THERMODYNAMIC STUDIES OF GYPSUM
IN WATER AND AQUEOUS SOLUTIONS

by

CHARLES CLIFFORD BRIGGS

Thesis submitted for the Degree of
Doctor of Philosophy

Department of Chemistry
University of Sheffield

November 1972

SUMMARY

The object of the work described in this thesis was to investigate some aspects of the thermodynamics of calcium sulphate in aqueous solutions containing mixed electrolytes.

A large portion of the thesis describes the experimental determination of the thermodynamic solubility product of gypsum ($CaSO_4 \cdot 2H_2O$) by an electromotive force method. The procedure used is novel and involved the use of a calcium responsive membrane electrode in conjunction with a lead two phase amalgam — lead sulphate electrode. The standard potential of the latter electrode and some thermodynamic properties of calcium sulphate solutions were obtained in the course of this work.

Gypsum solubility measurements were made up to ionic strengths of six molal in binary and ternary electrolyte solutions in the system Ca^{2+} - Na^{+} - SO_4^{2-} - Cl^{-} - H_2O. A second estimate of the gypsum solubility product was obtained from the results. Activity coefficients in the mixed electrolyte solutions were investigated using some recent approaches in electrolyte thermodynamics.

An electromotive force method was used to obtain calcium chloride activity coefficients in mixed solutions with calcium sulphate. The experiment was designed to provide confirmation of a theoretical limiting law for mixtures of electrolytes having asymmetric charge types. It was concluded that such confirmation was not possible for the system investigated. Literature osmotic coefficients for mixtures of 1:1 and 2:1 charge type chlorides were analysed to check if the data conformed to a related limiting law for solvent properties. The theoretical concentration dependence trend was not observed, but the data were concordant with primitive model calculations.

ACKNOWLEDGEMENTS

I would like to dedicate this thesis to my wife for her constant encouragement. I would also like to acknowledge the assistance of the following:

Dr. M. Elder:	for valuable help with computer programming.
Professor H. L. Friedman:	for his useful comments on the work described in Part III.
Professor G. J. Hoytink:	for provision of laboratory facilities within the Department of Chemistry of the University of Sheffield.
Dr. T. H. Lilley:	for his excellent supervision and for numerous ideas and suggestions without which this work would not have been possible.
Dr. C. W. Outhwaite:	for carrying out the calculations referred to in Part I.
Mrs. C. A. Richardson:	for her efficient typing.
Professor G. Scatchard:	for permission to reproduce some of his equations.
The Science Research Council:	for the award of a grant.
The Steetley Company:	for generous provision of facilities and for financial assistance.

CONTENTS

Page Number

PART I: THE THERMODYNAMIC SOLUBILITY PRODUCT OF CALCIUM SULPHATE DIHYDRATE IN AQUEOUS SOLUTION AT 25°C

PART II: SOLUBILITY OF CALCIUM SULPHATE DIHYDRATE IN THE SYSTEM Ca^{2+} - Na^+ - SO_4^{2-} - Cl^- - H_2O AT 25°C

PART III: SOME ASPECTS OF THE THERMODYNAMIC PROPERTIES OF DILUTE BINARY ELECTROLYTE SOLUTIONS

PART IV: EVALUATION OF AN ALTERNATIVE TO THE DEBYE-HÜCKEL EXPRESSION

PART I

THE THERMODYNAMIC SOLUBILITY PRODUCT OF CALCIUM SULPHATE DIHYDRATE (GYPSUM) IN AQUEOUS SOLUTION AT 25^{o}C

1. INTRODUCTION

1.1 STATEMENT OF PROBLEM

The thermodynamic solubility product (K_{sp}) for the dissolution process

$$CaSO_4.2H_2O_{(s)} \quad = \quad Ca^{2+}_{(aq)} \; + \; SO_4^{2-}{}_{(aq)} \; + \; 2H_2O_{(\ell)}$$

is defined by

$$K_{sp} \quad = \quad m_{Ca^{2+}}\, m_{SO_4^{2-}}\, \gamma_\pm^2\, a_W^2 \qquad \text{(E.1.1.1)}$$

$m_{Ca^{2+}}$ and $m_{SO_4^{2-}}$ are the molalities of calcium and sulphate ions in equilibrium with solid phase gypsum, $\gamma_\pm$ is the mean ionic molal activity coefficient and a_W is the water activity.

