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KINETIC STUDIES OF MAJOR SEAWATER CHEMICAL EQUILIBRIA.(U)  
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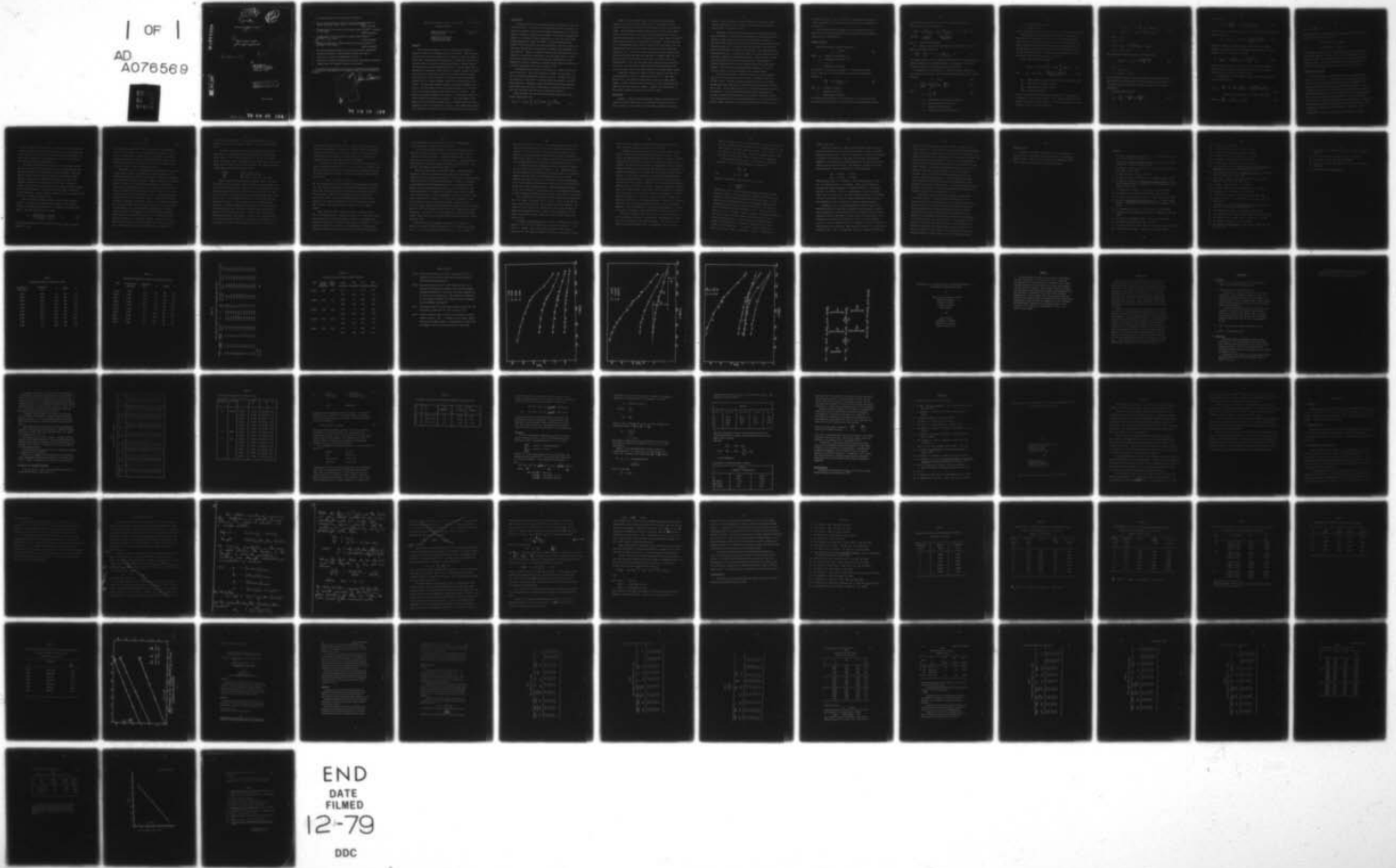
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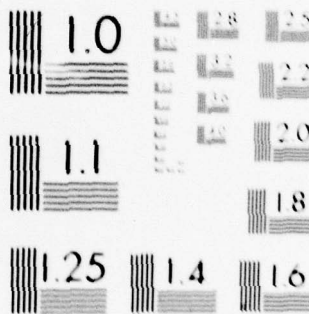
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*This report contains reprints or preprints of the following papers:*

The following papers are the results of the contract.

1. "On Ion Selective Electrode Study of Calcium and Magnesium Sulfate in Aqueous Solution". *2* Analyt. Letters. All (10) 797 (1978).  
Reprint enclosed.
2. "Thermodynamics of Ion Association in Aqueous Copper Sulfate" *2* I. (accepted J. Soln. Chem.).  
Preprint enclosed.
3. "Thermodynamics of Ion Association in Aqueous Copper Sulfate II."  
(accepted J. Soln. Chem.).  
Preprint enclosed.
4. "Ultrasonic Absorption in Aqueous Alkali Metal Sulfate Solutions" *2*.  
(accepted J. Phys. Chem.).  
Preprint enclosed.

The following additional papers are in the final stages of preparation.

5. "Ultrasonic Absorption in Aqueous  $MgSO_4$  Solutions from 5-25°C."
6. "The Kinetics of Boric Acid Dissociation at 5-25°."
7. "Simulation of Ultrasonic Absorption in the Ocean under Ambient Conditions."
8. "Chemical Model for Inorganic Speciation in the Ocean."

The principal investigator and his numerous co-workers are deeply grateful to the Office of Naval Research for the generous support they have provided for our work.

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Ultrasonic Absorption in Aqueous Alkali Metal  
Sulfate Solutions

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Abstract

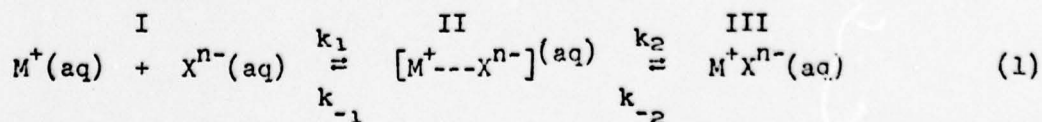
The ultrasonic absorption of the five alkali metal sulfates was measured in water in the frequency range from 25-520 MHz. Only one relaxation was found for all the salts and in all systems it was in the region of 100-400 MHz. The amplitude of the absorption increased with increasing concentration while the relaxation frequency decreased or remained constant. The amplitude and relaxation frequency behaved in a similar manner when the temperature was decreased. These results were analysed in terms of a three state mechanism of association where the two reaction steps are coupled. The experimental results included a B' parameter which was the residual absorption due to a higher frequency relaxation and solute-solvent interactions. The three-state mechanism yielded forward rate constants at 0.5 M and 25° C for the formation of the inner-sphere complex of  $1.0 \times 10^9 \text{ sec}^{-1}$  for all salts except potassium sulfate which was  $2.0 \times 10^9 \text{ sec}^{-1}$ . This mechanism successfully explained the decrease in the relaxation frequency of sodium sulfate with increasing concentration. The volume change for the reactions can be calculated and they exhibit a temperature and concentration dependence similar to the absorption amplitude. At the higher concentrations it was possible to treat the two steps as decoupled to a good approximation.

### Introduction

The alkali metal ions are extremely important constituents of the sea<sup>1</sup> and of biofluids.<sup>2</sup> In the past the characteristic kinetics of reaction of these ions in aqueous solution were considered immeasurably fast. With the advent of relaxation methods Eigen and Maass<sup>3,4</sup> were able to investigate the kinetics of association of these simple metal ions with the complex multi-dentate ligands NTA<sup>3-</sup>, EDTA<sup>4-</sup> and DGLTA<sup>4-</sup>. In addition other kinetic studies<sup>4,5</sup> have been carried out on the interaction of the alkali metal ions with other large molecules, particularly in methanol where association is very extensive. However, no systematic studies have been carried out on the kinetics of association of alkali metal ions with simple anions. We were particularly interested in the association with sulfate because of the importance of sulfate association in seawater and the extensive studies made of sulfate association with +2 and +3 cations.<sup>6,7,8,9</sup>

The problems with the study of alkali metal ion - sulfate kinetics in water are two-fold. First, the association constants are very small<sup>11</sup> as are the important thermodynamic parameters  $\Delta H$  and  $\Delta V$ . Secondly, the rates are expected to be very fast.<sup>10</sup> For these reasons we decided to use ultrasonic absorption. Preliminary results showed measurable effects although it was clear very early that we could expect an unpleasant combination of very short relaxation times and very low absorption amplitudes.

Eigen and Maass<sup>3</sup> used the following mechanism to treat the results of their alkali metal work:



State I is the separated aqueous ions; state II an outer-sphere complex; and state III an inner-sphere complex. The fact that only one relaxation was observed for these systems makes the above the most appropriate scheme. The characteristic water substitution rates<sup>3</sup> for the alkali metal ions are all on the order of  $10^9 \text{ sec}^{-1}$  so slow relaxations are not to be expected in these systems. The four state model of Eigen, Diebler and Tamm<sup>9,12</sup> seems overly complex for the alkali metal ion reactions. In this model step I is a diffusion-controlled approach of the aquo ions while steps II and III represent the step-wise loss of waters from anion and cation to give the contact ion pair. For metal ions whose characteristic water exchange rates are fairly slow the three steps can be observed. For alkali metal ions with their high water exchange rates, the steps are too close in rate to be distinguishable. Thus, the three-state model seems to be most appropriate to our case. The first step is the diffusion controlled approach of the aquo ions and the second is the slower formation of the inner-sphere complex.

Inner-sphere complexes of  $\text{LiSO}_4^-$  and  $\text{NaSO}_4^-$  have been observed by IR spectrophotometry in fairly concentrated solutions.<sup>13, 14</sup> Other Raman studies<sup>15</sup> have indicated that sodium sulfate forms only an outer-sphere complex. However, the Raman studies were done at lower concentrations than either the IR or our ultrasonic studies. Therefore, the concentration of inner-sphere complexes was probably too small to detect.

#### Experimental

**Materials:** Lithium sulfate monohydrate, anhydrous sodium sulfate and anhydrous potassium sulfate were Fisher Certified ACS reagents and were used as received. Cesium sulfate was Fisher reagent grade and was used as

received. Rubidium sulfate was prepared from silver sulfate and rubidium chloride and purified. Stock solutions of all the salts were prepared volumetrically using deionized water.

**Apparatus:** The send-receive pulse technique was used for all ultrasonic measurements. In this technique measurement of pulse attenuation as a function of path length yields the ultrasonic absorption coefficient. A Matec 6600 pulse modulator and receiver with different plug-in units furnished the basic electronics. The plug-in units used were Model 760 (10-90 MHz), Model 765 (90-300 MHz) and Model 770 (300-700 MHz). The output signal from the appropriate plug-in is gated into a Matec 1235 A pulse amplitude monitor. This device, basically a peak-reading-voltmeter, provides a direct reading of the amplitude of the selected pulse in decibels. The frequency is measured by beating the pulse with a Hewlett-Packard 608D or 612A signal generator, then measuring the signal generator frequency at zero beat frequency by means of a Hewlett-Packard 5327C frequency counter.

Two cells were employed. The medium frequency cell uses a matched pair of 5 MHz X-cut quartz transducers and has an effective range of 15-205 MHz in water. The high frequency cell employs 30 MHz X-cut crystals permanently bonded to quartz delay rods and has a effective range of 90-520 MHz in water. For the high frequency cell a new path-length measuring device was developed. We used a Hewlett-Packard displacement transducer that develops a voltage directly proportional to distance. This device enables us to semi-automate the high frequency measurements since we can automatically process signals related to pulse amplitude, path length and frequency using

a computing calculator. The medium frequency technique has been described in the literature<sup>16</sup> and the high frequency technique will be submitted for publication.<sup>17</sup>

The temperature of the jacketed cells was controlled to  $\pm 0.05^\circ \text{C}$  with a Lauda TK 30-D temperature bath and monitored with a Yellow Springs Instrument 425 C Telethermometer.

#### Treatment of Data

The data obtained are based on the equation

$$I_x = I_0 e^{-2\alpha x} \quad (2)$$

where  $I_0$  = intensity of sound wave at  $x_1$

$I_x$  = intensity of sound wave at  $x_2$

$x$  =  $x_2 - x_1$

$\alpha$  = absorption coefficient

By measuring  $\alpha$  as a function of frequency,  $f$ , we generate our basic  $(\alpha_i, f_i)$  data set. For a single chemical relaxation the theoretical function is

$$\frac{\alpha}{f^2} = \frac{A}{1 + (f/f_r)^2} + B \quad (3)$$

where  $f_r$  = relaxation frequency

$A$  = relaxation amplitude

$B$  = high frequency background

In dilute solutions exhibiting only one relaxation  $B$  is very close to the pure solvent absorption value. In the case of the concentrated alkali metal

sulfate solutions examined here, we should assume that the measured  $(\alpha/f^2)$  should really be considered as

$$\left(\frac{\alpha}{f^2}\right) = \frac{A}{1 + (f/f_r)^2} + \left( \frac{A'}{1 + (f/f_r')^2} + \Delta B + B \right) \quad (4)$$

measured                      observed                      high frequency  
relaxation                      relaxation                      relaxation

and  $B$  = pure solvent absorption

$\Delta B$  = change in pure solvent absorption caused by presence of solute.

Then we shall treat our data by

$$\left(\frac{\alpha}{f^2}\right) = \left(\frac{\alpha}{f^2} - B\right) \equiv \frac{A}{1 + (f/f_r)^2} + B' \quad (5)$$

So  $B'$  simply includes any small amplitude relaxation above our high frequency limit plus changes in the solvent background. It should be a constant for a particular salt at a given concentration and temperature.

