

AN ABSTRACT OF THE THESIS OF

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Title: ION ASSOCIATION OF SODIUM, MAGNESIUM, AND  
CALCIUM WITH SULFATE IN AQUEOUS SOLUTION

Abstract approved: Redacted for privacy  
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An association model was used to describe the specific interactions between sodium, magnesium, calcium, and sulfate ions. The formation of ion-pairs by a generic ion  $M^{v+}$  and  $SO_4^{2-}$  was characterized by the stoichiometric association constant:

$$K^*_{MSO_4} = \frac{[MSO_4^{(v+ - 2)}]}{[M^{v+}][SO_4^{2-}]}$$

The brackets denote the molality of each species.

Values of  $K^*_{NaSO_4}$  were determined over the ranges of temperature, ionic strength, and pressure encountered in the ocean.

$K^*_{NaSO_4}$  did not vary with the composition of NaCl- $Na_2SO_4$  solutions at the ionic strength of seawater. Values of  $K^*_{MgSO_4}$  were obtained in solutions with an ionic strength of 0.67 at 25° C and at 1.7° C.

A value of the thermodynamic association constant  $K_{MgSO_4} = \frac{a_{MgSO_4}}{(a_{Mg} a_{SO_4})} = 209$ , where  $a$  represents the activity of each species, was obtained at 25° C by extrapolation of  $K^*_{MgSO_4}$  to

infinite dilution.  $K^*_{\text{CaSO}_4}$  was found to be 10.8 at 25° C and at an ionic strength of 0.67.

Harned's rule for the behavior of activity coefficients in mixed electrolyte solutions was derived from the association model. Thus, ion association may be regarded as a possible interpretation of Harned's rule behavior.

The molalities of the unassociated and the ion-paired major species in seawater were calculated from the stoichiometric association constants. The results were shown to account for several of the chemical properties of seawater such as the relatively large solubility of calcite, the values of activity coefficients of several solutes, the ultrasonic absorption of seawater, and the colligative properties of seawater.

Ion Association of Sodium, Magnesium, and Calcium  
With Sulfate in Aqueous Solution

by

Dana Ray Kester

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# ION ASSOCIATION OF SODIUM, MAGNESIUM, AND CALCIUM WITH SULFATE IN AQUEOUS SOLUTION

## I. INTRODUCTION

A knowledge of the interactions between ions in concentrated aqueous solutions of mixed electrolytes is important for an understanding of many of the chemical properties of seawater. These interactions affect the dissociation of weak acids (Weyl, 1961; Kester and Pytkowicz, 1967; Disteché and Disteché, 1967; Culberson and Pytkowicz, 1968), the solubility of minerals (Garrels, Thompson, and Siever, 1961; Pytkowicz and Kester, 1967), the colligative properties, the electrical conductance, and the viscosity. The interactions between magnesium and sulfate ions are particularly important in accounting for the large ultrasonic absorption of seawater (Liebermann, 1949).

Two models have been employed to describe the ionic interactions in electrolytic solutions with ionic strengths greater than 0.1. These models are not as fundamental as the Debye-Hückel model for the ionic interactions in dilute solutions, because they only attempt to describe the departures of thermodynamic properties of a particular solution from those of an arbitrarily defined standard solution. The characteristics of these two models will be described briefly in the theoretical section of this work. One model is

developed in terms of specific ionic interactions without specifying their mechanistic nature; while in the other model, the departures of a particular solution from the standard solution are attributed to the formation of ion-paired or complexed species. The ion association model has been more widely used to account for ionic interactions in seawater than the specific interaction model.

In a brief note related to the chemistry of bicarbonate and carbonate in seawater, Greenberg and Moberg (1932) suggested that the low values for the activity coefficients of these two ions in seawater may be due to the presence of complexes with the divalent cations in seawater. Garrels, Thompson, and Siever (1961) investigated experimentally the effect of sodium and magnesium ions on the activity coefficients of bicarbonate and carbonate ions at various ionic strengths, which bracketed the ionic strength of seawater. They concluded that ion-pairs formed by  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$  reduced the activity coefficients of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ .

Goldberg (1954) made one of the early estimates of the chemical species in seawater by calculating the concentrations of several complexes formed by  $\text{Cu}^{2+}$  and  $\text{Cl}^-$  from thermodynamic equilibrium constants, assuming that all activity coefficients were unity. Krauskopf (1956) introduced typical values for activity coefficients based on the electrical charge of each species in his consideration of the most likely species which were formed by 11 trace elements

(Zn, Cu, Pb, Bi, Cd, Ni, Co, Hg, Ag, Cr, and V) with chloride and hydroxide ions in seawater.

Goldberg and Arrhenius (1958) calculated the concentrations of various chemical species in seawater using estimated values for activity coefficients and thermodynamic equilibrium constants. They concluded that less than 1% of the sodium and potassium ions in seawater existed as sulfate ion-pairs, and that these ion-pairs did not significantly affect the sulfate ion concentration. They also estimated that about 7% of the magnesium and calcium ions in seawater existed as sulfate ion-pairs.

Garrels and Thompson (1962) made a comprehensive estimate of the major ion-pairs in seawater. They calculated the distribution of chemical species in seawater at 25<sup>o</sup> C and one atmosphere pressure from thermodynamic dissociation constants and estimated values of activity coefficients (Table 1). The activity coefficients of the free ions were calculated by the mean-salt-method, with the exception of  $\gamma_{Na}$ , which was determined with a sodium ion-sensitive glass electrode. The activity coefficients of the univalent ion-pairs were assumed to be equal to that of the free bicarbonate ions. They assumed a value of 1.13 for the activity coefficient of the uncharged ion-pairs. Their calculations provided a valuable first approximation of the major chemical species in seawater. Their model of ion-pairs in seawater successfully accounted for the small activity

coefficients of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  and for the enhanced solubility of  $\text{CaSO}_4$  in synthetic seawater relative to dilute solutions.

Table 1. The activity coefficients of ion-pairs and free ions at 25° C and at 0.70 ionic strength, used by Garrels and Thompson (1962).

	$\text{SO}_4^{2-}$	$\text{HCO}_3^-$	$\text{CO}_3^{2-}$	Free
$\text{Na}^+$	0.68	1.13	0.68	0.76
$\text{Mg}^{2+}$	1.13	0.68	1.13	0.36
$\text{Ca}^{2+}$	1.13	0.68	1.13	0.28
$\text{K}^+$	0.68	----	----	0.64
Free	0.12	0.68	0.20	

Gieskes (1966) has applied the specific interaction model to describe the behavior of the activity coefficient of sodium chloride in mixed electrolytic solutions similar to seawater. He found that the relatively strong interactions between magnesium and sulfate ions affected the activity coefficient of sodium chloride, and that this could best be accounted for by considering the ion-pairing of magnesium and sulfate. Thus, his final result was a combination of the two models in which some interactions were described by the specific interaction model (i. e. Harned's rule) while others were described by ion association. This approach provided an adequate description

of the activity coefficient of sodium chloride in the mixed electrolytic solutions. However, it is not internally consistent, because ion-pairs are disregarded for sodium ion interactions. Gieskes work is significant because it represents an approach to ionic interactions in seawater based on experimental data rather than on estimates.

In this work the ion association model was selected because it provided an interpretation of ionic interactions in seawater which was consistent with experimental results. Garrels and Thompson (1962) estimated that sulfate ion-pairs were the most significant for the major cations in seawater. The experimental aspects of this work were, therefore, confined to the interactions of sodium, magnesium, and calcium ions with sulfate ions. The measurements were initially made at 25° C and one atmosphere pressure. Where possible, they were then extended to lower temperatures and to higher pressures to determine the variations in these ionic interactions which occur in the ocean. A more complete analysis for the interactions of the cations in seawater will require consideration of the interactions with chloride, with bicarbonate and carbonate (Garrels and Thompson, 1962), and with bromide, iodide, phosphate, hydroxide, and silicate (Goldberg and Arrhenius, 1958).

## II. THEORY

Two types of approaches have been used to describe the effects of short range interactions on activity coefficients in seawater. The first is based on the association model of Bjerrum (Harned and Owen, 1958) which was modified by Garrels and Thompson (1962) and by Kester and Pytkowicz (1967). The basic assumptions in this approach are that short range interactions in seawater can be represented by the formation of ion-pairs and that there are solutions in which no ion-pairs are formed. When the association model is used it is necessary to show that the equilibrium constant for ion-pair formation is constant over a range of compositions, if the ionic strength is unchanged (Sillén, 1958).

An alternative approach to short range interactions, the specific interaction model, can be exemplified by the equation of Guggenheim (1935). Robinson and Stokes (1959) have shown that the empirical relation known as Harned's rule can be obtained from Guggenheim's equation. This rule, for an electrolyte MX in the presence of an electrolyte NY, may be written as:

$$\log f_{MX} = \log f_{(0)MX} + k\mu_{MX} = \log f_{MX(0)} - k\mu_{NY}, \quad (1)$$

where  $f_{MX}$  is the total mean activity coefficient of MX,  $f_{(0)MX}$  and  $f_{MX(0)}$  are the activity coefficients at zero ionic strength of MX and



in pure MX respectively. The  $\mu$  terms refer to the ionic strength contributions of the salts indicated by the subscripts. This equation is only valid when the sum of the ionic strengths,  $\mu_{MX} + \mu_{NY}$ , is kept constant.

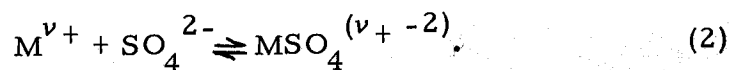
Both of these models involve Brönsted's principle of specific ionic interactions, which asserts that specific interactions occur only between oppositely charged ions (Brönsted, 1922).

Gieskes (1966) concluded that ion association did not occur in solutions containing mixtures of NaCl and Na<sub>2</sub>SO<sub>4</sub> because Harned's rule was followed. There is an alternative conclusion, as will be shown later (page 26), because Harned's rule can be derived not only from Guggenheim's equation but also from the association model. Also, the interaction terms in Guggenheim's equation, which are present in the constant k of equation (1), include the effects of ion association (Harned and Owen, 1958).

There are conflicting interpretations regarding the significance of ion-pairs formed by chloride and the alkali metal and the alkaline earth cations in aqueous solutions of ionic strengths 0.1 to 1.0. Davies (1927) and Righellato and Davies (1930) concluded from an examination of conductance data that NaCl, MgCl<sub>2</sub>, and CaCl<sub>2</sub> could be considered completely dissociated for concentrations up to 0.5 M. Stokes (1945) has shown that the activity coefficient of MgCl<sub>2</sub> does not indicate significant association up to 5.5 M. However,

Fuoss and Hsia (1967) concluded that ion association can be used to account for the conductance of NaCl, KCl, and CsI in dioxane-water mixtures of varying dielectric constant. When their results are extrapolated to the dielectric constant of pure water, the magnitude of association becomes uncertain due to the extreme dependence of the association constant on the dielectric constant. Ion association of  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  with  $\text{Cl}^-$  deserves further examination, but on the basis of available data it was assumed that these ion-pairs are not significant in seawater.

The association of a metal ion  $\text{M}^{v+}$  with sulfate to form the  $\text{MSO}_4^{(v+ - 2)}$  ion-pair is represented by the equilibrium:



The term "ion-pair" is used to refer to those species which most likely result from electrostatic forces (see page 76), thereby reserving the term "complex" for covalently bonded species (Nancollas, 1966). The techniques used in this study of ion-pairs in seawater do not reveal the structural form of the ion-pairs; operationally, a species will be considered an ion-pair when it does not contribute to the activity of  $\text{M}^{v+}$ . Structural information about sulfate ion-pairs has been obtained from ultrasonic absorption (Eigen, 1957) and from Raman spectra (Hester and Plane, 1964). These studies indicate that sulfate ion-pairs contain some water of hydration between the

interacting ions and that contact ion-pairs are less significant than outer-sphere interactions.

In the association model a distinction is made between free activity coefficients,  $\gamma$ , and total activity coefficients,  $f$ , which are related to the activity,  $a_X$ , by (Pytkowicz, Duedall, and Connors, 1966):

$$a_X = \gamma_X [X] = f_X T(X). \quad (3)$$

The  $[X]$  denotes the molality of unassociated X;  $T(X)$  is the total (free plus paired) molality of X. In the association model it is assumed that  $\gamma$  depends only on the ionic strength, and any difference of  $f$  in two solutions of the same ionic strength, but of different compositions, is ascribed to a difference in the extent of ion-pairing of X in the two solutions. Even though this interpretation is an oversimplification, it will be shown that it provides a manageable and self-consistent representation of short range interactions in concentrated mixed electrolyte solutions.

The formation of ion-pairs in seawater may be represented by a stoichiometric association constant, which is defined by (Rossotti and Rossotti, 1961):

$$K_{MSO_4}^* = \frac{[MSO_4^{(v^+ - 2)}]}{[M^{v^+}][SO_4^{2-}]} = \frac{\gamma_M \gamma_{SO_4}}{\gamma_{MSO_4}} K_{MSO_4}. \quad (4)$$

The brackets denote molalities, and  $K_{\text{MSO}_4}$  represents the thermodynamic association constant, which is defined in terms of the activities of the species. Stoichiometric constants are used in preference to thermodynamic constants because concentrations rather than activities are usually measured in seawater, and because the activity coefficients of ion-pairs are not known. The determination of a stoichiometric constant is an alternative to evaluating the quotient of activity coefficients in equation (4).

A consequence of the ion association model is the distinction between the effective and the total ionic strengths. The effective ionic strength,  $\mu_{\text{E}}$ , is defined in terms of the species present; for an NaCl-MgCl<sub>2</sub>-Na<sub>2</sub>SO<sub>4</sub> solution  $\mu_{\text{E}} = 1/2 ( [\text{Na}^+] + [\text{NaSO}_4^-] + 4[\text{Mg}^{2+}] + 4[\text{SO}_4^{2-}] + [\text{Cl}^-] )$ . The total ionic strength of this solution is  $\mu_{\text{T}} = m_{\text{NaCl}} + 3m_{\text{MgCl}_2} + 3m_{\text{Na}_2\text{SO}_4}$ , where  $m$  is the molality of the salt indicated by the subscript.

When treating ionic interactions in multicomponent solutions such as seawater, it is convenient to refer to activities and to activity coefficients of individual ions. The use of these individual ionic quantities requires a non-thermodynamic assumption. Kortüm (1965) cites two methods for resolving mean ionic activity coefficients into individual ionic activity coefficients. The method of Guggenheim (1930) sets  $\gamma_+ = \gamma_- = \gamma_{\pm}$  for all uni-univalent electrolytes. In dilute solutions this convention receives support from the Debye-Hückel

theory of ionic interaction, in which the electrostatic interactions of ions are considered to be independent of the sign of their charge. However, this support cannot be applied at higher concentrations where mean ionic activity coefficients depart from the Debye-Hückel limiting law. A second convention asserts that the activity coefficient of chloride ions in any solution is the same as the mean ionic activity coefficient of KCl at the same ionic strength (Mac Innes, 1961). Support for the Mac Innes assumption has been based on the similar electronic structures of  $K^+$  and  $Cl^-$ , on their similar masses, and on their similar mobilities (Mac Innes, 1919; Mac Innes, 1961; Kortüm, 1965). This convention has been commonly used for estimating individual ionic activity coefficients in concentrated natural solutions, and this estimate has been called the mean-salt-method (Garrels and Christ, 1965).

Studies of activity coefficients in mixed electrolyte solutions of variable composition, but of constant total ionic strength, reveal variations in total activity coefficients which frequently follow Harned's rule (Lanier, 1965; Gieskes, 1966; Butler and Huston, 1967; Butler, Hsu, and Synnott, 1967). These observations may seem to invalidate the use of the mean-salt-method; however, if the mean-salt-method is restricted to the calculation of free activity coefficients, then the variations in total activity coefficients in accordance with Harned's rule may be formalistically accounted for

by ion-pair formation. The usefulness of this approach will be determined by the extent to which it provides a consistent explanation for the ionic properties of mixed electrolyte solutions.

Equation (4) indicates that one criterion for the consistency of the association model is that  $K_{M\text{SO}_4}^*$  may depend on the effective ionic strength, but it should not vary with composition at a constant effective ionic strength. This hypothesis will be tested experimentally for  $K_{\text{NaSO}_4}^*$  in NaCl-Na<sub>2</sub>SO<sub>4</sub> solutions.

## III. SODIUM SULFATE ASSOCIATION

Determination of  $K^*$  NaSO<sub>4</sub>

The determination of  $K^*$  NaSO<sub>4</sub> was based on the following potentiometric method which was outlined in part by Rechnitz (1965). The e. m. f. of a sodium sensitive glass electrode (Beckman No. 39278 or Corning No. 476210) and a fiber junction calomel electrode (Beckman No. 39170) was measured in 125 ml of test solution (NaCl and Na<sub>2</sub>SO<sub>4</sub> of varying composition). The electrodes were then transferred to 125.0 ml of a standard NaCl solution, and the e. m. f. was measured after adding increments of a titrant solution (2.000 molal NaCl). The titration was continued until the e. m. f. in the standard solution, E(std), bracketed the value obtained in the test solution. The electrode e. m. f. was then measured again in the test solution to detect any drift in the electrode e. m. f. The initial and final e. m. f. values in the test solution usually differed by less than 0.03 mv, and they were averaged to obtain E(test), the e. m. f. of the electrode couple in the test solution.

The concentration of unassociated sodium ions in the test solution was obtained in the following manner. When E(test) = E(std), the activity of sodium ions was the same in the test solution and in the standard solution, provided that the asymmetry potential of the glass electrode and the liquid junction potential of the salt bridge were the

same in the two solutions. The validity of this assumption was not verified experimentally; however, the results obtained from these measurements were consistent with values obtained by electrode measurements without a salt bridge (page 32), which suggests that any differences in the liquid junction potential in the test and in the standard solutions did not introduce a significant error. Thus, when  $E(\text{std}) = E(\text{test})$ :

$$a_{\text{Na}}(\text{test}) = a_{\text{Na}}(\text{std}), \quad (5)$$

or

$$[\text{Na}^+]_{\text{test}} = \frac{\gamma_{\text{Na}}(\text{std})}{\gamma_{\text{Na}}(\text{test})} [\text{Na}^+]_{\text{std}}. \quad (6)$$

Assuming that there is no association of  $\text{Na}^+$  and  $\text{Cl}^-$ ,  $[\text{Na}^+]_{\text{std}}$  and the effective ionic strength of the standard solution,  $\mu_E(\text{std})$ , are equal to the molality of  $\text{NaCl}$  in the standard solution.

An iterative procedure was used to calculate  $[\text{Na}^+]_{\text{test}}$ . The ratio of the activity coefficients in equation (6) was initially set as 1.000 yielding a first estimate of  $[\text{Na}^+]_{\text{test}}$ . The molalities of  $\text{NaSO}_4^-$  and  $\text{SO}_4^{2-}$  were then computed from the following two equations:

$$[\text{NaSO}_4^-]_{\text{test}} = T(\text{Na})_{\text{test}} - [\text{Na}^+]_{\text{test}}; \quad (7)$$

$$[\text{SO}_4^{2-}]_{\text{test}} = T(\text{SO}_4)_{\text{test}} - [\text{NaSO}_4^-]_{\text{test}}. \quad (8)$$

The total sodium  $T(\text{Na})$  and the total sulfate  $T(\text{SO}_4)$  were known from



the composition of the test solution. It was then possible to estimate the effective ionic strength of the test solution:

$$\mu_E(\text{test}) = 1/2 \left\{ [\text{Na}^+] + [\text{NaSO}_4^-] + 4[\text{SO}_4^{2-}] + [\text{Cl}^-] \right\}. \quad (9)$$

The ratio of the activity coefficients in equation (6) was then estimated using the mean-salt-method (page 11), and the effective ionic strengths of the test and the standard solutions. Refined values of  $[\text{Na}^+]_{\text{test}}$ ,  $\mu_E(\text{test})$ , and  $\gamma_{\text{Na}}(\text{test})$  were then calculated until the ratio of activity coefficients in equation (6) did not vary by more than one part in  $10^5$  upon successive iterations. The stoichiometric association constant for  $\text{NaSO}_4^-$  ion-pairs was calculated from

$$K^*_{\text{NaSO}_4} = \frac{[\text{NaSO}_4^-]}{[\text{Na}^+][\text{SO}_4^{2-}]} \quad (10)$$

### Experimental Procedure

The experimental procedure will be described in sufficient detail to serve as a guide for future workers.

All solutions were prepared by weight so that their molalities would be known to better than 0.1%. The salts used in this work were Baker Analyzed reagent grade. They were dried at  $125^\circ \text{C}$ , at 0.5 atm pressure, for at least four hours and then cooled in a desiccator before weighing. The test solution was prepared by weighing out the desired amounts of  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$  to within one part in  $10^5$ .

Distilled water was added by weight to within two parts in  $10^5$ . The initial standard solution and the titrant solution contained only NaCl; they were prepared in the same manner as the test solution.

The 125 ml of initial standard solution were placed in the thermostated beaker (Figure 1) with a pipet. The pipet was calibrated in terms of the mass of initial standard solution delivered. A similar quantity of test solution was placed in a second thermostated beaker.

The sodium-sensitive electrode couple was immersed in the test solution, and the e. m. f. was recorded until a stable value was obtained (drift rate less than 0.06 mv per hour). The electrodes were then removed from the test solution, rinsed with the initial standard solution, and placed in the thermostated beaker containing the initial standard solution. The e. m. f. was recorded until a stable value was obtained.