In Part II of this thesis the solubility product is required in order to calculate activity coefficients from measured solubilities. Unfortunately literature values for K_{sp} differ by factors as large as two. The solubility of gypsum may be measured with reasonable accuracy, and the water activity is so close to unity that an error in its estimation would be negligible. The difficulty in obtaining K_{sp} arises in deducing the value of $\gamma_\pm$ at the solubility limit.

1.2 LITERATURE RESULTS

1.2.1 Standard free energies of formation

K_{sp} may be estimated at 25°C in an indirect manner from the tables of standard free energy of formation given by Latimer (1). The result is $K_{sp} = 2.45 \times 10^{-5}$ mol^2 kg^{-2}. The reliance which can be placed on the accuracy of this result for the solubility product, depends upon the manner in which the values given by Latimer were reached. The quoted standard free energies of formation are self consistent and for liquid water for example are probably very accurate. In the case of aqueous multivalent ions, serious problems exist. Consider the sulphate ion. The standard free energy of formation in aqueous solution is calculated from the standard enthalpy and standard entropy of formation. One method of calculating the latter quantity requires the following information:

(i) the standard entropy of gypsum;
(ii) the standard enthalpy of solution of gypsum;
(iii) the standard entropy of the aqueous Ca^{2+} ion;
(iv) the thermodynamic solubility product of gypsum.

This is the method used by Latimer *et al* (8). It is clear that circular arguments are involved if the tabulated standard free energies of formation are used to calculate K_{sp} for gypsum. This situation is somewhat modified by the fact that the figures quoted in reference (1) are derived from various sets of data and averaged so as to give values which are self consistent with all other data presented in the monograph (1).

1.2.2 Freezing point measurements

The most reliable estimates of K_{sp} were probably those based on the freezing point measurements of Brown and Prue (5). The latter measured freezing point depressions of calcium sulphate solutions in the concentration range 0.00418 to 0.011 molal, and five other 2:2 sulphates up to concentrations of about 0.1 molal. They were able to account for the observed osmotic coefficients (ϕ) to about 0.02 molal by assuming ion pairing. Above this concentration serious discrepancies were evident.

Gardner and Glueckauf (2) treated the same data assuming that further association into either triplets or quadruplets occurs. Both these assumptions gave a reasonable fit to the experimental osmotic coefficients for all six sulphates. Electrostatic contributions were expressed by the equations advocated by Glueckauf (6), and three additional parameters were introduced giving terms linear in concentration ostensibly to account for hydration. Sets of parameters giving a satisfactory fit to the osmotic coefficient data were deduced. Activity coefficients were calculated at 0^oC by using these sets of parameters in equations linked to the osmotic coefficient equations via the Gibbs-Duhem relationship. A value for the thermodynamic solubility product of gypsum at 25^oC was derived using the solubility data of Marshall and Slusher (7), and the assumption that activity coefficients are invariant over the temperature range 0^oC to 25^oC. This procedure gave $K_{sp} = 2.49 \times 10^{-5}$ mol^2 kg^{-2}.

In a second paper (3) restricted to calcium sulphate solutions, Gardner and Glueckauf used the same treatment as in (2), but the temperature dependence of the activity coefficients was taken into account. It was assumed that the temperature dependence of the ion pair dissociation constant was correctly given by the electrostatic treatment of Bjerrum (9). The distance of closest approach (a) was taken to be independent of temperature. This proposition was made on the reasonable grounds that at the value of "a" deduced from the results at 0^oC, the interaction energy between two doubly charged ions would be 8 kT at that temperature and 11 kT at 200^oC. Consequently the closest possible contact, consistent with short range repulsive forces, would be achieved at all temperatures. This argument is supported by the work of Marshall and Slusher (7). This modified proceedure resulted in a value for the solubility product at 25^oC of 2.26×10^{-5} mol^2 kg^{-2}. In 1971 Gardner and Glueckauf (4) presented a third paper dealing with calcium sulphate activity coefficients. In this paper the Bjerrum concept of ionic association was dispensed with, and activity coefficients were derived using a numerical integration of the Poisson-Boltzmann (P-B) equation. The authors carried out extensive calculations for 2:2 electrolytes, based on Müller's (10) method for the exact solution of the P-B equation. Eight extension terms to the linearised Debye-Hückel term were used, compared with only two extension terms used by Gronwall, La Mer and Sandved (11). Using this approach the only variable parameter in the electrostatic contribution to activity or osmotic coefficients is the distance of closestapproach. The authors deduced this value for $CaSO_4$ by once again using the freezing point data of Brown and Prue. The Debye-Hückel term was again replaced by Glueckauf's approximation to Kirkwood's equation (12), allowing a term linear in concentration to be added to account for statistical contributions. It was found that the distance of closest approach required to fit the observed osmotic coefficients was not markedly dependent on the chosen value for the constant in the statistical term. The same assumption that "a" is independent of temperature was used to calculate activity coefficients at temperatures greater than 0°C, giving a value at 25°C which together with the solubility data of Marshall and Slusher (7) gave a value for the thermodynamic solubility product of 2.23×10^{-5} mol^2 kg^{-2}.