The amplitude of the relaxation,  $A$ , and the relaxation frequency,  $f_r$ , are related to the relaxation time and thermodynamic properties of the process occurring

$$\tau^{-1} = 2\pi f_r \quad (6)$$

$$A = \frac{2\pi^2 v^2}{RT^2 x} \frac{(C_P - C_V)}{C_P C_V} \left(\Delta H^\circ - \frac{C_P \Delta V^\circ}{v\theta}\right)^2 \quad (7)$$

where

$$x = \frac{1}{V} \sum_i \frac{v_i}{C_i} \quad (8)$$

$v_i$  = stoichiometric coefficient of reactant  $i$

$C_i$  = molar concentration of reactant  $i$

$\theta$  = expansibility of solution

$v$  = velocity of sound in the solution

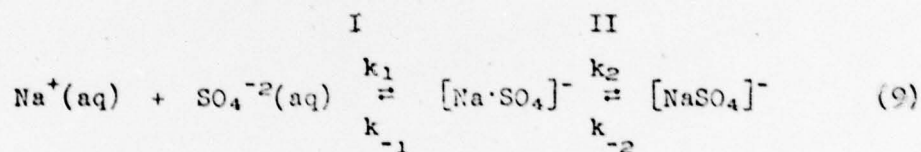
$\beta$  = compressibility of solution

$V$  = volume of solution

and the other symbols have their normal meanings for a chemical equilibrium.<sup>18</sup>

The expression for the relaxation time in terms of individual rate constants can be derived from a consideration of the three-state model given above.<sup>19</sup> We shall not assume that the two steps are decoupled but shall assume that the activity coefficients are not changing appreciably with concentration in the range of interest, 0.30 to 1.0 molar. Since the activity coefficients show a broad minimum with concentration in the range, this latter assumption should be quite good.<sup>19</sup>

Using sodium sulfate as an example



$$\text{Then } K_{\Sigma} = K_I(1 + K_{II}) = \frac{[\text{NaSO}_4]^- + [\text{Na}\cdot\text{SO}_4]^-}{[\text{Na}^+][\text{SO}_4^{-2}]} \quad (10)$$

$K_{\Sigma}$  = overall association constant (available from equilibrium data)

$K_I$  = outer-sphere association constant

$K_{II}$  = inner-sphere association constant

$[A]$  = activity of species A

We shall calculate  $K_I$  from the Eigen-Fuoss equation.<sup>20,21</sup>  $K_{II}$  can then be evaluated. Using the rate equations for the formation of  $(\text{Na}\cdot\text{SO}_4)^-$  and  $(\text{NaSO}_4)^-$  and the mass balance conditions, we can obtain expressions for the relaxation times using standard techniques.

$$\begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \begin{pmatrix} \delta_{(\text{NaSO}_4)^-} \\ \delta_{(\text{Na}\cdot\text{SO}_4)^-} \end{pmatrix} \quad (11)$$

$$a_{11} = -k_{-2}$$

$$a_{12} = k_2$$

$$a_{21} = -k'_1 = -k_1 \left( \frac{Y_+ Y_-^{-2}}{Y_-} \right) (C_{\text{Na}^+} + C_{\text{SO}_4^{-2}})$$

$$a_{22} = -k'_1 - k_{-1} - k_2$$

The eigenvalues of the matrix give the relaxation times

$$(\tau_{\text{I,II}})^{-1} = \lambda_{\text{I,II}} = \frac{-B \mp (B^2 - 4AC)^{1/2}}{2A} \quad (12)$$

$$A = 1$$

$$B = -(a_{11} + a_{22})$$

$$C = -a_{12}a_{21} + a_{11}a_{22}$$

We will put this equation in more usable form by using the experimental  $K_{\Sigma}$ , the theoretically calculated  $K_{\text{I}}$  and the theoretical value for  $k_{-1}^{20,22}$ . In addition we shall use Pitzer's theoretical equation<sup>25</sup> for activity coefficients.

The expression for  $K_{\text{I}}$  is<sup>21</sup>

$$K_{\text{I}} = \left( \frac{k_1}{k_{-1}} \right) = \frac{4 \pi \text{Na}^3}{3000} \exp \left( -\frac{Z_+ Z_- e^2}{aDkT} \right) \quad (13)$$

and for  $k_{-1}$  is<sup>20</sup>

$$k_{-1} = \frac{3 Z_M Z_X e^2}{a^3 D k T} \left[ \left( \frac{D_M + D_X}{1 - \exp(-Z_M Z_X e^2 / a D k T)} \right) \right] \quad (14)$$

If the diffusion coefficients,  $D_M$  and  $D_X$  are not known they can be estimated<sup>23</sup> from the expression

$$D_0 = D_M + D_X = 8.94 \times 10^{-10} \left( \frac{v_M + v_X}{v_M |Z_M|} \right) \left( \frac{\lambda_M^\circ \lambda_X^\circ}{\Lambda^\circ} \right) T \quad (15)$$

Robinson and Stokes<sup>24</sup> give  $\lambda_i^\circ$  as a function of temperature. Pitzer's equation for activity coefficients fits the experimental data up to ionic strengths of 5 M. It is given in the form

$$\ln \gamma = |Z_M Z_X| f^Y + m \left[ \frac{2 v_M v_X}{v} \right] B_{MX}^Y + m^2 \frac{2(v_M v_X)^{3/2}}{v} C_{MX}^Y \quad (16)$$

where  $f^Y$ ,  $B_{MX}^Y$  and  $C_{MX}^Y$  are explicit functions of the ionic strength and three adjustable parameters that vary from salt to salt. The original paper<sup>25</sup> should be consulted for further details.

The combination of these calculations gives the following expression for the relaxation times

$$\frac{1}{\tau_{I,II}} = \frac{k_{-1}(1 + K_I')}{2} + \frac{k_2(1 + \frac{K_I'}{K_\Sigma - K_I'})}{2} \pm \frac{1}{2} \left\{ \frac{k_2 K_I'}{K_\Sigma - K_I'} \left[ k_2 \left( \frac{K_I'}{K_\Sigma - K_I'} + 2 \right) - 2k_{-1}(K_I' + 1) \right] + k_{-1} \left[ k_{-1}(K_I' + 1)^2 + 2k_2(1 - K_I') \right] + k_2^2 \right\}^{\frac{1}{2}} \quad (17)$$

$$\text{where } K_I' = \left( \frac{k_1}{k_{-1}} \right) = K_I \gamma_{\pm} [C_{Na^+} + C_{SO_4^{2-}}] \quad (18)$$

since 
$$\left(\frac{\gamma_+ \gamma_-}{\gamma_{\pm}}\right) = \gamma_{\pm}$$

The activity coefficient identity results from treating  $M_2SO_4$  as a mixture of  $(2M^+, SO_4^{-2})$  and  $(M^+, MSO_4^-)$  where

$$\gamma_+^2 (M^+) \gamma_- (SO_4^{-2}) = \gamma_{\pm}^3 (M_2SO_4)$$

and 
$$\gamma_+ (M^+) \gamma_- (MSO_4^-) = \gamma_{\pm}^2 (M_2SO_4)$$

One can then solve for  $\gamma_+ \gamma_-$  and  $\gamma_{\pm}$  in terms of  $\gamma_{\pm}$  which is then available from Pitzer's equation. When  $K_{\Sigma}$  is known all the rate constants for the three state model can be determined once an 'a' value for the outer-sphere complex is known. At the lower temperatures where  $K_{\Sigma}$  values are not available, estimated values must be used to obtain  $(k_2, k_{-2})$  values.

### Results and Discussion\*

The excess ultrasonic absorption for different concentrations of  $Na_2SO_4$  is shown in Fig 1. The precision of the individual data points is very good for all solutions measured with the largest deviation of any individual point from a derived single relaxation line being 1%. With the low amplitude relaxations in these systems, such precision is necessary for meaningful data treatment. As can be seen from Fig 1 the excess absorption does increase with increasing salt concentration. Below 0.10 M  $Na_2SO_4$  it is difficult to detect a relaxation in this frequency range. Increasing the concentration increases the absorption amplitude and results in either a decreased or unchanged relaxation frequency. This lowering of the

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\* Tabulated  $(\alpha, f)$  values are available from G. Atkinson on request.

relaxation frequency with increasing ion concentration makes it clear that we are not dealing with a simple bimolecular process. The individual data points represent the average of at least three separate determinations of  $\alpha$  at a given frequency in a given experimental run, and, in most cases the average of different experimental runs.

Fig 2 shows the temperature dependence of a 0.50 M  $\text{Na}_2\text{SO}_4$  solution. For all of the solutions measured, lowering the temperature increased the absorption amplitude and decreased the relaxation frequency. The shaded symbols are data taken with the high frequency cell and show excellent agreement in their overlap with the medium frequency cell data. The relaxation parameters are illustrated for the 25° data. The data are fitted to A,  $f_r$ , and B' using a non-linear least squares analysis programmed for an HP 9800 calculator. In no case did  $(\alpha'/f^2)$  reach a constant value at high frequencies. However, with the exception of the 5.5° results,  $(\alpha'/f^2)$  did reach a constant low frequency value.

Table I lists the relaxation parameters for the  $\text{Na}_2\text{SO}_4$  solutions studied. The results can be qualitatively understood if we assume the existence of a rapid pre-equilibrium for the formation of the outer-sphere complex. Then the relaxation time is simply

$$\tau^{-1} = \frac{k_2 K_I \gamma_{\pm} (C_{\text{Na}^+} + C_{\text{SO}_4^{-2}})}{1 + K_I \gamma_{\pm} (C_{\text{Na}^+} + C_{\text{SO}_4^{-2}})} + k_{-2} \quad (19)$$

As the  $\text{Na}_2\text{SO}_4$  concentration is increased the term  $[K_I \gamma_{\pm} (C_{\text{Na}^+} + C_{\text{SO}_4^{-2}})]$  becomes  $\gg 1$  and

$$\tau^{-1} \rightarrow k_2 + k_{-2} \quad (20)$$

So at high salt concentration  $\tau$  becomes independent of concentration. This is seen for  $\text{Na}_2\text{SO}_4$  at  $25^\circ$  at concentrations greater than 0.30 and at  $15^\circ$  for concentrations greater than 0.50. Although it is useful in explaining the above observation, eq (19) should not be used in quantitatively interpreting our data since it is based on the assumption that  $k_1, k_{-1} \gg k_2, k_{-2}$ . This is unlikely in our case.

The changes in  $B'$  with concentration and temperature can be related to the solvent structuring associated with "structure-making" and "structure-breaking" ions,<sup>27-29</sup> and to changes in the excess absorption due to the higher frequency relaxation.  $\text{Na}_2\text{SO}_4$ , classified as a "structure maker,"<sup>28</sup> would cause increased solvent structuring with increased concentration increasing the  $\Delta B$  value. The increased association at the higher concentrations would cause the  $A'$  value to increase. As a result we would expect the increased  $B'$  shown in Table I. A tetramethylammonium bromide (TMA-Br) gave a  $(\alpha'/f^2)$  value that was independent of frequency indicating no measurable association. However, a 1.5 M solution of TMA-Br, the same ionic strength as 0.50 M  $\text{Na}_2\text{SO}_4$ , gave a  $B'$  of -3.5. All of this is attributable to the solute-solvent interaction of the "structure breaking" TMA-Br.<sup>30</sup> The measurement of a (0.60 M TMA-Br/0.30M  $\text{Na}_2\text{SO}_4$ ) mixture gave values of  $(\alpha'/f^2)$  that are 1.0 to 1.2 units lower at each frequency than the pure 0.30 M  $\text{Na}_2\text{SO}_4$  solution. This gives  $A$  and  $f_r$  values that are the same as the pure solution but a  $B'$  that is 1.1 units lower. For the same mixture at  $15^\circ$ ,  $(\alpha'/f^2)$  values are lower by 2.2 -

2.5 units at each frequency. In essence the added TMA-Br has a drastic effect on  $\Delta B$  but little effect on  $A'$  and this is mirrored by the changes in  $B'$ .

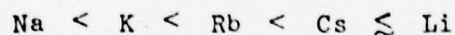
In order to compare our results with the other results on alkali metal ions<sup>3,4</sup> we extended the ultrasonic measurements to all the alkali metal sulfates.<sup>1</sup> Fig 3 shows our results at 25° and 0.50 M for all the salts. As in Eigen's work, the amplitude of the sodium salt is substantially greater than the others under the same conditions. The relative amplitude for the other four ions depends on the anion<sup>31</sup>

EDTA <sup>-4</sup>	Na >> K > Li ~ Rb ~ Cs
NTA <sup>-3</sup>	Na >> Cs ~ K > Li > Rb
SO <sub>4</sub> <sup>-2</sup>	Na >> K ~ Rb ~ Cs ~ Li (This work)

Table II gives the fitted relaxation parameters for the five salts. The results show one important difference from those reported by Eigen for the large multidentate ligands. Eigen and Maass found relaxation times that increases monotonically from Li<sup>+</sup> to Cs<sup>+</sup> for each anion. At 5.5° we find this same order of increasing relaxation time with increasing ionic radius. However, at 25°, the relaxation time for the Li<sup>+</sup> salt has gone from the slowest to the fastest. In this particular case, the three-parameter fit yields a relaxation frequency of 560 MHz. This is at the far edge of our measurement range and, therefore, the fitted results are subject to larger errors than in the other cases. For this reason we also tried a two-parameter fit for Li<sub>2</sub>SO<sub>4</sub> fixing  $B'$ . For a  $B'$  of 1.0,  $A$  has decreased to 4.5 and  $f_r$  to 505 MHz. When  $B'$  is increased to 2.0,  $A$  becomes 3.6 and  $f_r$  decreases to 397 MHz. Since the measured ( $\alpha'/f^2$ ) is 3.0 at 521 MHz,

the expected  $B'$  should be somewhat lower. However, the  $B'$  of 0.4 obtained with the three-parameter fit is too low. The best value for the relaxation frequency of  $\text{Li}_2\text{SO}_4$  should lie between the 560 MHz value and the 330 MHz value found for 1.00 M  $\text{Li}_2\text{SO}_4$ . In all the other cases, increasing the concentration either lowered the  $f_r$  or left it unchanged.

In conclusion we feel that the best values for the 0.50 M  $\text{Li}_2\text{SO}_4$  are those from the two parameter fit:  $B' = 2.0$ ,  $A = 3.6$  and  $f_r = 397$  MHz. This still makes the relaxation time for  $\text{Li}_2\text{SO}_4$  substantially faster than would be expected from Eigen's results. Thus at 25° the order of the relaxation times would be



One can speculate that this is due to the very strong hydration of the  $\text{Li}^+$  ion. This diminishes the extent of inner-sphere complexation so that the bulk of the absorption results from the much faster outer-sphere process. The multidentate ligands used in the Eigen and Maass work could have reversed this effect. At 5.5° the differences caused by difference in hydration of the cations is diminished since the entire solvent is much more structured. This permits the  $\text{Li}^+$  to behave in a more "normal" fashion.

The  $B'$  values for the  $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$  salts are close to zero. This is consistent with our qualitative correlation of  $B'$  with the structural effects of these ions and the contribution of the fast step amplitude to the measured amplitude. All three of these cations are classed as "structure breakers" while  $\text{SO}_4^{-2}$  is classed as a "structure-maker". The opposing cation-anion effects on the solvent tend to cancel each other leaving only

a small amplitude due to the fast step.  $\text{Li}^+$  is a "structure-maker" so we would expect a larger  $B'$  value in its case.

To calculate the rate constants, we will use the equations given in the theory section. First an 'a' value must be chosen. This is the "distance of closest approach" in the outer-sphere complex. This is then used to calculate  $K_1'$  and  $k_{-1}$ . We have assumed  $k_{-1}$  is independent of ionic strength so increases in  $K_1'$  are reflected by increases in  $k_1'$ . The  $K_2$  values were obtained from the literature.<sup>11, 32-35</sup>

Table III contains the most important results. The concentration dependence of the rate constants for  $\text{Na}_2\text{SO}_4$  reveals the same unusual behavior seen in the relaxation frequencies. In Table II we saw the relaxation frequency decrease with increasing concentration. Normally no dependence on concentration would be expected since this is a unimolecular process. However, in this system the coupling between  $k_1'$  and  $k_2$  is closest at the lowest concentration. This results in a higher  $k_2$  than would be expected if no coupling existed. As the concentration increases  $k_1'$  increases. This tends to decouple the two steps. At 1.00 M  $k_1'$  and  $k_2$  differ by a factor of 16 so the two steps are essentially decoupled. Calculation of  $k_2$  for 1.00 M  $\text{Na}_2\text{SO}_4$  using the rapid pre-equilibrium method and a  $K_2$  of 5.2 (ref 11) gives  $5.1 \times 10^{-8} \text{ sec}^{-1}$  instead of the  $5.2 \times 10^3 \text{ sec}^{-1}$  given by the extended calculation. Only at 0.30 M do the two methods give appreciably different results. When a  $K_2$  of 6.6 is used (ref 35) the results are slightly altered (see Table III).