The initial standard solution was stirred as increments of the titrant solution were added with a piston buret (Man-o-stat 71-634 or Gilmont S-1200). Stirring was discontinued and the e. m. f. was recorded after each addition of titrant solution. The titration was continued until the e. m. f. of the electrodes in the standard solution bracketed their e. m. f. in the test solution. The piston burets were calibrated in terms of the mass of titrant which was added. After the titration the electrodes were rinsed with the test solution, immersed in the beaker containing test solution, and the e. m. f. was

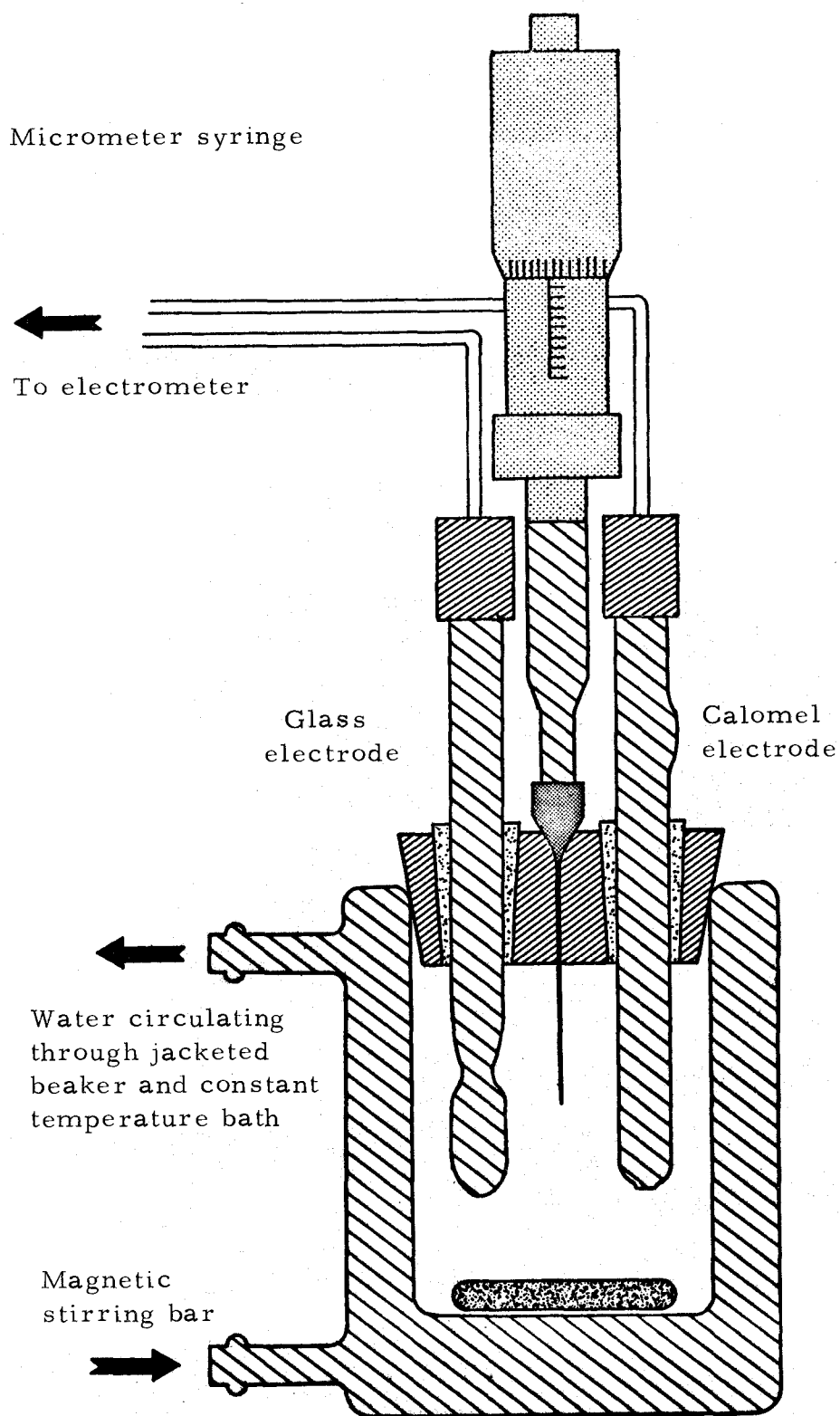


Figure 1. Thermostated beaker with electrodes.

measured. This value was normally within 0.03 mv of the value measured before the titration. The titration data were discarded if the electrode e. m. f. in the test solution differed by more than 0.05 mv before and after the titration.

The raw data for a typical titration are shown in Table 2. The e. m. f. of the electrodes in the test solution was taken as the average of the e. m. f. before and after the titration. The change in electrode e. m. f. with the amount of titrant added was essentially linear, due to the small interval over which the titration was performed (Figure 2). The amount of titrant necessary to make  $E(\text{std}) = E(\text{test})$  was obtained by a least squares regression of the titration data.

The calculation of  $[Na^+]_{\text{test}}$  from equation (6) required an estimate of the ratio of  $\gamma_{Na}$  in the test and the standard solutions. Values of  $\gamma_{Na}$ , based on the mean-salt-method, were obtained as a function of the effective ionic strength from the expression:

$$\gamma_{Na} = \frac{f_{NaCl}^2}{f_{KCl}} \quad (11)$$

The mean ionic activity coefficients of sodium chloride ( $f_{NaCl}$ ) and of potassium chloride ( $f_{KCl}$ ) at various effective ionic strengths were obtained from Harned and Owen (1958). The iterative calculation of  $[Na^+]_{\text{test}}$  was performed by a computer; therefore, it was convenient to express  $\gamma_{Na}$  as a function of  $\mu_E$ . A series of quadratic equations were used to obtain a smooth curve between the values of  $\gamma_{Na}$  obtained

Table 2. Example of data for the determination of  $K^*$   $NaSO_4$ .

Determination of  $K^*$   $NaSO_4$

Date: 6 Nov. 1967

Molality of solutions:

	<u>NaCl</u>	<u>MgCl<sub>2</sub></u>	<u>CaCl<sub>2</sub></u>	<u>Na<sub>2</sub>SO<sub>4</sub></u>
Test solution	0.5617	-----	-----	0.06720
Initial standard	0.6307	-----	-----	-----
Titrant solution	2.000	-----	-----	-----

Mass of initial standard solution: 127.80 g.

Titration data:

TEST SOLUTION			STANDARD SOLUTION			
Time	T <sup>o</sup> C	EMF (mv)	Time	T <sup>o</sup> C	EMF (mv)	Titrant (ml)
1245	24.98	-34.41	1315	24.99	-33.32	0.000
1400	25.00	-34.39	1420	25.00	-34.12	1.75
			1440	24.99	-34.22	2.00
			1510	25.00	-34.34	2.25
			1540	25.00	-34.47	2.50
			1600	25.00	-34.58	2.75
1630	25.00	-34.40				

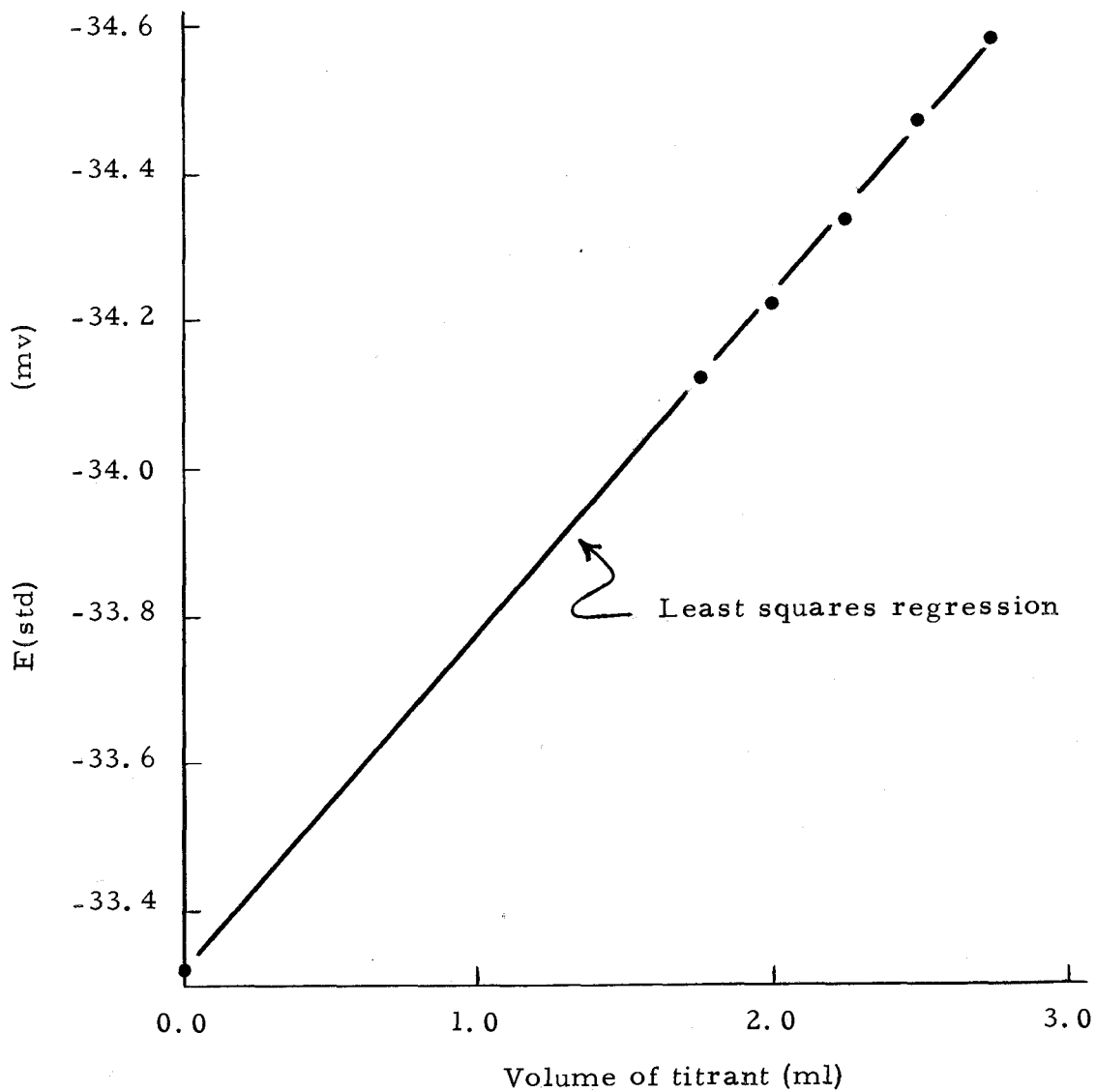


Figure 2. Variation of  $E(\text{std})$  during a titration.

from the data of Harned and Owen (1958). These equations are given in Table 3, and the resulting curve is shown in Figure 3. The calculation of  $K_{\text{NaSO}_4}^*$  was described on page 14. The experimental data from which  $K_{\text{NaSO}_4}^*$  was calculated are listed in Appendix II.

Table 3. Quadratic equations for  $\gamma_{\text{Na}}$  at various effective ionic strengths:  $\gamma_{\text{Na}} = A + B \mu_{\text{E}}^{\text{Na}} + C \mu_{\text{E}}^2$ .

Ionic Strength Interval	A	B	C
$0.1 < \mu_{\text{E}} \leq 0.2$	0.8409	-0.6285	0.9050
$0.2 < \mu_{\text{E}} \leq 0.5$	0.8036	-0.3177	0.2833
$0.5 < \mu_{\text{E}} \leq 1.0$	0.7389	-0.0700	0.04667

#### Results for Sodium Sulfate Association at 25°C

$K_{\text{NaSO}_4}^*$  was determined at 25°C in a series of NaCl-Na<sub>2</sub>SO<sub>4</sub> solutions of varying composition at an effective ionic strength between 0.683 and 0.690. The results, which are presented in Figure 4, show that  $K_{\text{NaSO}_4}^*$  is independent of the composition within the scatter of the data. The constancy of  $K_{\text{NaSO}_4}^*$  indicates that the association model, in terms of ion-pairs, provides an adequate description of short range interactions in these solutions. If other species besides NaSO<sub>4</sub><sup>-</sup> had been formed to an appreciable extent, the association constant calculated from equation (10) would vary with the extent of

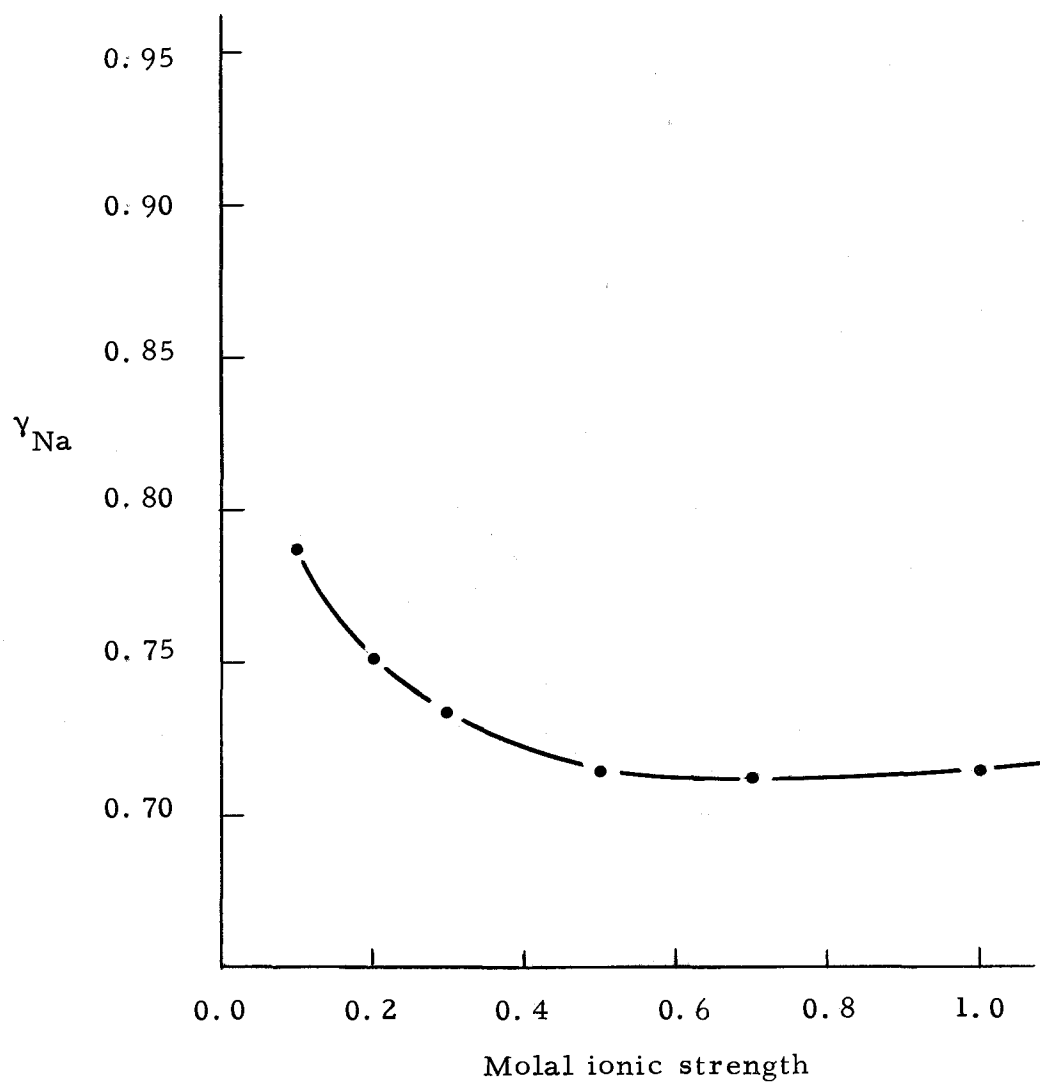


Figure 3. Interpolation curve for the estimation of  $\gamma_{Na}$  as a function of ionic strength.



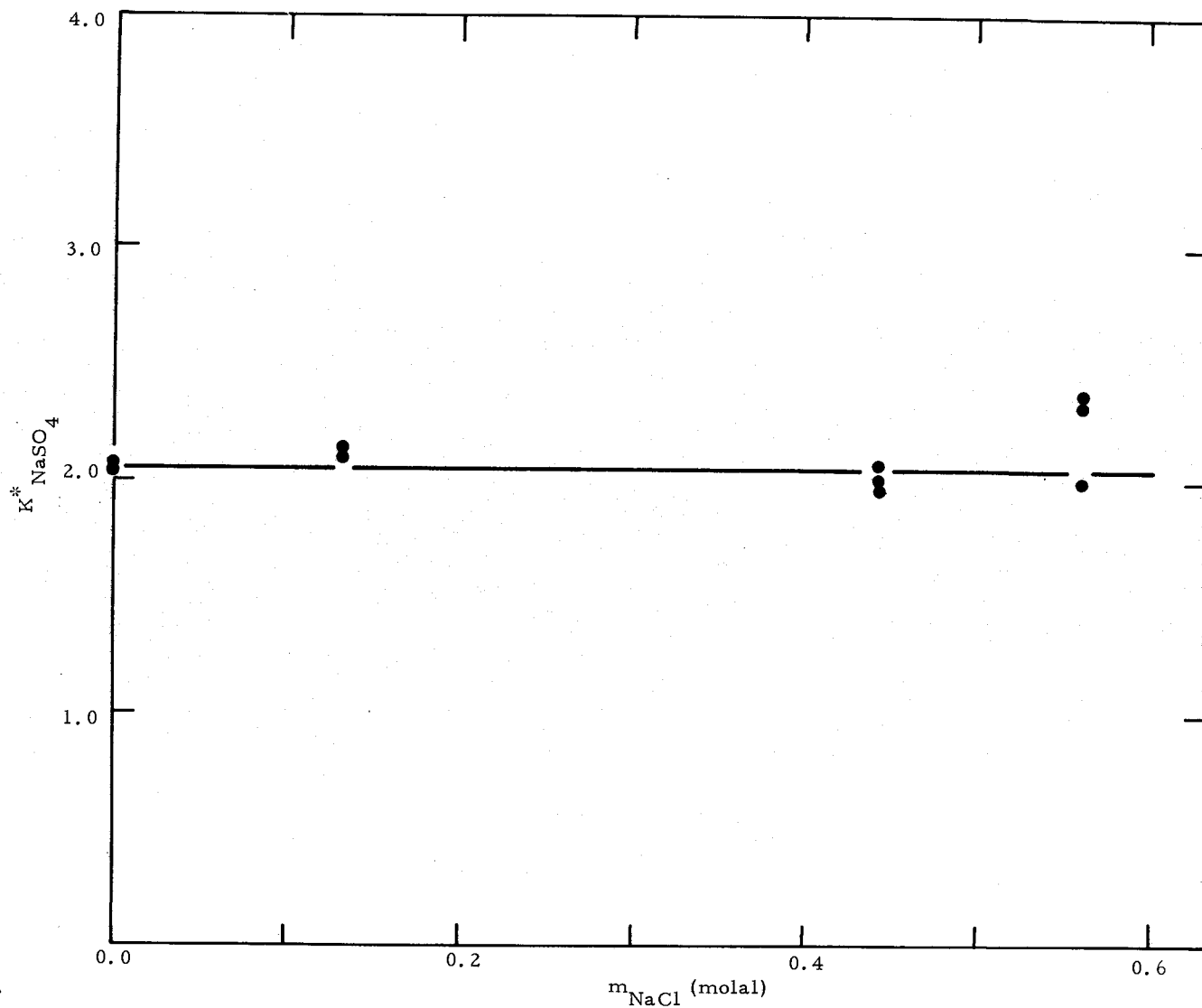


Figure 4. Values of  $K^*_{\text{NaSO}_4}$  at various compositions of NaCl- $\text{Na}_2\text{SO}_4$  solutions with  $\mu_E = 0.687 \pm 0.003$  at  $25^\circ\text{C}$ .

association which occurred when the composition was changed. It will be shown in Figure 5 that the slight changes in the effective ionic strength were negligible.

The reproducibility of the results shown in Figure 4 decreases with increasing concentration of NaCl because the extent of association decreases. Thus, the values of  $K_{\text{NaSO}_4}^*$  are most precise in pure  $\text{Na}_2\text{SO}_4$  solutions. For this reason the variation of  $K_{\text{NaSO}_4}^*$  with the effective ionic strength at  $25^\circ\text{C}$ , which is presented in Figure 5, was determined in a series of  $\text{Na}_2\text{SO}_4$  solutions.

Values of  $K_{\text{NaSO}_4}^*$  obtained from conductivity data at  $18^\circ\text{C}$  in dilute solutions (Righellato and Davies, 1930) are also shown in Figure 5. The trends suggest a systematic difference between the two sets of results shown in Figure 5. Subsequent results (page 34) will show that  $K_{\text{NaSO}_4}^*$  increases as temperature decreases. This difference may represent a systematic difference between the assumptions required by the conductometric and potentiometric methods. For example, the conductance method requires an assumed value for the mobility of the  $\text{NaSO}_4^-$  ion-pair, which cannot be verified experimentally (Righellato and Davies, 1930). The potentiometric method used in this work assumes that chloride ion-pairs are not significant, that free activity coefficients depend only on ionic strength, and that the liquid junction potential of the saturated KCl salt bridge is the same in solutions of similar ionic strengths but of different

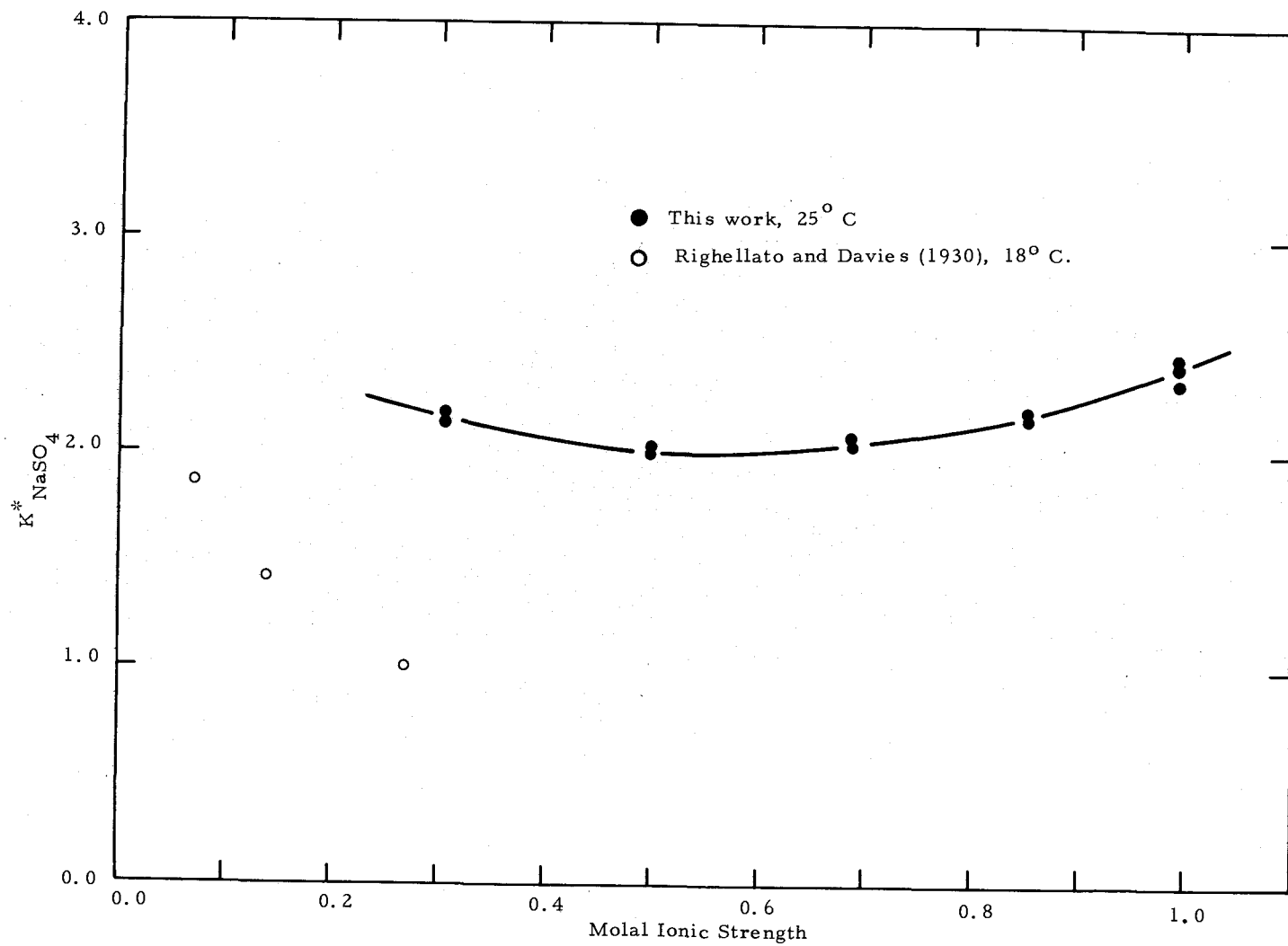


Figure 5. Variation of  $K^*_{NaSO_4}$  with  $\mu_E$  in  $Na_2SO_4$  solutions at 25°C.

composition. After deriving Harned's rule from the association model, it will be shown that the results of this work agree with values which do not require assumptions about activity coefficients and the liquid junction potential (page 32).

