-0.0213
			0.0029	0.0383	-0.0224
			0.0007	0.0323	-0.0284

Table XI (Cont.)

Total Ionic Strength I	pH	Q	R_{21}	α_{12}	α_{21}
0.5527	6.47	-0.0602	-0.0013	0.0275	-0.0327
			-0.0023	0.0255	-0.0347
			-0.0002	0.0305	-0.0297
pH of reference solution (Table X) is 8.01; average $\alpha_{12} = +0.028 \pm 0.002$, average $\alpha_{21} = -0.027 \pm 0.002$.					
0.9957	7.67	-0.0554	-0.0019	0.0299	-0.0255
			-0.0031	0.0313	-0.0241
			-0.0018	0.0298	-0.0256
1.0003	7.69	-0.0555	-0.0062	0.0365	-0.0190
			-0.0025	0.0313	-0.0242
			-0.0042	0.0336	-0.1219
			-0.0034	0.0325	-0.0230
1.0008	7.73	-0.0555	0.0032	0.0231	-0.0324
			0.0003	0.0273	-0.0282
			0.0062	0.0188	-0.0367
			0.0059	0.0193	-0.0362
1.0085	7.89	-0.0554	0.0017	0.0239	-0.0315
			0.0016	0.0242	-0.0312
			0.0015	0.0244	-0.0310
			0.0022	0.0228	-0.0326
1.0409	8.19	-0.0551	0.0028	0.0321	-0.0230
			0.0011	0.0293	-0.0258
			0.0012	0.0295	-0.0256
1.0494	7.60	-0.0551	0.0034	0.0313	-0.0238
			0.0036	0.0315	-0.0236
			0.0019	0.0296	-0.0255

Table XII. Activity Coefficient Measurements in
 NaCl-NaF Electrolytes at 25 °C
 (Cell: Na Glass/NaCl, NaF, H₂O/LaF₃ Membrane)

Total Ionic Strength, I	Ionic Strength Fraction NaF, X ₂	ΔE , mV		$-\log \gamma_{21}$	
		C	B	C	B
0.9931	1.0	0	0	0.2412	0.2412
1.0003	0.8853	3.3	4.1	0.2442	0.2509
		3.0	—	0.2416	—
1.0225	0.5294	15.82	15.05	0.2432	0.2366
		16.35	14.77	0.2476	0.2343
1.0494	0.0966	—	56.50	—	0.2233
		—	56.71	—	0.2251

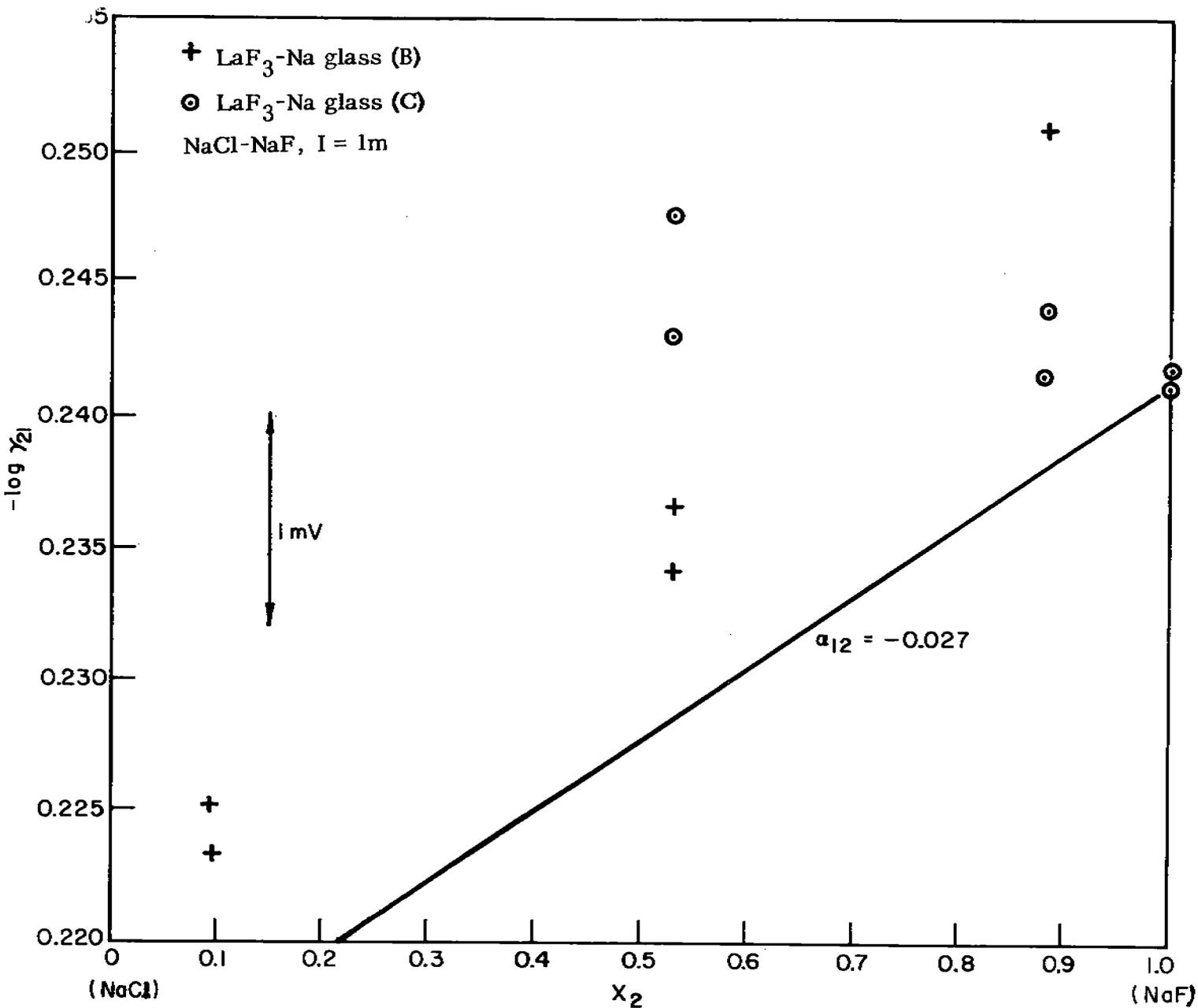


Fig. 21. Preliminary data for the activity coefficient of NaF in NaCl-NaF electrolytes at ionic strength 1.0m (the slope of the Harned rule line is obtained from the data in Table XI)

$$\begin{aligned}\alpha_{12} &= +0.028 \pm 0.002 && \text{at } I = 1.0\text{m} && (59) \\ \alpha_{21} &= -0.027 \pm 0.002\end{aligned}$$

(Note that the precision of the results improves greatly at the higher ionic strength.)

3. From direct measurements of α_{12} (Tables VII, VIII, and IX), the best values appear to be

$$\alpha_{12} = 0.0 \pm 0.03 \quad \text{at } I = 0.5\text{m} \quad (60)$$

$$\alpha_{12} = +0.03 \pm 0.01 \quad \text{at } I = 1.0\text{m} \quad (61)$$

which are in agreement with the above results.

4. The few data that we have for direct measurement of α_{21} (Table XII) confirm that it is negative, and we may tentatively conclude from these data that

$$\alpha_{21} = -0.02 \pm 0.01 \quad \text{at } I = 1.0\text{m} \quad (62)$$

5. Thus, we may take

$$\alpha_{12} = -\alpha_{21} = 0.027 \quad (63)$$

(for all ionic strengths) for a convenient summary of all results.

Within the general irreproducibility of these measurements in fluoride solutions, we may conclude that all three methods of obtaining activity coefficients yield concordant results. We hope that further work on this topic will improve the accuracy of the data.

We have also made measurements of mean activity coefficients, γ_{\pm} , in aqueous solutions containing only NaF by means of the cell

Na glass electrode/ Na^+ , F^- , H_2O /LaF membrane electrode from 10^{-4} to 1m (saturation). The glass electrode was a new NAS-11-18 electrode (C').

Four V-shaped cells were placed in a water bath maintained at 25.00 ± 0.02 °C. Potentials were recorded as a function of time by means of an expanded scale pH meter connected to a Sargent recorder. The reference solution was 0.0100m NaF, and its potential fluctuated between -10.12 and -10.40 mV over a 2-day period during which the experiment was completed. The electrodes were transferred from one solution to another only after a stable potential was reached; this usually took a few minutes with the exception of the most dilute solution, in which the time required was 20 min to 1 hr.

The potential of the above cell is expressed as follows:

$$E = E^\circ + (2 RT/F) \ln (m_{\text{NaF}} \gamma_{\pm\text{NaF}}) \quad (64)$$

Values of E° calculated for each solution using the mean activity coefficients from isopiestic data are listed in Table XIII.

Ratios of activity coefficients ($\gamma_{\pm}^r/\gamma_{\pm}^t$) were obtained using the following expression

$$\Delta E = +118.3 \log (m_{\text{NaF}}^r/m_{\text{NaF}}^t) + 118.3 \log (\gamma_{\pm}^r/\gamma_{\pm}^t) \quad (65)$$

The experimental mean activity coefficients of NaF were obtained by setting $\gamma_{\pm}^r = 0.901$. These are listed in Table XIII with the isopiestic values.

In Fig. 22 (data in Table XIV), the ratio of activity coefficients taken from isopiestic data are plotted against m_{NaF} as dark circles, and our potentiometric values as light circles. Note that our values are lower than those of the isopiestic, especially at high concentrations of sodium fluoride. This discrepancy might be a result of systematic errors due to the glass electrode, but could also be an error in the isopiestic data. If so, it could explain some of the inconsistencies observed in Harned rule coefficients calculated from osmotic coefficient data in NaCl-NaF mixtures in the previous section. Further work will resolve this question.

Table XIII. E° Values for the Cell: Na Glass/ Na^+ , F^- , $\text{H}_2\text{O}/\text{LaF}_3$ Membrane

NaF, m	E, mV	γ_{\pm} (Observed)	γ_{\pm}^*	E° , mV	pH
0.0010	-124.27	0.982	0.965	232.46	6.45
	-124.12	0.985		232.78	
	-123.95	0.988		232.61	
	-123.60	0.995		233.13	
0.0100	-10.12	Reference Solution	0.901	231.76	6.08
	-10.20			231.84	
	-10.40			231.56	
0.1001	100.10	0.773	0.765	232.22	6.25
	100.40	0.778		232.52	
	100.05	0.772		232.17	
0.4921	175.90	0.688	0.634	235.79	8.49
	176.22	0.682		236.11	
	175.95	0.688		235.84	
0.9533	203.60	0.609	0.577	234.30	9.30
	203.70	0.610		234.40	
	203.95	0.613		234.65	

*Isopiestic data from Robinson and Stokes¹² from 0.1 to 1.0m, and from Debye-Hückel theory below 0.1m. See Y. C. Wu and W. J. Hamer, Electrochemical Data part XIII, NBS report 10-002, (1969).

Table XIV. Activity Coefficients in NaF Solutions

NaF, m	$\Delta E (E_{\text{ref}} - E_{\text{test}}),$ mV	$\gamma_{\pm\text{ref}} \gamma_{\pm\text{test}}$ (Observed)	$\gamma_{\pm\text{ref}} \gamma_{\pm\text{test}}$ (Calculated)*
0.0010	113.87	0.9174	0.9337
	113.72	0.9147	
	113.55	0.9117	
	113.20	0.9055	
0.0100	0	1.0	1.0
0.1001	-110.50	1.1656	1.1793
	-110.80	1.1588	
	-110.45	1.1667	
0.4921	-186.30	1.3099	1.4223
	-186.32	1.3094	
	-186.62	1.3017	
0.9533	-214.00	1.4801	1.5623
	-214.10	1.4772	
	-214.35	1.4700	