1.2.3 Solubility measurements

Marshall and Slusher (7) measured gypsum solubilities in sodium chloride solutions for concentrations of NaCl from zero up to the solubility limit and at temperatures from 0 to 100°C. Values of K_{sp} were found at each temperature by using a Debye-Hückel (D-H) expression for the activity coefficients, extended by empirical terms in I and I^2:

$$\ln \gamma_{\pm} = - \frac{|z_+ z_-| S \sqrt{I}}{1 + (a/a_0)\sqrt{I}} + BI + CI^2 \qquad (E.1.2.1)$$

z_+ and z_- are the charges on the cation and anion;

S is the D-H limiting law constant = 1.172 kg$^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$ at 25°C;

a is the distance of closest approach of ions;

a_0 is a constant dependent only on temperature and the properties of the solvent;

B and C are empirically determined constants;

I is the ionic strength defined on the molality scale by $I = \frac{1}{2} \Sigma m_i z_i^2$;

m_i is the molality of the i'th species;

z_i is the charge on the i'th species.

It was assumed that calcium sulphate is fully dissociated in solution. The solubility data was fitted by a non linear least squares procedure to give best values of the solubility product, the distance of closest approach, and the proportionality constants for the extension terms in E.1.2.1. At 25°C this procedure gave a result of $K_{sp} = 4.23 \times 10^{-5}$ mol^2 kg^{-2}.

The authors also treated the data by assuming that ion pairing occurs. The details of this treatment are not clear, but it was concluded that the original assumption of full dissociation was adequate on the grounds that the variance of fit between observed and calculated results was essentially the same using the two treatments.

In this second method of analysis, the dissociation constant was treated as a variable parameter, and a value of 0.013 mol kg^{-1} was found for 25°C. This is higher than other literature values which are in the range 0.003 to 0.006 mol kg^{-1}. Since new results for the solubility product were not given, it is probable that K_{sp} was fixed at the original value rather than treated as a variable.

Other workers who have treated gypsum solubility measurements in sodium chloride solutions are Ostroff and Metler (13) and Denman (14). The former used their measurements at 28°C to calculate a value for K_{sp} of 4.5×10^{-5} mol^2 kg^{-2} by an unsophisticated extrapolation technique. Ion pairing was not considered and activity coefficients were calculated using the Debye-Hückel equation with an arbitrarily chosen value for the distance of closest approach. Denman (14) treated his measurements using a pre-Debye-Hückel approach, in that log $\gamma_\pm$ was assumed to be a linear function in the cube root of ionic strength. The results of his treatment could be interpreted as being equivalent to a solubility product of 2.9×10^{-5} mol^2 kg^{-2} at 25°C. In view of the empirical nature of this approach, Denman achieved a surprising degree of accuracy in his primary objective of predicting gypsum solubilities in a number of electrolyte solutions.

Moreno and Osborn (15) measured gypsum solubilities in sulphuric acid solutions at 25°C. Single ion activity coefficients were calculated using a Debye-Hückel equation in which different values for the distance of closest approach were used for each species. The value of Bell and George (16) was used for the dissociation constant of $CaSO_4$ ion pairs; and the value of Lietzke *et al* (17) was used for the dissociation constant of the bisulphate ion. The equations were solved by an iterative technique in order to obtain free ion concentrations which were consistent with the ionic strength used to calculate the activity coefficients. Calculated values of K_{sp} remained remarkably constant around 2.45×10^{-5} mol^{2}kg^{-2} over a range of sulphuric acid concentration from zero to 0.05 molal.