The values of  $K_{\text{NaSO}_4}^*$  and of the free ion and ion-pair concentrations, which correspond to the results shown in Figures 4 and 5, are presented in Tables 4 and 5. The following interpolation formula, which was used to construct the curve shown in Figure 5, can be used to obtain interpolated values of  $K_{\text{NaSO}_4}^*$ :

$$K_{\text{NaSO}_4}^* = 2.73 - 2.58 \mu_E + 2.28 \mu_E^2. \quad (12)$$

$K_{\text{NaSO}_4}^*$  is independent of the composition of the NaCl-Na<sub>2</sub>SO<sub>4</sub> solutions within the precision of the results (Figure 5). Thus, values of  $K_{\text{NaSO}_4}^*$  determined in sodium sulfate solutions may be applied to seawater of the same effective ionic strength. However, the values of  $[\text{Na}^+]$ ,  $[\text{NaSO}_4^-]$ , and  $[\text{SO}_4^{2-}]$  depend on the composition of the solution because of competitive association with other ions. The results which are obtained when  $K_{\text{NaSO}_4}^*$  is used to calculate  $[\text{Na}^+]$  in seawater agrees well with measured values (page 85).

#### Explanation of Harned's Rule by the Association Model

Harned's rule, represented by equation (1), can be derived from the association model if the extent of association is slight, as will be shown below. This conclusion is in contrast to those in earlier studies (Gieskes, 1966; Lanier, 1965; Butler, Hsu, Synnott, 1967).

Table 4. Values of  $K^*_{\text{NaSO}_4}$  and the molality of the species in the NaCl-Na<sub>2</sub>SO<sub>4</sub> solutions at an effective ionic strength of  $0.687 \pm 0.003$  at 25° C. The limits of uncertainty are the average deviations from the mean; the solution numbers correspond to those listed in Appendix I.

Solution Number	$m_{\text{Na}_2\text{SO}_4}$ molal	$m_{\text{NaCl}}$ molal	$\mu_E$	$K^*_{\text{NaSO}_4}$	$[\text{Na}^+]$ molal	$[\text{NaSO}_4^-]$ molal	$[\text{SO}_4^{2-}]$ molal
1	0.34998	0.0000	0.6987	2.04 $\pm$ 0.02	0.5198	0.1801	0.1699
2	0.28740	0.13239	0.6852	2.11 $\pm$ 0.01	0.5525	0.1547	0.1327
3	0.12976	0.44425	0.6887	2.00 $\pm$ 0.04	0.6314	0.0724	0.0573
4	0.06720	0.56167	0.6834	2.23 $\pm$ 0.16	0.6562	0.0399	0.0273

Table 5. Values of  $K_{\text{NaSO}_4}^*$  and the molality of species in  $\text{Na}_2\text{SO}_4$  test solutions of various effective ionic strengths at 25° C. The limits of uncertainty are the average deviations from the mean; the solution numbers correspond to those listed in Appendix I.

Solution Number	$m_{\text{Na}_2\text{SO}_4}$ molal	$\mu_E$	$K_{\text{NaSO}_4}^*$	$[\text{Na}^+]$ molal	$[\text{NaSO}_4^-]$ molal	$[\text{SO}_4^{2-}]$ molal
5	0.13046	0.3081	2.14±0.02	0.2193	0.0417	0.0888
6	0.23210	0.5001	2.00±0.01	0.3661	0.0981	0.1340
1	0.34998	0.6897	2.04±0.02	0.5198	0.1801	0.1699
7	0.46810	0.8520	2.18±0.01	0.6600	0.2762	0.1919
8	0.58835	0.9933	2.41±0.03	0.7908	0.3859	0.2025

These authors examined NaCl-Na<sub>2</sub>SO<sub>4</sub> solutions and disregarded ion association because  $f_{\text{NaCl}}$  varied linearly with composition at constant ionic strength.

The following derivation of Harned's rule refers only to the test solution, so the subscript, test, will not be used. The molality of total chloride is equal to the molality of free chloride, provided that chloride ion-pairs are not significant. Thus, it follows from equation (3) that:

$$f_{\text{NaCl}} = \gamma_{\text{NaCl}} \left\{ \frac{[\text{Na}^+]}{T(\text{Na})} \right\}^{1/2} \quad (13)$$

Equation (10) may be written:

$$[\text{NaSO}_4^-] = K^*_{\text{NaSO}_4} [\text{Na}^+] [\text{SO}_4^{2-}] \quad (14)$$

From equations (7) and (14) it follows that:

$$\frac{[\text{Na}^+]}{T(\text{Na})} = \frac{1}{1 + K^*_{\text{NaSO}_4} [\text{SO}_4^{2-}]} \quad (15)$$

Substituting equation (15) into equation (13) and taking the logarithm yields:

$$\log f_{\text{NaCl}} = \log \gamma_{\text{NaCl}} - 1/2 \log (1 + K^*_{\text{NaSO}_4} [\text{SO}_4^{2-}]) \quad (16)$$

If  $K^*_{\text{NaSO}_4} [\text{SO}_4^{2-}] < 1$ , which will be true as long as  $[\text{NaSO}_4^-] < [\text{Na}^+]$ ,

then the last term in equation (16) can be expressed by the series:

$$\log (1 + K_{\text{NaSO}_4}^* [\text{SO}_4^{2-}]) = \frac{K_{\text{NaSO}_4}^* [\text{SO}_4^{2-}]}{2.303} - \frac{K_{\text{NaSO}_4}^* [\text{SO}_4^{2-}]^2}{4.606} \dots (17)$$

Equation (18) may be obtained by a procedure similar to that used for equation (15):

$$[\text{SO}_4^{2-}] = \frac{T(\text{SO}_4)}{1 + K_{\text{NaSO}_4}^* [\text{Na}^+]} \quad (18)$$

Introducing equation (18) into equation (17), with  $T(\text{SO}_4) = m_{\text{Na}_2\text{SO}_4}$ , and then inserting equation (17) into equation (16), with  $\log \gamma_{\text{NaCl}} = \log f_{\text{NaCl}(0)}$  yields:

$$\log f_{\text{NaCl}} = \log f_{\text{NaCl}(0)} - k_1 m_{\text{Na}_2\text{SO}_4} + k_2 (m_{\text{Na}_2\text{SO}_4})^2 - \dots (19)$$

with

$$k_i = \frac{(K_{\text{NaSO}_4}^*)^i / (1 + K_{\text{NaSO}_4}^* [\text{Na}^+])^i}{2(2.303) i} \quad (20)$$

At constant ionic strength equation (19) reduces to Harned's rule (equation 1) if two conditions are satisfied. First,  $K_{\text{NaSO}_4}^* [\text{SO}_4^{2-}] \ll 1$ ; this condition will permit the omission of the second and higher order terms in equations (17) and (19). Second, either  $[\text{Na}^+]$  must be approximately constant or  $K_{\text{NaSO}_4}^* [\text{Na}^+] \ll 1$  to assure that  $k_i$  will be a constant. These conditions will be satisfied only when the extent of association is slight. The results of Table 5 show that for  $\text{NaSO}_4^-$  ion-pairs the first condition may be acceptable, but that the second condition is not satisfied. Thus, in the calculations which follow,



equation (16) will be used in place of equation (19), because equation (16) does not require these mathematical approximations. However, the principle that Harned's rule may be derived from the association model for systems in which the extent of association is slight is still valid. Thus, the association model predicts that as a first approximation  $f_{\text{NaCl}}$  will vary linearly with composition at a constant effective ionic strength,  $\mu_{\text{E}}$ . Investigations of activity coefficients in accordance with Harned's rule are normally carried out at a constant total ionic strength,  $\mu_{\text{T}}$ . Therefore, these activity coefficients would be expected to conform to equation (19) only when the difference between  $\mu_{\text{E}}$  and  $\mu_{\text{T}}$  is slight, that is, when the extent of association is slight.

A comparison was made between calculations of  $f_{\text{NaCl}}$ , based on the results of sodium sulfate association, and measured values of  $f_{\text{NaCl}}$  which obey Harned's rule. Equation (16) was used to calculate  $\log f_{\text{NaCl}}$  in NaCl-Na<sub>2</sub>SO<sub>4</sub> solutions of various compositions. Values for  $\log \gamma_{\text{NaCl}}$  were obtained from Robinson and Stokes (1959);  $K_{\text{NaSO}_4}^*$  was calculated from equation (12); and  $[\text{SO}_4^{2-}]$  was obtained by solving the following quadratic equation, which is derived in

Appendix VI:

$$K_{\text{NaSO}_4}^* [\text{SO}_4^{2-}]^2 + \{1 + \{T(\text{Na}) - T(\text{SO}_4)\} K_{\text{NaSO}_4}^*\} [\text{SO}_4^{2-}] - T(\text{SO}_4) = 0.$$

(21)

The results are shown in Figure 6. The circles represent the values of  $\log f_{\text{NaCl}}$  when  $\mu_{\text{E}}$  is kept constant at 0.70. They show a linear variation of  $\log f_{\text{NaCl}}$  with  $m_{\text{Na}_2\text{SO}_4}$  over the entire range of compositions. The triangles are for a constant  $\mu_{\text{T}} = 0.70$ . A constant total ionic strength is the condition under which studies related to Harned's rule are normally performed. For  $\mu_{\text{T}} = 0.70$  the effective ionic strength varies non-linearly from 0.70 at  $m_{\text{Na}_2\text{SO}_4} = 0$  to 0.5 at  $m_{\text{Na}_2\text{SO}_4} = 0.233$ . This variation of  $\mu_{\text{E}}$  and the non-linear change of  $\log \gamma_{\text{NaCl}}$  with ionic strength (Robinson and Stokes, 1959) cause the values of  $\log f_{\text{NaCl}}$  at  $\mu_{\text{T}} = 0.70$  to be non-linear and slightly more positive than those at  $\mu_{\text{E}} = 0.70$ . The shaded region in Figure 6 is the range of values measured by Gieskes (1966) at  $\mu_{\text{T}} = 0.70$ . There is good agreement between his measured values and those calculated from the results of this work. Gieskes did not detect any non-linearity in  $\log f_{\text{NaCl}}$  at  $\mu_{\text{T}} = 0.70$ , because the non-linearity was within the precision of his measurements over the range of compositions that he used.

The agreement between Gieskes values of  $\log f_{\text{NaCl}}$  and those calculated from the results of this work demonstrates the consistency of these two sets of measurements. Gieskes data were obtained with a glass sodium-sensitive electrode and a silver-silver chloride electrode without a salt-bridge. The agreement between these two sets of results indicates that the assumptions required in this work

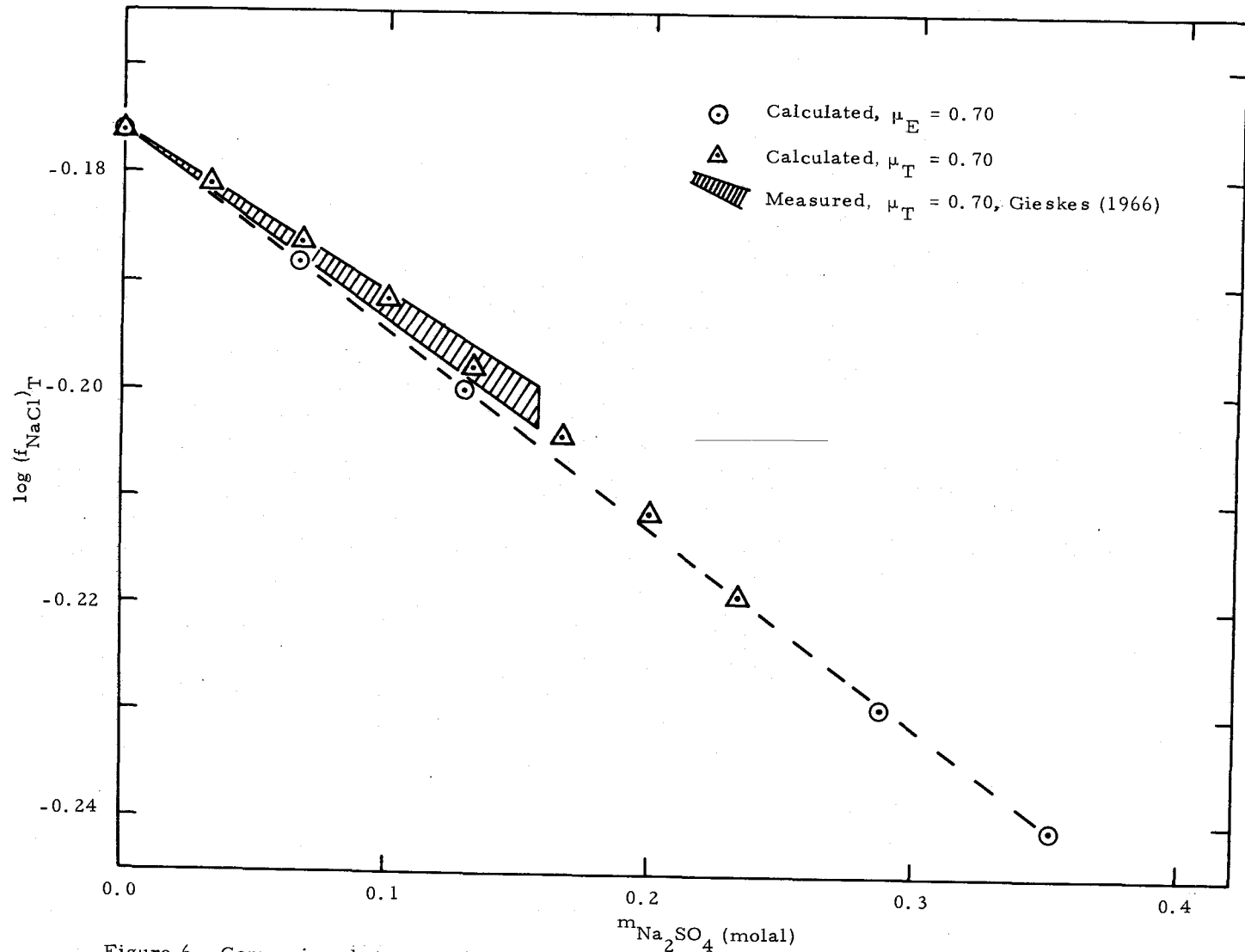


Figure 6. Comparison between values of  $\log (f_{\text{NaCl}})_T$  calculated from the results of this work and measured by Gieskes (1966).

(i. e. neglecting differences in the liquid junction potential in equation (5), estimating the ratio of the activity coefficients in equation (6) by the mean-salt-method, and neglecting chloride ion-pairs) did not introduce significant errors into the final results. This agreement, however, does not prove that ion association is the only significant type of specific interaction in NaCl-Na<sub>2</sub>SO<sub>4</sub> solutions. A more refined specific interaction model might also be able to account for the behavior of activity coefficients in these solutions.

Effect of Temperature on  $K^*$  NaSO<sub>4</sub>

$K^*$  NaSO<sub>4</sub> was determined at 2.40° C by the procedure described previously (page 15). The compositions of the test, the initial standard, and the titrant solutions are shown in Table 6; the reason for the choice of the composition of the test solution will become evident in the next section (page 42).

Table 6. Molal composition of solutions for determining  $K^*$  NaSO<sub>4</sub> at 2.40° C.

	Test Solution	Initial Standard Solution	Titrant Solution
NaCl	0.1099	0.4949	4.905
Na <sub>2</sub> SO <sub>4</sub>	0.2865	-----	-----

The ratio of activity coefficients in equation (6) was calculated at 2.4° C using equation (11) and the data of Harned and Owen (1958).

The results of three determinations of  $K_{\text{NaSO}_4}^*$  are shown in Table 7. The data of Tables 4 and 7 show that there is more association between sodium and sulfate ions at 2.4° C than at 25.0° C.

The experimental data are listed in Appendix III.

The temperature dependence of  $K_{\text{NaSO}_4}^*$  may be used to calculate the change in enthalpy which occurs upon formation of  $\text{NaSO}_4^-$  ion-pairs at  $\mu_E = 0.61$ . It is possible to designate the  $\text{NaCl-Na}_2\text{SO}_4$  medium of  $\mu_E = 0.61$  as the standard state, in which case the expression for the change in enthalpy follows directly from the standard thermodynamic relationships. Alternatively, the more usual standard state of the solutes at infinite dilution may be used along with expressions for activity coefficients to relate the change in  $K_{\text{NaSO}_4}^*$  with temperature to the change in enthalpy. Either choice of standard states will yield the same expression for the change in enthalpy. The standard state at infinite dilution will be used in the following expressions, so that changes in thermodynamic properties upon changes in the composition or in ionic strength of the solutions may be described by activity coefficients rather than by shifts in the standard state.

It follows from equation (4) that:

$$\ln K_{\text{NaSO}_4}^* = \ln K_{\text{NaSO}_4} + \ln \gamma_{\text{Na}} + \ln \gamma_{\text{SO}_4} - \ln \gamma_{\text{NaSO}_4} \quad (22)$$

Table 7. The molalities of species, the effective ionic strength, and the values of  $K^*_{\text{NaSO}_4}$  determined in the test solution at 2.4° C.

	$[\text{Na}^+]_{\text{test}}$	$[\text{NaSO}_4^-]_{\text{test}}$	$[\text{SO}_4^{2-}]_{\text{test}}$	$\mu_{\text{F}}(\text{test})$	$K^*_{\text{NaSO}_4}$
	0.5022	0.1807	0.1058	0.608	3.40
	0.5010	0.1819	0.1046	0.606	3.47
	0.5024	0.1805	0.1060	0.608	3.39
Average	0.5019	0.1810	0.1055	0.607	3.42
Ave. dev.	$\pm 0.0006$	$\pm 0.0006$	$\pm 0.0006$	$\pm 0.001$	$\pm 0.03$

The variation of  $\ln K_{\text{NaSO}_4}^*$  with temperature is given by:

$$\frac{\partial \ln K_{\text{NaSO}_4}^*}{\partial T} = \frac{\partial \ln K_{\text{NaSO}_4}}{\partial T} + \frac{\partial \ln \gamma_{\text{Na}}}{\partial T} + \frac{\partial \ln \gamma_{\text{SO}_4}}{\partial T} - \frac{\partial \ln \gamma_{\text{NaSO}_4}}{\partial T}. \quad (23)$$

At constant pressure,

$$\frac{\partial \ln K_{\text{NaSO}_4}}{\partial T} = \frac{\Delta \bar{H}_{\text{NaSO}_4}^{\circ}}{RT^2}, \quad (24)$$

where  $\Delta \bar{H}_{\text{NaSO}_4}^{\circ} = \bar{H}_{\text{NaSO}_4}^{\circ} - \bar{H}_{\text{Na}}^{\circ} - \bar{H}_{\text{SO}_4}^{\circ}$ .  $\bar{H}^{\circ}$  is the partial molal enthalpy of each species at infinite dilution. At constant pressure and composition,

$$\frac{\partial \ln \gamma}{\partial T} = - \frac{\bar{H}^* - \bar{H}^{\circ}}{RT^2}, \quad (25)$$

where  $\bar{H}^*$  is the partial molal enthalpy of the solute in the solution.

In the following development, the stipulation of constant composition for partial molal quantities will be approximated by the restraint of constant effective ionic strength. If partial molal quantities are treated in terms of the association model, it may be hypothesized that these quantities, for individual species, depend on the effective ionic strength rather than on the composition. There is insufficient data to test this hypothesis at the present time.

Substitution of equations (24) and (25) into equation (23) yields:

$$\frac{\partial \ln K_{\text{NaSO}_4}^*}{\partial T} = \frac{\bar{H}_{\text{NaSO}_4}^* - \bar{H}_{\text{Na}}^* - \bar{H}_{\text{SO}_4}^*}{RT^2} = \frac{\Delta \bar{H}_{\text{NaSO}_4}^*}{RT^2} \quad (26)$$

$\Delta \bar{H}_{\text{NaSO}_4}^*$  is the change in enthalpy which occurs on formation of one mole of  $\text{NaSO}_4^-$  ion-pairs in the  $\text{NaCl-Na}_2\text{SO}_4$  solution at a particular effective ionic strength. This enthalpy change is the net effect of the changes which occur due to (i) the electrostatic interaction between  $\text{Na}^+$  and  $\text{SO}_4^{2-}$ , (ii) the change in solute-solute interactions, and (iii) the change in solute-solvent interactions upon formation of  $\text{NaSO}_4^-$  ion-pairs in this particular ionic medium.