Since the value for  $k_2$  depends on the value of 'a' assumed, we varied 'a' for the 0.5 M  $\text{Na}_2\text{SO}_4$  calculations at 25°. With  $K_1'$  at a minimum near 'a' = 5 Å and  $k_{-1}$  increasing with increasing 'a',  $k_2$  is smaller at

both 4 and 6 Å than it is at 5 Å. If one were to suppose that 'a' did vary with concentration, the size would be inversely related to the concentration. The effect of this on the  $\text{Na}_2\text{SO}_4$  results would be to give a smaller  $k_2$  at lower concentrations while leaving the high concentration values largely unchanged. This would bring the results more in line with the more aesthetically pleasing concentration independent rate constant.

To examine the effect of temperature on  $k_2$  we evaluated the results for 0.50 M  $\text{Na}_2\text{SO}_4$  at 15.0° and 5.5° using 'a' = 5 Å. The values for  $K_\Sigma$  at these temperatures were obtained by using the  $\Delta H$  value of +1.1 Kcal/mole reported by Austin and Mair.<sup>32</sup> The calculated  $k_2$  at 15.0° is very slightly larger than the value at 25° while the 5.5° value is appreciably less. We would expect the decrease of  $k_2$  from 25° to 5.5° to hold true for all the alkali metal sulfates since the relaxation frequencies decrease for all and all should have positive  $\Delta H$  values. As the temperature decreases  $k_{-1}$  also decreases due primarily to the decrease in the diffusion coefficients.

The two parameter fit results were used to evaluate the rate constants for 0.50 M  $\text{Li}_2\text{SO}_4$ . The  $K_\Sigma$  used was 4.5 (ref 35). The use of the other  $K_\Sigma$  value in the literature (5.9 in ref 35) altered the results somewhat. The results are given in Table III. The initial  $K_\Sigma$  values used for  $\text{Rb}_2\text{SO}_4$  and  $\text{Cs}_2\text{SO}_4$  are from Reardon (ref 35). However it was necessary to use a  $K_\Sigma$  somewhat larger than Reardon's value since Reardon's value of  $K_\Sigma$  was the same as our  $K_I$ .

For  $\text{K}_2\text{SO}_4$  two different  $K_\Sigma$  values were used. The value of 9.1 (ref 11) gives  $k_2 = 2.02 \times 10^9 \text{ sec}^{-1}$  while the 7.1 value (ref 34) yields  $k_2 = 1.79 \times 10^9 \text{ sec}^{-1}$ . Reardon's work indicates that the smaller value of  $K_\Sigma$  is a better choice. The results for  $\text{Rb}_2\text{SO}_4$  and  $\text{Cs}_2\text{SO}_4$  are very similar to those

for  $\text{Li}_2\text{SO}_4$  since only the  $k_{-1}$  values differ appreciably. This effect is due to the larger diffusion coefficients of  $\text{Rb}^+$  and  $\text{Cs}^+$ .

Treatment of these systems using the simple three-state model has greatly facilitated the understanding and analysis of the data. Fig 4 gives a more detailed picture of the  $\text{Na}_2\text{SO}_4$  system as an example. However, pursuing this more detailed mechanism in our calculations does not seem fruitful. In essence we have one measured relaxation time and one measured equilibrium constant for each salt at each concentration and temperature. In addition, thermodynamic data is lacking for the secondary equilibria shown in Fig 4. In all of these systems we are dealing with electrolytes that are very largely dissociated. In addition most of the kinetic processes are close to diffusion control. Therefore, we do not believe more elaborate kinetic analysis is fruitful at this time. Given the experimental concentrations, the assumptions made and the small size of the association constants, the value of  $k_2$  at 0.50 M for Li, Na, Rb, and Cs is the same,  $1 \times 10^9 \text{ sec}^{-1}$ . Potassium is higher at  $2 \times 10^9 \text{ sec}^{-1}$ . Since all but the  $\text{K}^+$  system have similar  $K_\Sigma$  values, this is not a surprising result. However, it is surprising that  $\text{K}_2\text{SO}_4$  with a larger  $K_\Sigma$  than  $\text{Na}_2\text{SO}_4$  should give a smaller absorption amplitude. The only explanation, if one accepts the  $K_\Sigma$  values, is that the  $\Delta V$  for the  $\text{K}^+$  association is much smaller than for the  $\text{Na}^+$  association.

The excess absorption values,  $A$ , can be used to calculate the values of  $\Delta V$ , the change in volume on ion association. Experimentally we obtain  $\Delta V_{\text{II}}$  the volume change for the slower relaxation.  $\Delta V_{\text{I}}$  is not available except for a maximum possible value. The formation of the outer-sphere

complex should have a small  $\Delta V$  since, presumably, no water is displaced in the process. Therefore, the contribution of this coupled step to  $\Delta V_2$ , the volume change for the second step will be small. If  $\Delta V_1$  were zero or  $\tau_{II} \ll \tau_I$ , then  $\Delta V_2$  would equal  $\Delta V_{II}$ . In these calculations we shall always assume that the contribution of  $\Delta H$  to the amplitudes is negligible.

The amplitude expression given in eq 7 can then be simplified. Assuming  $\Delta H = 0$  and using the thermodynamic identities<sup>26</sup>

$$\frac{C_P}{C_V} = \frac{\beta}{\kappa}$$

and

$$C_P - C_V = \frac{TV\theta^2}{\beta}$$

Where  $\beta$  is the adiabatic compressibility, eq 7 becomes

$$A = \frac{2\pi^2 v \rho \Delta V^2}{RTV\chi} \times \tau$$

Marks<sup>26</sup> gives values for the velocity and density of the alkali sulfate solutions studied.  $\chi$  can be evaluated from the known concentrations and equilibrium constant plus the calculated activity coefficients. We also assume that the activity coefficients are not changing appreciably with concentration in this range. We obtain values of  $\Delta V_{II} = -4.4 \text{ cm}^3/\text{mole}$  for 0.50 M  $\text{Na}_2\text{SO}_4$  at 25° and  $-6.6 \text{ cm}^3/\text{mole}$  at 5.5°. The  $\Delta V_{II}$  for 1.00 M  $\text{Na}_2\text{SO}_4$  at 25° is  $-5.3 \text{ cm}^3/\text{mole}$ . Since  $\Delta V_{II}$  changes little with concentration, the large increases in A with increasing concentration must be due to increased association together with the changes in solution velocity, density and relaxation time. Using the two parameter fit for 0.50 M  $\text{Li}_2\text{SO}_4$  at 25° we obtain  $\Delta V_{II} = -3.8 \text{ cm}^3/\text{mole}$ . For 0.50 M  $\text{K}_2\text{SO}_4$  at 25° the  $K_\Sigma$  of 9.1 gives a  $\Delta V_{II} = -4.4 \text{ cm}^3/\text{mole}$ . The  $K_\Sigma$  of 7.1 gives only a

slightly lower value.

To obtain the best  $\Delta V_2$  we should do a normal mode analysis of  $\Delta V_{II}$  to find the contribution from the coupled first step.<sup>40</sup> To do this we need both eigenvalues for the system. These can be obtained by using the rate constants to evaluate the coefficients of the original matrix then solving for the eigenvalues. The smaller value should correspond to the slower step and the larger one to the rapid first step. The eigenvalues are then used to find the eigenvectors. For 0.50 M  $\text{Na}_2\text{SO}_4$  at 25° this method yields

$$\Delta V_I = 6.79 \Delta V_1 + 1.00 \Delta V_2$$

$$\Delta V_{II} = 0.73 \Delta V_1 + 1.00 \Delta V_2$$

The experimental  $\Delta V_{II}$  is  $-4.4 \text{ cm}^3/\text{mole}$ . If we first assume  $\Delta V_I = 0$  then  $\Delta V_1 = 0.7 \text{ cm}^3/\text{mole}$  and  $\Delta V_2 = -5.0 \text{ cm}^3/\text{mole}$ . Even if  $\Delta V_I$  is allowed to equal all the residual amplitude ( $-7.2 \text{ cm}^3/\text{mole}$ ) then  $\Delta V_1 = -0.5 \text{ cm}^3/\text{mole}$  and  $\Delta V_2 = -4.2 \text{ cm}^3/\text{mole}$ . So even a large change in  $\Delta V_I$  has a relatively small effect on our  $\Delta V_2$  value. We could confidently expect it to lie between  $-4.2$  and  $-5.0 \text{ cm}^3/\text{mole}$ . Thus it is a good approximation that  $\Delta V_2 \simeq \Delta V_{II}$ , the experimental value, and that the two steps are largely decoupled.

Furthermore  $\Delta V_2 \gg \Delta V_1$  which seems eminently sensible when we think about the formation of inner-sphere complexes versus outer-sphere complexes. Table IV gives the  $\Delta V$  values calculated with and without coupling as well as showing the effect of different  $\Delta V_I$  values on the  $\Delta V_1$  and  $\Delta V_2$  values. It is interesting to note that for 0.50 M  $\text{Na}_2\text{SO}_4$  at 5.5°,  $\Delta V_2 = -9.6 \text{ cm}^3/\text{mole}$  if  $\Delta V_I$  is 0 and  $-8.5 \text{ cm}^3/\text{mole}$  is  $\Delta V_I$  is  $-7 \text{ cm}^3/\text{mole}$ . At the lower temperature the coupling is more pronounced. These results would give a  $\Delta V^\circ$  for the overall reaction of  $(\Delta V_1 + \Delta V_2) = -8.5 \text{ cm}^3/\text{mole}$ . This can be compared with the much

larger value of  $-15.8 \text{ cm}^3/\text{mole}$  obtained by Kester and Pytkowicz<sup>37</sup> for  $0.50 \text{ M Na}_2\text{SO}_4$  at  $2^\circ$ . Their value was obtained from the pressure dependence of the equilibrium constant determined with a specific ion electrode. One should note that the Kester and Pytkowicz  $\Delta V^\circ$  for  $\text{Na}_2\text{SO}_4$  is even larger than that determined by other workers<sup>38,39</sup> for  $\text{MgSO}_4$ . This seems improbable. Fisher has measured the pressure dependence of the conductance of aqueous  $\text{Na}_2\text{SO}_4$  solutions. His recent re-calculations<sup>41</sup> gave him a  $\Delta V^\circ$  of  $-8.25 \text{ cm}^3/\text{mole}$  for  $\text{Na}^+ -\text{SO}_4^{-2}$  ion pair formation. This is in very good agreement with our results. Millero<sup>33</sup> has predicted that  $\Delta V^\circ$  will increase with decreasing temperature. This is observed in our work. Thus a substantial amount of the increased sound absorption at lower temperatures is due to an increase in  $\Delta V^\circ$  not changes in density, velocity and degree of association. These last three effects would only increase amplitude by about 15% as one goes from  $25^\circ$  to  $5.5^\circ$ .

In conclusion we have shown that alkali metal ion association with sulfate proceeds at nearly a diffusion controlled rate. The association process is best described as the fast formation of an outer-sphere complex followed by rapid conversion to inner-sphere complexes. As the concentration of the solution decreases the rates of the two steps approach each other. The low degree of association gives low amplitude sound absorption with most of the amplitude being attributable to the outer-sphere to inner-sphere conversion. The combination of low amplitudes and coupled fast steps will make it very difficult to gain additional information about these systems using this technique. At higher concentrations it does appear possible to treat the two steps as largely decoupled and thereby derive very useful kinetic information.

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Table I

Relaxation Parameters for  $\text{Na}_2\text{SO}_4$  in Water

Concentration (Molarity)	Temperature (°C)	A	$f_r$ (MHz)	B'
0.30M	25.0	4.3	313	1.8
0.50M	25.0	8.4	221	4.3
0.70M	25.0	13.3	221	7.4
1.00M	25.0	22.7	217	9.8
0.30M	15.0	8.7	293	0.7
0.50M	15.0	15.9	221	4.3
0.70M	15.0	21.9	153	12.3
1.00M	15.0	34.7	155	18.1
0.30M	5.5	17.3	233	-0.7
0.50M	5.5	29.6	169	6.8

Table II

## Relaxation Parameters for Alkali Metal Sulfates in Water

Salt	Concentration (Molarity)	Temperature (°C)	A	$f_r$ (MHz)	B'
Li <sub>2</sub> SO <sub>4</sub>	0.50M	25.0	5.1	560	0.4
Li <sub>2</sub> SO <sub>4</sub>	1.00M	25.0	7.5	330	4.3
K <sub>2</sub> SO <sub>4</sub>	0.50M	25.0	5.0	299	1.6
Rb <sub>2</sub> SO <sub>4</sub>	0.50M	25.0	7.2	356	-1.5
Cs <sub>2</sub> SO <sub>4</sub>	0.50M	25.0	4.7	320	-0.3
Li <sub>2</sub> SO <sub>4</sub>	0.50M	5.5	9.1	142	5.3
Li <sub>2</sub> SO <sub>4</sub>	1.00M	5.5	15.8	128	10.5
K <sub>2</sub> SO <sub>4</sub>	0.50M	5.5	14.8	178	2.0
Rb <sub>2</sub> SO <sub>4</sub>	0.50M	5.5	12.6	161	1.0
Cs <sub>2</sub> SO <sub>4</sub>	0.50M	5.5	10.1	219	-1.1

Table III

## Rate Constants - Equilibrium Constants for Selected Alkali Sulfates

Cation	Concentration	Temperature	$\frac{1}{\tau} \times 10^{-9}$	$K_I$	$K'_I$	$K_\Sigma$	$k_2 \times 10^{-9}$	$k_{-2} \times 10^{-9}$	$k'_1 \times 10^{-9}$	$k_{-1} \times 10^{-9}$
		ature	sec <sup>-1</sup>		M <sup>-1</sup>	M <sup>-1</sup>	M <sup>-1</sup> sec <sup>-1</sup>	sec <sup>-1</sup>	sec <sup>-1</sup>	sec <sup>-1</sup>
Na	0.3	25	1.97	5.53	1.63	6.6	2.50	0.82	4.16	2.55
Na	0.5	25	1.39	5.53	2.25	6.6	1.21	0.62 <sub>g</sub>	5.74	2.55
Na	0.7	25	1.39	5.53	2.75	6.6	0.99 <sub>1</sub>	0.70 <sub>g</sub>	7.01	2.55
Na	1.0	25	1.36	5.53	3.38	6.6	0.76 <sub>o</sub>	0.79 <sub>g</sub>	8.62	2.55
*Na	0.5	25	1.29	5.79*	2.35	5.2	0.97 <sub>g</sub>	0.80 <sub>7</sub>	3.60	1.53
Na	0.5	25	1.39	5.93 <sub>l</sub>	2.41	5.2	0.81 <sub>5</sub>	0.70 <sub>4</sub>	8.58	3.56
Na	0.5	15	1.39	5.35	2.17	4.9	0.99 <sub>g</sub>	0.79 <sub>4</sub>	4.32	1.99
Na	0.5	5.5	1.06	5.20	2.03	4.6	0.77 <sub>7</sub>	0.61 <sub>4</sub>	3.07	1.51
Li	0.5	25	2.49	5.53	2.71	5.9	1.39	1.18	5.83	2.15
K	0.5	25	1.88	5.53	2.18	7.1	1.79	0.79 <sub>3</sub>	7.00	3.21
Rb	0.5	25	2.24	5.53	2.36	4.0	1.08	1.55 <sub>4</sub>	7.67	3.25
Cs	0.5	25	3.20	5.53	2.46	4.0	1.00	1.59 <sub>7</sub>	8.00	3.25

\* a = 4Å

J a = 6Å

Table IV

## Reaction Volumes for Selected Alkali Sulfates

Salt	Concentration (Molarity)	Temperature (°C)	$\Delta V_{II}$ (cm <sup>3</sup> /mole)	$\Delta V_I$ (cm <sup>3</sup> /mole)	$\Delta V_1$ (cm <sup>3</sup> /mole)	$\Delta V_2$ (cm <sup>3</sup> /mole)
Na <sub>2</sub> SO <sub>4</sub>	0.5M	25.0	-4.4	0	+0.7	-5.0
			-4.4	-7.2	-0.5	-4.2
Na <sub>2</sub> SO <sub>4</sub>	0.5M	5.5	-6.6	0	+1.7	-9.6
			-6.6	-7.0	-0.1	-8.5
Na <sub>2</sub> SO <sub>4</sub>	1.0M	25.0	-5.3	0	+0.5	-10.6
			-5.3	-10.0	-1.5	-9.6
Li <sub>2</sub> SO <sub>4</sub>	0.5M	25.0	-3.8	0	+0.6	-3.6
			-3.8	-5.2	-0.2	-3.4
K <sub>2</sub> SO <sub>4</sub>	0.5M	25.0	-4.4	0	+0.5	-2.5
			-4.4	-6.0	-0.2	-2.1

### Figure Captions

- Fig 1: The excess absorption,  $\alpha'/f^2 \times 10^{17}$  nepers  $\text{sec}^2 \text{cm}^{-1}$ , as a function of the log of the frequency for sodium sulfate at 25°C and varying concentration.
- Fig 2: The excess absorption,  $\alpha'/f^2 \times 10^{17}$  nepers  $\text{sec}^2 \text{cm}^{-1}$ , as a function of the log of the frequency for 0.50M sodium sulfate at varying temperatures. The values from a three parameter fit at 25°C are A, the amplitude,  $f_r$ , the relaxation frequency and B', the residual absorption due to higher frequency relaxation and solute-solvent interactions.
- Fig 3: Experimental data for all the alkali sulfates at 25°C and 0.50M are plotted in terms of  $\alpha'/f^2 \times 10^{17}$  nepers  $\text{sec}^2 \text{cm}^{-1}$ .
- Fig 4: Possible additional steps for the ionic association of sodium sulfate are shown. The "." indicates an outer sphere complex, while the inner sphere complex is represented as a contact pair. The charges on the ions have been omitted for simplicity.