Nakayama and Rasnick (18) measured calcium sulphate solubilities in solutions of NaCl and Na_2SO_4 up to 0.1 molal at 25°C. "Calcium ion activities" were measured by using a calcium responsive membrane electrode in conjuntion with a calomel reference electrode. The degree of dissociation of $CaSO_4$ ion pairs was calculated by an iterative method using a D-H expression for the activity coefficients of free ions. The solubility product and dissociation constant were then calculated for each solution, making a correction for ion-pairing of sodium and sulphate ions in the case of Na_2SO_4 solutions. Values of K_{sp} were in the range 2.4 to 2.9×10^{-5} mol^2 kg^{-2} and values of the ion pair dissociation constant (K_D) were in the range 0.0051 to 0.0066 mol kg^{-1}.

Tanji (19), measured gypsum solubilities in NaCl, $MgCl_2$, $CaCl_2$, Na_2SO_4 and $MgSO_4$ solutions of ionic strengths up to 0.2 molal. Calcium ion activities were measured in the same solutions by means of a membrane electrode. The author did not use these measurements to derive values for K_{sp} and K_D, but instead used literature values of $K_{sp} = 2.4 \times 10^{-5}$ mol^2 kg^{-2} and $K_D = 0.0049$ mol kg^{-1} in order to compare observed and calculated gypsum solubilities and calcium ion activities. Activity coefficients of free ions were expressed by using Davies' (74) modification of the Debye-Hückel equation:

$$\ln \gamma_i = - z_i^2 S \left[\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2 I \right] \qquad \text{(E.1.2.2)}$$

Account was taken of the formation of $MgSO_4$ and $NaSO_4^-$ ion pairs. The agreement between calculated and observed quantities was good. This implies that if Tanji (19) had used his measurements to derive K_{sp} and K_D with the same system of equations, values close to 2.4×10^{-5} mol^2 kg^{-2} and 0.0049 mol kg^{-1} would have resulted.

1.2.4 Critical discussion of accuracy for the various methods

In view of the problem of circular arguments, and the comments made by Latimer (1) on the accuracy of oxidation potentials calculated indirectly, it would be unwise to set the standard free energy change for gypsum dissolution within closer limits than 6.3 ±0.3 k cal. This corresponds to a solubility product of $(2.5 \pm 1.0) \times 10^{-5}$ mol^2 kg^{-2}.

The most thermodynamically sound methods are those of Gardner and Glueckauf (2,3,4) and their results are thought to be the most reliable. A number of factors do, however, contribute to uncertainty in the values of K_{sp} deduced. These factors are outlined below:

(i) the difficulty of accurately measuring small changes in the freezing point leads to scatter in the results. This may be seen in Fig. 6 of reference 4, where experimental osmotic coefficients are plotted against concentration.

(ii) The restricted concentration range, in combination with scatter of the results, allows relatively wide variations in sets of parameters, all of which fit the experimental data with insignificant changes in the variance of fit. As a consequence, the accuracy with which osmotic coefficients can be estimated at concentrations above and below the experimental range is severely limited.

(iii) The accurate evaluation of activity coefficients by analytical Gibbs-Duhem integrations, is limited both by the imperfect nature of the functions used for $\gamma_\pm$ and ϕ, and by errors in the parameters used in the equations.

(iv) The necessity of a long extrapolation of activity coefficients from the solubility limit at 0°C (0.011 molal) to the solubility limit at 25°C (0.0152 molal).

(v) The necessity of correcting activity coefficients for the temperature change from 0° to 25°C.

(vi) The possibility of error in the value of the stoichiometric solubility of gypsum at 25°C.

The authors do not discuss accuracy in any of their papers, but in view of the above considerations a value of $(2.3 \pm 0.4) \times 10^{-5}$mol^2 kg^{-2} seems appropriate.