Assuming that  $\Delta \bar{H}_{\text{NaSO}_4}^*$  is constant between absolute temperatures  $T_1$  and  $T_2$  and then integrating equation (26) yields:

$$\Delta \bar{H}_{\text{NaSO}_4}^* = \frac{R \{ \ln(K_{\text{NaSO}_4}^*)_2 - \ln(K_{\text{NaSO}_4}^*)_1 \}}{\left\{ \frac{1}{T_1} - \frac{1}{T_2} \right\}} \quad (27)$$

$\Delta \bar{H}_{\text{NaSO}_4}^*$  was calculated for the  $\text{NaCl-Na}_2\text{SO}_4$  medium of  $\mu_E = 0.61$  using  $K_{\text{NaSO}_4}^* = 3.42 \pm 0.03$  at  $275.6^\circ \text{K}$  (Table 7) and using  $K_{\text{NaSO}_4}^* = 2.01 \pm 0.02$  at  $298.2^\circ \text{K}$  (equation 12). The result was  $\Delta \bar{H}_{\text{NaSO}_4}^* = -3.84 \pm 0.14 \text{ kcal mole}^{-1}$ . There have been no other determinations of the temperature dependence of sodium sulfate association, neither at infinite dilution nor in any other ionic medium. Thus, there is little comparative basis for an interpretation of the



preceding value for  $\Delta\bar{H}^*_{\text{NaSO}_4}$ . Some general observations regarding the significance of enthalpy changes at 0.67 effective ionic strength will be made in a subsequent section (page 72).

The value of  $\Delta\bar{H}^*_{\text{NaSO}_4}$  was used to obtain values of  $K^*_{\text{NaSO}_4}$  at temperatures other than 25° C and 2.4° C from the following expression:

$$\ln(K^*_{\text{NaSO}_4})_{T^\circ\text{K}} = \frac{\Delta\bar{H}^*_{\text{NaSO}_4}}{R} \left\{ \frac{1}{298.2} - \frac{1}{T^\circ\text{K}} \right\} + \ln 2.01. \quad (28)$$

The resulting values of  $K^*_{\text{NaSO}_4}$  at selected temperature are listed in Table 8. At 25° C the variation of  $K^*_{\text{NaSO}_4}$  with  $\mu_E$  was within the experimental precision over the range of  $\mu_E = 0.60$  to 0.75 (Figure 5), which is the normal range of seawater. Assuming that the ionic strength dependence of  $K^*_{\text{NaSO}_4}$  does not change greatly with temperature, the values in Table 8 may be applied over this limited range of effective ionic strengths.

Table 8. Variation of  $K^*_{\text{NaSO}_4}$  with temperature at  $\mu_E = 0.61$ .

$T^\circ\text{C}$	0	5	10	15	20	25
$K^*_{\text{NaSO}_4}$	3.64	3.21	2.84	2.52	2.25	2.01

Effect of Pressure on  $K^*$  NaSO<sub>4</sub>

The pressure dependence of  $K^*$  NaSO<sub>4</sub> was determined at 1.5° C using potentiometric techniques similar to those of Disteché (1959) and of Culberson and Pytkowicz (1968). The measurements were made with a pressure-compensated sodium ion sensitive glass electrode and a Ag;AgCl reference electrode without a salt bridge (Figure 7). The e. m. f. of this electrode couple at pressure P is given by:

$$E_p = -S \log \frac{\{(a_{Na})_P (a_{Cl})_P\}_e}{\{(a_{Na})_P (a_{Cl})_P\}_i} + E(\text{asym})_P. \quad (29)$$

S is the slope of the electrode couple e. m. f. response to the logarithm of activity. The e and i subscripts refer to the solutions placed outside the glass electrode shell and to the solution placed inside the glass electrode shell. E(asym) is the asymmetry potential of the electrode couple, which is determined by placing identical solutions inside and outside the glass shell.

The change in e. m. f. in going from 1 to P atm is,

$$E_p - E_1 = -S \log A + \Delta E(\text{asym}), \quad (30)$$

where  $\Delta E(\text{asym}) = E(\text{asym})_P - E(\text{asym})_1$ . A is the quotient of activities, which may be written as:

$$A = \frac{(\gamma_{Na})_{P,e} [Na^+]_{P,e} (\gamma_{Cl})_{P,e} [Cl^-]_{P,e} (\gamma_{Na})_{1,i} [Na^+]_{1,i} (\gamma_{Cl})_{1,i} [Cl^-]_{1,i}}{(\gamma_{Na})_{P,i} [Na^+]_{P,i} (\gamma_{Cl})_{P,i} [Cl^-]_{P,i} (\gamma_{Na})_{1,e} [Na^+]_{1,e} (\gamma_{Cl})_{1,e} [Cl^-]_{1,e}}. \quad (31)$$

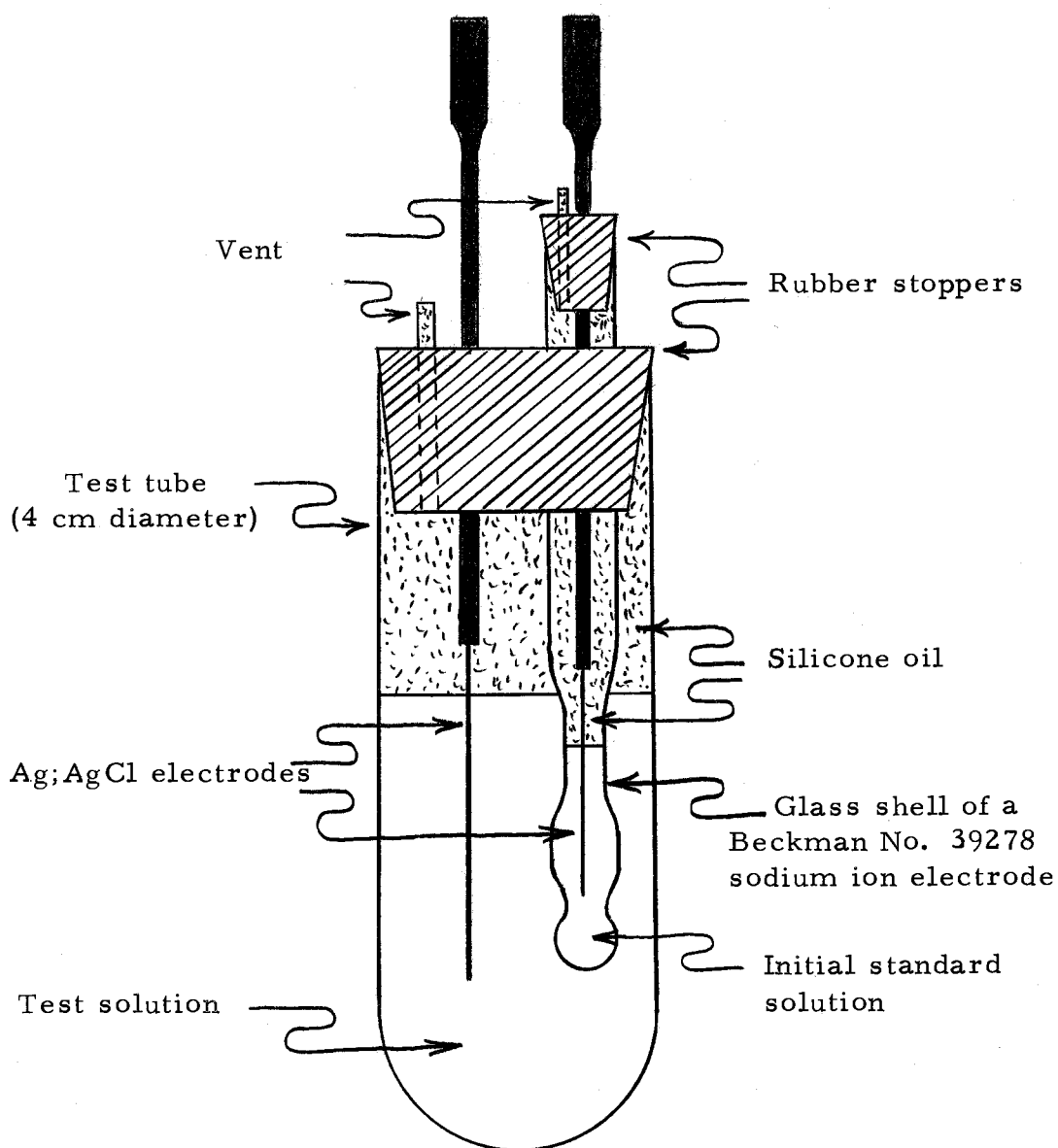


Figure 7. Illustration of the pressure-compensated sodium ion sensitive electrode cell.

Equation (30) is valid only if  $S$  does not change significantly with pressure. The variation of  $S$  with pressure will be examined below (Table 9).

The initial standard solution (Table 6) was placed inside the glass electrode shell, and the test solution (Table 6) was placed outside the shell. The composition of the test solution was selected so that it contained sufficient chloride ions to assure that the Ag;AgCl electrode would give a stable potential, and so that there was sufficient ion-pairing to yield precise values of  $K^*_{\text{NaSO}_4}$  (Figure 4). Assuming that there are no ion-pairs formed by  $\text{Na}^+$  and  $\text{Cl}^-$  in the initial standard or in the test solutions, it follows that:

$$[\text{Cl}^-]_{1,i} = [\text{Cl}^-]_{P,i}; [\text{Cl}^-]_{1,e} = [\text{Cl}^-]_{P,e}; \text{ and } [\text{Na}^+]_{1,i} = [\text{Na}^+]_{P,i}$$

Therefore, since  $\gamma_{\text{NaCl}} = f_{\text{NaCl}}$  equation (31) may be written:

$$A = \frac{(f_{\text{NaCl}})_{P,e}^2 (f_{\text{NaCl}})_{1,i}^2 [\text{Na}^+]_{P,e}}{(f_{\text{NaCl}})_{1,e}^2 (f_{\text{NaCl}})_{P,i}^2 [\text{Na}^+]_{1,e}}, \quad (32)$$

where  $f_{\text{NaCl}}$  is the mean ionic activity coefficient of sodium chloride.

If the effect of pressure on  $f_{\text{NaCl}}$  is assumed to be the same in the test and initial standard solutions, then:

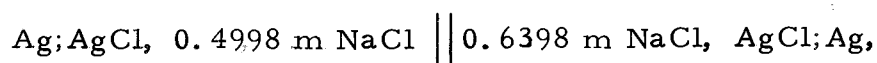
$$\frac{(f_{\text{NaCl}})_{P,e}}{(f_{\text{NaCl}})_{1,e}} = \frac{(f_{\text{NaCl}})_{P,i}}{(f_{\text{NaCl}})_{1,i}}. \quad (33)$$

Thus, from equation (32) and (33) equation (30) may be written:

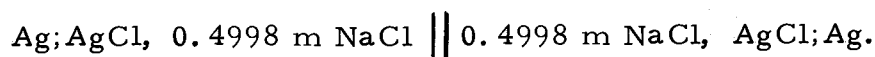
$$E_p - E_1 = -S \log \frac{[\text{Na}^+]_{P, e}}{[\text{Na}^+]_{1, e}} + \Delta E(\text{asym}). \quad (34)$$

Disteche (1959) and Culberson (1968) found that  $S$  was independent of pressure for glass pH electrodes at pressures up to 1000 atm.

Table 9 shows that the change in the e. m. f.,  $E(S)_p$ , of the cell:



is not significantly different from that of  $E(\text{asym})$  of the cell:



This observation indicates that  $S$  does not change significantly with pressure for the sodium-sensitive electrode couple up to 1000 atm.

It also substantiates the assumption that the pressure dependence of

$\gamma_{\text{NaCl}}$  is the same at  $\mu_E = 0.50$  as it is at  $\mu_E = 0.64$ .

Table 9. The e. m. f. data for examining the effect of pressure on  $S$ .

E. M. F.	1 atm	500 atm	1000 atm
$E(\text{asym})$	+26.32 mv	+26.92 mv	+27.55 mv
$\Delta E(\text{asym})$	0.00	+0.60	+1.22
$E(S)_p$	+15.58	+16.22	+16.84
$\Delta E(S)_p$	0.00	+0.64	+1.26

The effect of pressure on  $K^*_{NaSO_4}$  was determined in the following manner. The initial standard solution was placed inside and outside the glass shell, and the e. m. f. of the electrode couple was measured at 1, 500, and 1000 atm. These measurements yielded  $\Delta E(\text{asym})$ , because  $[Na^+]_{P, e} = [Na^+]_{1, e}$ . The external compartment was then filled with the test solution and the e. m. f. was again measured at 1, 500, and 1000 atm. The ratio of unassociated sodium ion molalities at P and 1 atm was calculated from equation (34). Then,  $[Na^+]_P$  was calculated using this ratio and the value of  $[Na^+]_1$ , which was obtained at 1.5° C from equations (21), (28) and (35):

$$[Na^+] = T(Na) - \{T(SO_4) - [SO_4^{2-}]\}. \quad (35)$$

Equations (7) and (8) were used to obtain  $[NaSO_4^-]_P$  and  $[SO_4^{2-}]_P$  which then permitted the calculation of  $K^*_{NaSO_4}$  at pressure P.

One additional factor had to be considered because it was found that an increase in pressure caused a breakdown in ion-pairs, which resulted in an increase in the effective ionic strength from 0.61 to 0.64 to 0.68 in going from 1 to 500 to 1000 atm. Thus, part of the observed change in e. m. f. with pressure,  $E_P - E_1$ , was due to the change in  $f_{NaCl}$  caused by the increase in the effective ionic strength. The value of  $f_{NaCl}$  at the effective ionic strength  $\mu_E(P, e)$ , of the test solution in the external compartment at pressure P will be

denoted by  $(f_{\text{NaCl}})_{\mu_{\text{E}}(\text{P}, \text{e})}$ . The effect of  $\mu_{\text{E}}(\text{P}, \text{e})$  on  $f_{\text{NaCl}}$  may be accounted for by modifying equation (34) to be:

$$\log \frac{[\text{Na}^+]_{\text{P}, \text{e}}}{[\text{Na}^+]_{\text{l}, \text{e}}} = - \frac{E_{\text{P}} - E_{\text{l}} - \Delta E(\text{asym})}{S} - \log \frac{(f_{\text{NaCl}})_{\mu_{\text{E}}(\text{P}, \text{e})}^2}{(f_{\text{NaCl}})_{\mu_{\text{E}}(\text{l}, \text{e})}^2} \quad (36)$$

The last term in equation (36) accounts for the change in e. m. f. due to the change in the effective ionic strength of the test solution in the external compartment as the pressure changes from 1 to P atm.

Values of  $f_{\text{NaCl}}$  at the appropriate ionic strength, at 1.5° C, and at 1 atm pressure were obtained from Harned and Owen (1958). In practice it was necessary to determine the correction factor by successive approximations, because  $\mu_{\text{E}}(\text{P}, \text{e})$  depended on  $[\text{Na}^+]_{\text{P}, \text{e}}$ . Three iterations were required to obtain a constant value for the correction factor.

The e. m. f. response, S, of the pressure-compensated sodium ion electrode was determined from e. m. f. measurements relative to a calomel electrode with a saturated KCl salt bridge. The measurements were made in 0.4802 m and in 0.5811 m sodium chloride solutions at 1.5° C at atmospheric pressure. Neglecting any differences in the liquid junction and asymmetry potentials in these two solutions, the value of S is given by:

$$-S = \frac{E_2 - E_1}{\log \frac{\gamma_{\text{Na}}(2) m_{\text{Na}}(2)}{\gamma_{\text{Na}}(1) m_{\text{Na}}(1)}} \quad (37)$$

where the 1 and 2 refer to the two sodium chloride solutions. The values of  $\gamma_{\text{Na}}$  were obtained at 1.5° C from equation (11). The value of  $S = 53.5$  mv per decade change in activity was obtained, which is 98% of the theoretical value,  $(RT \ln 10)/F$ .

The results of three measurements of  $K^*_{\text{NaSO}_4}$  at 500 and 1000 atm are listed in Table 10. The experimental data from which these results were derived are presented in Appendix III.

Table 10. Values of  $K^*_{\text{NaSO}_4}$  at 1.5° C and various pressures obtained from three sets of measurements.

	Pressure (atm)		
	1	500	1000
--		2.51	1.71
--		2.42	1.70
--		2.55	1.81
Average	3.50*	2.49	1.74
Average deviation	$\pm 0.03^{**}$	$\pm 0.05$	$\pm 0.05$

\* Obtained from equation (28)

\*\* Based on the results of Table 7.



The change in volume which occurs upon formation of  $\text{NaSO}_4^-$  ion-pairs at  $\mu_{\text{F}} = 0.61$  may be calculated from the data of Table 10. From equation (22) the pressure dependence of  $K_{\text{NaSO}_4}^*$  may be written as:

$$\frac{\partial \ln K_{\text{NaSO}_4}^*}{\partial P} = \frac{\partial \ln K_{\text{NaSO}_4}}{\partial P} + \frac{\partial \ln \gamma_{\text{Na}}}{\partial P} + \frac{\partial \ln \gamma_{\text{SO}_4}}{\partial P} - \frac{\partial \ln \gamma_{\text{NaSO}_4}}{\partial P}. \quad (38)$$

At constant temperature,

$$\frac{\partial \ln K_{\text{NaSO}_4}}{\partial P} = \frac{-\Delta \bar{V}_{\text{NaSO}_4}^{\circ}}{RT}, \quad (39)$$

where  $\Delta \bar{V}_{\text{NaSO}_4}^{\circ} = \bar{V}_{\text{NaSO}_4}^{\circ} - \bar{V}_{\text{Na}}^{\circ} - \bar{V}_{\text{SO}_4}^{\circ}$ .  $\bar{V}^{\circ}$  is the partial molal volume of each species at the standard state of infinite dilution. The pressure dependence of the activity coefficients in equation (38) at constant temperature and at constant composition is given by:

$$\frac{\partial \ln \gamma}{\partial P} = \frac{\bar{V}^* - \bar{V}^{\circ}}{RT}, \quad (40)$$

where  $\bar{V}^*$  is the partial molal volume of the solute in the solution.

Substituting equations (39) and (40) into equation (38) yields:

$$\frac{\partial \ln K_{\text{NaSO}_4}^*}{\partial P} = \frac{-\left\{ \bar{V}_{\text{NaSO}_4}^* - \bar{V}_{\text{Na}}^* - \bar{V}_{\text{SO}_4}^* \right\} - \Delta \bar{V}_{\text{NaSO}_4}^*}{RT} \quad (41)$$

The variation of  $\ln K_{\text{NaSO}_4}^*$  with pressure was linear within the precision of the data (Figure 8). Thus, no variation in  $\Delta \bar{V}_{\text{NaSO}_4}^*$

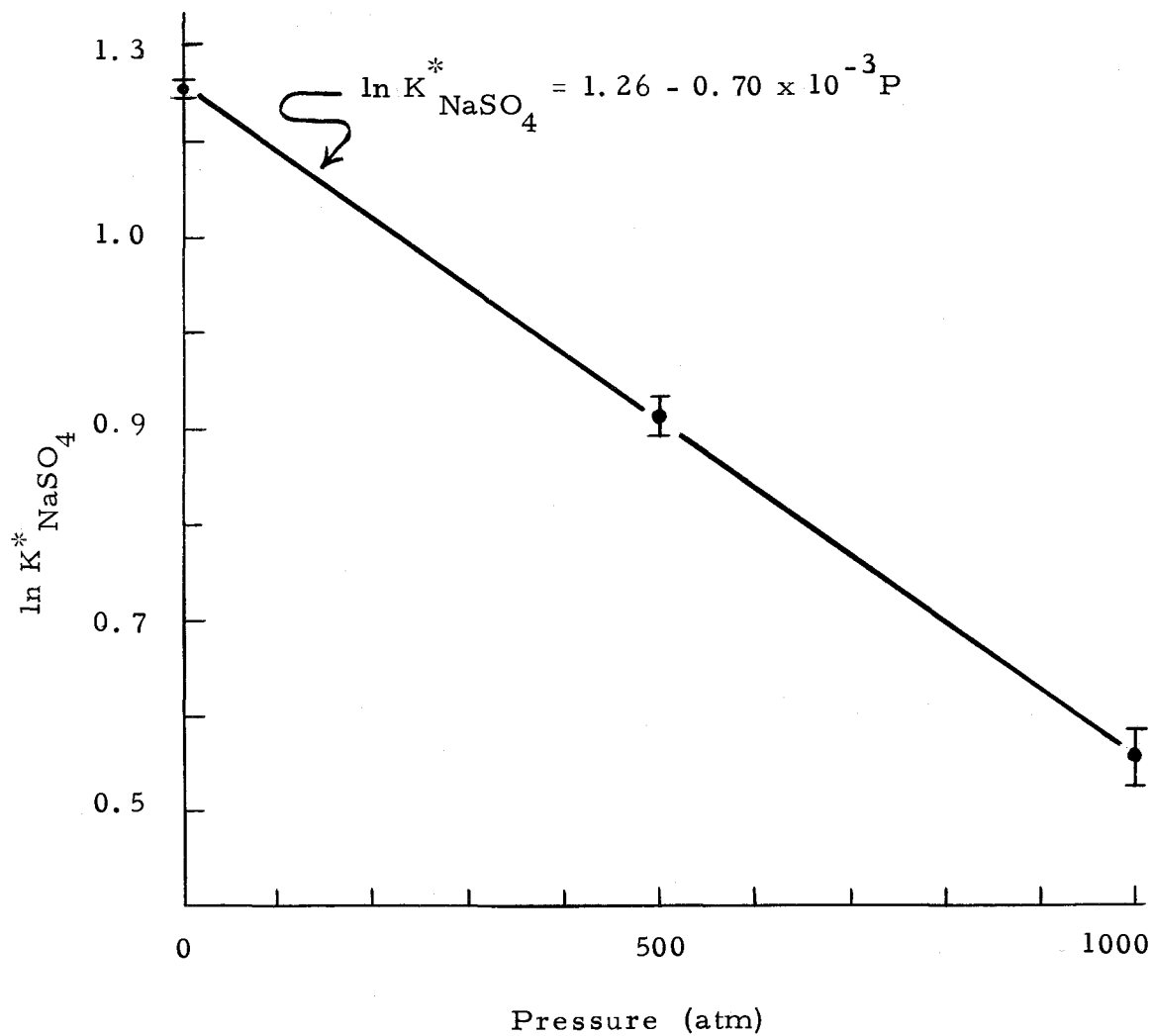


Figure 8. Variation of  $\ln K^* \text{NaSO}_4$  with pressure at  $1.5^\circ \text{C}$  and  $\mu_{\text{F}} = 0.61$ . The vertical bars represent the average deviation from the mean (Table 10).

could be detected between 1 and 1000 atm. The solid line through the data points in Figure 8 was obtained by a least squares regression; it yields a value of  $\Delta\bar{V}_{\text{NaSO}_4}^* = 15.8 \text{ cm}^3 \text{ mole}^{-1}$ . Therefore, the formation of one mole of  $\text{NaSO}_4^-$  ion-pairs in the  $\text{NaCl-Na}_2\text{SO}_4$  medium of  $\mu_E = 0.61$  at  $1.5^\circ \text{C}$  results in an increase in volume of  $15.8 \text{ cm}^3$ . It is possible that much of this increase in volume is due to the release of electrostricted water molecules upon formation of the  $\text{NaSO}_4^-$  ion-pair.