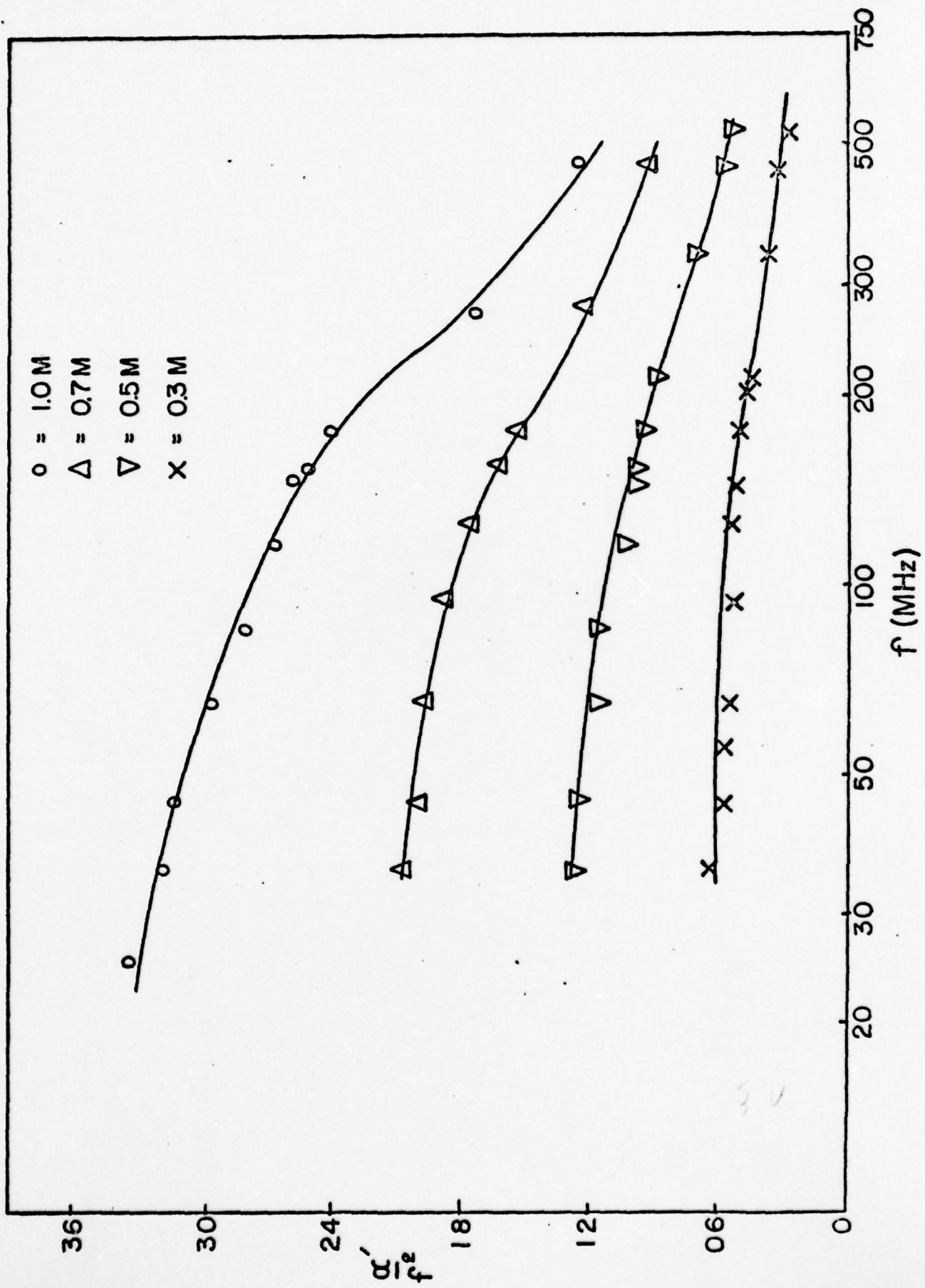


Fig. 1. Dependence of  $\alpha_f^2$  on frequency  $f$ .

30

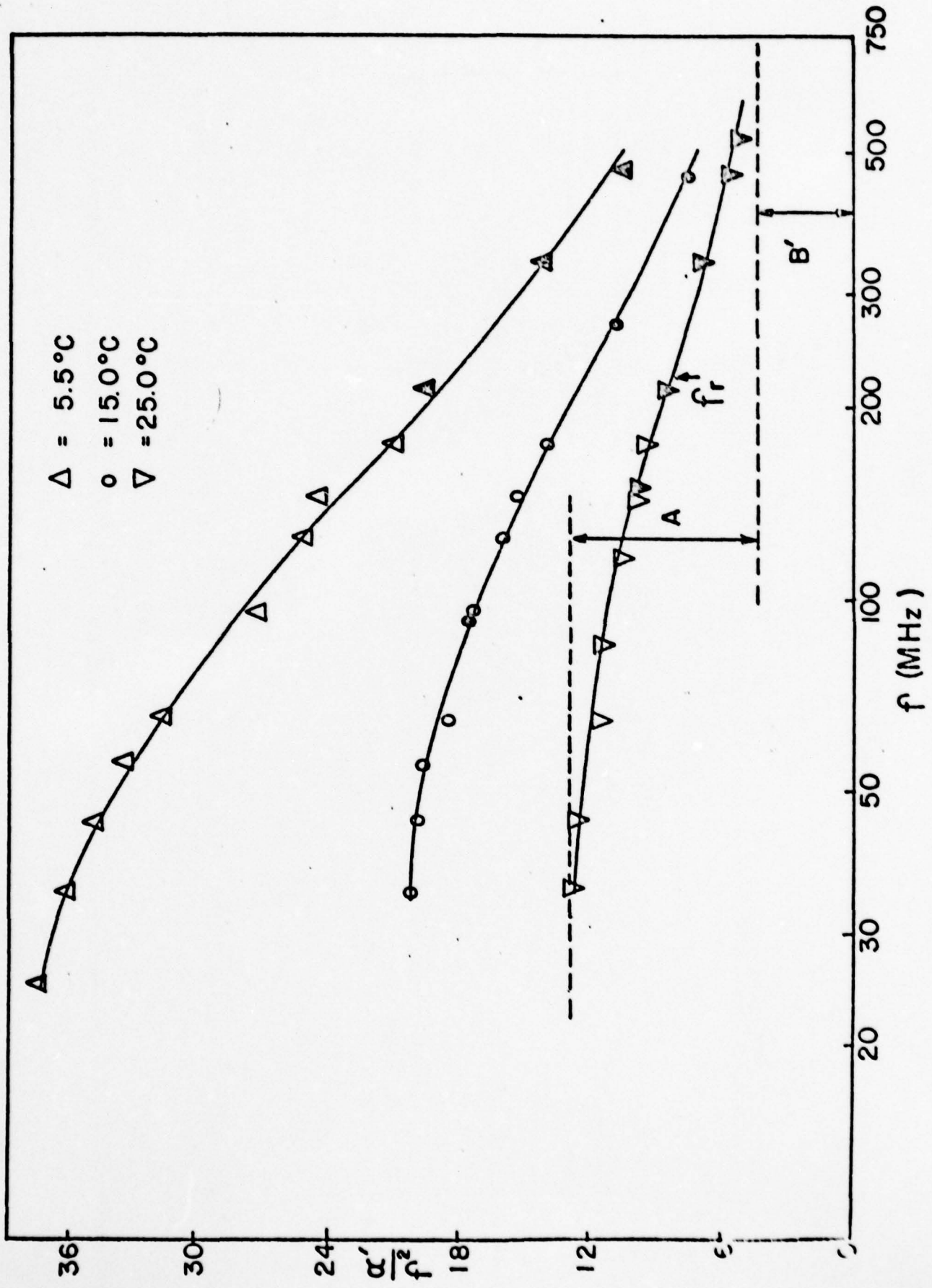


Fig. 2. Gitterkonstante und Frequenzabhängigkeit der Gitterkonstante

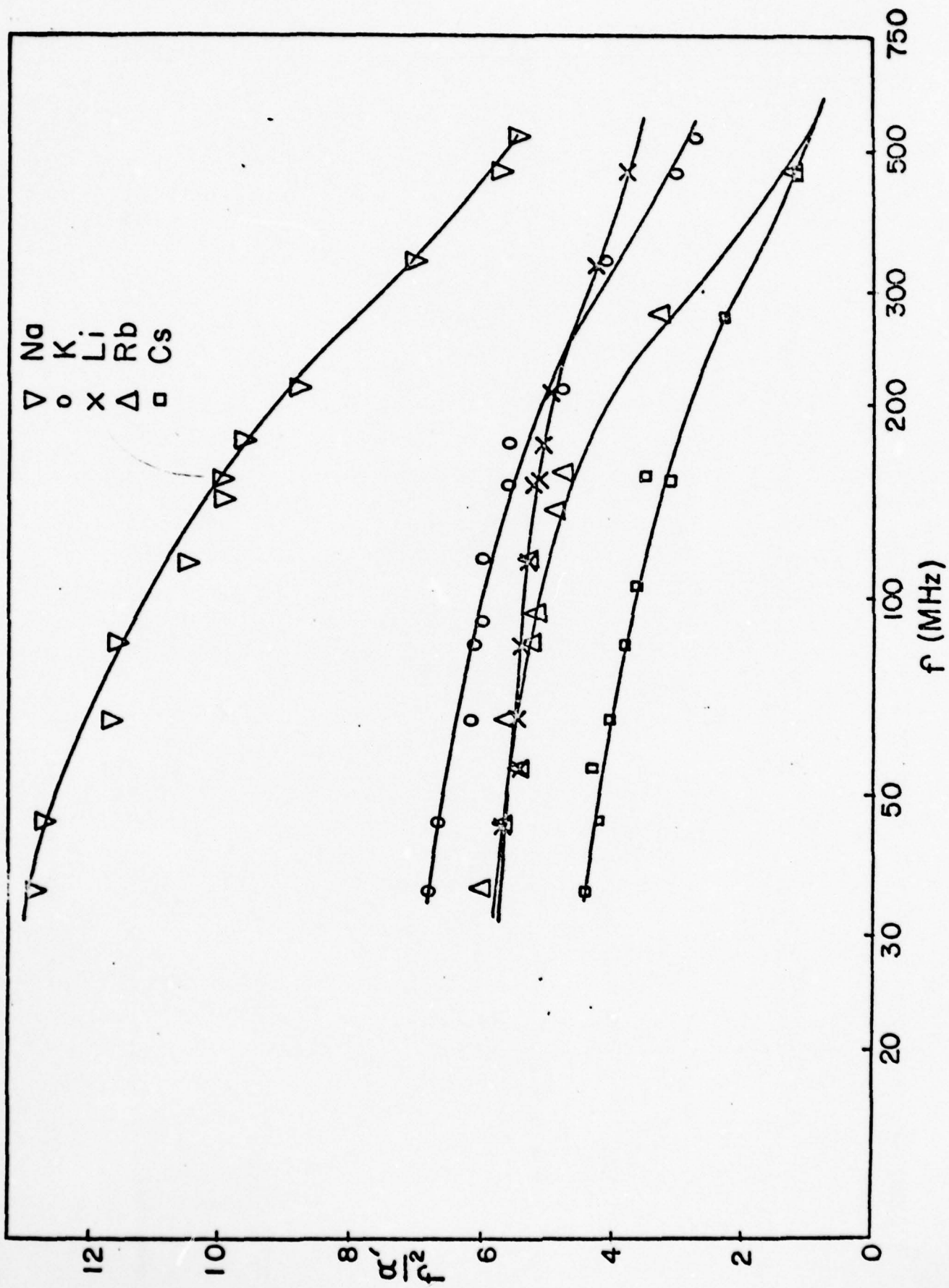
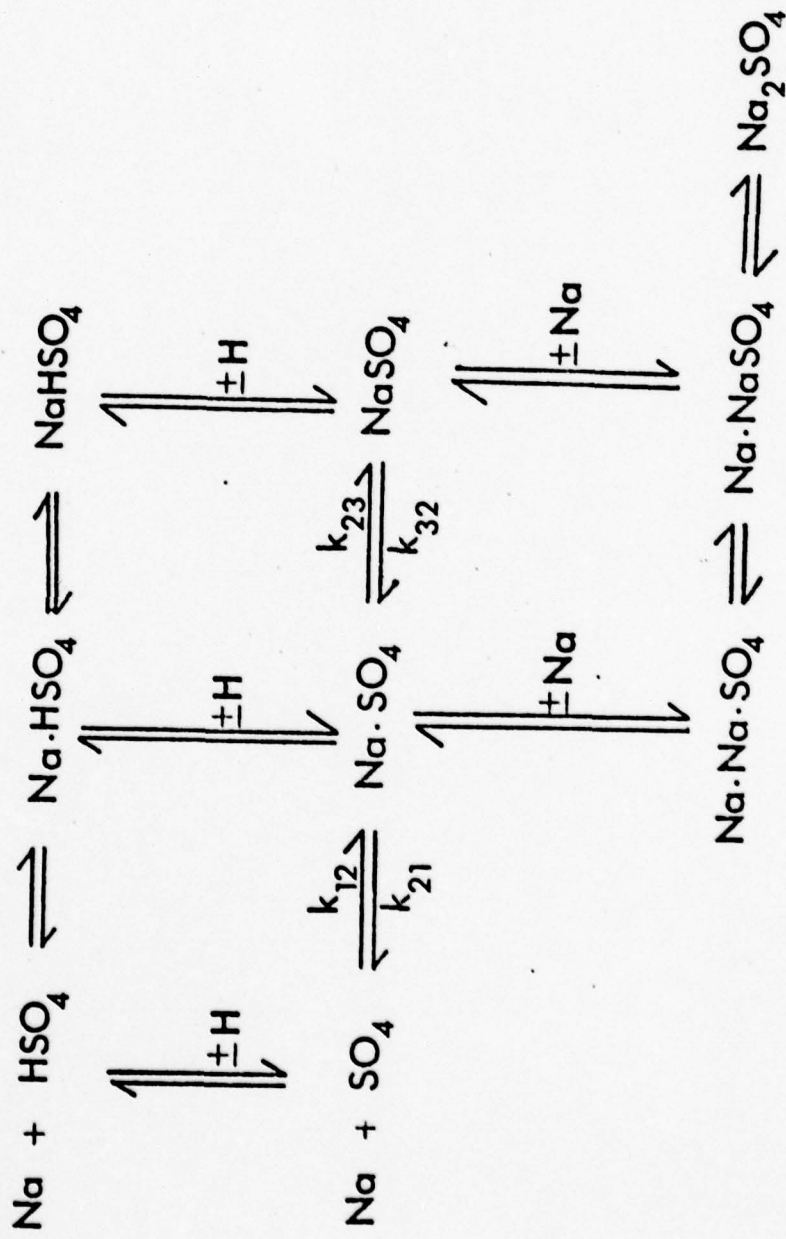


Fig. 2. C.V. ...