The method of Marshall and Slusher (7) would appear to be unsound, primarily since it is well known (20) that the activity coefficients of 2:2 electrolytes cannot be represented by a simple Debye-Hückel expression. The addition of higher order empirical terms would not affect the invalidity of the least squares extrapolation to zero ionic strength. A further criticism of the method is that ionic strength dependence of the activity coefficients must be different in the regions above and below the solubility limit. Below this limit, only changes in $CaSO_4$ concentration contribute to changes in I, but above the limit, changes in NaCl concentration provide the major contribution. Consequently, changes in the environment of the Ca^{2+} and SO_4^{2-} ions will be of a different nature in the two situations. It is therefore inappropriate to use the ionic strength dependence of the activity coefficients in the high concentration region to predict changes in $\gamma_\pm$ below the solubility limit.

Similar objections can be made against the previously discussed methods of Ostroff (13) and of Denman (14).

All the remaining procedures use the useful concept of ion association to account for deviation of activity coefficients from the D-H expression. Unfortunately ion pair dissociation constants are not true thermodynamic constants since they depend upon the expression used for the activity coefficients of the free ions. More specifically if a D-H equation is used, the distance of closest approach parameter, should be the distance defining association and should therefore be linked to the dissociation constant. This was not the case in any of the treatments: somewhat arbitrary values were used for this parameter, more appropriate to the distance of closest approach of ions rather than the distance defining association. The concept of single ion activities is also unfortunately involved in these procedures, and in the case of Nakayama's work (18), variability of the liquid junction potential between the reference electrode and the test solutions is a further source of error. While these theoretical objections should be borne in mind, the results obtained by using the ion pairing treatments are fairly consistent and would indicate a value of K_{sp} in the range (2.5 ±0.8) × 10^{-5} mol^2 kg^{-2}.

1.3 THE PRESENT METHOD

In order to reduce the uncertainty in the value of K_{sp} a method was required which was more direct than freezing point measurements, but was still thermodynamically sound. The obvious solution was to use electrodes which were reversible to calcium and sulphate ions. Measurement of the cell e.m.f. of an aqueous solution saturated with gypsum at 25°C, would then lead directly to the solubility product using the Nernst equation and the definition of K_{sp}:

$$E_{cell} = E^o_{cell} + \frac{RT}{2F} \ln K_{sp} - \frac{RT}{F} \ln a_W$$

This method clearly requires that the standard cell potential and the water activity, are either known, or can be accurately determined.

1.3.1 Sulphate responsive electrode

The choice of sulphate electrode was controlled by the solubility of suitable sulphates (21). Only lead sulphate has a sufficiently low solubility, especially since it was desired to make measurements at calcium sulphate concentrations below saturation. Lead-lead sulphate electrodes may be used with either pure or amalgamated lead. Pure lead suffers from the disadvantage that its electrochemical properties depend markedly on the physical state of its surface (21), so that the only sulphate reversible electrode suitable for this investigation was the lead amalgam-lead sulphate electrode.

At 25°C, lead amalgams in the concentration range 1.8 to 66% Pb are two phase systems in which solid $HgPb_2$ (containing a little excess mercury in solid solution) is in equilibrium with the liquid phase (22,23,24). Consequently the e.m.f. of a lead amalgam electrode should be independent of amalgam composition over this range. Pushin (24) confirmed this prediction, but later users of two phase lead amalgams as sulphate responsive electrodes, used lead concentrations in the restricted range 2.5% to 6% (25,26,27,28,29). Following Bray (26), the detrimental effect of oxygen on the electrode was emphasised by later workers, and great care was taken at most stages of cell preparation. Examination of experimental procedures does however show that a situation where serious oxidation of amalgam could occur, was present at least once in all of the methods used. The stages involved are the transfer of amalgam from preparation cell to storage vessel, and from storage vessel to experimental cell. In order to transfer portions of amalgam of the same composition as the bulk, the amalgam must be heated to give a single phase. This requires a temperature of about 60°C for a 4% lead amalgam and, when exposed to air, oxidation occurs rapidly at this temperature. It was consequently found necessary to filter off surface oxide by passing the hot amalgam through either a glass capillary tube or a filter paper with a pin hole opening. It is obvious that oxidation also occurred at this stage, so that the amalgams could not have been free from oxide impurities. Although the detrimental effect of oxygen was emphasised, the magnitude of observed e.m.f. errors for neutral or nearly neutral solutions was not given in any of the literature. Evidence that cell e.m.f. values are not critically dependent upon the degree of oxidation may be obtained by comparison of results for the cell

$$\mathrm{Pb\ (Hg)\ |\ Pb\ SO_4\ |\ Na_2SO_4 \cdot 10H_2O\ |\ Na_2SO_4\ (sat)\ |\ Hg\ SO_4\ |\ Hg.}$$