## IV. MAGNESIUM SULFATE ASSOCIATION

Determination of  $K_{MgSO_4}^*$ 

The association of  $Mg^{2+}$  and  $SO_4^{2-}$  to form  $MgSO_4^0$ , represented by the equilibrium  $Mg^{2+} + SO_4^{2-} \rightleftharpoons MgSO_4^0$ , was characterized by the stoichiometric association constant  $K_{MgSO_4}^*$ :

$$K_{MgSO_4}^* = \frac{[MgSO_4^0]}{[Mg^{2+}][SO_4^{2-}]} = \frac{\gamma_{Mg} \gamma_{SO_4}}{\gamma_{MgSO_4}} K_{MgSO_4} \quad (42)$$

In accordance with the previous notation, the brackets denote molalities,  $\gamma$  represents the activity coefficients of each species, and  $K_{MgSO_4}$  is the thermodynamic association constant defined in terms of activities.

$K_{MgSO_4}^*$  was determined potentiometrically, using a magnesium-sensitive electrode (Orion No. 92-32 Divalent Cation Electrode) and a calomel reference electrode with a saturated KCl salt bridge (Beckman No. 39170). The composition of the test solution in which  $K_{MgSO_4}^*$  was determined was based on the composition of seawater of 34.8‰ salinity (Kester et al., 1967). The procedure used required that all the ion-pairs involving magnesium and sulfate ions that occurred in the test solution be known. Therefore, in order to eliminate ion-pairs of  $Mg^{2+}$  and  $SO_4^{2-}$  which could not be accounted for, NaCl was substituted for  $NaHCO_3$ , KCl, KBr, and NaF;  $CaCl_2$  and  $SrCl_2$  were replaced by  $MgCl_2$ ; and  $H_3BO_3$  was omitted. The

composition of the test solution, initial standard solution, and titrant solution are shown in Table 11.

The substitution of salts does not affect the value of  $K^*_{\text{MgSO}_4}$ , if the basic assumption regarding free activity coefficients is correct. It is evident from equation (42) that at constant temperature and pressure if the activity coefficients depend only on the effective ionic strength,  $K^*_{\text{MgSO}_4}$  will also depend only on the effective ionic strength and not on the composition of the test solution. This assumption was verified for the stoichiometric association constant of  $\text{NaSO}_4^-$  ion-pairs in  $\text{NaCl-Na}_2\text{SO}_4$  solutions (Figure 4). The validity of this assumption was tested further in this section of the work. The value of  $K^*_{\text{NaSO}_4}$  obtained in an  $\text{Na}_2\text{SO}_4$  solution at  $\mu_E = 0.670$  was used to calculate  $[\text{Na}^+]$ , the molality of unassociated sodium ions, in an  $\text{NaCl-MgCl}_2\text{-Na}_2\text{SO}_4$  solution of the same effective ionic strength. A sodium-sensitive electrode (Corning No. 476210) was then used to measure  $[\text{Na}^+]$  in the  $\text{NaCl-MgCl}_2\text{-Na}_2\text{SO}_4$  solution. The measured and calculated values of  $[\text{Na}^+]$  agreed to within 0.1%. This is within the reproducibility of the sodium-sensitive electrode couple. Therefore, the value of  $K^*_{\text{NaSO}_4}$  determined in  $\text{Na}_2\text{SO}_4$  solutions adequately accounted for the amount of unassociated sodium ions in an  $\text{NaCl-MgCl}_2\text{-Na}_2\text{SO}_4$  solution of the same effective ionic strength. The ultimate test of the assumptions made by applying the value of  $K^*_{\text{MgSO}_4}$  determined in an  $\text{NaCl-MgCl}_2\text{-Na}_2\text{SO}_4$  solution to seawater

Table 11. Molalities of the constituents in the solutions used to determine  $K^*_{MgSO_4}$  at 25° C and  $\mu_E = 0.67$ .

Solution	Cl <sup>-</sup>	Na <sup>+</sup>	Mg <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup>
Test	0.5660	0.4928	0.06567	0.02908
Initial Standard	0.5829	0.4829	0.04999	-----
Titrant	2.535	0.4829	1.026	-----

will be the comparison of the calculated and the measured molality of unassociated magnesium ions in seawater (page 85).

All solutions were prepared using reagent grade salts. The NaCl and Na<sub>2</sub>SO<sub>4</sub> were weighed after drying at 120° C and 0.5 atm pressure for several hours. A one molal solution of MgCl<sub>2</sub>·6H<sub>2</sub>O was prepared and was standardized by titrating the chloride with silver nitrate using the Mohr method (Blaedel and Meloche, 1957). This solution was used in the preparation of the solutions shown in Table 11. All solutions were prepared by weight so that their molalities would be accurate to within 0.1%.

The concentration of unassociated magnesium ions in the test solution, [Mg<sup>2+</sup>], was determined by first measuring E(test), the e. m. f. of the magnesium-sensitive electrode couple in 100 ml of the test solution. The electrode couple was then inserted into 100 ml of the initial standard solution and the e. m. f. was measured while the magnesium chloride concentration was increased by adding 0.1 ml increments of the titrant solution. The titration was continued until the e. m. f. of the electrode couple in the standard solution, E(std), bracketed the value obtained in the test solution.

The dependence of the e. m. f. on the activity of magnesium ions,  $a_{\text{Mg}}$ , and on the activity of sodium ions,  $a_{\text{Na}}$ , at 25° C in solutions similar to the standard solution was found to be:

$$E = -80.06 - 28.92 \log \{a_{\text{Mg}} + 0.043(a_{\text{Na}})^2\} \text{ mv.} \quad (43)$$

Therefore, assuming that the liquid junction and asymmetry potentials of the electrode couple were the same in the standard and in the test solutions,  $a_{\text{Mg}}(\text{std})$  was equal to  $a_{\text{Mg}}(\text{test})$  when  $E(\text{std}) = E(\text{test})$ , provided that  $a_{\text{Na}}(\text{std}) = a_{\text{Na}}(\text{test})$ . The latter condition was verified by measuring the e. m. f. of a sodium-sensitive electrode and of the calomel reference electrode in the two solutions. These two e. m. f. values were the same within 0.02 mv, which was the reproducibility of this pair of electrodes. The assumed invariance of the liquid junction and asymmetry potentials could not be verified. It probably was a reasonable assumption because the compositions and the ionic strengths of the test and standard solutions were similar when  $E(\text{std}) = E(\text{test})$ . The effective ionic strengths of the standard and test solutions differed by 1.5% when  $E(\text{std}) = E(\text{test})$ . This difference in ionic strength resulted in less than a 0.1% difference in the activity coefficients of the unassociated magnesium ions in the two solutions, according to calculations based on the mean-salt-method. Thus, when  $E(\text{std}) = E(\text{test})$ ,

$$[\text{Mg}^{2+}]_{\text{std}} = [\text{Mg}^{2+}]_{\text{test}}, \quad (44)$$

is valid to within 0.1%. Assuming that there was no complexing between  $\text{Mg}^{2+}$  and  $\text{Cl}^-$  in these solutions,  $[\text{Mg}^{2+}]_{\text{std}}$ , and hence  $[\text{Mg}^{2+}]_{\text{test}}$ , were equal to the known molality of  $\text{MgCl}_2$  in the



standard solution.

The calculation of  $K^*_{MgSO_4}$  required the following expressions, which apply to the test solution:

$$\text{Total magnesium} \equiv T(\text{Mg}) = [\text{Mg}^{2+}] + [\text{MgSO}_4^0], \quad (45)$$

$$\text{Total sulfate} \equiv T(\text{SO}_4) = [\text{SO}_4^{2-}] + [\text{MgSO}_4^0] + [\text{NaSO}_4^-], \quad (46)$$

$$\text{Total sodium} \equiv T(\text{Na}) = [\text{Na}^+] + [\text{NaSO}_4^-]; \quad (47)$$

and

$$K^*_{NaSO_4} = \frac{[\text{NaSO}_4^-]}{[\text{Na}^+][\text{SO}_4^{2-}]}. \quad (48)$$

The following equation may be derived from equations (42), (45), (46), (47), and (48) (Appendix VI):

$$a(K^*_{MgSO_4})^2 + b(K^*_{MgSO_4}) + c = 0, \quad (49)$$

with  $a = [\text{Mg}^{2+}]^2 \{T(\text{SO}_4) - [\text{MgSO}_4^0]\}$ ,

$$b = [\text{Mg}^{2+}][\text{MgSO}_4^0] \{K^*_{NaSO_4} \{T(\text{SO}_4) - T(\text{Na}) - [\text{MgSO}_4^0]\} - 1\},$$

and  $c = -[\text{MgSO}_4^0]^2 K^*_{NaSO_4}$ .

The coefficients  $a$ ,  $b$ , and  $c$  in equation (49) were calculated by the use of equations (44) and (45), the composition of the test solution (Table 11), and the value of  $K^*_{NaSO_4} = 2.02$  obtained previously (equation 12, with  $\mu_E = 0.67$ ),  $K^*_{MgSO_4}$  was then calculated as the following root of equation (49);  $K^*_{MgSO_4} = (-b + \sqrt{b^2 - 4ac})/2a$ .

Results of Magnesium Sulfate Association  
at 25° C and  $\mu_F = 0.67$

The values of  $K_{MgSO_4}^*$  and the molalities of the chemical species in the NaCl-MgCl<sub>2</sub>-Na<sub>2</sub>SO<sub>4</sub> test solution at 25.00 ± 0.03° C are given in Table 12. The average value of  $K_{MgSO_4}^*$  is slightly larger than the value of 8.8, which may be computed from the estimates of Garrels and Thompson (1962). The experimental data from which  $K_{MgSO_4}^*$  was obtained are given in Appendix IV. There have been no other values of  $K_{MgSO_4}^*$  reported near  $\mu_E = 0.67$ .

Variation of  $K_{MgSO_4}^*$  with Ionic Strength at 25° C

$K_{MgSO_4}^*$  was determined in a series of solutions of various effective ionic strengths with the intent of extrapolating the results to infinite dilution to obtain a value of  $K_{MgSO_4}$  at 25° C. The test solution contained MgCl<sub>2</sub> and MgSO<sub>4</sub> in various proportions; MgCl<sub>2</sub> was the only solute in the standard solution and in the titrant solution. The results are shown in Table 13.

Table 12. Results obtained from six measurements at 25° C in the test solution: 0.4347 m NaCl, 0.06567 m MgCl<sub>2</sub>, and 0.02908 m Na<sub>2</sub>SO<sub>4</sub>. (Brackets indicate molal concentration.)

Experiment	[Mg <sup>2+</sup> ]	[MgSO <sub>4</sub> <sup>0</sup> ]	[SO <sub>4</sub> <sup>2-</sup> ]	[NaSO <sub>4</sub> <sup>-</sup> ]	[Na <sup>+</sup> ]	K <sub>MgSO<sub>4</sub></sub> *
1	0.05861	0.00706	0.01114	0.01089	0.4819	10.8
2	0.05976	0.00691	0.01121	0.01094	0.4819	10.5
3	0.05905	0.00662	0.01135	0.01108	0.4817	9.9
4	0.05878	0.00689	0.01123	0.01099	0.4818	10.4
5	0.05893	0.00674	0.01130	0.01103	0.4818	10.1
6	0.05927	0.00640	0.01147	0.01122	0.4816	9.4
Average	0.05890	0.00677	0.01128	0.01102	0.4818	10.2
Standard deviation	±0.00024	±0.00024	±0.00013	±0.00012	±0.0001	±0.5

Table 13. The variation of  $K_{\text{MgSO}_4}^*$  with  $\mu_{\text{F}}$  at 25° C.

$\mu_{\text{F}}$	$K_{\text{MgSO}_4}^*$	Test Solution $m_{\text{MgCl}_2}$	$m_{\text{MgSO}_4}$
0.0118	110	0.00300	0.00100
0.0371	67	0.01000	0.00319
0.0623	51	0.00984	0.01582
0.0820	60	0.02491	0.00478
0.228	24	0.06870	0.01504

These data were extrapolated to infinite dilution using the same procedure as that used by Marshall (1967). The value of  $\log K_{\text{MgSO}_4}^*$  was plotted as a function of  $\sqrt{\mu_{\text{F}}}/(1 + \sqrt{\mu_{\text{F}}})$  (Figure 9). The solid line in Figure 9 was obtained by a least squares linear regression which yielded:

$$\log K_{\text{MgSO}_4}^* = 2.32 - 2.84 \frac{\sqrt{\mu_{\text{F}}}}{1 + \sqrt{\mu_{\text{F}}}} \quad (50)$$

The value at infinite dilution of  $\log K_{\text{MgSO}_4}^* = 2.32$  may be compared with those reported by various workers using different types of measurements (Table 14). The value obtained in this work is in good agreement with those from other sources. This agreement indicates that the techniques used to determine  $K_{\text{MgSO}_4}^*$  yield values which are consistent with other methods, at least when extrapolated to infinite dilution. The observation that different techniques produce

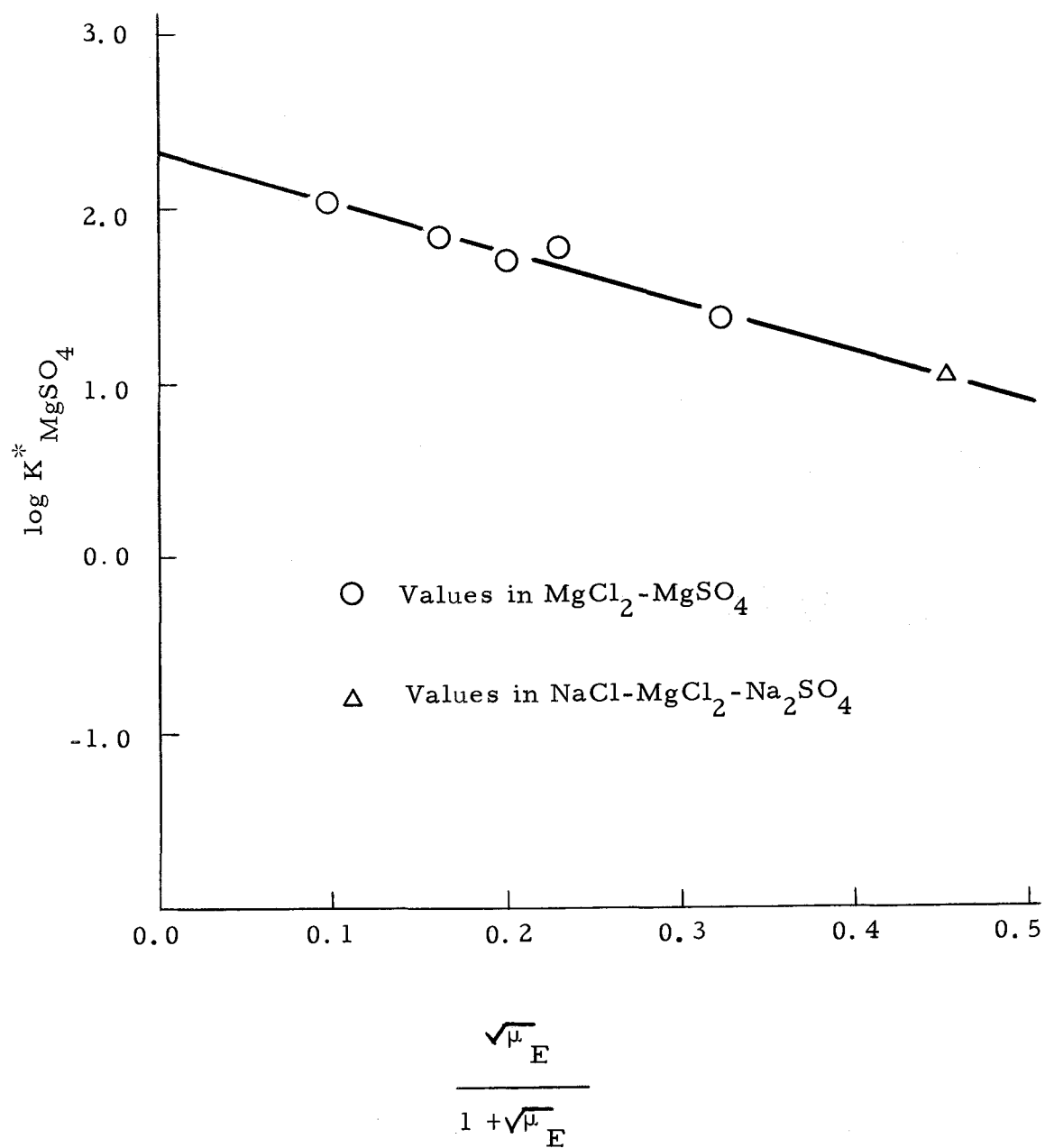


Figure 9. Extrapolation of  $\log K^*_{\text{MgSO}_4}$  to infinite dilution.

Table 14. Values of  $\log K_{\text{MgSO}_4}$  reported by various workers at 25° C.

$\log K_{\text{MgSO}_4}$	Method	Source
2.27	Conductivity	Jones and Monk (1952)
2.36	E. M. F. : Hydrogen ion electrode	Jones and Monk (1952)
2.25	E. M. F. : Hydrogen ion electrode	Nair and Nancollas (1958)
2.29	Ultrasonic absorption	Eigen and Tamm (1962)
2.22	Ultrasonic absorption	Atkinson and Petrucci (1966)
2.40	Solubility of $\text{CaSO}_4$	Marshall (1967)
2.32	E. M. F. : Magnesium ion electrode	This work

similar values for the association constant, provides support for the explanation of specific interactions between magnesium and sulfate ions in terms of ion association.

The value of  $\log K_{\text{MgSO}_4}^*$  based on measurements in the NaCl-MgCl<sub>2</sub>-Na<sub>2</sub>SO<sub>4</sub> test solution (Tables 11 and 12) was also plotted in Figure 9 to demonstrate the consistency between measurements obtained in different media. These results show that the value of  $K_{\text{MgSO}_4}^*$  obtained in an NaCl-MgCl<sub>2</sub>-Na<sub>2</sub>SO<sub>4</sub> solution agrees with the values of  $K_{\text{MgSO}_4}^*$  determined in MgCl<sub>2</sub>-MgSO<sub>4</sub> solutions of various relative compositions. This observation supports the contention that  $K_{\text{MgSO}_4}^*$  may be considered to be a function of  $\mu_E$  and not a function of composition.

To facilitate the calculation of association between magnesium and sulfate ions in solutions of various effective ionic strengths,  $K_{\text{MgSO}_4}^*$ , computed from equation (50), was plotted as a function of  $\mu_E$  (Figure 10).

#### Effect of Temperature on $K_{\text{MgSO}_4}^*$

$K_{\text{MgSO}_4}^*$  was determined at  $1.70 \pm 0.03^\circ \text{C}$  using the same procedure as that described at  $25^\circ \text{C}$ . The compositions of the solutions used are shown in Table 15, and the results of three determinations are listed in Table 16. The experimental data are given in Appendix IV.

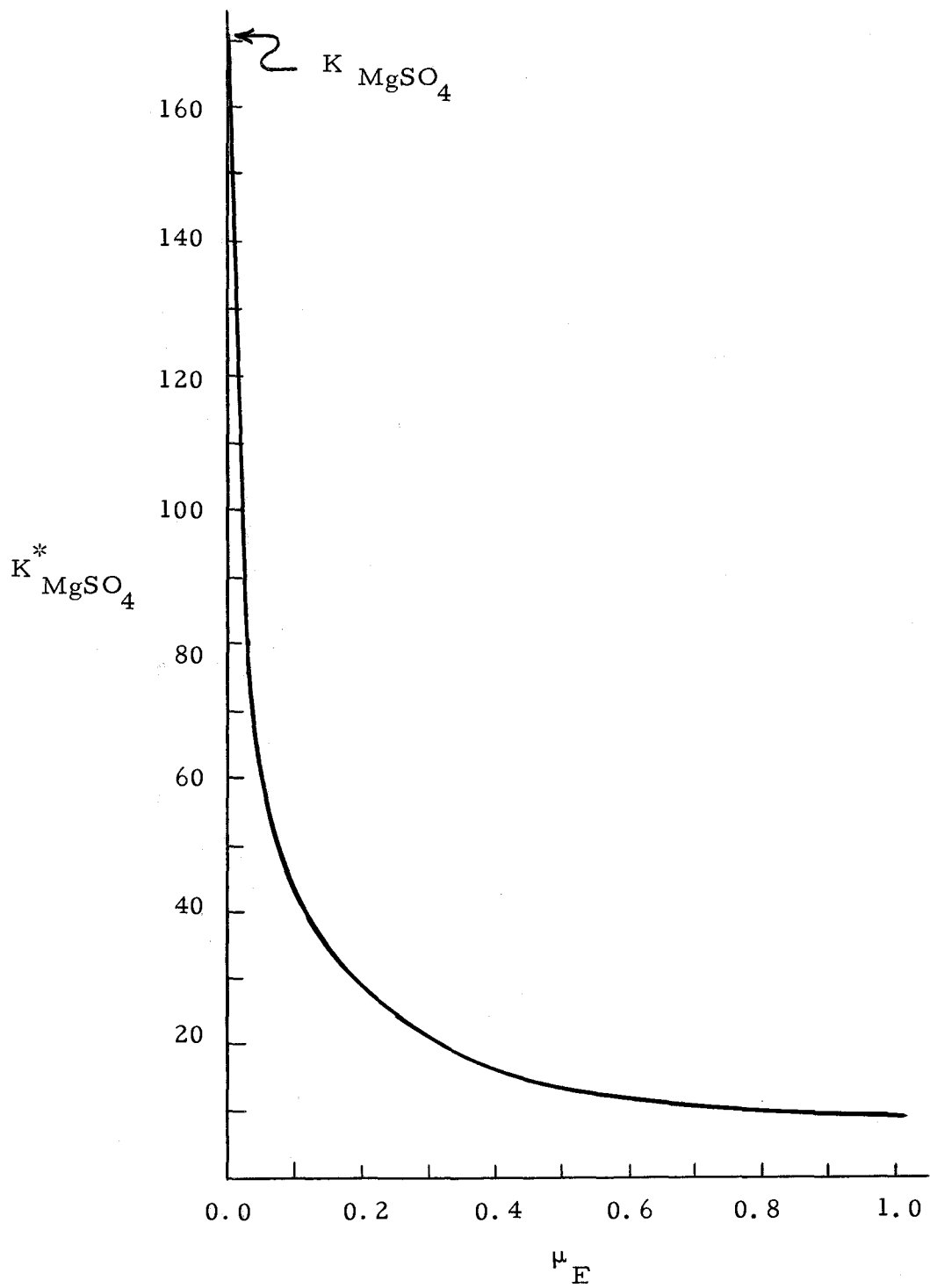


Figure 10. Variation of  $K^* \text{MgSO}_4$  with  $\mu_E$ .