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THERMODYNAMICS OF IONIC ASSOCIATION IN AQUEOUS COPPER SULFATE. II.  
ION SPECIFIC ELECTRODE MEASUREMENTS

by

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### Abstract

The stoichiometric constants,  $K_c$ , for  $\text{CuSO}_4$  ion association have been measured at  $15^\circ$ ,  $25^\circ$ , and  $35^\circ$  in water, aqueous  $\text{NaCl}$  and aqueous  $\text{NaClO}_4$  using a divalent ion electrode. The  $K_c$  values were converted to the infinite dilution  $K_A$  values using standard activity coefficient methods. The  $K_A$  values found by this method are significantly higher than those measured spectrophotometrically. This difference is attributed to the fact that the electrode technique can be used to measure both inner and outer sphere ion pairs while the spectral method only measures the inner sphere pairs. Combining the results from the two methods allows us to calculate the thermodynamic parameters for the individual steps. At  $25^\circ$  we find  $K_I = 99.2$  (free ions to outer sphere) and  $K_{II} = 1.62$  (outer to inner sphere).

## Introduction

Recent years have seen a greatly increased interest in ion specific electrodes. The utility of the now classical glass electrode selective for hydronium ions was demonstrated in the late 1930's.<sup>1</sup> The development of glass electrodes specific for univalent cations occurred in the late 1950's.<sup>2,3</sup> But the development in the 1960's of liquid membrane and solid state electrodes for a wide variety of cations and anions marked the beginning of the new era.<sup>4,5</sup> The new electrodes together with high precision solid state, digital pH-mv meters makes broader application of potentiometry in physical and inorganic chemistry a certainty.

We have been concerned with the measurement of ion association for years. Although numerous techniques have been used to measure association in classical systems such as  $\text{MgSO}_4$  and  $\text{CuSO}_4$ , the situation is still not very satisfactory. One of the problems is the tendency of investigators to choose a single experimental technique. This makes it very difficult at times to compare results on the same system done by different investigators. The differences in ion association constants for  $\text{CuSO}_4$  in water at 25° seem large compared to the precision of the different methods. Therefore, we decided to apply a variety of methods to the same system. In the first paper<sup>6</sup> we repeated and extended the use of UV-visible spectroscopy to measure ion association in aqueous  $\text{CuSO}_4$ . In this paper we will examine the same system using the potentiometric technique with a ion specific electrode.

## Experimental

### A. Materials

1.  $\text{CuSO}_4$ : This was Fisher Reagent Grade recrystallized twice from distilled and deionized water.

2.  $\text{CuBDS}$  (Copper (II) m-benzenedisulfonate)

Crude  $\text{H}_2\text{BDS}$ , as obtained from Eastman Kodak, contains excess  $\text{H}_2\text{SO}_4$ . The crude  $\text{H}_2\text{BDS}$  in aqueous solution is treated with  $\text{Ba}(\text{OH})_2$  until no more  $\text{BaSO}_4$  is formed. The resulting  $\text{BaBDS}$  solution is passed through a cation exchange resin in the hydrogen form to obtain a pure  $\text{H}_2\text{BDS}$  solution which can be standardized.

To prepare  $\text{CuBDS}$  equivalent amounts of the pure acid solution and dried  $\text{CuCO}_3$  are reacted. The resulting solution is evaporated until crystals form. The product is recrystallized twice from deionized water. Purity is checked by EDTA analysis for the Cu and ion exchange for the BDS.

3.  $\text{NaCl}$ : This was Fisher Reagent grade dried at  $105^\circ\text{C}$ .

4.  $\text{NaClO}_4$ : Fisher Reagent grade.

### B. Measurements

The potentiometric measurements were made using an Orion Model 801 pH-mv meter equipped with an Orion Model 92-32 divalent cation electrode and a 90-01 single junction reference electrode. The 92-32 was modified for  $\text{Cu}^{+2}$  selectivity using the internal and filling solutions suggested and supplied by Orion.

Measurements were carried out in a large volume jacketed glass cell whose working solution temperature could be controlled to  $\pm 0.05^\circ$ .

All working and reference solutions were prepared by weight dilution techniques. The  $\text{Cu}^{+2}$  concentration of each solution was checked by EDTA titration.

The primary problem in ion specific electrode measurements is establishing a standard curve of potential versus activity. We elected to use CuBDS as our standard reference because of the strong evidence<sup>7,8</sup> that it is essentially completely unassociated in aqueous solution. It is therefore advantageous to use it as an activity reference for CuSO<sub>4</sub> since it is also a 2-2 salt. The use of 2-1 salts such as Cu(NO<sub>3</sub>)<sub>2</sub> as reference presents additional problems in activity-concentration conversions.

A standard reference curve was run before and after each set of "unknown" measurements. Unless the curves agreed the data were discarded. It is our experience that the liquid membrane electrode cannot be trusted to be stable for more than 1-2 hours.

Three different media were used in the CuSO<sub>4</sub> measurements: pure water, aqueous NaCl, and aqueous NaClO<sub>4</sub>. Standard reference curves were run with CuBDS in the same three media. All systems were examined at 15°, 25°, 35°.

The activity of Cu<sup>+2</sup> in the "unknown" solutions was calculated from the standard reference curve and converted to [Cu<sup>+2</sup>] using the known activity coefficients of CuSO<sub>4</sub><sup>9</sup> at the given ionic strength. The ( [Cu<sup>+2</sup>], I ) values must, of course, be obtained by an iterative procedure.

All measurements were made at a pH of 4 to remove the necessity of correcting for Cu<sup>+2</sup> hydrolysis.

Table I is an example of a data set showing the calculation of the stoichiometric association constants, K<sub>c</sub>, for CuSO<sub>4</sub> in H<sub>2</sub>O at 25°C. Table II summarizes the K<sub>c</sub> results in the three media.

#### Evaluation of Association Constants

It is now useful to convert the stoichiometric constants, K<sub>c</sub>, to the infinite dilution state values, K<sub>A</sub>.

Table I  
 $\text{CuSO}_4$  in  $\text{H}_2\text{O}$  at  $25^\circ$  Results

$[\text{Cu(m)BDS}]$ $\text{Cx}10^3$	$[\text{CuSO}_4]$ $\text{Cx}10^3$	mV Cu BDS	mV $\text{CuSO}_4$	$^a \text{Cu}^{2+}$ $\text{x}10^3$	$\nu_{\pm}(\text{Cu}^{2+})$	$[\text{Cu}^{2+}]$ $\text{Cx}10^3$	I	$K_c$ $\text{C}^{-1}$
10.03	15.12	25.6	24.9	4.70 <sub>4</sub>	0.4991	9.431	0.03773	63.99
12.01	18.01	27.2	26.4	5.31 <sub>1</sub>	0.4662	11.08	0.04432	56.39
15.18	22.52	29.3	27.9	6.01 <sub>2</sub>	0.4381	13.18	0.05271	53.65
17.42	26.11	30.5	29.0	6.51 <sub>3</sub>	0.4213	14.77	0.05911	51.87
18.72	33.48	31.0	30.9	7.75 <sub>1</sub>	0.4121	18.72	0.07492	42.12
25.04	43.79	33.8	33.0	9.04 <sub>2</sub>	0.3862	23.31	0.0932	37.60
37.25	55.55	35.8	34.7	10.2 <sub>5</sub>	0.3682	27.81	0.1112	35.82
37.44	62.90	37.6	36.0	11.2 <sub>5</sub>	0.3561	31.53	0.1261	31.51
43.64	77.28	39.5	37.7	12.8 <sub>0</sub>	0.3383	37.64	0.1505	28.00
52.45	99.36	41.1	39.2	14.7 <sub>0</sub>	0.3241	45.30	0.1810	26.30
74.93	187.4	41.5	42.4	24.2 <sub>0</sub>	0.2953	81.94	0.3217	15.71
99.91	249.9	44.7	45.1	29.9 <sub>1</sub>	0.2928	102.1	0.4085	14.16
150.0	374.9	49.1	48.6	44.5 <sub>2</sub>	0.3058	145.6	0.5822	10.82
199.9	400.0	52.1	49.1	45.0 <sub>1</sub>	0.3212	168.2	0.6729	8.191

Table II

Stoichiometric Association Constants of  $\text{CuSO}_4$ .

Temperature °C	Medium	I	$\sqrt{I}$	$\gamma_{\pm}$	$K_c$
25	$\text{NaClO}_4$	0.05011	0.2239	0.4616	51.61
		0.07172	0.2678	0.4188	42.53
		0.1011	0.3180	0.3794	34.90
		0.1251	0.3537	0.3569	30.89
		0.1483	0.3851	0.3417	25.80
		0.1962	0.4429	0.3176	20.59
25	$\text{NaCl}$	0.1256	0.3544	0.3566	29.37
		0.1998	0.4470	0.3177	19.95
25	$\text{H}_2\text{O}$	0.05272	0.2296	0.4381	53.65
		0.07491	0.2737	0.4122	42.12
		0.1112	0.3335	0.3682	35.81
		0.1263	0.3554	0.3562	31.52
		0.1505	0.3879	0.3381	28.01
		0.1811	0.4256	0.3243	26.30

$$K_A \equiv \frac{a_{\text{CuSO}_4}}{a_{\text{Cu}^{2+}} a_{\text{SO}_4^{2-}}} = \frac{[\text{CuSO}_4] \gamma_p}{[\text{Cu}^{2+}] [\text{SO}_4^{2-}] \gamma_{\pm}^2} \quad (1)$$

$$= K_c / \gamma_{\pm}^2 \quad \text{assuming } \gamma_p = 1$$

We have used the same methods described in paper I. In the first method the Davies equation<sup>10</sup> is used to calculate  $\gamma_{\pm}$  for each  $K_c$  at a given I and an average  $K_A$  is obtained. In the second method<sup>11</sup> eq (1) is rearranged to

$$\log K_c - \log \gamma_{\pm}^2 = \log K_A \quad (2)$$

Then the extended Debye-Hückel equation<sup>12</sup> is used to calculate  $\gamma_{\pm}$  at different I values with a series of  $a^{\circ}$ , mean distance of closest approach values. Then a plot of the L.H.S. of eq(2) versus I gives  $\log K_A$  as the intercept. Both techniques can be made to agree to within 5%. The  $K_A$  values and the other thermodynamic parameters are given in Table III (pure H<sub>2</sub>O).

It is interesting to compare the  $K_A$  values in the three different media at 25°

Medium	$K_A$ (C <sup>-1</sup> )
H <sub>2</sub> O	259.8 ± 11.5
Na <sub>2</sub> ClO <sub>4</sub> (aq)	232.3 ± 12.8
NaCl (aq)	214.4 ± 13.2

Although the values are close to being the same within experimental error, they are somewhat different. These apparent differences could arise in two general ways. First, the  $K_A$ 's have been calculated using a pure electrolyte activity coefficient approach, that is assuming  $\gamma_{\pm}$  depends only on ionic strength. This is known to be generally not true. However, appropriate corrections would

Table III

Association Constants and Thermodynamic Parameters for  $\text{CuSO}_4$  in  $\text{H}_2\text{O}$ .

T °C	$K_{\Delta}$ $\text{C}^{-1}$	$\Delta H^{\circ}$ KCal/Mole	$\Delta G^{\circ}$ KCal/Mole	$\Delta S^{\circ}$ Cal/Mole - °K
15	$235.4 \pm 12.1$	1.40	- 3.142	+ 15.8
25	$259.8 \pm 11.5$	1.40	- 3.310	+ 15.8
35	$274.2 \pm 3.8$	1.40	- 3.454	+ 15.8



The comparison of the various association concepts is conceptually simplified by considering a pure  $\text{CuSO}_4$  solution. If we let

$$a_i = \text{Activity of species } i$$

$$\text{then } K_I = \frac{a_2}{a_1^2}$$

$$K_{II} = \frac{a_3}{a_2}$$

Now the "real" thermodynamic  $K_A$  must be for the formation of an equilibrium mixture of (2) and (3) from (1)

$$K_A = \frac{a_2 + a_3}{a_1^2}$$

$$\equiv K_I + K_I K_{II}$$

This should be equivalent to the  $K_A$  determined by I.S.E. since in this method we measure  $a_1$  and obtain the sum of  $(a_2 + a_3)$  from stoichiometry.

However, in the spectrophotometric method we measure  $C_3$  (corresponding to  $a_3$ ) directly and assume everything else is "free" ion. Therefore, this method lumps (1) and (2) together.

$$\text{So } K_S \equiv K_A \quad (\text{spectrophotometric})$$

$$= \frac{a_3}{(a_1 + a_2)^2}$$

We can now show that

$$K_S = K_I K_{II}$$

Therefore, knowing both  $K_A$  and  $K_S$ , we can calculate  $K_I$  and  $K_{II}$ . The results are given in Table IV.

Table IV				
T (°C)	$K_S$ ( $C^{-1}$ )	$K_A$ ( $C^{-1}$ )	$K_I$ ( $C^{-1}$ )	$K_{II}$
15	145.0	235.4	90.4	1.604
25	160.6	259.8	99.2	1.619
35	169.6	274.2	104.6	1.621
45	201.4	-	-	-

With real trepidation because of the large errors involved, we can use these values to estimate the  $\Delta H$  parameters and other parameters of the two steps.

Note that

$$\Delta X_S^\circ = \Delta X_I^\circ + \Delta X_{II}^\circ$$

$$\text{while } \Delta X_A^\circ = \Delta X_I^\circ + \frac{K_{II}}{K_{II} + 1} \Delta X_{II}^\circ$$

for any parameter X

The derived 25° values are given in Table V.