This cell e.m.f. was measured at 25°C by a number of workers giving the following results in international volts: 0.96464 (25); 0.96466 (30); 0.96463 (31); 0.96462 (32); 0.96471 (33). The results span a range of only 0.09 mv while the care taken to exclude oxygen varied from almost no precautions in references 25 and 30 to fairly extensive precautions in the case of reference 33. Whether the same result would be obtained if a truly oxygen free cell was used is unknown.

In studies using acid solutions, such high precision has not been obtained. Harned and Hamer (22) found unreproducibility of the order of 2 mv occurred in moderately dilute sulphuric acid, even though "the greatest precautions were taken to eliminate air". At concentrations of H_2SO_4 below 0.006 molal, the results of Baumstark (34) are within experimental error of those given by Shrawder and Cowperthwaite (29) but his two results at higher concentrations are inconsistent by about 2 mv. Thus the importance of excluding oxygen, and the maximum permissible level before its presence becomes significant, are not easily ascertained from the literature. It was decided therefore to exclude the lead amalgam from oxygen at all stages of experimental work.

The standard electrode potential of the two phase lead amalgam-lead sulphate electrode was determined from the cell

$$\mathrm{Pt,\ H_2\ /\ H_2\ SO_4\ /\ Pb\ SO_4\ /\ Pb\ (Hg)} \qquad \text{Cell I}$$

by Baumstark (34) and Shrawder (29). It has already been mentioned that the e.m.f. results of these workers were in good agreement, but the values of $E^0_{PbSO_4/Pb(Hg)}$ obtained were - 0.35217 int. volts and - 0.35052 int. volts. respectively. The reason for this discrepancy lay in the extrapolation techniques used. Baumstark (34) assumed a linear relationship between cell e.m.f. and the square root of ionic strength, while Shrawder (29) took account of incomplete dissociation of the bisulphate ion in a similar extrapolation. Neither treatment was satisfactory and it was decided to re-examine both sets of results in order to obtain a more reliable value for E^o. In addition it was decided to make measurements to low calcium sulphate concentrations so that an independent result for the standard electrode potential could be obtained. This would also enable values for the ion pair dissociation constant of $CaSO_4$ to be determined.

1.3.2 Calcium responsive electrode

Calcium amalgam electrodes were considered to measure calcium ion activity, but were discarded on the grounds that the standard potential was unreliable. Butler (35) has supported the reversibility of this electrode, and after re-evaluating all previous experimental results, he concluded that $E^o_{Ca^{2+}/Ca(Hg)} = -1.996 \pm 0.002$ v. The uncertainty of ±2 mv quoted by Butler is thought to be over-optimistic since the experimental results give individual values for E^o covering a much wider range. Even if the uncertainty of ±2 mv was considered reasonable, this would still be an unsatisfactory electrode to use, since the corresponding uncertainty in the solubility product of gypsum would be $\pm 0.4 \times 10^{-5}$ mol^2 kg^{-2}.

Calcium responsive membrane electrodes do not have a standard electrode potential in the normal sense of the term, and the effective contribution to the electrode potential of the standard term is unfortunately subject to drift with time (38). These electrodes do however, have the great advantage that they can be conveniently transferred from one solution to another in a similar manner to hydrogen ion responsive glass electrodes (38). If the potentials of two cells between which the electrode is transferred are combined, the unknown "standard potential" of the calcium electrode may be eliminated. Membrane electrodes reversible to calcium ions may be subdivided into those using solid ion exchangers, and those using liquid ion exchangers. The former only recently reached the stage where a conveniently handlable electrode was used in satisfactory experiments (36), but the latter have been used successfully since 1966 by a number of workers in the form of the commercial Orion model 92-32 electrode. It was shown by Ross (37) that the electrode gave a Nernstian response over a wide concentration range, that it was insensitive to pH changes in the range 5.5 to 10, and that anions did not in general show any interference. These conclusions have since been confirmed by other workers (38). It was therefore decided to use the Orion electrode for this work.