*From isopiestic data.¹²

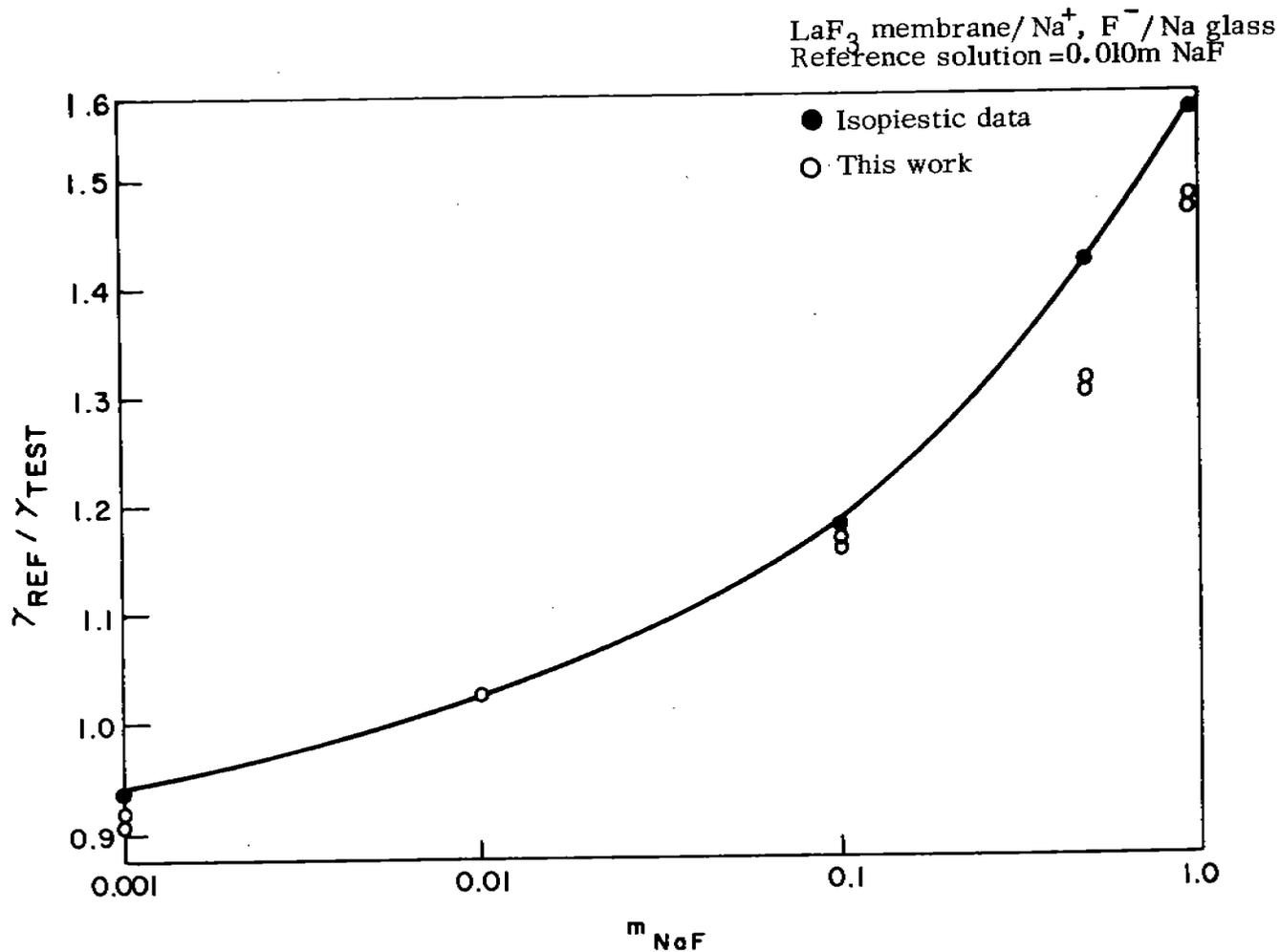
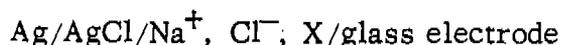


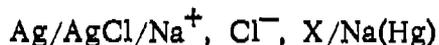
Fig. 22. Mean activity coefficient γ_{\pm} for NaF in aqueous solutions containing no additional salts [our experimental results (○) are expressed as a ratio to the 0.01m reference solution for more accurate comparison with the isopiestic data (-), from reference 12]

E. NaCl-KCl Electrolytes

Electrodes made from sodium aluminum silicate and lithium aluminum silicate glasses are well known to be selective for sodium in the presence of other cations, particularly H^+ and K^+ . This selectivity and thermodynamic reversibility is well documented in dilute solution,⁵² as well as in concentrated solutions containing a single salt component.⁵³ Relatively concentrated multicomponent solutions have been studied by means of cells such as^{15, 21}



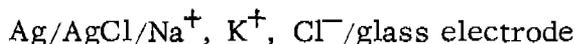
where X is a cation or anion which does not interfere with the operation of either the Ag/AgCl or glass electrode. Such data have been verified (for $X = Mg^{2+}$, Ca^{2+} , and SO_4^{2-}) by measurements with amalgam electrode cells such as^{5, 18, 20}



and (for $X = Mg^{2+}$, Ca^{2+} , Ba^{2+} , SO_4^{2-} , NO_3^- , and ClO_4^-) by isopiestic measurements.^{5, 6}

Although considerable attention has been paid to analytical measurements of sodium ion activity in solutions containing potassium ion,^{52, 54, 55} verification of the selectivity of these glass electrodes has generally been done in dilute solutions for two reasons. First, the activity coefficients of the two ions can be calculated from the Debye-Hückel theory for ionic strengths less than 0.1m and are essentially equal in this region. Second, most analytical measurements are made with a reference electrode employing a saturated KCl salt bridge, and the potential of this liquid junction cannot be assumed constant if the test solution is much more concentrated than 0.1m.

Neither of these objections applies to the cell without liquid junction which we have studied:



If the glass electrode responded only to sodium ion and not at all to potassium ion, the potential of this cell would give directly the activity coefficient, γ_{12} , of NaCl in the mixed electrolyte:

$$E = E^\circ + \frac{RT}{F} \ln (m_{\text{Na}} m_{\text{Cl}} \gamma_{12}^2) \quad (66)$$

The temperature (T), Faraday constant (F), and Gas constant (R), as well as the molal concentration of sodium (m_{Na}) and chloride (m_{Cl}) ions in the electrolyte are known accurately. The standard potential, E° , is determined by calibrating the glass electrode in an electrolyte containing only NaCl at known concentration, where the activity coefficients are known.¹²

A few measurements of this cell at ionic strength 1m were reported by Lanier,⁵⁶ but the electrode he used (Beckman 39137) was made with a glass (NAS-27-5) which shows essentially no selectivity for Na^+ over K^+ . We have previously attempted to measure the activity coefficients (γ_{12}) of NaCl in NaCl-KCl electrolytes using sodium amalgam electrodes, but have found that, since the kinetic interference between the sodium and potassium electron transfer reactions was sufficiently large, we were unable to obtain results of the desired accuracy.^{5, 19} The only other measurements of activity coefficients in this multicomponent system are the isopiestic studies of Robinson,⁵⁷ which have been recently reevaluated by Rush and Robinson.⁵⁸

In this section, we report our measurements of activity coefficients in the NaCl-KCl- H_2O system using two highly sodium selective commercial glass electrodes (of different composition) in a cell without liquid junction. These data verify the isopiestic results by a completely independent method, and also indicate that the glass electrodes indeed measure sodium ion activity in concentrated solutions with much the same selectivity as they do in dilute solutions.

Experiments were conducted as described previously.^{5, 21} The glass electrode was either a Beckman sodium ion electrode no. 39278 (electrode B) or a Corning sodium ion electrode no. 476210 (electrode C). Electrode C is made from a glass containing⁵⁹ 11% Na₂O, 18% Al₂O₃, and 71% SiO₂ (NAS-11-18). The glass composition of electrode B is not given by the manufacturer, but is probably^{60, 61} close to 10.4% Li₂O, 22.6% Al₂O₃, and 67% SiO₂ (LAS-10-23). Two samples of electrode B obtained more than a year apart were used and agreed within experimental error, indicating a reproducible glass composition.

Two cells with matched Ag/AgCl electrodes were used, and the glass electrode transferred back and forth between the two cells while the potential was being recorded as a function of time. One cell contained the mixed NaCl-KCl electrolyte and the other contained a solution of NaCl at the same ionic strength. Equilibrium was reached within 1 min, and the precision of the readings was ± 0.2 mV. All measurements were made at pH = 7.0 ± 0.5 and 25.00 ± 0.02 °C. Solutions were analyzed for chloride by potentiometric titration with standard silver nitrate solution.

From the experimental potential differences (ΔE), the activity coefficient of NaCl was calculated, according to Eq. 66, and then corrected to a round value of ionic strength as described previously.²¹ Both the corrected and uncorrected values are given in Table XV. The measurements made with the glass electrode cell at ionic strength 4.0m are shown in Fig. 23, together with the line corresponding to Harned's rule¹²

$$\log \gamma_{12} = \log \gamma_{10} - \alpha_{12} X_2 I \quad (67)$$

with $\alpha_{12} = 0.024$ obtained from the isopiestic measurements.⁵⁸ In Eq. 67, I is the total ionic strength, X_2 is the ionic strength fraction of KCl, and γ_{10} is the activity coefficient of NaCl alone in aqueous solution at ionic strength I .

Table XV. Activity Coefficients of NaCl in NaCl-KCl Electrolytes at 25 °C

Total Ionic Strength	X_1	ΔE , mV	$-\log \gamma_{12}$ (Experimental)	$-\log \gamma_{12}$ (Corrected)*	Selectivity Ratio
Electrode B					
0.4805	1.0000	0	0.1664	0.1668	—
0.4834	0.8564	2.25	0.1531	0.1542	0.42 (?)
0.4876	0.6585	10.7	0.1660	0.1669	-0.014
0.4911	0.4722	18.4	0.1644	0.1651	0.022
0.4952	0.2706	31.7	0.1574	0.1578	0.023
0.4983	0.1145	53.4	0.1563	0.1564	0.0099
Electrode C					
0.4805	1.0000	0	0.1664	0.1668	—
0.4834	0.8564	3.1	0.1611	0.1622	0.20 (?)
0.4876	0.6583	11.3	0.1713	0.1722	-0.060 (?)
0.4911	0.4722	19.0	0.1694	0.1701	-0.0001
0.4952	0.2706	33.4	0.1738	0.1742	-0.0030
0.4983	0.1145	54.9	0.1706	0.1707	0.0017
Electrode B					
0.9323	1.0000	0	0.1816	0.1824	—
0.9466	0.7030	7.0	0.1697	0.1708	0.22 (?)
0.9548	0.5329	13.5	0.1675	0.1686	0.14 (?)
0.9703	0.2111	38.0	0.1788	0.1797	0.024
1.0554	0.0108	115.2	—	—	0.0037
1.0554	0.00137	154.8	—	—	0.0018
1.0554	<0.00001	154.4	—	—	0.0033

* To 0.500, 1.000, 3.000, or 4.000m ionic strength.

Table XV (Cont.)

Total Ionic Strength	X_1	ΔE , mV	$-\log \gamma_{12}$ (Experimental)	$-\log \gamma_{12}$ (Corrected)*	Selectivity Ratio
Electrode C					
0.9323	1.0000	0	0.1816	0.1824	—
0.9466	0.7030	9.4	0.1892	0.1903	-0.033
0.9548	0.5329	16.7	0.1985	0.1996	-0.024
0.9703	0.2111	40.0	0.1908	0.1917	0.0006
1.0554	0.0108	114.6	—	—	0.0040
1.0554	0.00137	161.8	—	—	0.0010
1.0554	<0.00001	184.9	—	—	0.0010
1.0554	<0.00001	203.9	—	—	0.0005
Electrode B					
3.1134	1.0000	0	0.1424	0.1463	—
3.0675	0.7492	9.7	0.1612	0.1632	0.12 (?)
3.0210	0.4957	21.7	0.1696	0.1701	0.12 (?)
2.9522	0.2667	39.4	0.1852	0.1848	0.067
2.9791	0.1202	60.7	0.1955	0.1948	0.023
3.1008	0.0100	121.7	—	—	0.0034
3.1008	0.00096	161.2	—	—	0.0022
3.1008	<0.00001	176.0	—	—	0.0019
Electrode C					
3.1134	1.0000	0	0.1424	0.1463	—
3.0675	0.7492	10.2	0.1631	0.1651	0.040
3.0210	0.4957	23.0	0.1781	0.1786	0.051 (?)
2.9522	0.2667	40.8	0.1919	0.1915	0.040
2.9791	0.1202	63.0	0.2110	0.2103	0.0071

Table XV (Cont.)