The composition of the test solution was only slightly different from that used at 25<sup>o</sup> C (Table 11). However, the effective ionic strength was 0.66 instead of 0.67 due to the greater extent of sodium sulfate and magnesium sulfate association at 1.7<sup>o</sup> C than at 25.0<sup>o</sup> C. This slight change in  $\mu_E$  with temperature does not produce a significant change in  $K^*_{MgSO_4}$  (Figure 10). Thus, for practical purposes the effective ionic strength of the test solution may be considered to be constant over the range of 1.7 to 25.0<sup>o</sup> C.

Table 15. Molalities of the constituents in the solutions used to determine  $K^*_{MgSO_4}$  at 1.7<sup>o</sup> C.

Solution	Cl <sup>-</sup>	Na <sup>+</sup>	Mg <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup>
Test	0.5656	0.4925	0.06563	0.02906
Initial Standard	0.5804	0.4826	0.04888	-----
Titrant	1.4728	0.4826	0.4951	-----

The variation of  $K^*_{MgSO_4}$  with temperature may be used to obtain a value for the change in enthalpy,  $\Delta\bar{H}^*_{MgSO_4}$ , which occurs upon formation of  $MgSO_4^0$  ion-pairs at  $\mu_E = 0.67$  in the NaCl-MgCl<sub>2</sub>-Na<sub>2</sub>SO<sub>4</sub> test solution. Following an argument similar to the one used in deriving equation (27) yields:

Table 16. Results of the determination of  $K^*_{MgSO_4}$  at  $1.7^\circ C$ .

	$[Na^+]$	$[NaSO_4^-]$	$[Mg^{2+}]$	$[MgSO_4^0]$	$[SO_4^{2-}]$	$K^*_{MgSO_4}$
	0.4788	0.01366	0.05839	0.00724	0.00816	15.2
	0.4789	0.01355	0.05827	0.00736	0.00815	15.5
	0.4787	0.01378	0.05866	0.00697	0.00831	14.3
Average	0.04788	0.01366	0.05844	0.00718	0.00821	15.0
Average Deviation	$\pm 0.0001$	$\pm 0.00008$	$\pm 0.00015$	$\pm 0.00015$	$\pm 0.00007$	$\pm 0.5$

$$\Delta H^*_{\text{MgSO}_4} = \frac{R \{ \ln(K^*_{\text{MgSO}_4})_2 - \ln(K^*_{\text{MgSO}_4})_1 \}}{\left\{ \frac{1}{T_1} - \frac{1}{T_2} \right\}} \quad (51)$$

As before, it was assumed that  $\Delta \bar{H}^*_{\text{MgSO}_4}$  was constant between absolute temperatures  $T_1$  and  $T_2$ . The data in Tables 12 and 16 yield a value of  $\Delta \bar{H}^*_{\text{MgSO}_4} = -2.7 \pm 0.5 \text{ kcal mole}^{-1}$ .

The values of  $K^*_{\text{MgSO}_4}$  at various temperatures may be calculated from:

$$\ln(K^*_{\text{MgSO}_4})_{T^\circ\text{K}} = \frac{\Delta \bar{H}^*_{\text{MgSO}_4}}{R} \left\{ \frac{1}{298.2} - \frac{1}{T^\circ\text{K}} \right\} + \ln 10.2 \quad (52)$$

A few selected values of  $K^*_{\text{MgSO}_4}$  at various temperatures are given in Table 17.

Table 17. Values of  $K^*_{\text{MgSO}_4}$  calculated from equation (52) at various temperatures and at  $\mu_E = 0.67$ .

$T^\circ\text{C}$	0	5	10	15	20	25
$K^*_{\text{MgSO}_4}$	15.5	14.2	13.0	12.0	11.0	10.2

Attempts were made to determine the effect of pressure on  $K^*_{\text{MgSO}_4}$  by a procedure similar to the one used for  $K^*_{\text{NaSO}_4}$  (page 40). However, the values of  $\Delta E(\text{asym})$  at 500 and 1000 atm varied by 1.6 mv and 4.9 mv in replicate determinations. This lack of

reproducibility of the magnesium-sensitive electrode couple at various pressures prevented even a qualitative estimate of the effect of pressure on  $K^* \text{MgSO}_4$ . The two most likely causes of the erratic electrode behavior at high pressure are the possible degeneration of the internal Ag;AgCl electrode and the possible alteration of the liquid ion exchanger at high pressure.

## V. CALCIUM SULFATE ASSOCIATION

To obtain  $K^*_{CaSO_4}$ , the concentration of unassociated calcium ions in the test solution,  $[Ca^{2+}]_{test}$ , was determined by first measuring  $E(test)$ , the e. m. f. in 100 ml of the test solution. The electrodes were then transferred to 100 ml of the initial standard solution (Table 18), and the e. m. f.,  $E(std)$ , was measured while the calcium concentration was increased by adding 0.1 ml increments of the titrant solution (Table 18). The e. m. f. depends on the activities of sodium, magnesium, and hydrogen ions as well as on the activity of calcium ions (Rechnitz and Lin 1968). The e. m. f. due to cations other than calcium was the same in the standard and in the test solutions. This condition was verified by observing that the e. m. f. of sodium, magnesium, and hydrogen ion sensitive electrode couples were the same in the two solutions. Thus, when  $E(std) = E(test)$ , the activity of calcium ions was the same in the two solutions, that is,

$$[Ca^{2+}]_{test} = \frac{\gamma_{Ca}(std)}{\gamma_{Ca}(test)} [Ca^{2+}]_{std} \quad (53)$$

In this equation it was assumed that the liquid junction and asymmetry potentials of the electrode couple were the same in the two solutions. This assumption is reasonable because the effective ionic strengths and the compositions of the two solutions were similar.

The ratio of the activity coefficients in equation (53) was 1.003 as estimated by the mean-salt-method. The  $[Ca^{2+}]_{std}$  is equal to the molality of  $CaCl_2$  in the standard solution when  $E(std) = E(test)$ , provided there are no ion-pairs formed by calcium ions and chloride ions in the standard solution.

Table 18. Composition of solutions used to determine  $K^* CaSO_4$ .

Ion	Molality of Solutions		
	Test	Initial Standard	Titrant
$Na^+$	0.4922	0.4813	0.4817
$Mg^{2+}$	0.05498	0.04943	0.04953
$Ca^{2+}$	0.01073	0.00932	0.1588
$Cl^-$	0.5655	0.5988	0.8984
$SO_4^{2-}$	0.02905	-----	-----

Having obtained  $[Ca^{2+}]_{test}$  from equation (53), it was then possible to calculate  $K^* CaSO_4$  as the positive root of the following equation, which is derived in Appendix VI.

$$a(K^* CaSO_4)^3 + b(K^* CaSO_4)^2 + c K^* CaSO_4 + d = 0, \quad (54)$$

$$\begin{aligned}
\text{with } a &= [\text{Ca}^{2+}]^3 \{T(\text{SO}_4) - [\text{CaSO}_4^0]\}, \\
b &= [\text{Ca}^{2+}]^2 [\text{CaSO}_4^0] \{K_{\text{MgSO}_4}^* \{T(\text{SO}_4) - T(\text{Mg}) - [\text{CaSO}_4^0]\} + \\
&\quad K_{\text{NaSO}_4}^* \{T(\text{SO}_4) - T(\text{Na}) - [\text{CaSO}_4^0]\} - 1\}, \\
c &= [\text{Ca}^{2+}] [\text{CaSO}_4^0]^2 \{K_{\text{NaSO}_4}^* K_{\text{MgSO}_4}^* \{T(\text{SO}_4) - T(\text{Na}) \\
&\quad - T(\text{Mg}) - [\text{CaSO}_4^0]\} - K_{\text{NaSO}_4}^* - K_{\text{MgSO}_4}^*\}, \\
\text{and } d &= [\text{CaSO}_4^0]^3 K_{\text{NaSO}_4}^* K_{\text{MgSO}_4}^*.
\end{aligned}$$

T(A) represents the total (unassociated plus ion-paired) molality of the generic ion A, and  $[\text{CaSO}_4^0] = T(\text{Ca}) - [\text{Ca}^{2+}]$ . All the molalities in equation (54) refer to the test solution. The previously determined values of  $K_{\text{NaSO}_4}^* = 2.02$  (equation 12) and  $K_{\text{MgSO}_4}^* = 10.2$  (Table 12) were used to calculate  $K_{\text{CaSO}_4}^*$  at 25° C and  $\mu_E = 0.67$ .

The results of six determinations of  $K_{\text{CaSO}_4}^*$  are listed in Table 19. The average value of  $K_{\text{CaSO}_4}^*$  is similar to the corresponding value for  $K_{\text{MgSO}_4}^*$  (Table 12), but it is significantly larger than the value of 6.1 which may be computed from the estimates of Garrels and Thompson (1962). The experimental data are listed in Appendix V.

Of the three cation-sensitive electrodes used in this work, the calcium ion electrode was the least reliable. At 25° C its e. m. f. relative to the calomel reference electrode in either the test or the standard solutions frequently varied by about 1 mv in six hours.

Under favorable conditions the reproducibility of  $\Delta E = E(\text{test}) - E(\text{std})$

Table 19. The results of six determinations of  $K_{CaSO_4}^*$  at  $25^\circ C$  and  $\mu_E = 0.67$ .

Run	$[Ca^{2+}]$	$[CaSO_4^0]$	$[SO_4^{2-}]$	$[Na^+]$	$[NaSO_4^-]$	$[Mg^{2+}]$	$[MgSO_4^0]$	$K_{CaSO_4}^*$
1	0.00965	0.00108	0.01130	0.4812	0.01098	0.04930	0.00568	9.9
2	0.00948	0.00125	0.01124	0.4813	0.01093	0.04932	0.00565	11.7
3	0.00954	0.00119	0.01126	0.4812	0.01094	0.04932	0.00566	11.1
4	0.00962	0.00111	0.01129	0.4812	0.01097	0.04930	0.00568	10.2
5	0.00954	0.00119	0.01126	0.4812	0.01094	0.04932	0.00566	11.1
6	0.00954	0.00119	0.01126	0.4812	0.01094	0.04932	0.00566	11.1
Average	0.00956	0.00117	0.01127	0.4812	0.01095	0.04931	0.00567	10.8
Standard Deviation	$\pm 0.00006$	$\pm 0.00006$	$\pm 0.00004$	$\pm 0.0000$	$\pm 0.00003$	$\pm 0.00001$	$\pm 0.00001$	$\pm 0.6$



was  $\pm 0.1$  mv. Measurements were also made with a Corning No. 476230 calcium ion electrode; this electrode was unsuitable for this study because it frequently gave values of  $\Delta E$  that varied by 0.5-1.2 mv. Attempts were made to determine the value of  $K_{CaSO_4}^*$  at low temperature, but they were unsuccessful due to the lack of reproducibility of the electrode couple potential. Measurements of  $K_{CaSO_4}^*$  at high pressure, similar to those of  $K_{NaSO_4}^*$  were not attempted due to the observations with the magnesium-sensitive electrode at high pressure (page 65).

## VI. THERMODYNAMIC PARAMETERS FOR SULFATE ION ASSOCIATION

Several thermodynamic parameters may be calculated from the results of this work. These parameters include the change in free energy at constant temperature and pressure,  $\Delta \bar{F}$ , and the changes in enthalpy,  $\Delta \bar{H}$ , in entropy,  $\Delta \bar{S}$ , and in volume,  $\Delta \bar{V}$ , which occur upon formation of the various sulfate ion-pairs. The change in free energy at the ionic strength of seawater, upon formation of  $\text{MSO}_4^{(\nu_+ - 2)}$  is given by:

$$\Delta \bar{F}_{\text{MSO}_4}^* = -RT \ln K_{\text{MSO}_4}^* \quad (55)$$

The expressions for  $\Delta \bar{H}^*$  and  $\Delta \bar{V}^*$  were presented previously in equations (27) and (41) (pages 38 and 47). The change in entropy is obtained from:

$$\Delta \bar{S}_{\text{MSO}_4}^* = \frac{\Delta \bar{H}_{\text{MSO}_4}^* - \Delta \bar{F}_{\text{MSO}_4}^*}{T} \quad (56)$$

These four thermodynamic parameters were computed from the results of this work (Table 20).

The significance of the parameters in Table 20 depends upon the validity of the association model for describing the ionic interactions in sulfate solutions at  $\mu_E = 0.67$ . A possible extension of this work would be to measure some of these parameters directly by calorimetry or densitometry. Such a series of measurements could provide additional support for the ion association model, or could show the

limitations of the model. The values of Table 20 may be useful in evaluating the feasibility of direct measurements.

Differences in the thermodynamics of ion association at  $\mu_F = 0.67$  and at infinite dilution may be seen by comparing the parameters in Table 20 with their corresponding values at infinite dilution (Table 21).

Table 20. Thermodynamic parameters for sulfate ion-pairs at  $\mu_F = 0.67$ .

	$\Delta \bar{F}^*_{\text{MSO}_4}$ 25° C kcal mole <sup>-1</sup>	$\Delta \bar{H}^*_{\text{MSO}_4}$ 2-25° C kcal mole <sup>-1</sup>	$\Delta \bar{S}^*_{\text{MSO}_4}$ 25° C cal deg <sup>-1</sup> mole <sup>-1</sup>	$\Delta \bar{V}^*_{\text{MSO}_4}$ 2° C cm <sup>3</sup> mole <sup>-1</sup>
NaSO <sub>4</sub> <sup>-</sup>	-0.42	-3.8	-11	+15.8
MgSO <sub>4</sub> <sup>o</sup>	-1.38	-2.7	-4	-----
CaSO <sub>4</sub> <sup>o</sup>	-1.41	-----	---	-----

Table 21. Thermodynamic parameters for sulfate ion-pairs at 25° C and at infinite dilution.

	$\Delta \bar{F}^*_{\text{MSO}_4}$ kcal mole <sup>-1</sup>	$\Delta \bar{H}^*_{\text{MSO}_4}$ kcal mole <sup>-1</sup>	$\Delta \bar{S}^*_{\text{MSO}_4}$ cal deg <sup>-1</sup> mole <sup>-1</sup>	$\Delta \bar{V}^*_{\text{MSO}_4}$ cm <sup>3</sup> mole <sup>-1</sup>
NaSO <sub>4</sub> <sup>-</sup>	-0.98 <sup>a</sup>	+1.1 <sup>b</sup>	---	-----
MgSO <sub>4</sub> <sup>o</sup>	-3.22 <sup>c</sup>	+4.55 <sup>c</sup>	+26.1 <sup>c</sup>	+7.7 <sup>d</sup>
CaSO <sub>4</sub> <sup>o</sup>	-3.15 <sup>c</sup>	+1.65 <sup>c</sup>	+16.1 <sup>c</sup>	-----

<sup>a</sup>Jenkins and Monk (1950)

<sup>c</sup>Nancollas (1966)

<sup>b</sup>Austin and Mair (1962)

<sup>d</sup>Fisher (1965)

It appears that the thermodynamic parameters for ion association depend significantly on the ionic strength (or the medium) to which they apply. The values of  $\Delta\bar{H}$  and  $\Delta\bar{S}$  in Tables 20 and 21 are particularly intriguing because the change in sign in going from infinite dilution to  $\mu_E = 0.67$  indicates a significant difference in the relative interactions of the unassociated ions and ion-pairs in the two media.

The value of  $\Delta\bar{H}$  may be interpreted as indicating the net number and strength of "bonds" which are broken and formed upon association (Nancollas, 1966). Thus, the positive values of  $\Delta\bar{H}_{\text{MSO}_4}^{\ominus}$  indicate that at infinite dilution more energy is required to break the "bonds" between the free ions and the water molecules than is gained upon formation of the "bonds" in the ion-pair and between the ion-pair and the water molecules. The negative values of  $\Delta\bar{H}_{\text{MSO}_4}^{\ominus*}$  indicate that energy is released when the ions are transferred from the environment of the unassociated ions at  $\mu_E = 0.67$  to that of the ion-pair. This could mean that, relative to the unassociated ions, the ion-pair interacts more strongly with its surroundings at  $\mu_E = 0.67$  than it does at infinite dilution, which might be the case if the ion-pair is polarizable. Alternatively, the unassociated ions may interact less with their surroundings at  $\mu_E = 0.67$ , relative to the ion-pair, than they do at infinite dilution. This second possibility would arise if the unassociated ions are less hydrated at  $\mu_E = 0.67$  than at infinite dilution, while the degree of hydration of the ion-pair does

not change as much between the two media.

The  $\Delta\bar{S}$  has been considered to be an indication of the change in the degree of randomness which occurs upon formation of the ion-pair (Nancollas, 1966). The positive values of  $\Delta\bar{S}_{\text{MSO}_4}^{\circ}$  indicate that the formation of ion-pairs at infinite dilution results in an increased disorder of the system. The union between two independent ions to form an ion-pair would cause a decrease in entropy, but at infinite dilution, this decrease in entropy is overshadowed by the decrease in hydration which occurs when the unassociated ions form the ion-pair. The negative values of  $\Delta\bar{S}_{\text{MSO}_4}^*$  suggest that the hydration of the unassociated ions may not be as strong of an ordering influence at  $\mu_{\text{E}} = 0.67$  as it is at infinite dilution. This interpretation is consistent with the second possibility mentioned in the examination of  $\Delta\bar{H}_{\text{MSO}_4}^*$ .

The values of  $\Delta\bar{V}_{\text{MSO}_4}$  in Tables 20 and 21 are insufficient to compare differences between infinite dilution and  $\mu_{\text{E}} = 0.67$ . However, Millero (1969) has shown that for the major ions in seawater there is an increase in volume when they are transferred from infinite dilution to seawater. This increase in volume is consistent with the interpretation of  $\Delta\bar{H}_{\text{MSO}_4}$  and  $\Delta\bar{S}_{\text{MSO}_4}$  that the unassociated ions are less hydrated at the ionic strength of seawater than at infinite dilution.

There is a great deal of freedom in constructing molecular models of ionic solutions from macroscopic observations. Such an

attempt for the ions in seawater is further obstructed by the sparsity of data and by the fact that the structure of water in the absence of the ions has not been established. Some of the inconsistencies which may be encountered when interpreting thermodynamic parameters by molecular models such as inner-sphere and outer-sphere complexes and such as "structure-makers and structure-breakers" have been pointed out by Sprio, Revesz, and Lee (1968) and by Holtzer and Emerson (1969).

In spite of these limitations, a simple model will be used to demonstrate that the stoichiometric association constants determined in this work can result from electrostatic interactions between ions. The cations,  $M^{z_1+}$ , and the anions,  $A^{z_2-}$ , will be considered to be point charges. The ion-pair,  $MA^{z_1+z_2}$ , will be treated as a conducting sphere with radius  $r$ . Fuoss (1958) has shown that for this model the energy of electrostatic interaction between the point charges in the ion-pair is given by:

$$U = \frac{|z_1 z_2| e_o^2}{r D (1 + \kappa r)} \quad (57)$$

the value of  $\kappa$  is (Kortüm, 1965):

$$\kappa = \left\{ \frac{8\pi e_o^2 N \mu}{1000 D k T} \right\}^{1/2}$$

where  $e_o = 4.802 \times 10^{-10}$  e. s. u., the electronic charge;

$N = 6.024 \times 10^{23}$ , Avogadro's number;

$\mu = 0.67$ , the ionic strength;

$D = 78.5$ , the dielectric constant of water;

$k = 1.380 \times 10^{-16}$  erg deg<sup>-1</sup>, Boltzmann's constant;

$T = 298^{\circ}$  K, the absolute temperature.

The volume of an ion-pair is  $v = 4/3 \pi r^3$ .

Let  $(M)_T$  and  $(A)_T$  be the total number of M and A ions in a volume  $V$  of the solution. The portion of this volume which is available for an anion to form an ion-pair is  $(M)_T v$ . Thus, the fraction of anions which form ion-pairs is:

$$\frac{n_{MA}}{(A)_T} = \frac{(M)_T v e^{U/kT}}{V} \quad (58)$$

The  $n$  is the number of species designated by the subscript in a volume  $V$ . The Boltzmann factor  $e^{U/kT}$  provides statistical weighting for the ion-pair volume segments due to the electrostatic interaction between the ions. The fraction of anions which are not ion-paired is simply related to the volume fraction which is available to these ions:

$$\frac{n_A}{(A)_T} = \frac{V - (M)_T v}{V} \quad (59)$$

Similarly, the fractions of cations which are paired and free are given by:

$$\frac{n_{MA}}{(M)_T} = \frac{(A)_T v e^{U/kT}}{V} \quad (60)$$

and

$$\frac{n_M}{(M)_T} = \frac{V - (A)_T v}{V} \quad (61)$$

The following expressions are obtained from either equations (58) or (60) and from equations (59) and (61):

$$n_{MA} = (M)_T (A)_T \frac{v e^{U/kT}}{V} \quad (62)$$

$$n_M = \frac{\{V - (A)_T v\} (M)_T}{V} \quad (63)$$

$$n_A = \frac{\{V - (M)_T v\} (A)_T}{V} \quad (64)$$

Thus, the molar association constants is:

$$K_{MA}^* = \frac{N V}{10^3} \frac{n_{MA}}{n_M n_A} = \frac{N v e^{U/kT} V^2}{10^3 \{V - (M)_T v\} \{V - (A)_T v\}} \quad (65)$$

where  $V$  and  $v$  are expressed in  $\text{cm}^3$ .