Table V . Stepwise - Thermodynamics		
	Step I	Step II
K	99.2	1.619
$\Delta G^\circ$ (Kcal)	-2.72	-0.28 <sub>5</sub>
$\Delta H^\circ$ (Kcal)	1.29	0.09 <sub>6</sub>
$\Delta S^\circ$ (Gibbs)	13.4	1.2 <sub>8</sub>

The  $\Delta X$  parameters are reasonably consistent with those calculable from the  $K_A$  and  $K_S$  data, but clearly cannot be trusted very far. Neither experimental technique is very high precision. However, the results do encourage our belief that the different experimental techniques do, indeed, measure different aspects of ion association.

Another interesting comparison can be made if we compare the results from this work with results from previous ultrasonic investigations of step-wise association in 2-2 sulfates<sup>16</sup>. If we use  $MgSO_4$  as a contrast, we can lump the first two steps of this three-step system together to obtain a valid comparison with  $CuSO_4$  where only two steps have ever been observed.

	$CuSO_4$	$MgSO_4$
Free Ion to Outer Sphere Conversion K	99.2	154.2
Outer to Inner Sphere Conversion K	1.6 <sub>2</sub>	0.17 <sub>2</sub>

So we find a much greater conversion of outer sphere to inner sphere ion pairs in the case of  $CuSO_4$ . This can be related to the very high rate of  $H_2O$  exchange on  $Cu^{2+}$  as compared to  $Mg^{2+}$ .

In conclusion, we have shown that ion specific electrodes can be used for reasonable precise determinations for the thermodynamics of ion association of divalent metals. The method has an inherent advantage in that it determines free ion activity ignoring all association processes. A comparison of I.S.E. values with these obtained by a method sensitive only to inner-sphere complexation can be used to obtain useful step-wise association parameters.

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Thermodynamics of Ionic Association in Aqueous Copper Sulphate Solutions

I. Spectrophotometric Measurements<sup>+</sup>

by

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## Introduction

The problem of ion association in electrolytes has been an important subject of investigation for physical chemists for more than 160 years.<sup>1-3</sup>

Theories of ionic association began when Volta discovered a way of producing electricity by means of chemical reactions. After that, Faraday, Clausius, Arrhenius and Ostwald made substantial experimental studies in the last century. However, the first mathematical approaches to the problem were begun in this century by Bjerrum,<sup>4</sup> Muller,<sup>5</sup> Gronwell,<sup>6</sup> Fuoss<sup>7</sup> and Denison and Ramsey.<sup>8</sup> Detailed explanations of the full mathematical derivations of the various models can be found elsewhere.<sup>9</sup>

If we turn to the experimental methods by which one can study ion association, several ~~ones~~ have been in common use. The most important have been conductance, potentiometric, spectrophotometric, polarographic, ion-exchange, solubility, solvent extraction, Raman spectra and reaction kinetics. It is desirable to study the same system<sub>x</sub> by as many techniques as possible<sub>x</sub> so that the investigator can make meaningful comparisons.

Copper sulphate has been studied by many authors<sub>x</sub> using several techniques including conductance, E.M.F. and spectroscopic. However, most of the different measurements have been carried out under different conditions so that comparison becomes difficult and ambiguous. We shall only review the results obtained using the two major methods, conductance and spectrophotometric.

The thermodynamic association constant ( $K_A$ ) of  $\text{CuSO}_4$  in water at  $25^\circ\text{C}$  obtained from conductance<sup>10,11</sup> measurements ranged from 200 to  $232 \text{ M}^{-1}$ . The spectrophotometric method ~~resulted in~~ <sup>GAVE</sup> values for  $K_A$  ranging from 125 to  $285 \text{ M}^{-1}$ .

For example, Monk and co-workers<sup>12</sup> obtained values of 212.7 and 222.2  $M^{-1}$ , while Nasanen<sup>13</sup> obtained a value of 125  $M^{-1}$ . The latter author could not find an explanation for the large difference between the results.

Prue<sup>14</sup> obtained a value of 285.7, while Matheson<sup>15</sup> could not obtain a unique value for  $K_A$  without arbitrary conditions. He obtained values in the range of 170-250  $M^{-1}$ . Later, Petrucci and Hemmes<sup>17</sup> made UV spectroscopic studies on  $CuSO_4$  at 25°C and obtained a value of 220-230  $M^{-1}$  for  $K_A$ .

It is obvious that the values obtained, even using the same experimental method, differ greatly from author to author. It is also noticeable that the values of  $K_A$  obtained by the spectrophotometric method are smaller than those obtained from the conductance method.

This paper and the one which follows are the result of thorough investigations in our laboratories on  $CuSO_4$  in various aqueous media and under a wide range of experimental conditions. In this communication the spectrophotometric measurements are reported at four temperatures and for three ionic strengths at each temperature. The following paper includes the ion-selective electrode measurements and a comparison of the results found using both techniques.

## Experimental

### A. Materials:

Copper perchlorate was prepared from analar copper(II)oxide using a slight excess of analar perchloric acid, then filtering and crystallizing. The product was then recrystallized from 0.01 M  $\text{HClO}_4$ . Sodium sulphate was Baker analytical reagent. Sodium chloride was Fisher reagent.

### B. General Equipment:

Measurements were made using a Zeiss QM3 spectrophotometer equipped with a 1 cm cell. The temperature of the solution was maintained constant by circulating water through the cell compartment. The temperature was controlled to  $\pm 0.01^\circ\text{C}$ .

### C. Measurements and Collecting Data:

Optical density (D) was determined at each temperature using 1 cm cell for the solution (D') and the reference (D). Copper perchlorate was used as the reference and the sample contained  $\text{Na}_2\text{SO}_4$ ,  $\text{Cu}(\text{ClO}_4)_2$  and  $\text{NaClO}_4$ . (D-D') was read directly and the measurements were repeated several times. Duplicate solutions of sample were measured and the values reported are the average of these two readings for each concentration.

To check any possible error in the measurements, a series of  $\text{Cu}(\text{ClO}_4)_2$  solutions were carried out at 250 nm wavelength using an assortment of cells of different path lengths. The results showed that the optical density over the range of this work is good to within 1%. The source used for the UV work was

the hydrogen lamp.

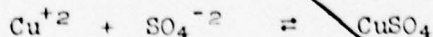
The cell used was 1 cm length quartz and was soaked in  $H_2SO_4$  over night, cleaned, and washed with distilled water, acetone, then dried with air before use. Stock solution of  $Cu(ClO_4)_2$  was prepared from reagent grade. It contained the required amount of  $HClO_4$  to prevent the hydrolysis of Cu.

Some exploratory experiments were carried out to study the possible hydrolysis of  $Cu^{+2}$  ion and determine the absorption peak. The results are given in Table I as the absorbance of  $Cu(ClO_4)_2$  in presence of varying amounts of  $HClO_4$  at  $25^\circ C$ . It is seen that the absorbance does not change after the concentration of  $HClO_4$  reaches a value above  $1.24 \times 10^{-3}$  M. This means that all our measurements must be carried out in the presence of at least this amount of  $HClO_4$  to prevent hydrolysis of  $Cu^{+2}$  at  $25^\circ C$ . In all the experiments  $HClO_4$  was added to minimize this hydrolysis.

## Results and Discussion

The primary aim of this work is to study the effect of temperature and medium on the association constant determined spectrophotometrically.  $\text{CuSO}_4$  has a particular interest both because it is a classical case of 2-2 electrolyte association and because the association can be measured directly by the spectrophotometric technique. Secondly, it is necessary to obtain more precise data under varying conditions so that the apparent differences in  $K_A$  determined by the different methods can be examined in detail. Finally, the present work is intended to lay a foundation for the investigation of the same system at high pressures.

As mentioned earlier, the method consists of measuring the difference in optical density between two solutions, a reference containing  $\text{Cu}(\text{ClO}_4)_2 - \text{NaClO}_4$  and a sample solution of  $\text{Cu}(\text{ClO}_4)_2 - \text{Na}_2\text{SO}_4$  and enough  $\text{NaClO}_4$  to maintain constant ionic strength. <sup>Let  $a$  be</sup>  $a$  is the  $[\text{Cu}(\text{ClO}_4)_2]_{\text{stoich}}$ ; <sup>Let  $b$  be</sup>  $b$  is  $[\text{Na}_2\text{SO}_4]_{\text{stoich}}$ ; <sup>Let  $c$  be</sup>  $c$  is  $[\text{NaClO}_4]_{\text{stoich}}$  and  $x = [\text{CuSO}_4]$  (ion pair). The reaction under investigation is represented by the equation:



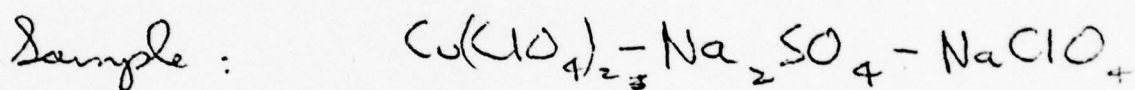
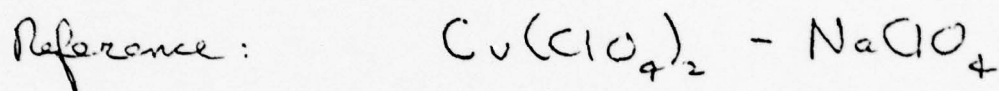
Concentration  $(a - x)$   $(b - x)$   $(x)$

It is well known that both free  $\text{Cu}^{+2}$  and the  $\text{CuSO}_4$  ion-pair absorb in the UV range. The measurements were carried out at a wavelength of 250 nm. If the  $\text{Cu}^{+2}(\text{aq})$  and  $[\text{CuSO}_4]$  are the only two species absorbing at 250 nm, then using Beer's law we have  $D = \epsilon l a$  but  $l = 1$ ; then  $D = \epsilon a$ ; where  $D$  is the optical density of  $\text{Cu}^{+2}$ ,  $\epsilon$  is the molar extinction coefficient of  $\text{Cu}^{+2}(\text{aq})$ ,  $a$  is the

A replace

A

The method consists of measuring the difference in optical density between a reference solution and a sample solution



The  $\text{Cu}(\text{ClO}_4)_2$  concentration is the same in both solutions. The  $\text{NaClO}_4$  in the "sample" is used to maintain a constant ionic strength while the  $\text{Na}_2\text{SO}_4$  concentration is varied.

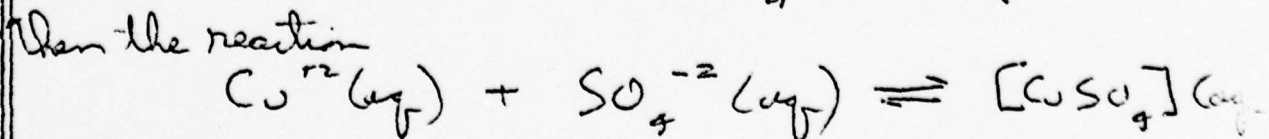
let  $\underline{a} = [\text{Cu}(\text{ClO}_4)_2]_{\text{stoich}}$

$\underline{b} = [\text{Na}_2\text{SO}_4]_{\text{stoich}}$

$\underline{c} = [\text{NaClO}_4]_{\text{stoich}}$

$x = [\text{CuSO}_4]_{\text{ion pair}}$

then the reaction



can be represented by the stoichiometric constant

$$K_c = \frac{x}{(a-x)(b-x)}$$

A

Both the free  $\text{Cu}^{+2}(\text{aq})$  and the  $\text{CuSO}_4$  ion pair absorb ~~isotically~~ at the 250nm wavelength used, and are the only absorbing species present. If the problem is simplified by using 1cm pathlength cells then

$$D = \epsilon a$$

$$D' = \epsilon' x + \epsilon (a - x)$$

where  $\epsilon$  = molar extinction coefficient of  $\text{Cu}^{+2}$   
 $\epsilon'$  = molar extinction coefficient of  $[\text{CuSO}_4]$

Using the fact that  $D - D' = (\epsilon - \epsilon')x$  and the definition of  $K_c$  we can derive

$$\frac{a - b}{D - D'} = \frac{a + b - x}{\Delta \epsilon} + \frac{1}{\Delta \epsilon \cdot K_c}$$

where  $\Delta \epsilon = \epsilon - \epsilon'$

The above derivation ignores the formation of small amounts of  $[\text{NaSO}_4^-]$  ion pairs. Corrections for this are within the error limits of the measurements.

concentration of  $\text{Cu}^{+2}(\text{aq})$  and  $D' = \epsilon'x + \epsilon(a - x)$  where  $D'$  = optical density of  $[\text{CuSO}_4]$  and the  $\text{Cu}^{+2}(\text{aq})$  ions.  $\epsilon'$  = extinction coefficient of  $[\text{CuSO}_4]$ ,  $a - x = [\text{Cu}^{+2}]$  in the sample solution  $D - D' = \Delta\epsilon \cdot x$ . But the stoichiometric association constant of  $\text{CuSO}_4$  is given by  $K_C = x/(a - x)(b - x)$ .

Combining the above equation, we obtain

$$\frac{ab}{D - D'} = \frac{a + b - x}{\Delta\epsilon} + \frac{1}{\Delta\epsilon \cdot K_C}$$

where  $\Delta\epsilon = \epsilon - \epsilon'$

Our task now is to calculate both  $K_C$  and  $\Delta\epsilon$ , since the other parameters in the last equation are known (except  $x$ ). Two methods were used to calculate  $K_C$  and  $\Delta\epsilon$ . The first is the graphical method, in which  $x$  is neglected first and  $ab/D - D'$  is plotted against  $(a + b)$ . From the slope and intercept both  $\Delta\epsilon$  and  $K_C$  are obtained. A value of  $x$  is then obtained by

$$x = (a + b) + \frac{1}{K_C} - \frac{ab}{D - D'} \cdot \Delta\epsilon$$

then a new graph is plotted between  $ab/D - D'$  against  $(a + b - x)$ . New values of  $K_C$  and  $\Delta\epsilon$  are obtained. This process is repeated several times until constant values of  $x$ ,  $K_C$  and  $\Delta\epsilon$  are obtained. Three iterations were necessary to obtain such constant values.

The second method in calculating  $K_C$  and  $\Delta\epsilon$  is simply using a least squares analysis with an iterative procedure similar to that used in the graphical method. A computer program was written and used in this case. The results obtained from both methods are essentially identical. Tables II and III give examples of the data analysis at  $32^\circ\text{C}$  and  $45^\circ\text{C}$ , respectively, while Fig. 1 shows the plots of  $ab/D - D'$  against  $(a + b - x)$  at  $25^\circ\text{C}$  for three ionic strengths. Table IV represents the stoichiometric association constants ( $K_C$ ) at various ionic strengths and temperatures. To correct for the ionic

strength effects the stoichiometric association constants at the various ionic strengths must be extrapolated to zero ionic strength. This simply means calculation of the thermodynamic association constants ( $K_A$ ) from  $K_C$  values. To carry out such a calculation activity coefficient ( $\gamma$ ) values must be known or estimated.  $K_A$  is related to  $K_C$  by the following relationship

$$K_A = K_C \cdot \frac{\gamma_{\text{CuSO}_4}}{\gamma_{\text{Cu}^{+2}} \cdot \gamma_{\text{SO}_4^{-2}}} \quad \text{gamma}$$

which can be rewritten as

$$K_A = K_C \cdot \frac{1}{f^{+2}} \quad \frac{1}{\gamma_{\pm}^2}$$

where  $\gamma_{\text{CuSO}_4}$  = activity coefficient of  $[\text{CuSO}_4]$  ion pair is considered to be unity

$\gamma_{\text{Cu}^{+2}} \approx \gamma_{\text{SO}_4^{-2}} = \gamma_{\pm}$  is the mean ionic activity coefficient of the free ions.