Total Ionic Strength	X_1	ΔE , mV	$-\log \gamma_{12}$ (Experimental)	$-\log \gamma_{12}$ (Corrected)*	Selectivity Ratio
Electrode C (Cont.)					
3.1008	0.0100	121.7	—	—	0.0031
3.1008	0.00096	175.3	—	—	0.00074
3.1008	<0.00001	203.5	—	—	0.00065
Electrode B					
4.3393	1.0000	0	0.0910	0.1062	—
4.3006	0.7884	8.0	0.1050	0.1173	0.32 (?)
4.2547	0.5329	22.1	0.1406	0.1494	0.080
4.2129	0.3099	39.4	0.1641	0.1703	0.027
4.1743	0.0986	71.3	0.1830	0.1872	0.0087
Electrode C					
4.3393	1.0000	0	0.0910	0.1062	—
4.3006	0.7884	9.6	0.1194	0.1317	-0.035
4.2547	0.5329	23.2	0.1485	0.1573	0.0095
4.2129	0.3099	40.9	0.1763	0.1825	-0.0084
4.1743	0.0986	72.5	0.1923	0.1965	0.0021

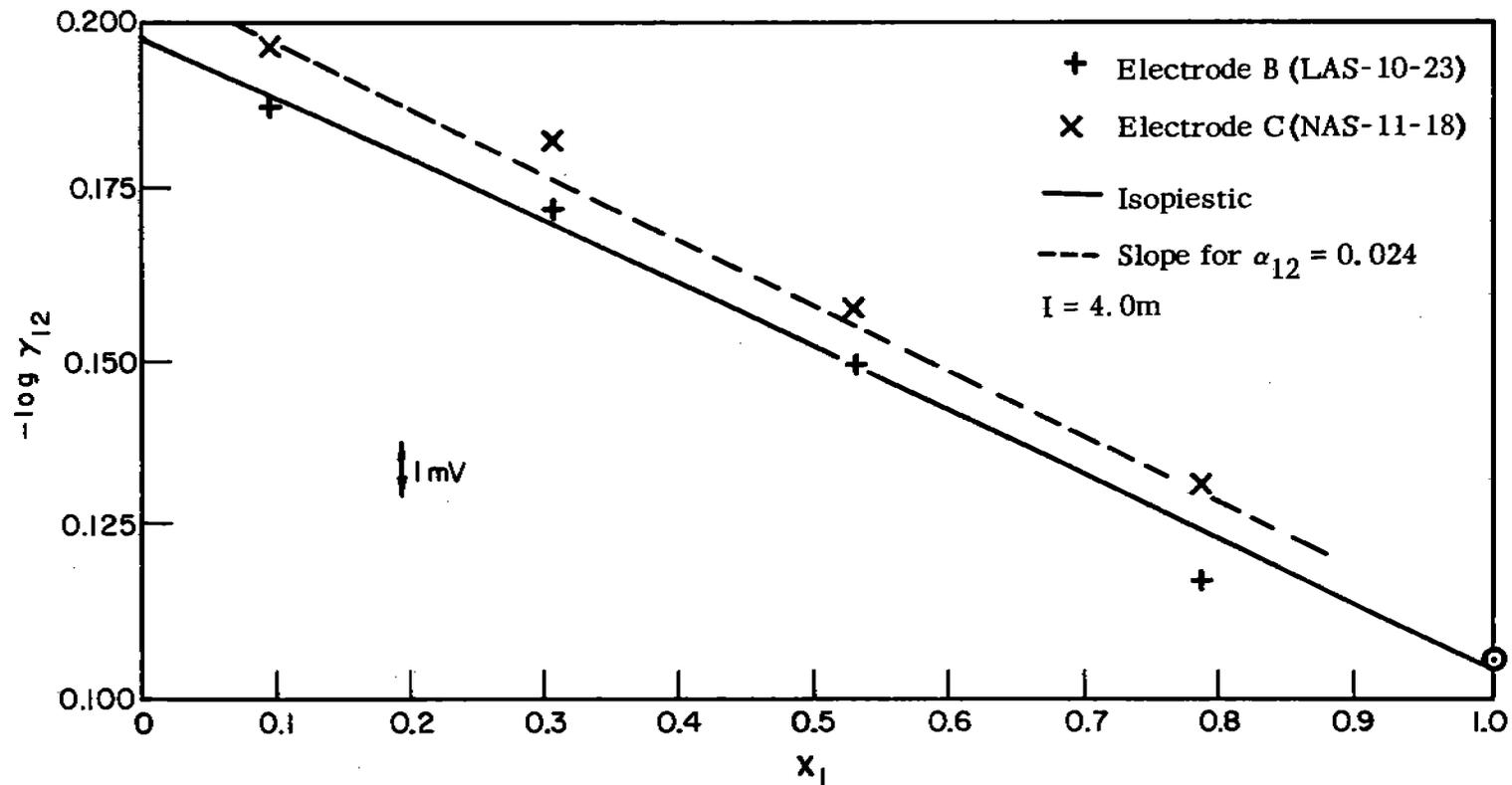


Fig. 23. Experimental activity coefficient data for NaCl in NaCl-KCl electrolytes at ionic strength 4.0m [the slope of the isopiestic line⁶ (which is not quite straight) corresponds approximately to a Harned rule coefficient $\alpha_{12} = 0.024$]

From the corrected values of γ_{12} , the Harned rule coefficient α_{12} was obtained for each data set in Table XV by the method of least squares, which also gave the 95% confidence limits for the coefficient. These values are listed in Table XVI.

In Table XVI, we also compare our results with the isopiestic data.⁵⁸ At most ionic strengths (0.5 to 3.0M), electrode B (LAS-10-23) shows substantial deviations from the isopiestic data, but the data obtained with electrode C (NAS-11-18) agree well within the confidence limits. At ionic strength 4.0, however, both types of electrode are in excellent agreement (Fig. 23) with the isopiestic data. The instability of the LAS-10-23 electrode has been noted by many workers.^{52, 60, 61}

An alternative way of looking at deviations from the isopiestic measurements is to calculate a selectivity ratio, K, defined by

$$E = E^\circ + \frac{RT}{F} \ln (m_{\text{Na}} \gamma_{12}^2 + K m_{\text{K}} \gamma_{21}^2) m_{\text{Cl}} \quad (68)$$

where γ_{21} is the mean activity coefficient of KCl in the mixed electrolyte. In these concentrated solutions, selectivity ratios must be calculated on the basis of multicomponent activity coefficients, or the deviations due to interionic attractions will completely obscure the actual selectivity effects.

Most of the selectivity ratio data published in the literature have been obtained by comparing the potential measured in 0.1M NaCl with that measured in 0.1M KCl (corresponding to $X_1 = 0$ in our measurements). For NAS-11-18 electrodes in dilute solutions at pH = 7, the selectivity ratio has been reported to be between 0.003^(52, 61) and 0.001.⁽⁵⁹⁾ For the LAS-10-23 electrodes, K has been reported to be as small as 10^{-5} , but depends strongly on glass composition.^{52, 61}

We have calculated values of selectivity ratio K from Eq. 68 using our potential measurements together with activity coefficient values based on isopiestic data. The empirical equations of Rush,⁶ fitted to the experimental isopiestic data of Robinson,^{57, 58} were evaluated to obtain γ_{12} and γ_{21} . The selectivity ratios obtained by solving Eq. 68 are listed in Table XV. Note that values of K obtained for $X_1 > 0.01$ are unreliable, since they tend to reflect small differences between the potential and isopiestic measurements.

Table XVI. Harned Rule Coefficients (α_{12}) for NaCl-KCl Electrolytes*

Ionic Strength	Electrode B (LAS-10-23)	Electrode C (NAS-11-18)	Isopiestic [†]
0.500	0.013 \pm 0.015	0.017 \pm 0.009	0.025 \pm 0.002
1.000	-0.003 \pm 0.014	0.013 \pm 0.011	0.023 \pm 0.001
3.000	0.018 \pm 0.002	0.023 \pm 0.002	0.022 \pm 0.001
4.000	0.024 \pm 0.002	0.025 \pm 0.001	0.024 \pm 0.001

* Errors are 95% confidence limits.

[†] Values from tables in reference 6, based on data from references 57 and 58, but neglecting quadratic terms in the expression for $\log \gamma_{12}$.

Our values of K (for $X_1 < 0.01$) obtained at high ionic strengths (1 and 3m) are of the order of 0.001, qualitatively confirming the low ionic strength results. However, since the exact glass compositions were not known, and only one sample of electrode C and two samples of electrode B were used, these measurements cannot be considered a definitive study of selectivity at high ionic strengths. Nevertheless, K seems to be somewhat smaller for electrode C than for electrode B, and this leads to the tentative conclusion that the NAS-11-18 glass is not only more stable than the LAS-10-23 glass at high ionic strengths, but is also more selective. The differences, however, are not large.

F. CaCl₂ and CaCl₂-NaCl Electrolytes

In previous reports,^{5,27} we gave the results of a number of measurements on NaCl-CaCl₂ electrolytes and on CaCl₂ alone, using a liquid ion exchange electrode selective for calcium (marketed commercially by Orion Research, Inc). We concluded that although thermodynamic reversibility with respect to Ca²⁺ was obtained if the chemical potential gradient across the membrane was not too large, the selectivity of the exchanger then available (Orion 92-20) for calcium over sodium was not adequate in concentrated solutions for proper thermodynamic measurements of activity coefficients in multicomponent mixtures.

Nevertheless, it would be desirable to have an independent check on α_{21} , which is presently obtainable only through isopiestic measurements or indirectly from potential measurements by using the Gibbs-Duhem relation with the osmotic coefficients. Recently, a more selective ion exchanger has been developed (Orion 98-20-02, formerly coded 130-18). We have made measurements using this exchanger in NaCl-CaCl₂ electrolytes and the results are listed in Table XVII. In Fig. 24, these data are compared with the line predicted from the isopiestic data ($\alpha_{21} = -0.0165$ at $I = 3.0m$) of Robinson and Bower.⁶² The curvature is substantial, and the deviations are outside the experimental precision, but are only a few millivolts. Thus, although this exchanger too is not sufficiently selective at high ionic strengths to be of use in accurate thermodynamic measurements, it gives a much more accurate estimation of calcium activity than the previous exchanger did.

We have also made some measurements with the new exchanger in solutions containing only CaCl₂. These are listed in Table XVIII. We have also summarized all the previous data obtained with the older ion exchanger which have never been reported in tabular form. From each of the points, an experimental value for the mean activity coefficient of CaCl₂ is obtained in the following way. In dilute solutions, the activity coefficient is calculated from an extended Debye-Hückel expression (Davies equation) for the most dilute solution measured, with the most dilute internal solution. Then, for the other data obtained with this same internal filling solution, activity

coefficients are given experimentally. The data obtained with a more concentrated filling solution are used, taking the activity coefficients from the previous set in the region of overlap. In this way, one can build up piecemeal a curve of mean activity coefficients from a number of different measurements, as is shown in Fig. 25.

One interesting observation is that with an internal filling solution of 0.1m CaCl_2 , the new ion exchanger gave excellent values for activity coefficients over the range from 0.01 to 5m, without having to use different internal solutions as we found was necessary with the 92-20 exchanger. Thus, not only is the new exchanger more selective for calcium over sodium, it is also more specific for calcium in CaCl_2 solutions of high ionic strength, and the liquid ion exchange membrane is Nernstian in its behavior, even when there are large chemical potential gradients between the internal and external solutions.

Table XVII. Activity Coefficients of CaCl_2 in NaCl-CaCl_2 Electrolytes*

Total Ionic Strength, I	Ionic Strength Fraction CaCl_2 , X_2	$E_{\text{ref}} - E_{\text{test}}$	$-\log \gamma_{\pm}^{\dagger}$
3.1827	1.0000	0	0.2924 [‡]
3.1686	0.7978	- 1.22	0.2721
		- 1.25	0.2718
		- 1.38	0.2703
		- 1.62	0.2676
3.1472	0.4885	- 0.20	0.2485
		- 0.22	0.2483
		- 0.25	0.2480
3.1315	0.2604	+ 2.85	0.2157
		2.90	0.2163
		2.95	0.2169
3.1274	0.2022	4.45	0.2029
		4.57	0.2043
		4.75	0.2063
		5.00	0.2091

* Measured using liquid ion exchanger 98-20-02 (formerly 130-18) with 0.1 M (Orion) internal solution.

[†]At the value of I given in column 1.

[‡]From the tables of Robinson and Stokes.¹²

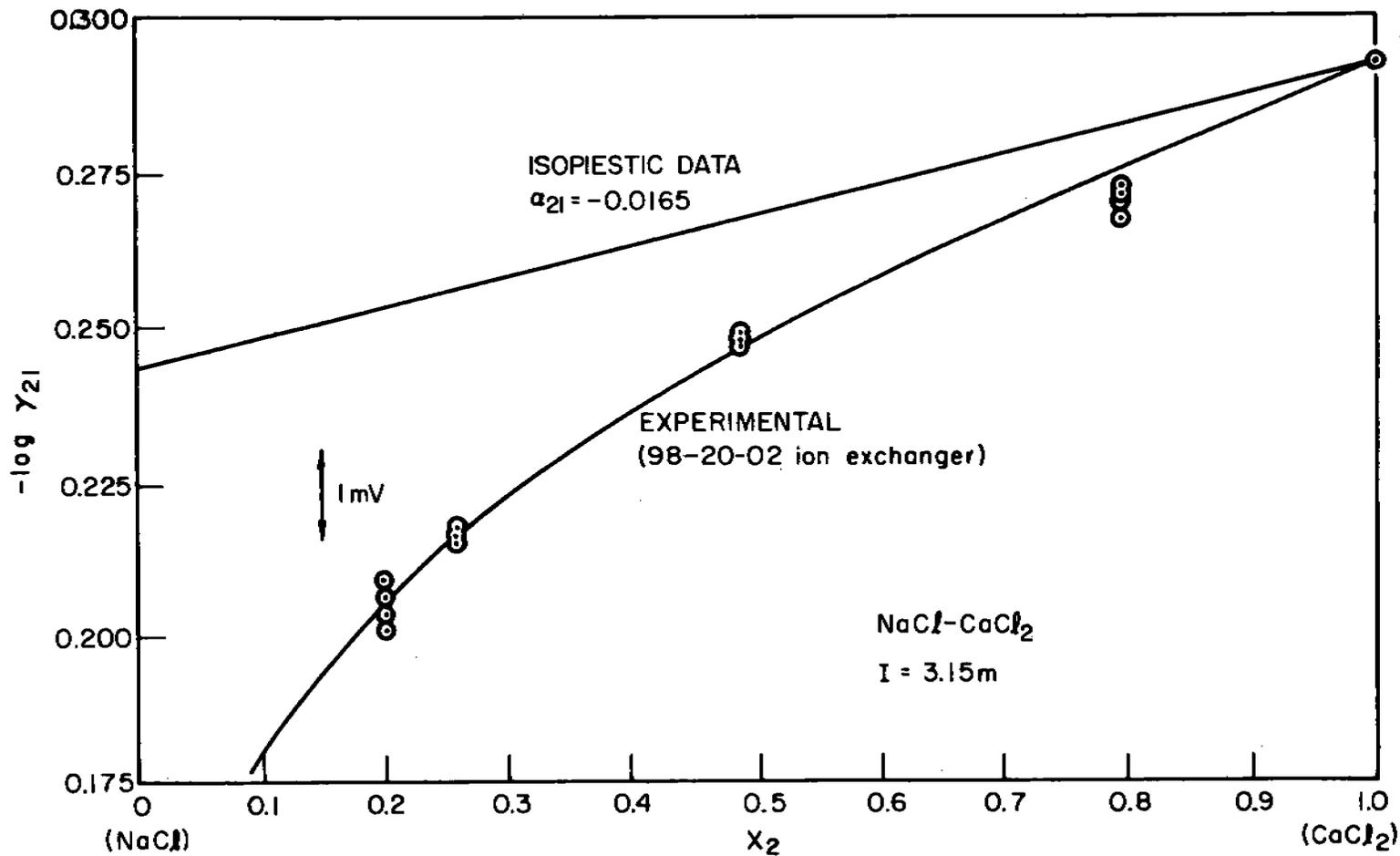


Fig. 24. Activity coefficient CaCl_2 in $\text{NaCl}-\text{CaCl}_2$ electrolytes at ionic strength 3.15m (note the systematic deviations at small values of X_2 due to the partial response of the ion exchanger to Na^+)