The numerical values used to calculate  $K_{\text{MSO}_4}^*$  are listed below equation (57) and in Table 22. The volume  $V$  was taken to be  $1 \text{ cm}^3$ .

The calculated stoichiometric association constants show that the measured constants can be adequately accounted for on the basis of electrostatic interactions.



Table 22. Comparison of the measured stoichiometric association constants with values calculated from an electrostatic model of ion-pairs.

	Ion			
	Na <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup>
Ionic radius (Å) <sup>a</sup>	0.95	0.65	0.99	2.05
Ions per cm <sup>3</sup> in seawater	2.95 x 10 <sup>20</sup>	3.31 x 10 <sup>19</sup>	6.63 x 10 <sup>18</sup>	1.75 x 10 <sup>19</sup>
K <sup>*</sup> <sub>M<sub>2</sub>SO<sub>4</sub></sub> (calculated) <sup>b</sup>	0.9	22	12	---
K <sup>*</sup> <sub>M<sub>2</sub>SO<sub>4</sub></sub> (measured) <sup>b</sup>	2.02	10.2	10.8	---

<sup>a</sup> Millero (1969).

<sup>b</sup> The difference between molar and molal constants is not significant.

## VII. MAJOR CHEMICAL SPECIES IN SEAWATER

The molalities of the chemical species in seawater may be calculated from stoichiometric association constants. The following expressions for the total molality of each constituent are based on the estimates of Garrels and Thompson (1962) which show the major chemical species in seawater:

$$T(\text{Na}) = [\text{Na}^+] + [\text{NaSO}_4^-] + [\text{NaHCO}_3^0] + [\text{NaCO}_3^-], \quad (66)$$

$$T(\text{Mg}) = [\text{Mg}^{2+}] + [\text{MgSO}_4^0] + [\text{MgHCO}_3^+] + [\text{MgCO}_3^0], \quad (67)$$

$$T(\text{Ca}) = [\text{Ca}^{2+}] + [\text{CaSO}_4^0] + [\text{CaHCO}_3^+] + [\text{CaCO}_3^0], \quad (68)$$

$$T(\text{K}) = [\text{K}^+] + [\text{KSO}_4^-], \quad (69)$$

$$T(\text{SO}_4) = [\text{SO}_4^{2-}] + [\text{NaSO}_4^-] + [\text{MgSO}_4^0] + [\text{CaSO}_4^0] + [\text{KSO}_4^-], \quad (70)$$

$$T(\text{HCO}_3) = [\text{HCO}_3^-] + [\text{NaHCO}_3^0] + [\text{MgHCO}_3^+] + [\text{CaHCO}_3^+], \quad (71)$$

$$T(\text{CO}_3) = [\text{CO}_3^{2-}] + [\text{NaCO}_3^-] + [\text{MgCO}_3^0] + [\text{CaCO}_3^0]. \quad (72)$$

The stoichiometric association constants for bicarbonate and carbonate ion-pairs may be defined in a manner similar to those for sulfate ion-pairs (equation 3):

$$K_{\text{MHCO}_3}^* = \frac{[\text{MHCO}_3^{(v+ -1)}]}{[\text{M}^{v+}] [\text{HCO}_3^-]} = \frac{\gamma_{\text{M}} \gamma_{\text{HCO}_3}}{\gamma_{\text{MHCO}_3}} K_{\text{MHCO}_3}; \quad (73)$$

$$K_{\text{MCO}_3}^* = \frac{[\text{MCO}_3^{(v+ -2)}]}{[\text{M}^{v+}] [\text{CO}_3^{2-}]} = \frac{\gamma_{\text{M}} \gamma_{\text{CO}_3}}{\gamma_{\text{MCO}_3}} K_{\text{MCO}_3}. \quad (74)$$

Equation (66) may, therefore, be written:

$$T(\text{Na}) = [\text{Na}^+] + K^*_{\text{NaSO}_4} [\text{Na}^+] [\text{SO}_4^{2-}] + K^*_{\text{NaHCO}_3} [\text{Na}^+] [\text{HCO}_3^-] + K^*_{\text{NaCO}_3} [\text{Na}^+] [\text{CO}_3^{2-}]. \quad (75)$$

Using equation (75) to obtain an expression for  $[\text{Na}^+]$  and using a similar procedure with equations (67) - (72) yields:

$$[\text{Na}^+] = \frac{T(\text{Na})}{1 + K^*_{\text{NaSO}_4} [\text{SO}_4^{2-}] + K^*_{\text{NaHCO}_3} [\text{HCO}_3^-] + K^*_{\text{NaCO}_3} [\text{CO}_3^{2-}]}, \quad (76)$$

$$[\text{Mg}^{2+}] = \frac{T(\text{Mg})}{1 + K^*_{\text{MgSO}_4} [\text{SO}_4^{2-}] + K^*_{\text{MgHCO}_3} [\text{HCO}_3^-] + K^*_{\text{MgCO}_3} [\text{CO}_3^{2-}]}, \quad (77)$$

$$[\text{Ca}^{2+}] = \frac{T(\text{Ca})}{1 + K^*_{\text{CaSO}_4} [\text{SO}_4^{2-}] + K^*_{\text{CaHCO}_3} [\text{HCO}_3^-] + K^*_{\text{CaCO}_3} [\text{CO}_3^{2-}]}, \quad (78)$$

$$[\text{K}^+] = \frac{T(\text{K})}{1 + K^*_{\text{KSO}_4} [\text{SO}_4^{2-}]}, \quad (79)$$

$$[\text{SO}_4^{2-}] = \frac{T(\text{SO}_4)}{1 + K^*_{\text{NaSO}_4} [\text{Na}^+] + K^*_{\text{MgSO}_4} [\text{Mg}^{2+}] + K^*_{\text{CaSO}_4} [\text{Ca}^{2+}] + K^*_{\text{KSO}_4} [\text{K}^+]}, \quad (80)$$

$$[\text{HCO}_3^-] = \frac{T(\text{HCO}_3)}{1 + K^*_{\text{NaHCO}_3} [\text{Na}^+] + K^*_{\text{MgHCO}_3} [\text{Mg}^{2+}] + K^*_{\text{CaHCO}_3} [\text{Ca}^{2+}]}, \quad (81)$$

$$[\text{CO}_3^{2-}] = \frac{T(\text{CO}_3)}{1 + K^*_{\text{NaCO}_3} [\text{Na}^+] + K^*_{\text{MgCO}_3} [\text{Mg}^{2+}] + K^*_{\text{CaCO}_3} [\text{Ca}^{2+}]}. \quad (82)$$

The stoichiometric association constants in equations (76) - (82) depend on the effective ionic strength, but not on the composition of the medium, according to the model used in this work. This condition was verified for  $K_{\text{NaSO}_4}^*$  in  $\text{Na}_2\text{SO}_4$ ,  $\text{NaCl-Na}_2\text{SO}_4$ , and  $\text{NaCl-MgCl}_2\text{-Na}_2\text{SO}_4$  solutions, and for  $K_{\text{MgSO}_4}^*$  in  $\text{MgCl}_2\text{-MgSO}_4$  and  $\text{NaCl-MgCl}_2\text{-Na}_2\text{SO}_4$  solutions. Thus, it is reasonable to expect that values of  $K_{\text{MSO}_4}^*$  determined in relatively simple electrolytic solutions may be used to calculate the major sulfate species in seawater. The stoichiometric association constants of bicarbonate, carbonate, and potassium ion-pairs have not been determined at the ionic strength of seawater. In order to calculate the major chemical species in seawater, the stoichiometric constants of these ion-pairs were estimated using the thermodynamic dissociation constants and the activity coefficients (Table 1, page 4) given by Garrels and Thompson (1962). The estimates of Garrels and Thompson for bicarbonate and carbonate ion-pairs were supported by the total activity coefficients measured by Berner (1965). The values of the stoichiometric association constants used in equations (76) - (82) are summarized in Table 23.

Table 23. The stoichiometric association constants used to calculate the major chemical species in seawater of 34.8‰ salinity at 25° C.

	$\text{SO}_4^{2-}$	$\text{HCO}_3^-$	$\text{CO}_3^{2-}$
$\text{Na}^+$	2.02 ± 0.03	0.26	4.16
$\text{Mg}^{2+}$	10.2 ± 0.5	5.22	160
$\text{Ca}^{2+}$	10.8 ± 0.7	5.10	78
$\text{K}^+$	1.03	---	---

The molalities of the chemical species in seawater were calculated in the following manner. Estimated values of the free anion concentrations were used in equations (76) through (79) to compute approximate free cation concentrations. These approximate values were then substituted into equations (80), (81), and (82) to obtain refined values of the free anion concentrations. Iterations within these two sets of equations were continued until successive free anion concentrations differed by less than  $1 \times 10^{-7}$  molal. The molality of each ion-pair was then calculated from the product of the free cation molality, the anion molality, and the stoichiometric association constant. The relative abundance of species in seawater at 25° C and 1 atm pressure was expressed as the percentage of each constituent which is present as free and as ion-paired species (Table 24). The uncertainties were determined by varying the

Table 24. Ionic species in 34.8‰ salinity seawater at 25° C calculated from the stoichiometric association constants.

Ion	Total molality	% Free	% MSO <sub>4</sub>	% MHCO <sub>3</sub>	%MCO <sub>3</sub>
Ca <sup>2+</sup>	0.01062	88.5±0.5	10.8±0.5	0.6	0.07
Mg <sup>2+</sup>	0.05485	89.0±0.3	10.3±0.3	0.6	0.13
Na <sup>+</sup>	0.4823	97.7±0.1	2.2±0.1	0.03	----
K <sup>+</sup>	0.01020	98.8±0.1	1.2±0.1	----	----

Ion	Total Molality	% Free	% CaA	% MgA	% NaA	% KA
SO <sub>4</sub> <sup>2-</sup>	0.02909	39.0±0.6	4.0±0.2	19.4±0.6	37.2±0.2	0.4
HCO <sub>3</sub> <sup>-</sup>	0.00186	70.0±0.1	3.3±0.1	17.8±0.1	8.6±0.1	---
CO <sub>3</sub> <sup>2-</sup>	0.00011	9.1	6.4	67.3	17.3	---

experimentally determined association constants by one standard deviation.

In order to test the validity of the distribution of species in seawater which was calculated from the stoichiometric association constants listed in Table 23, the cation-sensitive electrodes were used to measure the percentage of free sodium, magnesium, and calcium ions in seawater collected from 2000 m approximately 165 miles off Oregon. These measurements were made by the titration procedures described previously to measure the free cation molality in the test solutions. The average of three measurements, and the average deviation from the mean, are presented in Table 25 along with values reported by other workers.

A comparison of the calculated and the measured percentages of free cations based on this work shows fairly good agreement. The difference between the measured and the calculated free magnesium and free calcium is about two to three times the uncertainty of each value. While this difference could be attributed to the experimental uncertainties in the values, the measured free molality was lower than the calculated value in both cases. This may suggest that the stoichiometric association constants in Table 23 do not completely account for the magnesium and calcium species in seawater. The possible significance of this difference can be better evaluated when the stoichiometric association constants for

Table 25. The percentage of each cation which is unassociated in seawater at 25° C and 1 atm pressure.

Source	Free Na <sup>+</sup>	Free Mg <sup>2+</sup>	Free Ca <sup>2+</sup>
Garrels and Thompson (1962)	99	87	91
Thompson (1966) <sup>a</sup>	--	88	--
Thompson and Ross (1966) <sup>a</sup>	--	--	82 <sub>+2</sub>
Fisher (1967)	--	90	--
Pytkowicz and Gates (1968)	--	90	--
This work: calculated	97.7 <sub>+0.1</sub>	89.0 <sub>+0.3</sub>	88.5 <sub>+0.5</sub>
This work: measured	97.7 <sub>+0.1</sub>	88.1 <sub>+0.3</sub>	86.3 <sub>+0.9</sub>

<sup>a</sup>Thompson (1966) and Thompson and Ross (1966) did not consider the density factor in computing the molarity of ions in seawater. Therefore, their reported values were 2% too high, and they have been revised accordingly in this table. (Thompson, 1968).



bicarbonate and carbonate ion-pairs have been determined.

The agreement between the various values of free magnesium in seawater (Table 25) is significant, because different sets of assumptions were used in obtaining these values. The measurements in this work were similar to those of Thompson (1966) using a magnesium-sensitive electrode, though there were some slight differences in technique. The value reported by Fisher (1967) was based on ultrasonic absorption, and it represents an independent approach to evaluating chemical species in seawater. The value of Pytkowicz and Gates (1968) was obtained from solubility equilibria of  $Mg(OH)_2$  (brucite) using potentiometric pH measurements. Thus, several different methods yielded nearly the same result for the percentage of free magnesium ions in seawater, which supports the interpretation of ionic interactions of magnesium ions in terms of ion-pairs.

The percentage of free calcium ions measured in this work and by Thompson and Ross (1966) were both determined with calcium-sensitive electrodes. Part of the difference between these two measured values may be due to the greater experimental uncertainty of these values as compared with those of sodium and magnesium ion measurements. The sensitivity of the calcium ion electrode to the activity of hydrogen, sodium, and magnesium ions may also introduce errors into the results unless the techniques used

adequately account for this response.

The variation in the chemical species with salinity in the oceans may be inferred from the ionic strength dependence of the stoichiometric association constants. It was shown for  $K^*_{\text{NaSO}_4}$  (Figure 5) and for  $K^*_{\text{MgSO}_4}$  (Figure 10) that the variations of these constants between  $\mu_E = 0.60$  and  $0.75$  was about the same as the precision of the results. Thus,  $K^*_{\text{NaSO}_4}$  and  $K^*_{\text{MgSO}_4}$  may be considered to be constant for salinities between  $30^\circ/\text{oo}$  and  $36^\circ/\text{oo}$ , which include most of the open ocean. Assuming that this relatively slight dependence on the effective ionic strength in the range of seawater is also characteristic of the other stoichiometric association constants, the results of Table 24 may be applied to seawater between  $30^\circ/\text{oo}$  and  $36^\circ/\text{oo}$  salinity.

The effect of temperature on the distribution of sulfate species is significant. It is not possible to calculate completely the species in seawater at low temperature, because the required constants or activity coefficients of the bicarbonate and carbonate species are not known. However, the distribution of sulfate species has been computed at  $25^\circ\text{C}$  and at  $2^\circ\text{C}$  in a synthetic seawater in which the effect of bicarbonate and carbonate ion-pairs has been neglected, in order to illustrate the magnitude of the effect of temperature on the distribution of sulfate species. The effect of temperature on  $K^*_{\text{CaSO}_4}$  was assumed to be the same as that on  $K^*_{\text{MgSO}_4}$ . The

results (Table 26) show that a decrease in temperature causes a significant increase in the amount of  $\text{NaSO}_4^-$  ion-pairs, with a corresponding decrease in the free sulfate concentration. The amount of  $\text{MgSO}_4^0$  ion-pairs is only slightly greater at  $2^\circ\text{C}$  than at  $25^\circ\text{C}$ , and the amount of  $\text{CaSO}_4^0$  ion-pairs does not change significantly provided that the temperature dependence of  $\text{K}^*\text{CaSO}_4$  is similar to that of  $\text{K}^*\text{MgSO}_4$ .

Table 26. The effect of temperature on the distribution of sulfate species in seawater, neglecting the effect of bicarbonate and carbonate ion-pairs.

$T^\circ\text{C}$	Percentage of Sulfate as Each Species			
	Free $\text{SO}_4^{2-}$	$\text{NaSO}_4^-$	$\text{MgSO}_4^0$	$\text{CaSO}_4^0$
25	39	38	19	4
2	28	47	21	4

The pressure dependence of  $\text{K}^*\text{NaSO}_4$  shows that the distribution of sulfate species varies markedly with pressure in the oceans. The increase in pressure with depth causes a break-down of the  $\text{NaSO}_4^-$  ion-pairs. A quantitative estimate of the distribution of sulfate species at high pressure is not possible, because the effect of pressure on  $\text{K}^*\text{MgSO}_4$  and  $\text{K}^*\text{CaSO}_4$  could not be obtained.

## VIII. SIGNIFICANCE OF ION ASSOCIATION IN SEAWATER

The usefulness of the association model employed in this work depends on its ability to account for the chemical properties of seawater. A few selected examples of the application of this model to seawater will be presented in this section.

It is necessary to distinguish between the total and the effective ionic strength of seawater because of ion association. The total ionic strength is defined in terms of the total concentrations of the ions, and the effective ionic strength is expressed in terms of the concentrations of the species present. For seawater of salinity 34.8 ‰, the total ionic strength is 0.718 (Lyman and Fleming, 1940), whereas based on Table 24 the effective ionic strength is 0.668. This difference in ionic strength is important when comparing activity coefficients in seawater with those obtained in simple electrolytic solutions such as NaCl (Kester and Pytkowicz, 1967).

Ion association provides an explanation for the large solubility of various minerals in seawater as compared with that in pure water. This will be illustrated by the case of  $\text{CaCO}_3$  (calcite). The relationship between the solubility product of  $\text{CaCO}_3$  in seawater and in pure water is given by:

$$K'_{\text{SP}} = \frac{T(\text{Ca})}{[\text{Ca}^{2+}]} \frac{T(\text{CO}_3)}{[\text{CO}_3^{2-}]} \frac{1}{\gamma_{\text{Ca}}} \frac{1}{\gamma_{\text{CO}_3}} K_{\text{SP}} \quad (83)$$

where  $K'_{SP} = T(\text{Ca}) T(\text{CO}_3)$  in seawater saturated with  $\text{CaCO}_3$ , and  $K_{SP} = a_{\text{Ca}} a_{\text{CO}_3}$ , which is the thermodynamic solubility product.

The symbol  $a$  refers to the activity of the ions designated by the subscript, and the other terms were defined earlier. The calculated speciation for seawater (Table 24) yields:

$$\frac{T(\text{Ca})}{[\text{Ca}^{2+}]} \frac{T(\text{CO}_3)}{[\text{CO}_3^{2-}]} = 12.4; \quad (84)$$

Garrels and Thompson estimated that  $\gamma_{\text{Ca}} = 0.28$  and  $\gamma_{\text{CO}_3} = 0.20$ .

Therefore, we obtain  $K'_{SP}/K_{SP} = 220$ . This ratio is in reasonable agreement with  $K'_{SP}/K_{SP} = 190$ , which is obtained from the measurements of Wattenberg (Harvey 1960). Thus, in seawater there is a 12 fold increase in the solubility product of  $\text{CaCO}_3$  due to ion association and about an 18 fold increase due to the effect of ionic strength on activity coefficients, relative to the solubility product in pure water.

There have been several determinations of total activity coefficients in seawater which are frequently different from those based on single-salt solutions. The association model presented in this work can account for most of the differences between these two sets of measured activity coefficients. The second column of Table 27 lists several values for activity coefficients which have been measured in seawater; these are total activity coefficients according to the

Table 27. Illustration of the ability of the association model to account for the difference between the activity coefficients measured in seawater and obtained from single salt solutions at  $\mu_E = 0.67$  and  $25^\circ \text{C}$ .

Constituent	Measured Total Activity Coefficient	Single-Salt Solution Activity Coefficient	Calculated Total Activity Coefficient
$\text{Na}^+$	$0.67^a$	0.71	0.69
$\text{Ca}^{2+}$	$0.20 \pm 0.01^b$ $0.22 \pm 0.02^b$	0.26	0.23
$\text{HCO}_3^-$	$0.55 \pm 0.01^b$ $0.56 \pm 0.01^b$	0.68	0.48
$\text{CO}_3^{2-}$	$0.021 \pm 0.004^b$ $0.024 \pm 0.004^b$	0.20	0.018
NaCl	$0.67 \pm 0.01^c$ $0.668 \pm 0.003^d$	0.67	0.66
$\text{Na}_2\text{SO}_4$	$0.38 \pm 0.03^e$	0.31	0.34

<sup>a</sup>Platford (1965a)

<sup>d</sup>Gieskes (1966)

<sup>b</sup>Berner (1965)

<sup>e</sup>Platford and Dafoe (1965)

<sup>c</sup>Platford (1965b)

terminology of the association model. The values listed for single-salt solutions are based on direct measurements in the case of the NaCl and Na<sub>2</sub>SO<sub>4</sub> electrolytes, and those reported for individual ions are based on direct measurements and the mean-salt-method (Garrels and Thompson, 1962). Since these latter activity coefficients are derived from solutions in which there is assumed to be no ion association, they correspond to free activity coefficients. The total activity coefficient of the generic ion A was calculated from:

$$f_A = \gamma_A \frac{[A]}{T(A)}, \quad (85)$$

and for the generic electrolyte M<sub>m</sub>N<sub>n</sub>:

$$f_{M_m N_n} = \left\{ \left( \frac{[M]}{T(M)} \right)^m \left( \frac{[N]}{T(N)} \right)^n \gamma_M^m \gamma_N^n \right\}^{1/(m+n)} \quad (86)$$

The ratio of the unassociated to total ion molalities were obtained from Table 24. The free activity coefficients,  $\gamma$ , were calculated using the mean-salt-method. The value of  $\gamma_{SO_4}$  was obtained from:

$$\gamma_{SO_4} = \frac{f_{Na_2SO_4}^3}{\gamma_{Na}^2} \left( \frac{T(Na)}{[Na^+]} \right)^2 \frac{T(SO_4)}{[SO_4^{2-}]} = 0.21, \quad (87)$$

where  $f_{Na_2SO_4}$  is the mean total activity coefficient in an Na<sub>2</sub>SO<sub>4</sub> solution of  $\mu_E = 0.67$ .  $K_{Na_2SO_4}^*$  was used to calculate  $\frac{T(Na)}{[Na^+]}$  and  $\frac{T(SO_4)}{[SO_4^{2-}]}$  in this Na<sub>2</sub>SO<sub>4</sub> solution, and  $\gamma_{Na}$  was calculated from

equation (11). Ion association provides a reasonable explanation for the difference of activity coefficients in seawater and in single-salt solutions. The discrepancy between the calculated and the measured total activity coefficients of bicarbonate cannot be explained at the present time.