1.3.3 Reference cells

In order to eliminate the unknown standard potential of the calcium electrode, silver/silver chloride electrodes with pure calcium chloride solutions were employed as reference cells. The activity coefficients of $CaCl_2$ are known with a high degree of accuracy and silver/silver chloride electrodes can be prepared with low bias potentials. The standard e.m.f. of the Ag/AgCl electrode has been determined by a number of workers (21) and the three results quoted in reference 21 at 25°C are within 0.06 mv of the mean value.

1.3.4 Proposed experimental work

The intended work programme was split into three stages:

(i) a preliminary investigation using $CaCl_2$ solutions only. This was to check (a) that the response of the calcium electrode was Nernstian; (b) that solution pH was not critical in the expected working range and; (c) to examine the effect of other variables in order to determine optimum conditions.

(ii) Measurements over a wide concentration range, using pure $CaSO_4$ solutions in test cells with $CaCl_2$ in reference cells.

(iii) Measurements using test cells, filled with $CaCl_2$ solutions which were in equilibrium with gypsum. This was to check that the test cells responded accurately to $CaSO_4$ activity.

2. EXPERIMENTAL

2.1 MATERIALS AND APPARATUS

2.1.1 Water

Distilled water was passed through a column of mixed strong acid and strong base ion exchange resins (Permutit "Bio-Deminrolit") immediately prior to use.

2.1.2 Calcium sulphate dihydrate

Analar material was used. Purity was checked by calcium analysis using E.D.T.A., by loss on ignition determinations, and by powder X-ray diffraction. Details are given in Part II of this thesis.

2.1.3 Lead nitrate

Analar lead nitrate was dissolved in water at the boiling point. A concentration of about 1.2 kg per kg of water was used. The hot solution was filtered using a number 4 porosity filter stick and the filtrate cooled in the collection flask to 0°C. Large crystals resulted, enabling the supernatant solution to be decanted. Solutions for use in electrolysis were prepared by adding deionised water to the lead sulphate crystals and equilibrating the mixture at 0°C. This gave a solution of suitable concentration, with little chance of any contamination.

2.1.4 Calcium chloride solutions

Analar $CaCl_2 \cdot 6H_2O$ was recrystallised in the following manner: 0.73 kg of the solid was added to 0.52 kg of water and the mixture heated until the crystals dissolved. A clear solution was filtered off from a small residue of solid material using preheated filter sticks (No. 4 porosity). The filtrate was cooled to 0°C and crystallisation induced by adding a crystal of $CaCl_2 \cdot 6H_2O$. The shock crystallisation which resulted was considered undesirable, so the flask was heated until nearly all the crystals redissolved, and was then slowly cooled to 0°C.

The product was dissolved in water to give a stock solution approximately one molal. Solutions for the preliminary experiments were prepared by weight from this stock. The solutions were analysed for calcium by the E.D.T.A. method described in Part II of this thesis, and self consistancy calculations showed a maximum discrepancy of less than 0.3 per cent.

2.1.5 Calcium sulphate solutions

A stock solution of concentration 0.00998 molal was prepared by weight. The concentration was checked by E.D.T.A. titration and the two values were found to agree within 0.06%. Solutions were prepared by weight from this stock down to a lower limit of 0.000658 molal. A saturated solution of the di-hydrate was prepared by equilibration with excess solid phase for a minimum of 3 weeks at 25°C.

2.1.6 Calcium chloride-calcium sulphate solutions

Calcium chloride solutions were prepared by weight from the 1 molal stock and were equilibrated with excess gypsum. Equilibrium concentrations of $CaSO_4$ were deduced from the solubility data in Part II.

2.1.7 Silver oxide

This was prepared by dissolving 0.5 mole of Analar silver nitrate in 0.65 kg of water in a 1 litre conical flask. A solution of 0.5 mole of Analar sodium hydroxide in 0.2 kg water was slowly run into the $AgNO_3$ solution while the latter was vigorously stirred using a large magnetic stirrer. The flask was stoppered and stirring was continued for 20 min. When the precipitated Ag_2O had settled, the supernatant liquor was decanted (about 90% by volume) and replaced with deionised water. This washing procedure was repeated a further 30 times, the slurry being stirred for a minimum of 30 minutes at each stage.