Table XVIII. CaCl₂ Activity Measurements Using Liquid Ion Exchange Electrodes

m_1	$\log m_1 \gamma_1^*$	ΔE_{exp}	$\gamma_{\text{exp}}^\dagger$
Internal solution: 0.1M CaCl ₂ (Orion filling solution)			
Exchanger: 98-20-02 (formerly 130-18)			
A = -1.2775			
0.0344	-1.664	-33.8 -35.7 -35.9	-0.195 -0.217 -0.219
0.2515	-0.935	32.0 32.05	-0.317 -0.317
1.061	-0.267	94.5 94.6	-0.238 -0.237
2.085	0.237	125.65 127.2 129.25	-0.180 -0.163 -0.139
3.225	0.747	176.9 177.3	0.208 0.213
6.065	1.836	257.0	0.837

Internal solution: ~0.1M CaCl₂ (Orion filling solution)
 Exchanger: 92-20 (didecylphosphate)
 A = -1.4481

0.0157	-1.959	-46.0	-0.163
0.1103	-1.248	18.0	-0.288
0.2219	-0.983	40.8	-0.334
0.3266	-0.820	53.0	-0.365
0.5068	-0.644	71.2	-0.350
0.8426	-0.397	91.8	-0.339
1.398	-0.088	121.6	-0.223

* Using isopiestic values for γ_{\pm} of CaCl₂ (Robinson and Stokes,¹² Appendix 8.10, Table 13).

† Calculated using the equation

$$\log \gamma_{\text{exp}} = A - \log m_1 + \frac{\Delta E_{\text{exp}}}{88.7}$$

with values of A as given above each portion of the table.

Table XVIII (Cont.)

m_1	$\log m_1 \gamma_1^*$	ΔE_{exp}	$\gamma_{\text{exp}}^\dagger$
1.547	-0.013	128.8	-0.186
1.889	0.147	141.5	-0.129
2.899	0.604	170.4	0.011
4.046	1.087	193.1	0.122
5.484	1.647	202.4	0.095

Internal solution: 0.3266m CaCl_2
 Exchanger: 92-20
 $A = -0.8333$

0.0157	-1.959	-97.7	-0.131
0.1103	-1.252	-37.6 -38.1	-0.299 -0.305
0.2219	-0.983	-12.0 -12.1	-0.315 -0.316
0.3266	-0.830	0.0	-0.347
0.5068	-0.646	18.6 18.8	-0.328 -0.326
0.8426	-0.398	36.6 38.6	-0.346 -0.324
1.398	-0.088	64.9	-0.247
1.547	-0.013	71.1	-0.221
1.889	0.147	87.5	-0.123
3.270	0.765	142.0	0.253
5.484	1.647	160	0.231

Internal solution: 0.8426m CaCl_2
 Exchanger: 92-20
 $A = -0.4027$

0.2219	-0.983	-49.4	-0.306
0.5068	-0.644	-21.0 -21.5 -21.8	-0.344 -0.350 -0.353

Table XVIII (Cont.)

m_1	$\log m_1 \gamma_1^*$	ΔE_{exp}	$\gamma_{\text{exp}}^\dagger$
0.8426	-0.397	0	-0.328
1.398	-0.088	28.4	-0.228
		28.6	-0.226
		29.4	-0.217
1.547	-0.013	35.1	-0.196
		35.5	-0.192

Internal solution: 1.015m CaCl_2
 Exchanger: 92-20
 $A = -0.2898$

0.0157	-1.959	-139.2	-0.055
0.1103	-1.248	-85.8	-0.300
0.3266	-0.820	-50.9	-0.378
		-51.1	-0.380
0.5068	-0.644	-32.8	-0.364
		-34.1	-0.379
1.015	-0.295	0.0	-0.296
1.547	-0.013	19.8	-0.256
		20.6	-0.247
1.889	0.147	38.1	-0.136
		38.7	-0.130
2.899	0.604	79.2	0.141
		84.2	0.197
3.29	0.765	97.1	0.285
		99.3	0.311
4.045	1.087	122	0.479

Internal solution: 2.899m CaCl_2
 Exchanger: 92-20
 $A = 0.5823$

1.889	0.148	-5.6	0.243
		-6.2	0.236
2.899	0.603	0.0	0.120

Table XVIII (Cont.)

m_1	$\log m_1 \gamma_1^*$	ΔE_{exp}	$\gamma_{\text{exp}}^\dagger$
3.266	0.764	14.9	0.236
4.046	1.086	47.8	0.514
5.484	1.045	77.8	0.720
		78.9	0.732

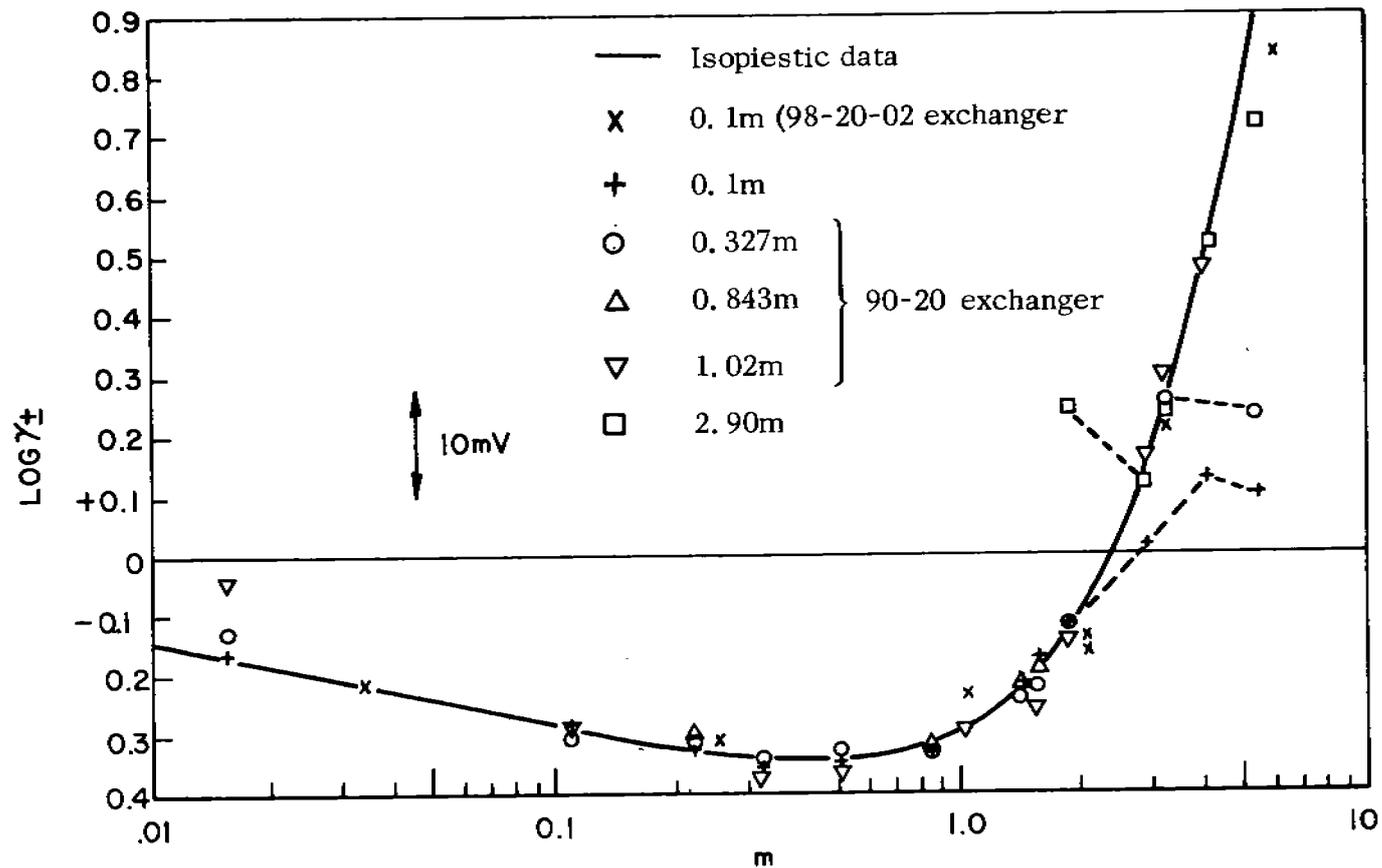


Fig. 25. Mean activity coefficients of CaCl_2 in aqueous solution obtained from liquid ion exchange electrode measurements (note that the 98-20-02 exchanger gives results agreeing with the isopiestic data over the entire range of concentrations without changing the internal solution; the 92-20 ion exchanger agrees only over a limited range of concentrations near the concentration of the internal solution)

IV. NOTES

In this part, we present information obtained in support of the primary goals of this program which is of sufficient scientific or technical interest to be permanently recorded. However, at this time we do not plan to publish this material in any other form.

A. Barium Amalgam Electrode Studies

The experiments described previously⁵ were continued. These were designed to obtain information about the kinetics of the barium amalgam electrode reaction by measuring potential-time curves at a dropping amalgam electrode where no external current flows. Under these conditions, the charging current from the expansion of the negatively charged drop drives the anodic dissolution reaction of the barium amalgam electrode.

The concentration of barium amalgam was varied in an attempt to verify whether the apparently strong dependence of the anodic transfer coefficient, β , on amalgam concentration was in fact true. These data, together with the data presented in the previous interim report,⁵ have been analyzed by the least squares method already described. A revised version of this computer program is given below, and the results are summarized in Table XIX. Values of the parameters β and i_0 are given both for the complete data set and for the set from which selected points of apparently high deviation had been discarded. The points discarded usually fell at the beginning of the set, and the deviations probably reflected the error in establishing the zero of the time scale. In general, discarding the points of high deviation resulted in a lower value for β and a larger value (less negative logarithm) for i_0 .

If the reaction were a simple electron transfer with rate determining step

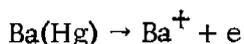


Table XIX. Transfer coefficients and Exchange Currents for Ba(Hg)
in BaCl₂ Solutions at 25 °C

Data Set	X_{Ba}	m_{BaCl_2}	$E_{\text{eq.}}$	All Points		Selected Points	
				β	$-\log i_o$	β	$-\log i_o$
1	7×10^{-5}	0.9642	-1.6459	$0.36 \pm .01$	$5.03 \pm .07$	$0.34 \pm .02$	$4.94 \pm .09$
3A	1.98×10^{-4}	0.06635	-1.6435	$0.29 \pm .01$	$3.75 \pm .03$	$0.26 \pm .01$	$3.71 \pm .02$
3B				$0.31 \pm .01$	$3.72 \pm .04$	$0.30 \pm .01$	$3.70 \pm .03$
2A	1.98×10^{-4}	0.3108	-1.6600	$0.42 \pm .02$	$3.76 \pm .05$	$0.40 \pm .01$	$3.70 \pm .02$
2B				$0.53 \pm .04$	$3.86 \pm .09$	$0.47 \pm .02$	$3.75 \pm .05$
11	7.17×10^{-4}	0.4589	-1.6559	$0.66 \pm .03$	$2.64 \pm .05$	$0.60 \pm .03$	$2.58 \pm .04$
12	1.70×10^{-3}	0.4589	-1.6670	$0.46 \pm .02$	$1.59 \pm .02$	$0.43 \pm .01$	$1.57 \pm .02$
13A	2.13×10^{-3}	0.4589	-1.6699	$0.80 \pm .07$	$1.89 \pm .06$	$0.60 \pm .04$	$1.64 \pm .04$
13B				$0.61 \pm .04$	$1.63 \pm .05$	$0.50 \pm .03$	$1.55 \pm .03$
13C				$0.67 \pm .02$	$2.13 \pm .07$	$0.55 \pm .01$	$1.99 \pm .02$
9A	2.86×10^{-3}	0.3108	-1.6779	$1.69 \pm .03$	$1.74 \pm .02$	$1.69 \pm .03$	$1.74 \pm .02$
9B				$3.4 \pm .3$	$2.03 \pm .05$	$3.1 \pm .3$	$1.99 \pm .05$
10A	2.86×10^{-3}	1.7053	-1.6556	$1.43 \pm .09$	$1.53 \pm .05$	$1.23 \pm .06$	$1.46 \pm .03$
10B				$1.59 \pm .08$	$1.65 \pm .05$	$1.27 \pm .03$	$1.55 \pm .01$

Note: Errors are standard deviations.

one would expect that β would be relatively independent of both amalgam and electrolyte concentration, and that the exchange current would be given by an equation of the approximate form

$$i_o = i_s (X_{Ba})^\alpha (m \gamma_{\pm})^\beta$$

where i_s , α , and β are constants, β has the same value as is obtained from the current-potential curves, $\alpha = 2 - \beta$, X_{Ba} is the mole fraction of barium in the amalgam, m is the molal concentration of $BaCl_2$ in the electrolyte, and γ_{\pm} is the mean activity coefficient of $BaCl_2$. Let us examine our data to see how well these relationships are obeyed.