In our calculations for obtaining  $K_A$  from  $K_C$  the mean ionic activity coefficients for the ionic species were obtained using the Davies equation

$$-\log \gamma_{\pm} = 0.5 Z_i^2 \left\{ \frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - 0.3 I \right\}$$

where  $Z_i$  = charge of ion and  $I$  is the ionic strength. The temperature effects on the activity coefficients are not considered. The values in Harned and Owen's tables indicate that  $\gamma_{\pm}$  for similar salts varies less than 1.5% in a 30°C range. The mean activity coefficients of the  $\text{Cu}^{+2}(\text{aq})$  ions as a function of temperature are not available.

$K_A$  is calculated at the same temperature, using all the ionic strengths at this temperature and an average value is obtained along with the standard error.

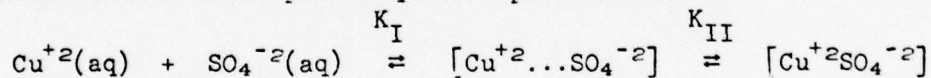
Another way of obtaining the thermodynamic association constant was developed by Petrucci. Here a plot of  $(\log K - \log \gamma_{\pm}^2)$  versus the ionic strength is made according to the equation

$$\log K_C - \log \gamma_{\pm}^2 = \log K_A$$

In this method several different values of  $\gamma_{\pm}$  are calculated by the extended Debye-Hückel activity coefficient equation using different values for closest distance of approach,  $a^{\circ}$ . When three values for  $a^{\circ}$  were used (0, 2.5 and 5 Å) they gave a thermodynamic association constant  $K_A$  within 5% ~~from~~<sup>of</sup> the value obtained by the other method. Table V shows the  $K_A$  values at 15, 25, 32 and 45°C. Also included in the same table are the thermodynamic parameters  $\Delta H^{\circ}$ ,  $\Delta G^{\circ}$  and  $\Delta S^{\circ}$  at the corresponding temperatures.

Then comparing these results with other workers using the same method we find that the agreement is very good with Petrucci's results at 25°C for the same ionic strengths (0.06 and 0.1). Table VI summarizes this comparison.

However, the  $K_A$  values obtained spectrophotometrically are distinctly lower than the values obtained by the other methods. Qualitatively this can be rationalized by considering that  $\text{CuSO}_4$  ion association is a multi-step process whose most simple adequate representation is



State	1	2	3
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Here State 1 = free ions

State 2 = outer-sphere ion pair

State 3 = inner-sphere ion pair

Such behavior has been amply demonstrated<sup>17</sup> for many such systems using the methods of relaxation kinetics. Therefore, in such systems there is an

equilibrium mixture of free ions, outer-sphere ion pairs and inner-sphere ion pairs. Then in comparing the results of different experimental methods for  $K_A$  it is important that we recognize what species the technique measures. Basically, methods such as conductance and E.M.F. measure the free ion concentration or activity. The ion pair concentrations are then obtained by difference (and by theory!). However, the spectrophotometric method, particularly in the UV, can distinguish between inner- and outer-sphere ion pairs. Smithson and Williams<sup>18</sup> pointed out in 1958 that outer-sphere ion pairs would probably have little effect on the UV spectrum of the absorbing species.

In the case of  $[\text{CuSO}_4]$ , then, the spectrophotometric method will "see" the outer-sphere ion pairs as free ions. This will lead to a lower  $K_A$  value. In principle the combination of this  $K_A$  value and a  $K_A$  from a conductance or E.M.F. method would allow the calculation of  $K_I$  and  $K_{II}$  stepwise association constants and the relative populations of inner- and outer-sphere species. This technique will be elaborated on in the following paper.

#### Acknowledgement

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Table I

Effect of Added  $\text{HClO}_4$  on the Absorbance of  $\text{Cu}(\text{ClO}_4)_2$   
at  $25^\circ\text{C}$  at  $\lambda = 250 \text{ nm}$

$[\text{Cu}(\text{ClO}_4)_2]$ $10^3 \text{ M}$	$[\text{HClO}_4]$ $10^4 \text{ M}$	Absorbance (A)
5	0.000	0.193
5	4.164	0.164
5	8.320	0.139
5	12.492	0.138
5	16.656	0.138
5	20.820	0.138

Table II

Stoichiometric Association Constant and Spectrophotometric Data

of  $\text{CuSO}_4$  at  $32^\circ\text{C}$   $[\text{Cu}(\text{ClO}_4)_2] = \underline{a} = 4.05 \times 10^{-3} \text{ M}$  $[\text{HClO}_4] = 1.01 \times 10^{-3} \text{ M}$ 

$[\text{Na}_2\text{SO}_4]$ $\text{M} \times 10^3$ (b)	$[\text{NaClO}_4]$ $\text{M} \times 10^3$ (c)	$D - D'$	$\frac{ab}{D - D'}$ $\times 10^4$	$(a + b - x)$ $\text{M} \times 10^3$
4	67.8	0.092	1.76	8.1
8	56.5	0.167	1.94	12.97
12	45.2	0.237	2.05	15.94
16	33.9	0.298	2.17	19.19
20	22.6	0.237	2.33	23.51
24	11.3	0.394	2.46	27.02
28	0.0	0.438	2.59	30.54

$$\gamma_{\pm} = 0.390; \Delta\epsilon = 270.3; K = 25.34 \text{ M}^{-1}; I = 0.091 \pm 0.001$$

Table III

Stoichiometric Association Constants and Spectrophotometric Data

of  $\text{CuSO}_4$  at  $45^\circ\text{C}$   $[\text{Cu}(\text{ClO}_4)_2] = \underline{a} = 3.04 \times 10^{-3} \text{ M}$  $[\text{HClO}_4] = 7.587 \times 10^{-4} \text{ M}$ 

$[\text{Na}_2\text{SO}_4]$ $\text{M} \times 10^3$ (b)	$[\text{NaClO}_4]$ $\text{M} \times 10^3$ (c)	$D - D'$	$\frac{ab}{D - D'}$ $\times 10^5$	$(a + b - x)$ $\text{M} \times 10^3$
3	23.6	0.119	7.66	6.412
4	21.0	0.163	7.46	5.722
6	15.7	0.216	8.44	9.101
8	10.5	0.277	8.79	10.308
10	5.2	0.318	9.56	12.963
12	0.0	0.364	10.02	14.550

$$\delta_{\pm} = 0.485; \Delta\epsilon = 338.9; K = 50.8_{\text{e}} \text{ M}^{-1}; I = 0.0418 \pm 0.002$$

Table IV

Stoichiometric Association Constants of  $\text{CuSO}_4$  at Various Ionic Strengths  
and Temperatures from Spectrophotometric Methods

Temp. °C	Ionic Strength I	$\Delta\epsilon$	$K_C$ $\text{LM}^{-1}$
15	$0.0435 \pm 0.0041$	215.1	31.63
	$0.0634 \pm 0.0013$	200.0	27.39
	$0.0922 \pm 0.0023$	200.0	22.93
25	$0.0421 \pm 0.0027$	250.0	35.10
	$0.0635 \pm 0.0030$	209.5	31.97
	$0.0910 \pm 0.0035$	242.1	24.43
32	$0.0429 \pm 0.0024$	266.60	38.26
	$0.0627 \pm 0.0023$	234.15	33.35
	$0.0912 \pm 0.0010$	270.27	25.34
45	$0.0418 \pm 0.0020$	338.98	50.86
	$0.0620 \pm 0.0019$	248.43	36.79
	$0.0995 \pm 0.0017$	384.61	28.57

The errors in  $\Delta\epsilon$  and  $K_C$  are  $\pm 5\%$ .

Additional digits are carried in the results to eliminate rounding off errors in other calculations.

Table V

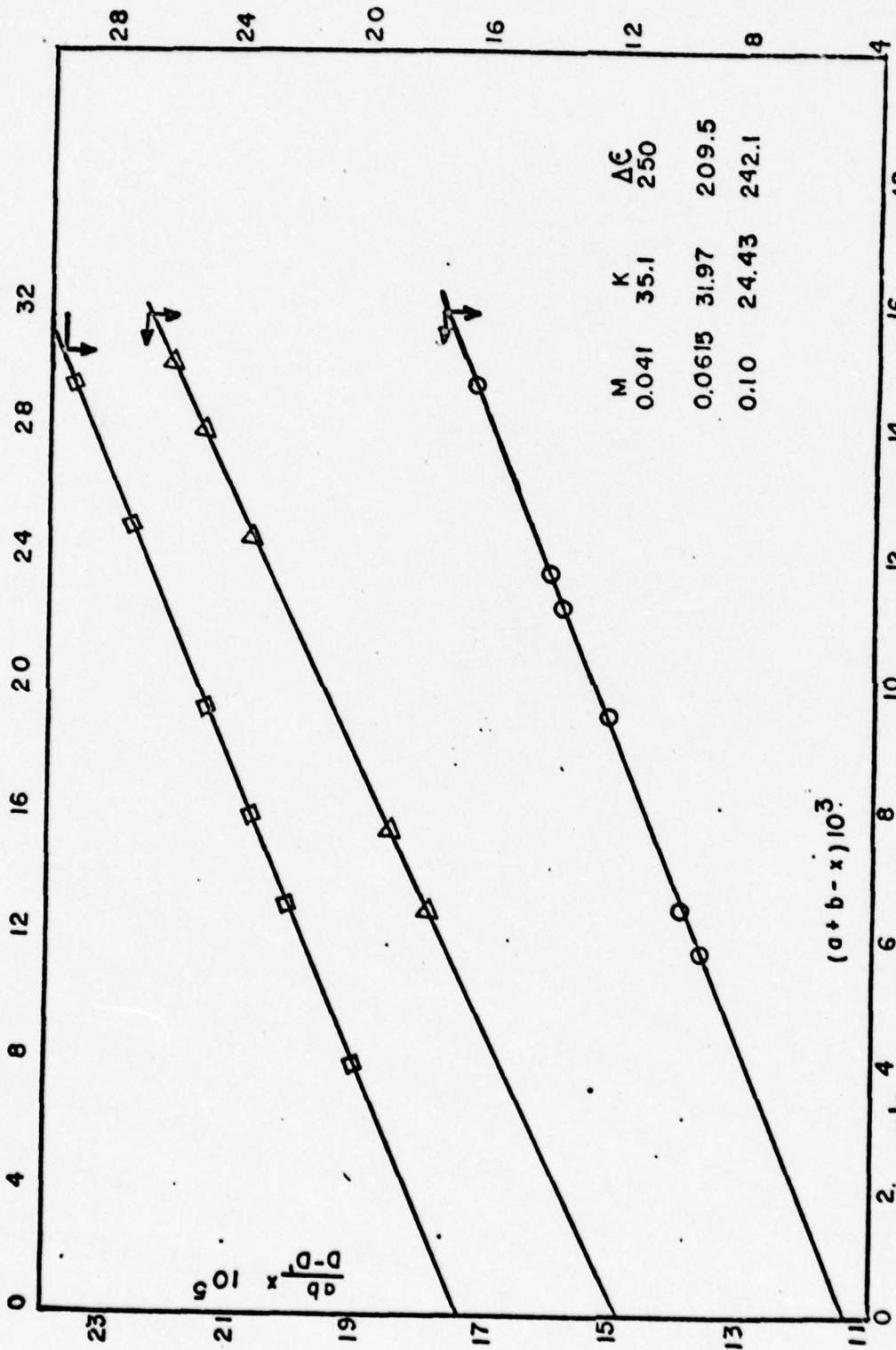
Thermodynamic Parameters of Ion Pair Formation of  $\text{CuSO}_4$ 

T °C	$K_A$ $\text{M}^{-1}$	$\Delta H^\circ$ Kcal $\text{M}^{-1}$	$\Delta G^\circ$ Kcal $\text{M}^{-1}$	$\Delta S^\circ$ cal $\text{M}^{-1} \text{K}^{-1}$
15	145.0	2.40	-2.86	18.0
25	160.6	2.40	-3.02	18.0
32	169.6	2.40	-3.12	18.0
45	201.4	2.40	-3.39	18.0

Table VI

Summary of the Spectrophotometrically Determined Stoichiometric  
Association Constants of  $\text{CuSO}_4$  at  $25^\circ\text{C}$   
in Aqueous  $\text{NaClO}_4$  Media

I	Reference	K $\text{M}^{-1}$
0.042	This work	35.1
0.064	This work	32.0
0.061	Petrucci	31.5
0.070	Petrucci	28.4
0.091	This work	24.4
0.103	Petrucci	18.9
0.095	Matheson	23.9



$\frac{ab}{D-D'} \text{ vs } (a+b-x)$  for  $\text{CuSO}_4$  at  $25^\circ\text{C}$  at  $I = 0.1(\square)$ ,  
 $0.615(\triangle)$  and  $0.041(\circ)$ .

Fig. 1

AN ION SELECTIVE ELECTRODE STUDY OF CALCIUM  
AND MAGNESIUM SULFATE IN AQUEOUS SOLUTION

KEY WORDS : Calcium, magnesium, ion-selective potentiometry,  
ion association

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ABSTRACT

A divalent cation-selective electrode was used to study the ion association thermodynamics of  $MgSO_4$  and  $CaSO_4$  at temperatures between 15 and 35 °C and at various ionic strengths. The ionic strength was adjusted with sodium chloride because it is the major salt in most natural waters. The thermodynamic association constants for  $MgSO_4$  and  $CaSO_4$  compare well with those determined from conductance studies.

INTRODUCTION

The study of ion association in solution has been an active area of chemical research for decades. Almost every known physico-chemical method has been applied to this problem. Potentiometric methods have not been

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particularly popular in the past due to the limited number of ions for which highly specific good quality electrodes were available. The present availability of the new generation of membrane and solid state ion selective electrodes should change that.

In this laboratory we are interested in the chemistry of natural waters such as seawater<sup>1,2</sup> and geothermal brines. Both in the laboratory and the field, new ways of measuring important components of such waters are badly needed. The availability of the new divalent cation electrodes encouraged us to examine their applicability to such measurements on  $Mg^{+2}$  and  $Ca^{+2}$  ions. As a test of such utility we decided to measure  $MgSO_4$  and  $CaSO_4$  ion association thermodynamics over a range of ionic strength and temperature.

Several investigators<sup>3,4,5</sup> have carried out limited range measurements on these systems using various techniques. After the measurements reported here were completed, Ainsworth<sup>6</sup> published some  $CaSO_4$  results obtained with an Orion Model 92-20 calcium electrode. His results at 25° agree in general with those reported here. However, his work was restricted to one ionic strength fixed with  $CaCl_2$ .

#### EXPERIMENTAL

All measurements were made with an Orion Model 801 Digital pH Meter equipped with an Orion Model 92-32 Divalent Cation electrode and an Orion 90-01 Single Junction reference electrode. Measurements were made in a large volume jacketed glass all whose contents could be controlled to  $\pm 0.05^\circ C$ .

Reagent grade  $MgCl_2$ ,  $MgSO_4$ ,  $CaCl_2$ ,  $CaSO_4$  and  $NaCl$  were used to prepare stock solutions. All solutions were analyzed using standard ion exchange and EDTA titration techniques.