The results of this work may be used to account for the relatively large ultrasonic absorption of seawater. The model used by Fisher (1967) in which the magnitude of the absorption is considered to be proportional to the concentration of  $\text{MgSO}_4^{\circ}$  ion-pairs will be employed. Kurtze and Tamm (1953) found that the absorption at a frequency of  $1 \times 10^5$  cps for a 0.1 molar  $\text{MgSO}_4$  solution was  $3.0 \pm 0.2 \times 10^3 \text{ sec}^2 \text{ m}^{-1}$ . The  $\text{MgSO}_4^{\circ}$  ion-pairs in this solution were calculated to be 0.0562 molal using equation (50). Thus, the molar absorption coefficient for  $\text{MgSO}_4^{\circ}$  for sound at  $1 \times 10^5$  cps is  $5.3 \pm 0.4 \times 10^4 \text{ sec}^2 \text{ m}^{-1} \text{ molal}^{-1}$ . Table 24 gives  $[\text{MgSO}_4^{\circ}] = 0.0056 \pm 0.0002$  molal in seawater at  $25^{\circ} \text{ C}$ . Therefore, the calculated absorption for seawater is  $3.0 \pm 0.3 \times 10^2 \text{ sec}^2 \text{ m}^{-1}$ . The published values of ultrasonic absorption in seawater range from  $3.4 - 5.0 \times 10^2 \text{ sec}^2 \text{ m}^{-1}$  (Kurtze and Tamm, 1953). The value of ultrasonic absorption for seawater calculated using the association model is in reasonable agreement with the observed values.

A simple non-thermodynamic approach may be used to illustrate the effect of ion association on the colligative properties of seawater.



In ideal dilute solutions a colligative property may be considered to be proportional to the concentration of solute species. The freezing point and the vapor pressure are the only colligative properties of seawater which have been determined experimentally. The osmotic pressure and the boiling point elevation have been computed from either of the other two colligative properties. In the illustration which follows the freezing point and the vapor pressure will be examined, but the osmotic pressure and the boiling point will not be considered because they would not provide any independent information.

The test solution used to determine  $K^*_{CaSO_4}$  (Table 18, page 68) may be regarded as a simplified form of synthetic seawater with a salinity of  $34.8^{\circ}/\text{oo}$ . The main difference between this solution and a more complete form of seawater is the substitution of NaCl for  $NaHCO_3$ . According to the results of Table 24 this substitution alters the concentration of solute species at  $25^{\circ} \text{C}$  by about 0.0006 molal, which is negligible in this consideration of colligative properties.

If ion association in this synthetic seawater is disregarded, that is if all the electrolytes are assumed to be completely dissociated, the solute molality is 1.152. An NaCl solution containing this number of solute species (i. e. 0.576 molal) has a freezing point of  $-1.94^{\circ} \text{C}$  (Washburn, 1928a). However, the freezing point of  $35^{\circ}/\text{oo}$  salinity seawater is  $-1.91 \pm 0.02^{\circ} \text{C}$  (Cox, 1965), which indicates that

seawater contains fewer solute species per kg of  $H_2O$  than is inferred from its analytical composition. The extent of association in the synthetic seawater at  $2^\circ C$  (Table 26) indicates that seawater actually contains a molality of 1.131 solute species. This corresponds to a 0.565 m NaCl solution, which has a freezing point of  $-1.90^\circ C$  (Washburn, 1928b). Ion association has a relatively small effect on the freezing point of seawater (about  $0.04^\circ C$ ), but when this effect is considered, the freezing point of seawater agrees with that of a single-salt solution, NaCl, containing the same concentration of solute species.

The solute species of the synthetic seawater at  $25^\circ C$  are 1.135 molal (Table 26) which corresponds to a 0.568 m NaCl solution. Robinson (1954) found from isopiestic measurements that seawater of  $34.8^\circ/oo$  salinity had the same vapor pressure as a 0.565 m NaCl solution. If ion association is neglected, the seawater would contain the same molality of solute species as a 0.576 m NaCl solution. Thus, ion association provides a reasonable explanation for the observation that the electrolytes in seawater exert less of an influence on the colligative properties than would be expected from the analytical composition of seawater.

The association model used in this work appears to be generally consistent with several of the chemical properties of seawater. The predictive capability of this model was examined by a preliminary

consideration of chloride ions in mixed electrolyte solutions. The e. m. f. of a Ag;AgCl and calomel electrode couple with a saturated KCl salt-bridge was measured in the two solutions shown in Table 28. Solution I represents a simplified form of synthetic seawater, and solution II is a sodium chloride solution with the same effective ionic strength as solution I, assuming complete dissociation of the chlorides.

Table 28. Molal composition of the constituents in the solutions used for the chloride activity measurements.

	Solution I	Solution II
Na <sup>+</sup>	0.4923	0.6689
Mg <sup>2+</sup>	0.05488	-----
Ca <sup>2+</sup>	0.01073	-----
Cl <sup>-</sup>	0.5654	0.6689
SO <sub>4</sub> <sup>2-</sup>	0.02905	-----
$\mu_E$	0.669	0.669

If the assumptions used in this work are correct, the difference in potential of the chloride-sensitive electrode couple in solutions I and II at 25° C should be given by:

$$E(I) - E(II) = \frac{2.303 RT}{F} \log \frac{0.5654}{0.6689} = -4.32 \text{ mv.} \quad (88)$$

The observed difference in potential at 25<sup>o</sup> C was  $-4.55 \pm 0.05$  mv based on two measurements. Thus, there is an inconsistency in the assumptions used in this work which amounts to 0.23 mv in the potential of the chloride-sensitive electrode couple in solutions I and II.

II. There are three possible explanations for this discrepancy:

- (1) The assumption that chloride ion-pairs are insignificant may not be valid.
- (2) The assumption that chloride ion activity coefficients are the same in solutions of the same  $\mu_F$  but of different compositions may not be valid.
- (3) The assumption that the liquid junction potential is the same in solutions of different compositions may not be valid.

If the first explanation is accepted, the measured difference in potential indicates that of the chloride ions which are unassociated in solution II,  $99.1 \pm 0.2\%$  remain unassociated in solution I. The  $0.9 \pm 0.2\%$  of the chloride which is ion-paired in solution I would be associated with 6-9% of the magnesium and calcium ions. The second explanation is merely an alternative expression of the first one, the only difference being that the discrepancy is assigned to the activity coefficient instead of to the formation of ion-pairs. If the third explanation is correct, these results indicate that the liquid junction potential is 0.23 mv larger in solution II than in solution I. This difference is not unreasonable based on various estimates of

liquid junction potentials in various solutions between 0.1 and 1.0 molar concentrations (Bates, 1964; Picknett, 1968).

The preceding observations indicate some of the limitations of the assumptions which have been employed in this work. However, the magnitude of their effect on the results of this work is not as large as indicated above, because the test and the standard solutions were more similar in composition than solutions I and II. For example, the expected difference in potential of the chloride-sensitive electrode couple in the initial standard and the test solutions used to determine  $K^*_{\text{CaSO}_4}$  (Table 18, page 68) is:

$$E(\text{test}) - E(\text{std}) = \frac{2.303 RT}{F} \log \frac{0.5655 \gamma_{\text{Cl}}^{(\text{test})}}{0.5988 \gamma_{\text{Cl}}^{(\text{std})}} = -6.52 \text{ mv}, \quad (89)$$

where the ratio of the activity coefficients of chloride is estimated by the mean-salt-method. The observed difference in potential was  $-6.59 \pm 0.04$  mv based on two measurements. Thus, the difference in the possible chloride ion-pairing, or in the activity coefficients, or in the liquid junction potential between the standard and the test solutions for determining  $K^*_{\text{CaSO}_4}$  was about 0.07 mv in the potential of the chloride-sensitive electrode couple.

This difference in potential cannot be explained by the formation of chloride ion-pairs. Since the observed potential difference is more negative than the expected difference, there would have to be more

chloride ion-pairs in the test solution than in the standard solution. The activity of the cations is the same in the test and the standard solutions, by experimental design; therefore, the extent of any chloride ion-pairing would be proportional to the activity of chloride ions. The chloride ion activity is greater in the standard solution than in the test solution. Thus, chloride ion-pairs would be expected to be more significant in the standard solution than in the test solution, which would not produce the observed difference in potential.

A difference of  $-0.07$  mv due to differences in the liquid junction potential in the test and standard solutions would result in values of  $[Ca^{2+}]_{test}$  which are about 0.5% too low. This error is slightly smaller than the reproducibility of the measurements (Table 19). In conclusion, the preceding considerations show that at least one of the assumptions used in this work is not entirely correct, and that the liquid junction potential is a likely suspect. The inconsistencies introduced by these assumptions, however, do not appear to exceed the experimental uncertainty of the results.

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## APPENDICES

APPENDIX I  
LIST OF FREQUENTLY USED SYMBOLS

- $a_X$  = the activity of X.
- $f_{M_m N_n}$  =  $(f_M^m f_N^n)^{1/(m+n)}$  = the mean ionic activity coefficient of the electrolyte  $M_m N_n$ .
- $f_X$  =  $\frac{a_X}{T(X)}$  = the total activity coefficient of X.
- F = the Faraday constant (96,490 coulombs equivalent<sup>-1</sup>).
- k = the proportionality constant of Harned's rule.
- $K_{MSO_4}$  =  $\frac{a_{MSO_4}}{a_M a_{SO_4}}$  the thermodynamic association constant for  $MSO_4^{(\nu+2)}$  ion-pairs.
- $K_{MSO_4}^*$  =  $\frac{[MSO_4^{(\nu+2)}]}{[M^{\nu+}][SO_4^{2-}]}$  = the stoichiometric association constant for  $MSO_4^{(\nu+2)}$  ion-pairs.
- ln = natural logarithm to the base e.
- log = common logarithm to the base 10.
- M = molar concentration.
- $m_{MX}$  = the molality of the electrolyte MX.
- R = the gas constant (1.987 cal deg<sup>-1</sup> mole<sup>-1</sup> or 82.06 cm<sup>3</sup> atm deg<sup>-1</sup> mole<sup>-1</sup>).
- T<sup>°</sup>C = the temperature in degrees Celcius.
- T<sup>°</sup>K = the temperature in degrees Kelvin.
- T(X) = the total molal concentration of all species involving X.
- [X] = the molal concentration of the species X.
- $\gamma_X$  =  $\frac{a_X}{[X]}$  = the free activity coefficient of X.
- $\mu_E$  = the effective ionic strength in terms of free and ion-pair species.
- $\mu_T$  = the total ionic strength in terms of total molalities.

APPENDIX II  
 DATA FOR THE DETERMINATION OF  $K^*_{NaSO_4}$   
 AT 25° C AND 1 ATM PRESSURE

The data listed below were used to calculate  $K^*_{NaSO_4}$  at 25° C and 1 atm pressure. The solution numbers correspond to those given in Tables 4 and 5. The  $m(\text{std})$  is the molality of the initial standard solution. The titrant solution was 2.001 molal NaCl. The grams of initial standard solution which were used in each titration are listed as  $G(\text{std})$ .  $G(\text{titrant})$  is the grams of titrant solution required to make  $E(\text{std}) = E(\text{test})$ .

Solution No.	$m(\text{std})$	$G(\text{std})$	$G(\text{titrant})$	$K^*_{NaSO_4}$
1	0.49990	127.1	1.62	2.06
1	0.49990	127.1	1.76	2.02
2	0.46537	126.9	6.93	2.11
2	0.46537	126.9	6.91	2.12
3	0.60001	127.6	3.17	1.96
3	0.60001	127.6	3.01	2.06
3	0.60001	102.1	2.52	1.98
4	0.63069	127.8	2.52	2.33
4	0.63069	127.8	2.49	2.35
4	0.63069	127.8	2.73	2.00
5	0.19023	125.6	1.90	2.13
5	0.19023	125.6	1.88	2.16
6	0.33990	101.1	1.43	2.00
6	0.33990	126.1	1.75	2.01
7	0.64294	127.8	1.78	2.18
7	0.64294	127.8	1.80	2.17
8	0.75136	128.4	5.05	2.37
8	0.75136	128.4	4.75	2.42
8	0.75136	128.4	4.68	2.44

APPENDIX III  
 DATA FOR THE EFFECT OF TEMPERATURE  
 AND PRESSURE ON  $K^*_{NaSO_4}$

Table IIIa (below) lists the data from which  $K^*_{NaSO_4}$  was calculated at  $2.4^\circ C$ . The notation is the same as that in Appendix II.

Table IIIa. Data for the determination of  $K^*_{NaSO_4}$  at  $2.4^\circ C$ .

No.	G(std)	G(titrant)	$K^*_{NaSO_4}$
1	101.48	0.064	3.40
2	101.47	0.031	3.47
3	101.48	0.069	3.39

Two sodium-sensitive electrode couples, which will be denoted as A and B, were used to determine the effect of pressure on  $K^*_{NaSO_4}$ . Table IIIb (below) lists the e. m. f. data for electrode couple A, and the data for electrode couple B is given in Table IIIc.  $E(\text{asym})$  was determined with the initial standard solution (Table 6) inside and outside the glass electrode. The large value of the asymmetry potential appeared to be a characteristic of the Beckman sodium-ion glass electrodes, because the potentials of the two  $Ag;AgCl$  electrodes differed by less than 0.5 mv.



Table IIIb. E. M. F. data for electrode couple A at 1.5° C.

E. M. F.	Pressure (atm)		
	1	500	1000
E(asymp)	-18.52	-18.98	-19.54
$\Delta E(\text{asymp})$	0.00	- 0.46	- 1.02
E(P)	+16.35	+15.22	+13.87
$E(P) - E(1) - \Delta E(\text{asymp})$	0.00	- 0.67	- 1.46

Table IIIc. E. M. F. data for electrode couple B at 1.5° C.

E. M. F.	Pressure (atm)		
	1	500	1000
E(asymp)	-27.80	-28.10	-28.76
$\Delta E(\text{asymp})$	0.00	- 0.30	- 0.96
E(P)	+ 7.60	+ 6.55	+ 5.23
$E(P) - E(1) - \Delta E(\text{asymp})$	0.00	- 0.75	- 1.41
E(P)	+ 7.29	+ 6.34	+ 4.98
$E(P) - E(1) - \Delta E(\text{asymp})$	0.00	- 0.65	- 1.35

APPENDIX IV  
DATA FOR THE DETERMINATION OF  $K^*_{MgSO_4}$

See Appendix II for an explanation of the notation.

Table IVa. Data for  $K^*_{MgSO_4}$  at 25° C.

No.	G(std)	G(titrant)	$K^*_{MgSO_4}$
1	101.85	0.990	10.8
2	101.84	1.007	10.5
3	101.85	1.041	9.9
4	101.83	1.010	10.4
5	101.87	1.027	10.1
6	101.85	1.066	9.4

Table IVb. Data for  $K^*_{MgSO_4}$  at 1.7° C.

No.	G(std)	G(titrant)	$K^*_{MgSO_4}$
1	101.91	2.32	15.2
2	101.90	2.29	15.5
3	101.91	2.39	14.3

APPENDIX V  
DATA FOR THE DETERMINATION OF  $K^* \text{CaSO}_4$ 

See Appendix II for an explanation of the notation.

No.	G(std)	G(titrant)	$K^* \text{CaSO}_4$
1	93.14	0.768	9.9
2	102.02	0.077	11.7
3	102.00	0.122	11.1
4	102.01	0.177	10.2
5	102.02	0.122	11.1
6	102.01	0.122	11.1

APPENDIX VI  
DERIVATION OF SPECIAL EQUATIONS

Derivation of Equation (21)

Equation (21) was derived in the following manner. The molality of unassociated sodium ions in an NaCl-Na<sub>2</sub>SO<sub>4</sub> solution may be obtained from equation (15) as:

$$[\text{Na}^+] = \frac{T(\text{Na})}{1 + K_{\text{NaSO}_4}^* [\text{SO}_4^{2-}]} \quad (21a)$$

Substituting equation (21a) into equation (14) yields:

$$[\text{NaSO}_4^-] = \frac{T(\text{Na}) K_{\text{NaSO}_4}^* [\text{SO}_4^{2-}]}{1 + K_{\text{NaSO}_4}^* [\text{SO}_4^{2-}]} \quad (21b)$$

The total sulfate molality of this solution is given by:

$$T(\text{SO}_4) = [\text{SO}_4^{2-}] + [\text{NaSO}_4^-] \quad (21c)$$

Substitution of equation (21b) into (21c) yields:

$$T(\text{SO}_4) = [\text{SO}_4^{2-}] + \frac{T(\text{Na}) K_{\text{NaSO}_4}^* [\text{SO}_4^{2-}]}{1 + K_{\text{NaSO}_4}^* [\text{SO}_4^{2-}]} \quad (21d)$$

Equation (21) is then obtained by multiplying equation (21d) by

$1 + K_{\text{NaSO}_4}^* [\text{SO}_4^{2-}]$  and rearranging:

$$K_{\text{NaSO}_4}^* [\text{SO}_4^{2-}]^2 + \{1 + \{T(\text{Na}) - T(\text{SO}_4)\} K_{\text{NaSO}_4}^*\} [\text{SO}_4^{2-}] - T(\text{SO}_4) = 0 \quad (21)$$

Derivation of Equation (49)

Substitution of equation (21b) from above into equation (46) yields:

$$T(\text{SO}_4) = [\text{SO}_4^{2-}] + [\text{MgSO}_4^0] + \frac{T(\text{Na})K^* \text{NaSO}_4 [\text{SO}_4^{2-}]}{1+K^* \text{NaSO}_4 [\text{SO}_4^{2-}]} \quad (49a)$$

From equation (42) we may write:

$$[\text{SO}_4^{2-}] = \frac{[\text{MgSO}_4^0]}{[\text{Mg}^{2+}] K^* \text{MgSO}_4} \quad (49b)$$

Thus, substituting equation (49b) into (49a) yields:

$$T(\text{SO}_4) = \frac{[\text{MgSO}_4^0]}{[\text{Mg}^{2+}] K^* \text{MgSO}_4} + [\text{MgSO}_4^0] + \frac{T(\text{Na})K^* \text{NaSO}_4 \frac{[\text{MgSO}_4^0]}{[\text{Mg}^{2+}] K^* \text{MgSO}_4}}{1+K^* \text{NaSO}_4 \frac{[\text{MgSO}_4^0]}{[\text{Mg}^{2+}] K^* \text{MgSO}_4}} \quad (49c)$$

Multiplying equation (49c) by  $[\text{Mg}^{2+}] K^* \text{MgSO}_4$  yields:

$$T(\text{SO}_4) [\text{Mg}^{2+}] K^* \text{MgSO}_4 = [\text{MgSO}_4^0] + [\text{MgSO}_4^0] [\text{Mg}^{2+}] K^* \text{MgSO}_4 + [\text{Mg}^{2+}] K^* \text{MgSO}_4 \frac{T(\text{Na}) K^* \text{NaSO}_4 [\text{MgSO}_4^0]}{[\text{Mg}^{2+}] K^* \text{MgSO}_4 + [\text{MgSO}_4^0] K^* \text{NaSO}_4} \quad (49d)$$

Multiplication of each term in equation (49d) by  $[\text{Mg}^{2+}] K^* \text{MgSO}_4 + [\text{MgSO}_4^0] K^* \text{NaSO}_4$  and then grouping the terms by powers of

$K^*_{MgSO_4}$  gives equation (49):

$$a(K^*_{MgSO_4})^2 + b K^*_{MgSO_4} + c = 0, \quad (49)$$

where  $a = [Mg^{2+}]^2 \{T(SO_4) - [MgSO_4^0]\}$ ,

$$b = [Mg^{2+}] [MgSO_4^0] \{K^*_{NaSO_4} \{T(SO_4) - T(Na) - [MgSO_4^0]\} - 1\},$$

and  $c = -[MgSO_4^0]^2 K^*_{NaSO_4}$ .

#### Derivation of Equation (54)

The derivation of equation (54) is analagous to that of equation (49), except that it involves one more order of complexity. The total sulfate for the test solution in Table 18 is given as:

$$T(SO_4) = [SO_4^{2-}] + [NaSO_4^-] + [MgSO_4^0] + [CaSO_4^0]. \quad (54a)$$

From the definition of  $K^*_{CaSO_4}$  we obtain:

$$[SO_4^{2-}] = \frac{[CaSO_4^0]}{[Ca^{2+}] K^*_{CaSO_4}}. \quad (54b)$$

The following equation may be derived in a manner similar to that used to obtain equation (21b) above:

$$[MgSO_4^0] = \frac{T(Mg) K^*_{MgSO_4} [SO_4^{2-}]}{1 + K^*_{MgSO_4} [SO_4^{2-}]}. \quad (54c)$$

Therefore, substitution of equation (54b) into equations (21b) and (54c), and then substituting these results and equation (54b) into equation (54a) yields:

$$T(\text{SO}_4) = \frac{[\text{CaSO}_4^0]}{[\text{Ca}^{2+}] K^*_{\text{CaSO}_4}} + \frac{T(\text{Na}) K^*_{\text{NaSO}_4} [\text{CaSO}_4^0]}{[\text{Ca}^{2+}] K^*_{\text{CaSO}_4} + [\text{CaSO}_4^0] K^*_{\text{NaSO}_4}} + \frac{T(\text{Mg}) K^*_{\text{MgSO}_4} [\text{CaSO}_4^0]}{[\text{Ca}^{2+}] K^*_{\text{CaSO}_4} + [\text{CaSO}_4^0] K^*_{\text{MgSO}_4}} + [\text{CaSO}_4^0] \quad (54d)$$

Equation (54d) becomes equation (54) upon clearing the fractions and rearranging the terms:

$$a(K^*_{\text{CaSO}_4})^3 + b(K^*_{\text{CaSO}_4})^2 + c K^*_{\text{CaSO}_4} + d = 0, \quad (54)$$

$$\text{with } a = [\text{Ca}^{2+}]^3 \{T(\text{SO}_4) - [\text{CaSO}_4^0]\},$$

$$b = [\text{Ca}^{2+}]^2 [\text{CaSO}_4^0] \{K^*_{\text{MgSO}_4} \{T(\text{SO}_4) - T(\text{Mg}) - [\text{CaSO}_4^0]\} + K^*_{\text{NaSO}_4} \{T(\text{SO}_4) - T(\text{Na}) - [\text{CaSO}_4^0]\} - 1\},$$

$$c = [\text{Ca}^{2+}] [\text{CaSO}_4^0]^2 \{K^*_{\text{NaSO}_4} K^*_{\text{MgSO}_4} \{T(\text{SO}_4) - T(\text{Na}) - T(\text{Mg}) - [\text{CaSO}_4^0]\} - K^*_{\text{NaSO}_4} - K^*_{\text{MgSO}_4}\},$$

$$\text{and } d = -[\text{CaSO}_4^0]^3 K^*_{\text{NaSO}_4} K^*_{\text{MgSO}_4}.$$