The transfer coefficient β is plotted in Fig. 26 as a function of amalgam concentration. As can be seen by examining Table XIX, there is also some dependence on electrolyte concentration, but not in any consistent fashion. If we compare sets 2 and 3, we see that the higher electrolyte concentration gives the higher value of β ; but if we compare sets 9 and 10, we see just the reverse. For all amalgam concentrations except the highest, β is between 0.3 and 0.7, which is consistent with a one-electron rate determining step as we have written above. Although the uncertainty from experiment to experiment is rather large (more than ten times the standard deviation of an individual experiment), it seems clear that β is smaller at the smaller amalgam concentrations, and levels out at approximately 0.35 in very dilute amalgams.

The very large values of β obtained for the most concentrated amalgams (sets 9 and 10) are strongly dependent on which points are retained for the curve fitting procedure. In other words, these data do not fit the theoretical form of the equations well.

Consider next the dependence of exchange current on amalgam and electrolyte concentration. Fig. 27 shows the dependence on amalgam concentration. A line of slope 1.5 (corresponding to $\alpha = 2 - \beta$) has been drawn through the data, but it is clear that a higher slope would give a better fit. Nevertheless, the predicted relation has been approximately verified.

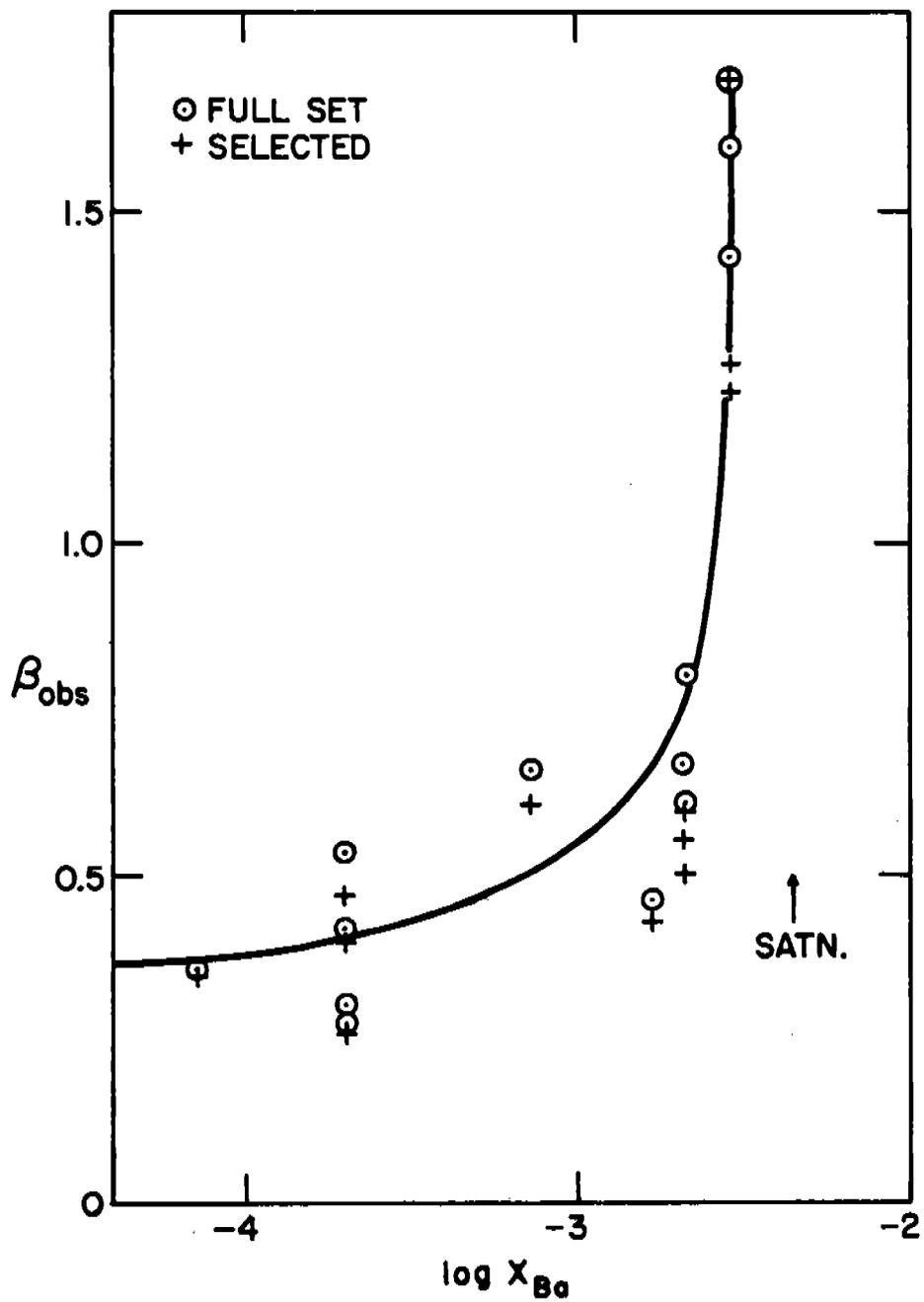


Fig. 26. Dependence of apparent transfer coefficient of barium amalgam concentration

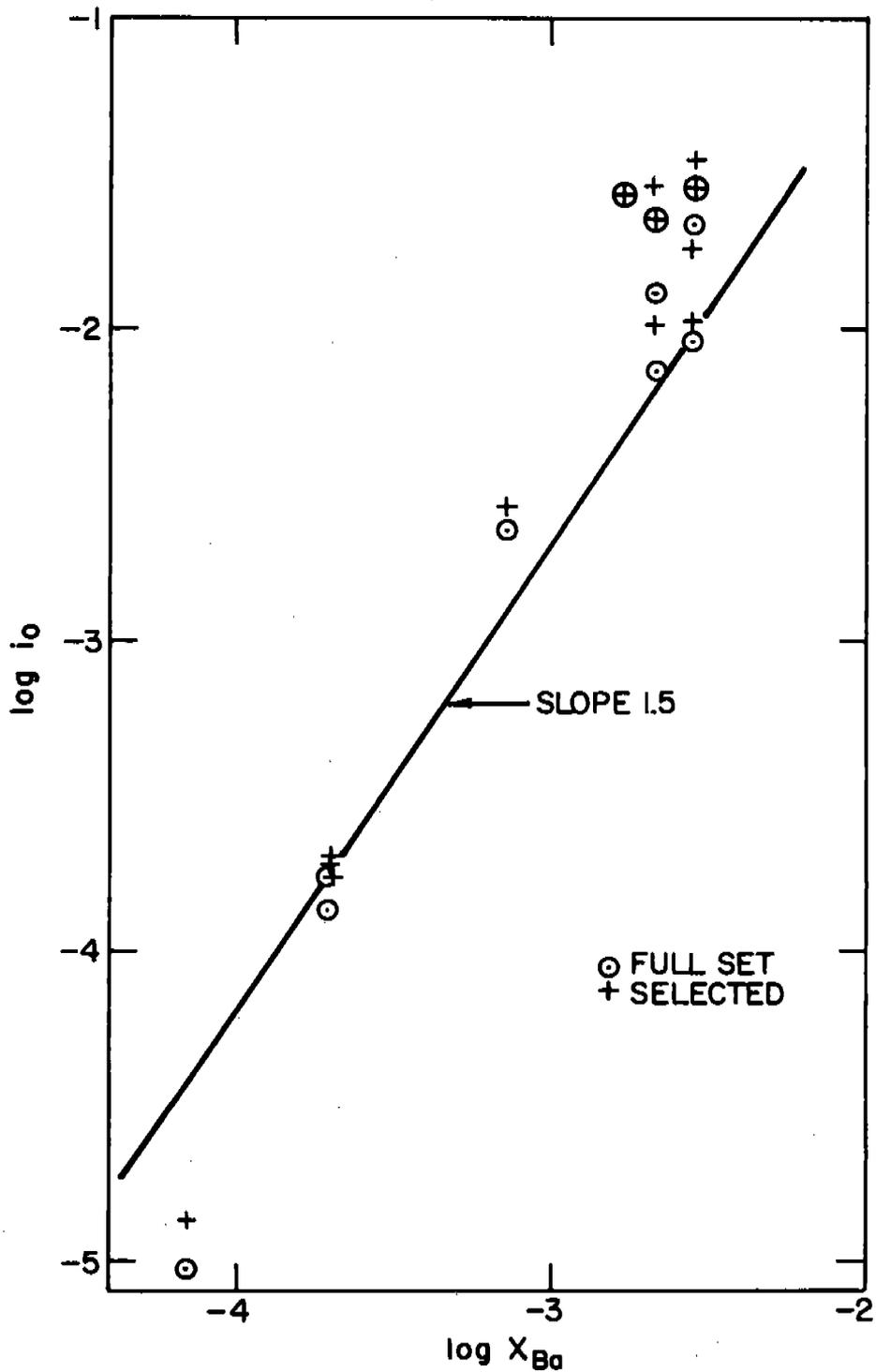


Fig. 27. Dependence of exchange current of barium amalgam concentration (the line has slope approximately $2 - \beta$, as predicted theoretically)

The dependence of electrolyte concentration is less well defined. Comparison of sets 2 and 3 shows no variation in exchange current with electrolyte concentration, but this may have been compensated for by the variation in β . Comparison of sets 9 and 10 shows a shift in i_0 in the predicted direction, and a rough calculation of the coefficient $d(\log i_0)/d(\log m \gamma_{\pm})$ for these two points gives a value of 0.33, in agreement with the value of β obtained from current-potential curves at low amalgam concentrations, but not in agreement with the apparent β obtained from sets 9 and 10. The explanation may lie in the failure of sets 9 and 10 to fit the theoretical equations, but a more detailed analysis has not yet been made.

B. Calcium Amalgam Electrode Studies

In addition to the experiments on barium amalgam electrodes, we have also made some preliminary experiments on calcium amalgam electrodes using the same technique. The results of these experiments are given in Fig. 28. All these current-time curves were taken using the same amalgam and electrolyte concentration and, as before, the letters A and B refer to curves on the same oscilloscope trace. From the plot of Fig. 28, it is clear that the data are far from self-consistent. Sets 8 and 9 agree fairly closely, but the two traces from set 5 disagree with each other, although the precision of each separate trace is excellent.

Full analysis of these data has not yet been made, but some preliminary results are given in Table XX. These computations have been made on the full data sets without discarding any points. If correction for hydrogen evolution is made using the same parameters as we used for the barium amalgam data, the hydrogen evolution current is many times greater than the net anodic current from the dissolution of calcium amalgam, and apparently this correction greatly overcompensates for the actual hydrogen evolution current. Note that in Table XX the results of computations including the hydrogen evolution correction give physically unrealistic parameters: negative transfer coefficients and extremely large values for i_0 . Thus, a more careful assessment of this source of error must be made.