In each set of measurements the first step is the calibration of the electrode pair using standard solutions of known activity. The standards for  $MgSO_4$  and  $CaSO_4$  were  $MgCl_2$  and  $CaCl_2$  respectively. The activities of these solutions are well known<sup>7,8</sup> These standard calibration curves gave

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the Nernst slope of 29.5 mv at 25°. The calibration was checked with standard solutions after each set of "unknowns" to test electrode drift. Measurements where such drift was found were discarded.

After the initial calibration curve was run, "unknown" solutions were prepared by weight and placed in the cell. A constant potential reading was normally obtained in 10-15 minutes with the approximately 200 cm<sup>3</sup> samples. The pH of each "unknown" was checked to detect any hydrolysis problems.

#### RESULTS AND DISCUSSION

##### A. MgSO<sub>4</sub>

Two of the authors have previously worked on the MgSO<sub>4</sub> system<sup>9</sup> using a spectrophotometric technique and potentiometry. However, these measurements were carried out at high ionic strengths. In this work we have used lower ionic strengths and have used NaCl as a medium. Although not commonly used to control ionic strength, NaCl is the common salt in most natural waters and, so, has been used here.

Measurements were made at four ionic strengths and three temperatures (15°, 25°, 35°) in the NaCl media. In addition, MgSO<sub>4</sub> measurements were made at 25° at seven concentrations in pure water. Tables I, II present sample data at ionic strength 0.108 (25°) and 0.027 (35°). Table III summarizes the pure water data. Table IV summarizes the NaCl media data at all three temperatures.

The potentiometric readings are converted to Mg<sup>+2</sup> activity using the calibration curve. The activities converted to concentration using the known activity coefficient

$$Mg^{+2} = a_{Mg^{+2}} / \gamma_{\pm}$$

It is then possible to calculate the stoichiometric association constant

$$K_c = \frac{[MgSO_4]}{[Mg^{+2}][SO_4^{-2}]}$$

The infinite dilution association constant is related to the stoichiometric



TABLE II  
 $MgSO_4$  in Aqueous NaCl 35°C + 0.05;  $\bar{V} + 0.554$ . I = 0.0272.

$[MgCl_2]$ Mx10 <sup>3</sup>	$[MgSO_4]$ in MgCl <sub>2</sub> Mx10 <sup>3</sup>	$[NaCl]$ in MgSO <sub>4</sub> Mx10 <sup>3</sup>	mV MgCl <sub>2</sub>	mV MgSO <sub>4</sub>	$[Mg^{2+}]$ Mx10 <sup>3</sup>	I	K <sub>C</sub> LM <sup>-1</sup>
2.460	2.883	17.26	-9.50	-9.40	2.462	0.0271	69.45
3.075	3.736	14.80	-7.00	-6.70	3.100	0.0272	66.18
3.690	4.643	12.34	-4.60	-4.40	3.720	0.0272	66.70
4.920	6.614	7.420	-1.20	-1.00	4.950	0.0272	67.91
6.150	8.797	2.500	+1.30	+1.30	6.150	0.0272	69.98
Mean =							68.04

TABLE III

MgSO<sub>4</sub> in H<sub>2</sub>O  
25°C

[MgCl <sub>2</sub> ] Mx10 <sup>-3</sup>	[MgSO <sub>4</sub> ] Mx10 <sup>-3</sup>	mV MgCl <sub>2</sub>	mV MgSO <sub>4</sub>	$\alpha_{Mg^{2+}}$ Mx10 <sup>3</sup>	$\gamma_{\pm}$ Mg <sup>+2</sup>	I Mx10 <sup>3</sup>	K <sub>c</sub>
7.380	10.20	-11.20	-13.00	3.750	0.555	0.0271	74.36
17.83	38.25	- 4.70	- 5.30	8.250	0.446	0.0740	57.80
24.60	51.63	- 3.30	- 3.10	11.10	0.410	0.1082	33.52
30.75	75.20	- 1.10	- 0.30	13.50	0.385	0.1400	32.60
41.82	102.60	2.10	2.40	16.70	0.360	0.186	25.73
55.35	137.00	4.70	4.70	20.35	0.328	0.248	19.47
64.57	154.20	6.80	5.80	22.00	0.318	0.277	17.76

TABLE IV  
SUMMARY OF STOICHIOMETRIC ASSOCIATION  
CONSTANTS OF  $MgSO_4$  IN AQUEOUS NaCl

T °C	I M	$\gamma_{\pm}$	$I^{1/2}$	$K_c$ LM <sup>-1</sup>
15	0.07470	0.4432	0.2732	32.17
	0.1075	0.4100	0.3278	27.76
	0.1402	0.3840	0.3744	24.42
	0.2462	0.3285	0.4962	16.06
25	0.07430	0.4455	0.2725	36.68
	0.1084	0.4100	0.3292	28.92
	0.1404	0.3860	0.3766	26.18
	0.2478	0.3275	0.4978	16.10
35	0.02720	0.5540	0.1648	68.04
	0.07460	0.4435	0.2730	37.74
	0.1085	0.4080	0.3293	28.33
	0.1412	0.3830	0.3757	24.72
	0.2480	0.3270	0.4979	16.97

constant by the equation

$$K_a = K_c / \gamma_{\pm}^2$$

where we have assumed the activity coefficient of the ion pair to be one.

For the calculation of  $K_a$  we have used the Davies equation.<sup>11</sup>

$$-\log \gamma_{\pm} = 0.5 z^2 \left[ \frac{I^{1/2}}{1 + I^{1/2}} - 0.3I \right]$$

Table V summarizes the results of the investigation. The  $K_a$  in NaCl is distinctly lower than the  $K_a$  in pure water. This is probably due to minor

TABLE V  
ASSOCIATION CONSTANTS AND THERMODYNAMIC  
PARAMETERS OF  $MgSO_4$ .

T		$K_T$	$\Delta H^\circ$	$\Delta G^\circ$	$\Delta S^\circ$
°C	Medium	$LM^{-1}$	KCal/Mole	KCal/Mole	KCal/Mole-°K
15	NaCl	$160.83 \pm 6.00$	1.15	- 2.92	0.0141
25	NaCl	$170.46 \pm 10.16$	1.15	- 3.09	0.0142
	H <sub>2</sub> O	$204.40 \pm 20.00$			
35	NaCl	$182.99 \pm 19.67$	1.15	- 3.20	0.0141

amounts of  $NaSO_4^-$  formation as well as the inadequacy of the Davies equation in the more complex NaCl/ $MgSO_4$  mixture.

The  $K_a$  (H<sub>2</sub>O) results agree reasonably well with the results obtained by conductance ( $K_a=187$ )<sup>12</sup> and other methods.<sup>13</sup>

#### B. $CaSO_4$

Measurements of the  $CaSO_4$  - NaCl system were carried out at four ionic strengths and three temperatures. Tables VI, VII and VIII give representative data. Each reported  $K_c$  is an average of five separate measurements.

Calculations were carried out exactly the same as in  $MgSO_4$ . Table IX summarizes the  $K_c$  results while Table X summarizes the  $K_a$  and other infinite dilution results. Fig. 1 gives the van'Thoff plot for  $K_a$ .

The  $K_a$  value at 25° is  $196.5 LM^{-1}$  in good agreement with the conductance value<sup>13</sup>( $200 LM^{-1}$ ) and the solubility value<sup>13</sup>( $204.2 LM^{-1}$ ). The  $\Delta H^\circ$  and  $\Delta S^\circ$  are in good agreement with those of Ainsworth.

TABLE VI

CaSO<sub>4</sub> in Aqueous NaCl: 15°C ± 0.05;  $\bar{Y}_+ = 0.5125$ ;  $\bar{Y}_- = 0.0402$ .

[CaCl <sub>2</sub> ] Mx10 <sup>3</sup>	[CaSO <sub>4</sub> ] Mx10 <sup>3</sup>	[NaCl] in CaCl <sub>2</sub> Mx10 <sup>3</sup>	[NaCl] in CaSO <sub>4</sub> Mx10 <sup>3</sup>	mV CaCl <sub>2</sub>	mV CaSO <sub>4</sub>	[Ca <sup>2+</sup> ] Mx10 <sup>3</sup>	I	K <sub>c</sub> LM <sup>-1</sup>
3.000	3.495	31.00	28.00	-5.00	-4.70	3.040	0.0402	49.23
4.000	4.880	28.00	24.00	-2.10	-1.80	4.050	0.0402	50.60
5.000	6.375	25.00	20.00	+0.50	+0.75	5.100	0.0404	45.02
6.000	7.980	22.00	16.00	2.60	2.70	6.050	0.0402	52.72
7.000	9.695	19.00	12.00	4.50	4.60	7.050	0.0402	53.21
Mean =								50.95

TABLE VII

$\text{CaSO}_4$  in Aqueous  $\text{NaCl}$ :  $25^\circ\text{C} \pm 0.01$ ,  $\bar{Y}_\pm = 0.586$  and  $I = 0.0206$ .

$[\text{CaCl}_2]$ $\text{M} \times 10^3$	$[\text{CaSO}_4]$ $\text{M} \times 10^3$	$[\text{NaCl}]$ in $\text{CaCl}_2$ $\text{M} \times 10^3$	$[\text{NaCl}]$ in $\text{CaSO}_4$ $\text{M} \times 10^3$	mV $\text{CaCl}_2$	mV $\text{CaSO}_4$	$[\text{Ca}^{2+}]$ $\text{M} \times 10^3$	I	$K_c$ $\text{L} \cdot \text{M}^{-1}$	
2.000	2.360	14.00	12.00	-9.40	-9.10	2.066	0.0203	68.90	
2.500	3.062	12.50	10.00	-7.80	-7.30	2.600	0.0204	68.41	
3.000	3.810	11.00	8.000	-5.60	-5.10	3.140	0.0206	68.60	
4.000	5.440	8.000	4.000	-2.10	-1.70	4.200	0.0208	70.29	
5.000	7.250	5.000	0.000	+0.40	+0.90	5.250	0.0210	72.56	
							Mean	=	69.63

TABLE VIII  
 $\text{CaSO}_4$  in Aqueous NaCl  $35^\circ\text{C} \pm 0.01$ ;  $\gamma_{\pm} = 0.595$  at  $I = 0.0201$

$[\text{CaCl}_2]$ $\text{Mx}10^3$	$[\text{CaSO}_4]$ $\text{Mx}10^3$	$[\text{NaCl}]$ in $\text{CaCl}_2$ $\text{Mx}10^3$	$[\text{NaCl}]$ in $\text{CaSO}_4$ $\text{Mx}10^3$	mV $\text{CaCl}_2$	mV $\text{CaSO}_4$	$[\text{Ca}^{2+}]$ $\text{Mx}10^3$	I	$K_c$ $\text{LM}^{-1}$
2.000	2.360	14.00	12.00	-9.90	-9.90	2.0	0.0200	90.00
2.500	3.063	12.50	10.00	-7.00	-6.80	2.52	0.0201	85.43
3.000	3.810	11.00	8.000	-4.80	-4.40	3.05	0.0202	81.70
4.000	5.440	8.000	4.000	-1.10	-1.00	4.02	0.0201	87.87
5.000	7.250	5.000	0.000	+1.40	+1.50	5.00	0.0200	90.00
						Mean =		87.00

TABLE IX

Summary of Association Constants of  $\text{CaSO}_4$  in Aqueous NaCl.

T °C	I	$I^{1/2}$	$\gamma_{\pm}$	$K_c$ $\text{LM}^{-1}$
15	0.0402	0.2006	0.5125	50.950
	0.0599	0.2447	0.4705	41.380
	0.0800	0.2826	0.4375	30.580
	0.0998	0.3159	0.4156	25.956
25	0.02060	0.1435	0.5860	69.630
	0.04075	0.2018	0.5110	54.600
	0.06080	0.2465	0.4690	42.380
	0.08010	0.2830	0.4360	37.300
	0.10010	0.3164	0.4150	31.240
35	0.02007	0.1416	0.5950	87.000
	0.04000	0.2001	0.5140	64.610
	0.06000	0.2450	0.4680	49.370
	0.08000	0.2827	0.4375	38.680
	0.09990	0.3160	0.4155	32.490

TABLE X

Association Constants and Thermodynamic Parameters of  $\text{CaSO}_4$ .

T °C	$K_T$ $\text{LM}^{-1}$	$\Delta H^\circ$ KCal/Mole	$\Delta G^\circ$ KCal/Mole	$\Delta S^\circ$ KCal/Mole $^{-\circ\text{K}}$
15	$172.74 \pm 14.18$	2.20	- 2.964	+ 0.0179
25	$196.51 \pm 7.53$	2.20	- 3.144	+ 0.0179
35	$221.21 \pm 18.91$	2.20	- 3.322	+ 0.0179

Our results show that the specific ion electrode is very capable of giving good thermodynamic data if proper care is taken. The main limitation is the need to make statements about activity coefficients in rather complex systems. This same problem will also intrude in natural water work.

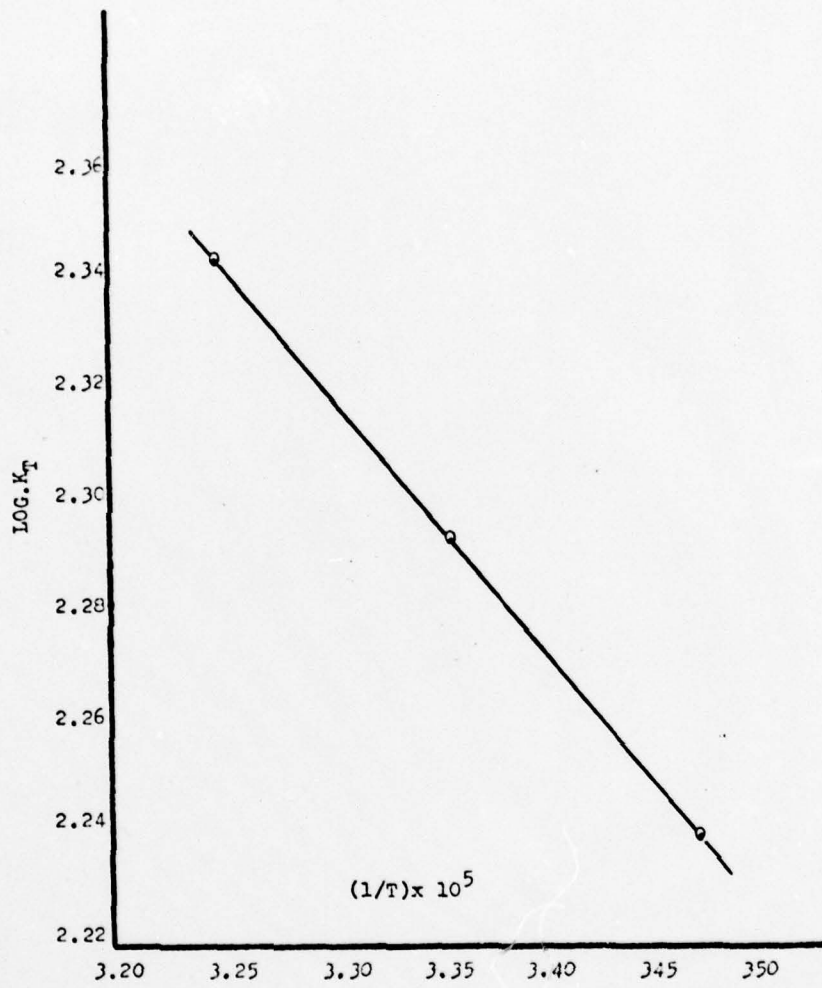


Fig. (1) Log  $K_T$  Vs.  $\frac{1}{T}$  of  $\text{CaSO}_4$

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