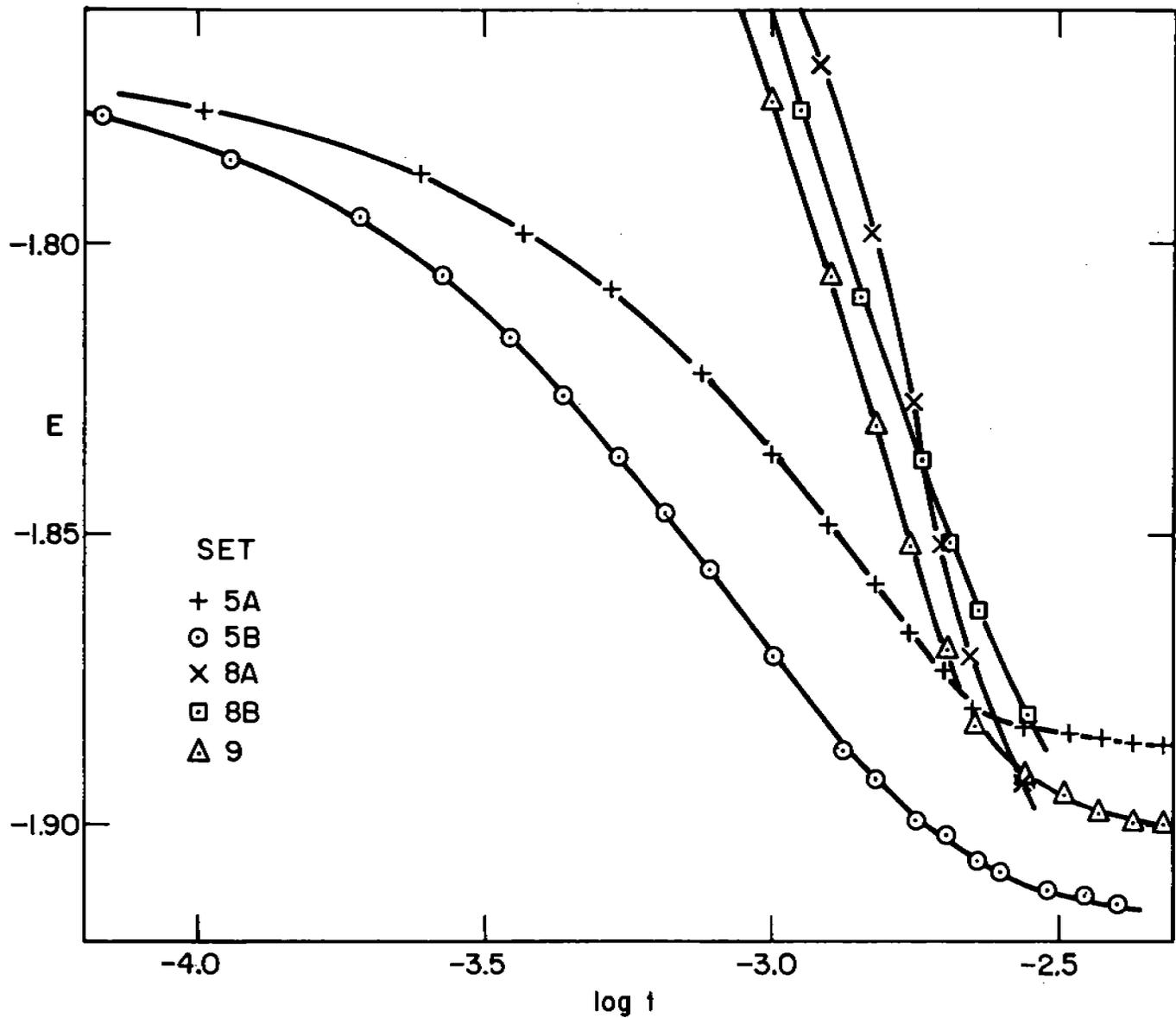


Fig. 28. Current-time curves for a dropping calcium amalgam electrode (see Table XIX)

Table XX. Kinetic Parameters for Ca(Hg) Electrode

Set No.	Including H ₂ Evolution		Neglecting H ₂ Evolution	
	β	$\log i_0$	β	$\log i_0$
5B	-0.47 ± 0.02	$+0.84 \pm 0.03$	$+0.57 \pm 0.02$	-2.22 ± 0.03
8A	-0.37 ± 0.04	$+0.61 \pm 0.11$	$+0.21 \pm 0.02$	-2.26 ± 0.07
8B	-0.37 ± 0.03	$+0.61 \pm 0.09$	$+0.25 \pm 0.01$	-2.31 ± 0.04

If hydrogen evolution is neglected entirely (an assumption which is also unlikely to be accurate), the computations give physically realistic values of β and $\log i_0$, with much the same internal consistency as the previous calculations.

An explanation both of the apparent irreproducibility of the measurements and the failure of the hydrogen evolution corrections to yield realistic parameters for the reaction kinetics can be found in the dissolution reaction of calcium amalgam itself. If there is hydrogen evolution occurring at much the same rates as on mercury, the dissolution of the drop as it forms will tend to raise the pH of the solution in the diffusion layer immediately adjacent to the amalgam drop, which in turn tends to suppress the contribution of hydrogen evolution to the charging current.

Depending on how long the amalgam has been in contact with the solution, this pH will attain different values, and thus the potential-time curves (reflecting the potential-current curve) will be different for different drops. Set 5, for example, apparently corresponds to a lower effective pH than set 8 or 9. This irreproducibility can be diminished in future experiments by adjusting the pH of the bulk of the solution to a value just below that at which Ca(OH)_2 is expected to precipitate ($\text{pH} \cong 11$).

Another possibility is that specific adsorption of Ca^{2+} in the electrical double layer may suppress the hydrogen evolution reaction. If this is so, then not only will corrections for hydrogen evolution be smaller than we would expect from data for mercury, but the capacitance of the double layer would be substantially larger, and would therefore change the constants used to calculate the charging current. One possible way of elucidating this effect is to make galvanostatic measurements of hydrogen evolution on mercury in the same electrolyte (1.0M CaCl_2). A more difficult experiment is to make impedance measurements at the amalgam electrode, but this would also yield kinetic data on the calcium amalgam couple.

C. Computer Programs

Throughout the research work described in this report, we have

made use of a time-shared computer system to carry out most of our calculations. The programs were written in CAL, a powerful and compact conversational algebraic language developed for the SDS-940 computer system, and operated by Dial-Data, Inc., Newton, Massachusetts.

Many of the programs we have used simply involved evaluation of a few algebraic expressions and were discarded after they were used. Others involved a more complicated mathematical analysis, sometimes using iterative procedures or logical decisions, and we have collected these programs here for future reference by workers in the field. Before each program, a brief description is given of the calculations carried out, and the variable names used are defined. In most cases, the required input data are easily recognized by the READ or DEMAND statements, and the program is started by asking the computer to do the first part number listed. Exceptions are noted. The programs are arranged in approximately the same order as the outline of this report, and references to sections of the report or published papers are made where appropriate.

PROGRAM/R3/

In this program, we have combined a number of the simpler calculations used in evaluating our experimental data. There are really four separate programs. Parts 10 and 20 take the raw experimental data and calculate the uncorrected values of activity coefficients, γ_{12} . Part 30 uses a value of the Harned rule coefficient, γ_{12} , given by the operator to calculate a set of theoretical activity coefficients and potential differences corresponding to the same experiments. Part 40 calculates values of γ_{21} from given values of γ_{21} and γ_{20} . Part 60 corrects the observed values of γ_{12} to round values of ionic strength.

Variable names used in the program are defined as follows:

RUN	Experiment number or name
"4C"	A typical data file name; this could be "RUN" also
N	Number of points in set
G	Activity coefficient (γ_{10}) of NaCl in reference solution
DR	Weight of NaCl per gram of H ₂ O in NaCl stock solution
DT	Weight of component 2 (KCl, NaF, NaHCO ₃) per gram of H ₂ O in stock solution of component 2
NR	Concentration of Na ⁺ in reference solution
CR	Concentration of Cl ⁻ in reference solution
KT	Concentration of cation in stock solution of component 2
CT	Concentration of anion in stock solution of component 2
I	Running index varying from 1 to N
X(I)	Weight of stock solution of NaCl taken in making up test solution
Y(I)	Weight of stock solution of component 2 taken in making up test solution
E(I)	Potential difference (reference minus test) between the AgCl electrodes in the double cell; E(I) is positive
FNA(I)	Ionic strength fraction of NaCl (X_1 in text of Section III)
LGO(I)	Log γ_{12} (experimental)
A(I)	Intermediate value defined by step 20. 2

IO(I)	Total ionic strength of test solution
ALP	Harned rule coefficient, α_{12}
LGI(I)	Calculated value of $\log \gamma_{12}$
GI(I)	Calculated value of γ_{12}
ALK	Harned rule coefficient, α_{21}
GK	Activity coefficient (γ_{20}) of pure second component at ionic strength IO(I)
LG2(I)	Calculated value of $\log \gamma_{21}$
D(I)	Calculated potential difference corresponding to the experimental difference E(I)
FK(I)	Ionic strength fraction of second component (i. e. , λ)
K(I)	Selectivity ratio, defined by step 40.30
IS	Round value of ionic strength
SLP	Slope of $\log \gamma_{10}$ curve: $\partial \log \gamma_{10} / \partial (IS)$
X2(I)	FK(I)
LGC(I)	Corrected value of $\log \gamma_{12}$ to round value of ionic strength (IS)

Listing of Program /R3/, August 1969

10.04 DEMAND RUN

10.05 OPEN "4C" FOR INPUT AS FILE 1

10.1 READ FROM 1: N, G, DR, DT, NR, CR, KT, CT

10.2 READ FROM 1: X(I), Y(I) FOR I=1 TO N

10.3 READ FROM 1: E(I) FOR I=1 TO N

10.35 CLOSE 1

10.4 TYPE

FNA(I) E(I) LGO(I) A(I) IO(I) I

10.5 DO PART 20 FOR I=1 TO N

10.6 PAGE

20.1 $XN(I)=X(I)/DR$, $YK(I)=Y(I)/DT$, $S(I)=XN(I)+YK(I)$, $FNA(I)=XN(I)/S(I)$,
 $FK(I)=YK(I)/S(I)$, $NAR(I)=FNA(I)*NR$, $CLR(I)=FNA(I)*CR$, $CLT(I)=FK(I)*CT$,
 $T(I)=CLR(I)+CLT(I)$, $NT(I)=NAR(I)$

20.2 $A(I)=59.15*LOG_{10}(((NR*CR)*G^2)/(NT(I)*T(I)))$, $LGO(I)=(E(I)-A(I))$
 $/118.3$, $IO(I)=(((FK(I)*KT)^2)+(FNA(I)*NR)+(FNA(I)*CR))/2$

20.3 TYPE IN FORM 3: FNA(I), E(I), LGO(I), A(I), IO(I), I

30.1 DEMAND ALP

30.2 $LG1(I)=LOG_{10}(G)-(ALP*FK(I)*IO(I))$, $G1(I)=10^{LG1(I)}$, $DE(I)=((NR*CR$
 $)*G^2)/((NT(I)*T(I))*((G1(I))^2))$, $D(I)=59.15*LOG_{10}(DE(I))$ FOR I=1 TO N

30.3 TYPE

LG1(I) FNA(I) G1(I) IO(I) DE(I) D(I) I

30.4 TYPE IN FORM 4: LG1(I), FNA(I), G1(I), IO(I), DE(I), D(I), I
 FOR I=1 TO N

30.5 PAGE

40.10 DEMAND ALK, GK

40.20 $LG2(I)=LOG_{10}(GK)-(ALK*FNA(I)*IO(I))$, $G2(I)=10^{LG2(I)}$, $C1(I)=$
 $10^{(E(I)/59.15)}$ FOR I=1 TO N

40.30 $ANA=(NR*CR*(G^2))$, $ANT(I)=C1(I)*(NAR(I)*T(I))*((G1(I))^2)$, $AKT(I)=$
 $C1(I)*(CLT(I)*T(I))*((G2(I))^2)$, $K(I)=(ANA-ANT(I))/(AKT(I))$ FOR I=1 TO N

40.40 TYPE

IO(I) FK(I) LG1(I) LG2(I) E(I) D(I) K(I) I

40.45 TYPE IN FORM 45: IO(I), FK(I), LG1(I), LG2(I), E(I), D(I),
 K(I), I, FOR I=1 TO N

40.50 TYPE $LOG_{10}(GK)$

40.55 TYPE $LOG_{10}(G)$

40.57 PAGE

60.0 DEMAND N, SLP, ALP, IS
 60.1 DEMAND X2(I), LGO(I), IO(I) FOR I = 1 TO N
 60.2 TYPE
 X2 IONIC STRENGTH LOG G EXP LOG G CORR I
 60.25 DO PART 61 FOR I = 1 TO N

61.0 LGC(I) = LGO(I)-SLP*(IO(I)-IS)-ALP*(X2(I)*(IO(I)-IS))
 61.1 TYPE IN FORM 5: X2(I), IO(I), LGO(I), LGC(I), I

FORM 3:

 ZZ.ZZZZ ZZZ.ZZZ ZZ.ZZZZ ZZZ.ZZZZ ZZ.ZZZZ ZZ

FORM 4:

 ZZ.ZZZZ ZZ.ZZZZ ZZ.ZZZZ ZZ.ZZZZ ZZZ.ZZZZ ZZZ.ZZZZ ZZ

FORM 45:

 ZZ.ZZZZ ZZ.ZZZZ ZZ.ZZZZ ZZ.ZZZZ ZZZ.ZZZZ ZZZ.ZZZZ ZZ.ZZZZ ZZ

FORM 5:

 ZZ.ZZZZ ZZ.ZZZZ ZZ.ZZZZ ZZ.ZZZZ ZZ

PROGRAM/NACKLCL/

This program is of interest primarily because it contains a subroutine to evaluate the activity coefficients, γ_{12} and γ_{21} , in NaCl-KCl electrolytes from the empirical relations derived by Rush.⁶ Part 10 sets all the constants required for this evaluation, and parts 11, 12, and 13 evaluate Rush's equations. We made use of these results in calculating selectivity ratios from our data. Parts 1 to 3 calculate deviations of the theoretical from observed ΔE values. Parts 4 and 5 calculate selectivity ratios for each point. Variable names used in the program are defined as follows:

"NAK"	Data file to be processed; the first number is N, followed by groups of three numbers (IS, FNA, DE); program recognizes the beginning of a set by the fact that DE = 0
N	Number of points in data file, including all sets
SDE	Sum of squared deviations (see step 2.41)
SD	Standard deviation of the mean (see step 1.5)
IS	Total ionic strength
FNA	Ionic strength fraction NaCl (X_1)
DE	ΔE , observed experimental difference in potentials between reference and test solutions (positive)
G10	γ_{10} , activity coefficient (calculated) of NaCl in reference solution
G12	γ_{12} , activity coefficient (calculated) of NaCl in test solution
G21	γ_{21} , activity coefficient (calculated) of KCl in test solution
DEC	Calculated value of ΔE
L10	$\log \gamma_{10}$
L12	$\log \gamma_{12}$
KSL	Selectivity ratio

Listing of Program/NACKLCL/, May 1969

```
1.05 DO PART 10
1.1 OPEN 'NAK' FOR INPUT AS FILE 1
1.15 READ FROM 1:N
1.23 SDE = 0
1.3 DO PART 2 FOR I = 1 TO N
1.4 CLOSE 1
1.5 SD = SQRT(SDE/(N*(N-1)))
1.51 TYPE SDE, SD

2.1 READ FROM 1: IS, FNA, DE
2.2 DO PART 3 IF DE = 0
2.25 Y(1) = FNA
2.26 DO PART 11
2.31 DEA = 118.3*LOG10(IS0*G10)
2.32 DEB = 59.15*LOG10(FNA*G12^2+KSL*(1-FNA)*G21^2)
2.33 DEC = DEA - DEB -118.3*LOG10(IS)
2.35 L10 = LOG10(G10), L12 = LOG10(G12)
2.4 DDE = DEC-DE
2.41 SDE = SDE+ DDE^2
2.5 TYPE IN FORM 2: IS, FNA, G10,G12,G21, DE,DEC,DDE, L10,L12

3.1 IS0 = IS
3.21 Y (1) =1
3.22 DO PART 11
3.3 G10 = G12

4.01 READ FROM 1: IS, FNA, DE
4.02 DO PART 3 IF DE =0
4.03 Y(1) = FNA
4.04 DO PART 11
4.11 QA = (IS0*G10/IS)^2
4.12 QB = 10^-(DE/59.15)
4.13 QC = FNA*G12^2
4.14 QD = (1-FNA)*G21^2
4.15 L12 = LOG10(G12)
4.21 KSL=0 IF FNA = 1
4.22 TO STEP 4.3 IF FNA = 1
4.23 KSL = (QA*QB-QC)/QD
4.3 TYPE IN FORM 3: IS, FNA, DE, L12, KSL

5.01 DO PART 10
5.1 TYPE
    IS      FNA      DE      L12      KSL"
```

```

5.11 LINE
5.2 OPEN "NAK" FOR INPUT AS FILE 1
5.25 READ FROM 1: N
5.3 DO PART 4 FOR I = 1 TO N
5.4 CLOSE 1

```

```

10.01 S = -1.17082, AP = 1.5, A = 1, B = 2
10.02 LB1 = -0.0253, LB2 = -0.00299
10.03 A(1,1) = .03684, A(1,2) = -.06408
10.04 A(2,1) = .02108, A(2,2) = .05244
10.05 A(3,1) = -0.001304, A(3,2) = -0.01124
10.06 A(4,1) = 0, A(4,2) = 0.000918

```

```

11.01 BET = (LB1 + LB2*IS)*IS
11.02 BB = (LB1 + LB2*IS/2)*IS
11.03 SQI = AP*SQRT(IS)
11.11 DO PART 12 FOR J = 1,2
11.22 Y(2) = 1 - Y(1)
11.31 J = A, K = B
11.32 DO PART 13
11.33 J =B, K = A
11.34 DO PART 13
11.41 G12 = EXP(LG(A)), G21 = EXP(LG(B))

```

```

12.01 AAA = 2*S*SQRT(IS)/(1+SQI) + 2*A(1,J)*IS + 1.5*A(2,J)*IS*IS
12.02 AAB = 4*A(3,J)*IS^3/3 + 1.25*A(4,J)*IS^4
12.03 AA(J) = AAA + AAB
12.11 ALA = 2*S/(AP^3*IS)
12.12 ALB = 1 + SQI - 1/(1+SQI) -2*LOG(1+SQI)
12.13 ALC = A(1,J)*IS + A(2,J)*IS^2 + A(3,J)*IS^3 + A(4,J)*IS^4
12.14 AL(J) = ALA*ALB + ALC

```

```

13.1 LG(J) = .5*(AA(J)+(AL(K)-AL(J))*Y(K)+BET*Y(K)+(BB-BET)*Y(K)^2)

```

```

FORM 1:
  IS          FNA          G10          G12          G21          DE          DEC          DDE          L10          L12
FORM 2:
  ??.?????  ??.?????  ?.???  ?.???  ?.???  ????.?  ????.?  ????.?  ?.?????  ?.?????
FORM 3:
  ??.?????  ?.?????  ????.?  ?.?????  ?.?????

```

PROGRAMS /PYT/ AND /PYT2/

These programs carry out the ion pairing calculations by the Pytkowicz method⁴⁵ described in detail in Section III. C of this report. The program /PYT/ applies to the system NaCl-Na₂CO₃ (or any other 1:2 salt, such as Na₂SO₄). The program /PYT2/ is identical, except for modifications in the equations necessary to apply to the system NaCl-NaHCO₃ (or any other 1:1 salt). In each program, part 3 calculates the ion pairing constant K* (K₁' or K₁'' in Section III. C) from a value of the Harned rule coefficient, α_{12} . Part 4 does the reverse calculation. Part 10 is a subroutine to calculate a value of γ_{10} , and part 11 is a subroutine to solve the quadratic equation which occurs in the calculations of part 4. Variable names used in the program are defined as follows:

A12	α_{12}
I	Ionic strength calculated on a formal basis
IPR	I' (ionic strength) calculated from equilibrium concentrations
M1	m_1 , concentration of NaCl
G1P	γ_1' , calculated activity coefficient of Na ⁺
L1P	$\log \gamma_1'$
M2	m_2 concentration of Na ₂ CO ₃ or NaHCO ₃
L12	$\log \gamma_{12}$
G12	γ_{12}
IPP	Stored value of IPR, which changes
NA	[Na ⁺], concentration of free sodium ion
NAC	[NaCO ₃ -] in /PYT/, [NaHCO ₃] in /PYT2/; concentration of the ion pair
CO3	[CO ₃ ²⁻], concentration of free carbonate
HCO3	[HCO ₃ ⁻], concentration of free bicarbonate ion
KS	K ₁ ' (/PYT/) or K ₁ '' (/PYT2/), ion association equilibrium constant

Listing of Program /PYT/, June 1969

```
3.10 TYPE "PYTKOWICZ METHOD, K* FROM ALPHA-12"  
3.11 DEMAND A12, I  
3.12 INDEX = 1, IPR = I  
3.13 LINE  
3.14 DEMAND M1  
3.15 M = I  
3.16 DO PART 10  
3.17 GIP = G10, LIP = L10  
3.21 M2 = (I-M1)/3  
3.22 L12 = L10 - A12*3*M2  
3.23 G12 = 10^L12  
3.24 TYPE IN FORM 31: M2, L12, G12, L10  
3.25 TYPE IN FORM 32:  
3.30 IPP = IPR  
3.31 NA = (M1+2*M2)*(G12/GIP)^2  
3.32 NAC = (M1 + 2* M2) - NA  
3.33 C03 = NA - M1 - M2  
3.34 IPR = M1 + M2 + 2*C03  
3.35 KS = NAC/(NA*C03)  
3.36 TO STEP 3.50 IF ABS(IPR-IPP) < 10^-4  
3.39 DO STEP 3.50  
3.40 M = IPR  
3.41 DO PART 10  
3.42 GIP = G10, LIP = L10  
3.44 TO STEP 3.30  
3.50 TYPE IN FORM 33: NA, NAC, C03, IPR, KS, LIP  
3.51 LINE  
3.52 M1 = M1 + .1*I  
3.53 TYPE M1  
3.54 TO STEP 3.15  
3.55 DONE IF M1>I  
  
4.10 TYPE "PYTKOWICZ METHOD, ALPHA-12 FROM K*"  
4.11 DEMAND KS, I  
4.12 LINE  
4.20 DEMAND M1  
4.21 M2 = (I - M1)/3  
4.215 TYPE M2  
4.22 DO PART 11  
4.23 C03 = X, NA = M1+M2+C03, NAC = M2-C03, IPR = M1+M2+2*C03  
4.24 TYPE IN FORM 42:  
4.30 M = IPR, INDEX = 1  
4.31 DO PART 10  
4.32 GIP = G10, LIP = L10  
4.33 L12 = L10 + .5*LOG10(NA/(M1+2*M2))
```

```

4.40 M = I
4.41 DO PART 10
4.42 DLG = L10 - L12
4.43 A12 = DLG/(3*M2)
4.44 TYPE IN FORM 44: IPR
4.50 TYPE IN FORM 45: NA, NAC, C03, DLG, A12, L12, L10, LIP
4.52 TYPE "ASSUMING I = I"
4.53 DLG = .5*LOG10(1+KS*C03)
4.54 A12 = DLG/(3*M2)
4.55 L12 = L10-DLG, LIP = L10
4.56 TYPE IN FORM 45: NA, NAC, C03, DLG, A12, L12, L10, LIP
4.57 LINE
4.58 MI = M1 + .1*I
4.59 TYPE M1
4.60 TO STEP 4.21 IF M1<I
4.61 TO STEP 4.20

```

```

10.1 S=-1.17082, SQM = SQRT(M)
10.2 LNG = S*SQM/(1+1.5*SQM)+.03684*M+.01581*M^2-.0008695*M^3
10.3 GI0 = EXP(LNG)
10.4 L10 = LNG/2.30258
10.45 DONE IF INDEX = 1
10.5 TYPE IN FORM 10: M , GI0, L10

```

```

11.10 B = 1 + KS*(M1+M2)
11.11 DIS = 4*M2*KS/B^2
11.20 X = .5*(-B+SQRT(B*B + 4*M2*KS))/KS
11.21 TYPE X
11.22 TO STEP 11.99 IF DIS >.01
11.50 X0 = M2, CNT = 0
11.51 TYPE "ITERATE"
11.60 X1 = (M2- KS*X0*X0)/B
11.61 TO STEP 11.70 IF ABS(X1-X0) < 10^-5*X0
11.62 X0 = X1, CNT = CNT+1
11.63 TO STEP 11.60 IF CNT<100
11.70 X = X1
11.71 TYPE X, CNT
11.99 DONE

```

```

FORM 10:
M1= ZZ.ZZZZ , GI0 = ZZ.ZZZZ, L10 = ZZ.ZZZZ
FORM 31:
M2= ZZ.ZZZZZ, L12= ZZ.ZZZZZ, GI2= ZZ.ZZZZZZ , L10 = ZZ.ZZZZZ
FORM 32:
[NA+] [NAC03-] [C03=] I-PRIME' K* LOG(GI-PRIME)
FORM 33:
ZZ.ZZZZZ ZZ.ZZZZZ ZZ.ZZZZZ ZZ.ZZZZZ ZZZZZ.ZZZZZ ZZ.ZZZZZ
FORM 42:
[NA+] [NAC03] [C03] DLG A12 L12 L10 LIP
FORM 44:
CALCULATED I = ZZ.ZZZZZ
FORM 45:
ZZ.ZZZZZ ZZ.ZZZZZ ZZ.ZZZZZ ZZ.ZZZZZ ZZ.ZZZZZ ZZ.ZZZZZ ZZ.ZZZZZ ZZ.ZZZZZ

```

Listing of Program /PYT2/, August 1969

```
3.10 TYPE "PYTKOWICZ METHOD, K* FROM ALPHA-12"  
3.11 DEMAND A12, I  
3.12 INDEX = 1, IPR = I  
3.13 LINE  
3.14 DEMAND M1  
3.15 M = I  
3.16 DO PART 10  
3.17 GIP = G10, LIP = L10  
3.21 M2=I-M1  
3.22 L12=L10-A12*M2  
3.23 G12 = 10^L12  
3.24 TYPE IN FORM 31: M2, L12, G12, L10  
3.25 TYPE IN FORM 32:  
3.30 IPP = IPR  
3.31 NA=(M1+M2)*(G12/GIP)^2  
3.32 NAC=(M1+M2)-NA  
3.33 HCO3=NA-M1  
3.34 IPR=M1+(M2+HCO3)/2  
3.35 KS = NAC/(NA*HCO3)  
3.36 TO STEP 3.50 IF ABS(IPR-IPP) < 10^-4  
3.39 DO STEP 3.50  
3.40 M = IPR  
3.41 DO PART 10  
3.42 GIP = G10, LIP = L10  
3.44 TO STEP 3.30  
3.50 TYPE IN FORM 33: NA, NAC, HCO3, IPR, KS, LIP  
3.51 LINE  
3.52 M1 = M1 + .1*I  
3.53 TYPE M1  
3.54 TO STEP 3.15  
3.55 DONE IF M1>I  
  
4.10 TYPE "PYTKOWICZ METHOD, ALPHA-12 FROM K*"  
4.11 DEMAND KS, I  
4.12 LINE  
4.20 DEMAND M1  
4.21 M2=I-M1  
4.215 TYPE M2  
4.22 DO PART 11  
4.23 HCO3=X, NA=M1+HCO3, NAC=M2-HCO3, IPR=M1+HCO3  
4.24 TYPE IN FORM 42:  
4.30 M = IPR, INDEX = 1  
4.31 DO PART 10  
4.32 GIP = G10, LIP = L10  
4.33 L12=L10+.5*LOG10(NA/(M1+M2))
```

```

4.40 M = I
4.41 DO PART 10
4.42 DLG = L10 - L12
4.43 A12=DLG/M2
4.44 TYPE IN FORM 44: IPR
4.50 TYPE IN FORM 45: NA, NAC, HCO3, DLG, A12, L12, L10, LIP
4.52 TYPE "ASSUMING I' = I
4.53 DLG = .5*LOG10(1+KS*HCO3)
4.54 A12=DLG/M2
4.55 L12 = L10-DLG, LIP = L10
4.56 TYPE IN FORM 45: NA, NAC, HCO3, DLG, A12, L12, L10, LIP
4.57 LINE
4.58 M1 = M1 + .1*I
4.59 TYPE M1
4.60 TO STEP 4.21 IF M1<I
4.61 TO STEP 4.20

```

```

10.1 S=-1.17082, SQM = SQRT(M)
10.2 LNG = S*SQM/(1+1.5*SQM)+.03684*M+.01581*M^2-.0008695*M^3
10.3 G10 = EXP(LNG)
10.4 L10 = LNG/2.30258
10.45 DONE IF INDEX = 1
10.5 TYPE IN FORM 10: M , G10, L10

```

```

11.10 B=1+KS*M1
11.11 DIS = 4*M2*KS/B^2
11.20 X = .5*(-B+SQRT(B*B + 4*M2*KS))/KS
11.21 TYPE X
11.22 TO STEP 11.99 IF DIS >.01
11.50 X0 = M2, CNT = 0
11.51 TYPE "ITERATE"
11.60 X1 = (M2- KS*X0*X0)/B
11.61 TO STEP 11.70 IF ABS(X1-X0) < 10^-5*X0
11.62 X0 = X1, CNT = CNT+1
11.63 TO STEP 11.60 IF CNT<100
11.70 X = X1
11.71 TYPE X, CNT
11.99 DONE

```

```

FORM 10:
M1= ZZ.ZZZZ , G10 = ZZ.ZZZZ, L10 = ZZ.ZZZZ
FORM 31:
M2= ZZ.ZZZZZ, L12= ZZ.ZZZZZ, G12= ZZ.ZZZZZZ , L10 = ZZ.ZZZZZ
FORM 32:
[NA+] [NAHCO3-] [HCO3-] I-PRIME K* LOG(GI-PRIME
FORM 33:
ZZ.ZZZZZ ZZ.ZZZZZ ZZ.ZZZZZ ZZ.ZZZZZ ZZZZZ.ZZZZZ ZZ.ZZZZ
FORM 42:
[NA+] [NAHCO3] [HCO3] DLG A12 L12 L10 LIP
FORM 44:
CALCULATED I' = ZZ.ZZZZZ
FORM 45:
ZZ.ZZZZZ ZZ.ZZZZZ ZZ.ZZZZZ ZZ.ZZZZZ ZZ.ZZZZZ ZZ.ZZZZZ ZZ.ZZZZZ ZZ.ZZZZZ

```

PROGRAM /BAHG/

This program gives the final version of the calculations used in evaluating our kinetic data on the Ba and Ca amalgam electrodes. Most of the details of these calculations were discussed in the previous Interim Report on this contract.⁵ The program begins by asking the computer to "DO PART 50." Part 60 is a subroutine for printing out the date and time of calculation. Part 96 is a subroutine to do a least squares fit to a straight line. This part is also used in many of our other calculations, particularly in evaluating the confidence limits of the Harned rule coefficients obtained from our activity coefficient measurements. Part 98 is a subroutine called by part 96. Part 99 is a subroutine called by the main part of the program, part 101.

Part 101 takes data as read from the oscilloscope photographs and converts it into a table of potential as a function of time; it then calculates the contributions from double layer charging (PP1), hydrogen evolution (PP2), and the back reaction (PP3). These quantities are defined by equations in part 99. The theoretical equation is then fit by a least squares straight line, and the best values of transfer coefficient, β (BET), and exchange current, i_0 (IQ), are obtained together with their confidence limits. The limits DBT and DLI are mean square errors and are multiplied by the Student "t" factor (approximately 2.0) to obtain 95% confidence limits. Because this factor varies with the size of the data set, it is not included in the program.

The program also makes provision for discarding points using subroutines given as parts 591, 592, 593, and 594. Part 502 is an emergency dump routine which saves all intermediate values if the calculation must be interrupted. Variable names used in the program are defined as follows:

FF	Name of data file or experiment
"1-9"	Typical data file name
EEQ	Equilibrium potential (versus NHE) of the amalgam used; see reference 5 for values
N	Number of points in the data set

H(I)	Voltage reading on oscilloscope trace (cm)
G(I)	Time reading on oscilloscope trace (cm)
MBA	Concentration of BaCl ₂ solution used
GBA	Mean activity coefficient of BaCl ₂ solution used
BAS	Baseline potential of the oscilloscope trace
C7	Time calibration factor
C8	Voltage calibration factor
C6	Standard potential of the Ag/AgCl electrode (versus NHE)
E(I)	Observed potential of the amalgam electrode (versus NHE)
T(I)	Time in seconds from the start of the drop
PP1	Contribution to current from double layer charging
PP2	Contribution to current from hydrogen evolution
PP3	Factor to correct for back reaction
BET	β , anodic transfer coefficient
DBT	Confidence interval parameter for β
LI	$\log i_0$ (i_0 is exchange current)
DLI	Confidence interval parameters for $\log i_0$

Listing of Program /BAHG/, October 1968

50.1 TO PART 101

60.1 DATE=@DATE, TIME=@TIME, MONTH=IP(DATE/100), DAY=100*FP(DATE/
100), HOUR=IP(TIME/3600), MINUTE=IP((TIME-3600*HOUR)/60),
SECOND=60*FP(TIME/60)

60.11 LINE FOR W=1 TO 3

60.2 TYPE IN FORM 60:MONTH, DAY, HOUR, MINUTE, SECOND, 'AM'
IF HOUR>2 AND HOUR<12

60.3 TYPE IN FORM 60:MONTH, DAY, HOUR-12, MINUTE, SECOND, 'PM'
IF HOUR >12

60.4 TYPE IN FORM 60:MONTH, DAY, HOUR, MINUTE, SECOND, 'PM'
IF HOUR=12

96.11 TYPE "

LEAST-SQUARES FIT TO A STRAIGHT LINE

96.14 SX=SUM(I=1 TO N: X(I)), SY=SUM(I=1 TO N: Y(I)), SXX=SUM(I=1 TO N
:X(I)*X(I)), SXY=SUM(I=1 TO N:X(I)*Y(I)), SYY=SUM(I=1 TO N:Y(I)*Y(I)),
AVX=SX/N, AVY=SY/N, M=N-1, S=SXX-SX*AVX, CVX=S/M, CVY=(SYY-SY*AVY)/M
96.15 CXY=(SXY-SX*AVY)/M, SDX=SQRT CVX, SDY=SQRT CVY, COR=-CXY/(SDY*
SDY), SLP=CXY/CVX, INT=AVY-SLP*AVX, RI=SQRT(M*(CVY-SLP*SLP*CVX)/(N-2

96.16 TYPE IN FORM 90: AVX, AVY, SDX, SDY, COR, SLP, INT

96.17 TYPE IN FORM 91: CS, CI

96.18 DEMAND ANS FOR YES=1 FOR NO=-1

96.181 PAGE IF ANS=YES

96.19 DF=0

96.20 DO STEP 93.11 FOR I=1 TO N IF ANS=NO

96.21 TO STEP 96.24 IF ANS=NO

96.22 TYPE

X	Y(OBS)	Y(CALC)	DIFF	I"
---	--------	---------	------	----

96.23 DO PART 93 FOR I=1 TO N

96.24 SDF=SQRT(DF/(N-1))

96.25 TYPE

STD. DEV. OF Y VALUES FROM LINE"

96.251 TYPE SDF

96.26 LINE FOR W=1 TO 6

96.27 DONE

93.11 YC=INT+SLP*X(I), DIF=YC-Y(I), DF=DF+DIF^2

93.12 TYPE IN FORM 93: X(I), Y(I), YC, DIF, I

93.13 DONE

99.1 X(I)=(E(I)-EEQ)/C1, PP1=-C2*(E(I)-EZ)/T(I),
PP2=(3E-13)*EXP(-.5*C3*(E(I)+(.059*PH))),
PP3=1-EXP(-2*C3*(E(I)-EEQ)), Y(I)=LOG10((PP1+PP2)/PP3)
99.2 TYPE IN FORM 99: E(I), PP1, PP2, PP3, I

```

101.11; BARIUM AMALGAM CALCULATION
101.115 DEMAND FF
101.12 OPEN "1-9" FOR INPUT AS FILE 1
101.13 READ FROM 1: EEQ, N
101.14 READ FROM 1: H(I), G(I) FOR I=1 TO N
101.141 CLOSE 1
101.142 DEMAND MBA, GBA, BAS, C7, C8
101.143 C5=.05915*LOG10(2*MBA*GBA), C6=.222
101.144 HE(I)=H(I)*C8, T(I)=G(I)*C7 FOR I=1 TO N
101.145 E(I)=BAS+(C6)+(-C5)-(HE(I)/1000) FOR I=1 TO N
101.146 TYPE "
      E(I)                T(I)                LOG10(T(I))"
101.148 T(I)=T(I)*1E-3 FOR I=1 TO N
101.149 TYPE IN FORM 105: E(I), T(I), LOG10(T(I)) FOR I=1 TO N
101.15 R=8.314, TT=298.15, F=96500, CIN=20E-6, EZ=-0.16,
C1=2.303*R*TT/F, C2=2*CIN/3, C3=F/(R*TT), PH=10
101.155 PAGE
101.16 DO PART 60
101.161 LINE
101.162 TYPE "
      E                PP1                PP2                PP3                I"
101.163 LINE
101.164 DO PART 99 FOR I=1 TO N
101.165 PAGE
101.166 DO PART 60
101.17 DO PART 96
101.18 BET=SLP, DBT=CS, LI=INT, DLI=CI, I0=10^LI
101.19 LINE FOR W=1 TO 3
101.20 TYPE BET, DBT, LI, DLI, I0, EEQ, FF
101.21 LINE FOR W=1 TO 3
101.289 PAGE
101.29 TYPE "DO YOU WISH TO DISCARD ANY POINTS?
TYPE BEG, END, RANDOM, OR NO."
101.3 DEMAND ANS FOR BEG=591 FOR RAN=592 FOR END=593 FOR RET=594
101.31 TO PART ANS IF ANS#1 IF ANS#-1
101.311 TO STEP 101.35 IF ANS=NO
101.32 TYPE "DO YOU WISH TO DISCARD ANY MORE POINTS?
TYPE BEG, END, RANDOM OR NO."
101.321 DEMAND ANS
101.33 TO PART ANS IF ANS#1 IF ANS#-1
101.339 DO STEP 99.1 FOR I=1 TO N
101.34 TO STEP 101.165
101.35 PAUSE

```

502.1 OPEN "ZPQ" FOR OUTPUT AS FILE 502
502.2 WRITE ON 502: ALL VALUES
502.3 CLOSE 502
502.4 RETURN

591. TYPE "THROW AWAY POINTS FROM 1 TO I"
591.2 DEMAND I
591.3 N=N-I
591.4 T(J)=T(J+I), E(J)=E(J+I) FOR J=1 TO N
591.5 TO PART RET

592. TYPE "THROW AWAY POINT I"
592.1 DEMAND I
592.2 N=N-1
592.3 T(J)=T(J+1), E(J)=E(J+1) FOR J=1 TO N
592.4 TYPE "ANYMORE? TYPE YES OR NO."
592.5 DEMAND ANS
592.6 TO PART 592. IF ANS=YES
592.7 TO PART RET

593 TYPE "THROW AWAY THE POINTS N-J TO N"
593.1 DEMAND J
593.2 N=N-J
593.3 TO PART RET

594 TO STEP 101.32

FORM 60: ZZ/ZZ/1968 ZZ:ZZ:ZZ ZZ

FORM 90:

AVERAGE VALUES OF VARIABLES
AVX=##### AVY=#####

STANDARD DEVIATION OF X AND Y FROM AVERAGE VALUES
SDX=##### SDY=#####

CORRELATION BETWEEN X AND Y
COR=#####

SLOPE AND INTERCEPT OF LSF LINE
SLP=##### INT=#####

FORM 91:

CONFIDENCE INTERVAL PARAMETERS FOR SLOPE AND INTERCEPT
CS=##### CI=#####

DO YOU WANT A TABLE OF CALCULATED AND OBSERVED VALUES?

FORM 92: ##### ##### ##### ##### 777
FORM 105: ### ##### 777.77777

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