2.1.8 Lead sulphate

A 0.4 molar solution of recrystallised AR lead nitrate was vigorously agitated using a magnetic stirrer, and a solution of Analar sodium sulphate was slowly run into the flask up to the stoichiometric proportion. After stirring a further 15 min, and allowing the precipitated $PbSO_4$ to settle, the supernatant liquor was decanted and replaced with deionised water. The washing procedure was repeated, and the slurry was then boiled for 15 min in order to increase crystal growth and give better settling characteristics. The precipitate was washed by decantation a further 15 times. Approximately 90% of the liquid phase was removed at each stage.

2.1.9 Mercury

High quality mercury was washed with 15% sodium hydroxide solution by bubbling filtered air through the contents of the flask. The NaOH solution was replaced at intervals until the aqueous phase remained almost clear after prolonged washing. This stage was reached very quickly since the starting material was essentially pure. After washing a number of times with distilled water, the process was continued with 1 molar perchloric acid for four days, changing the acid solution each day. The purified mercury was washed throroughly with distilled water, ethanol and ether, and was triply distilled under vacuum.

The product was once again treated with 1 molar perchloric acid before finally washing with water.

2.1.10 Lead amalgam

Amalgams containing about 4% lead were prepared electrolytically (21) in the cathode compartment shown in Figure 2.1.1. C and B are inlets and outlets for the water jacket, D is a platinum electrode, E is a stirrer (used at a very slow speed), F is a liquid junction to the anode compartment. The latter was a three necked flask with a large platinum anode, filled with 1 molal Analar nitric acid. Separate anode and cathode compartments were necessary, since discharge of nitrate ions at an anode in the presence of lead ions leads to the formation of lead peroxide (28). The cathode compartment was filled with 2 kg of mercury and an approx. 1 molal solution of the recrystallised lead nitrate. The quantity of lead nitrate solution used was twice that required for the electrolysis. This precaution was taken to ensure that the concentration of lead ions was always in vast excess over any impurity ions, thereby reducing the chance of discharging foreign cations in the latter stages of electrolysis. The liquid junction was made by applying a vacuum at an inverted "Y" connection between the compartments. Care was taken to ensure that the level of liquid was the same in both compartments, to avoid syphoning of solution between them. A current of 0.2 amp was required for about 104 hours in order to give an amalgam of the chosen composition. During electrolysis the amalgam was not susceptible to oxidation, but once the applied potential was removed, precautions were necessary. Immediately electrolysis was completed, the anode compartment was disconnected, and the stirrer and platinum electrode removed from the cathode compartment. The amalgam was washed 10 times with 1 kg aliquots of freshly distilled and deionised water. Inlet and outlet tubes for oxygen free nitrogen were inserted in the head of the vessel, and the amalgam outlet tube (X) was connected using a P.T.F.E. sleeve to the inlet (A) of the storage vessel (shown in Figure 2.1.2). The preparation vessel was flushed out with oxygen free nitrogen and partially evacuated using a water pump about 15 times. It was then maintained at a positive pressure by using a fairly fast nitrogen flow rate. Water at about 70 to 80^{o}C was passed through the water jacket for 10 minutes after the last traces of solid $HgPb_2$ disappeared. The solid phase normally floats just below the surface, but its presence is made clearly evident by "pimples" on the surface. During this heating stage, the small quantity of water on the surface of the amalgam evaporated and the storage vessel was evacuated with tap A open. The storage vessel was tested for leaks by its ability to hold a vacuum and was then alternately filled with oxygen free nitrogen and evacuated. After about 10 cycles, the vessel was partially evacuated and with a positive pressure of N_2 still flowing over the surface of the hot amalgam, tap X of the preparation cell was opened allowing the amalgam to run into the storage vessel. The last 10 c.c. of amalgam was retained in case any surface impurities were present. Taps X and A were closed, and the pressure of nitrogen in the storage vessel was increased to two atmospheres. On all the apparatus used, taps were of the P.T.F.E. type and P.T.F.E. sleeves were used on all the joints.

2.1.11 Silver-silver chloride electrodes

The method of preparation was based on the procedures given in Ives and Janz (21) for the

FIGURE 2.1.1 CATHODE COMPARTMENT OF LEAD AMALGAM PREPARATION APPARATUS

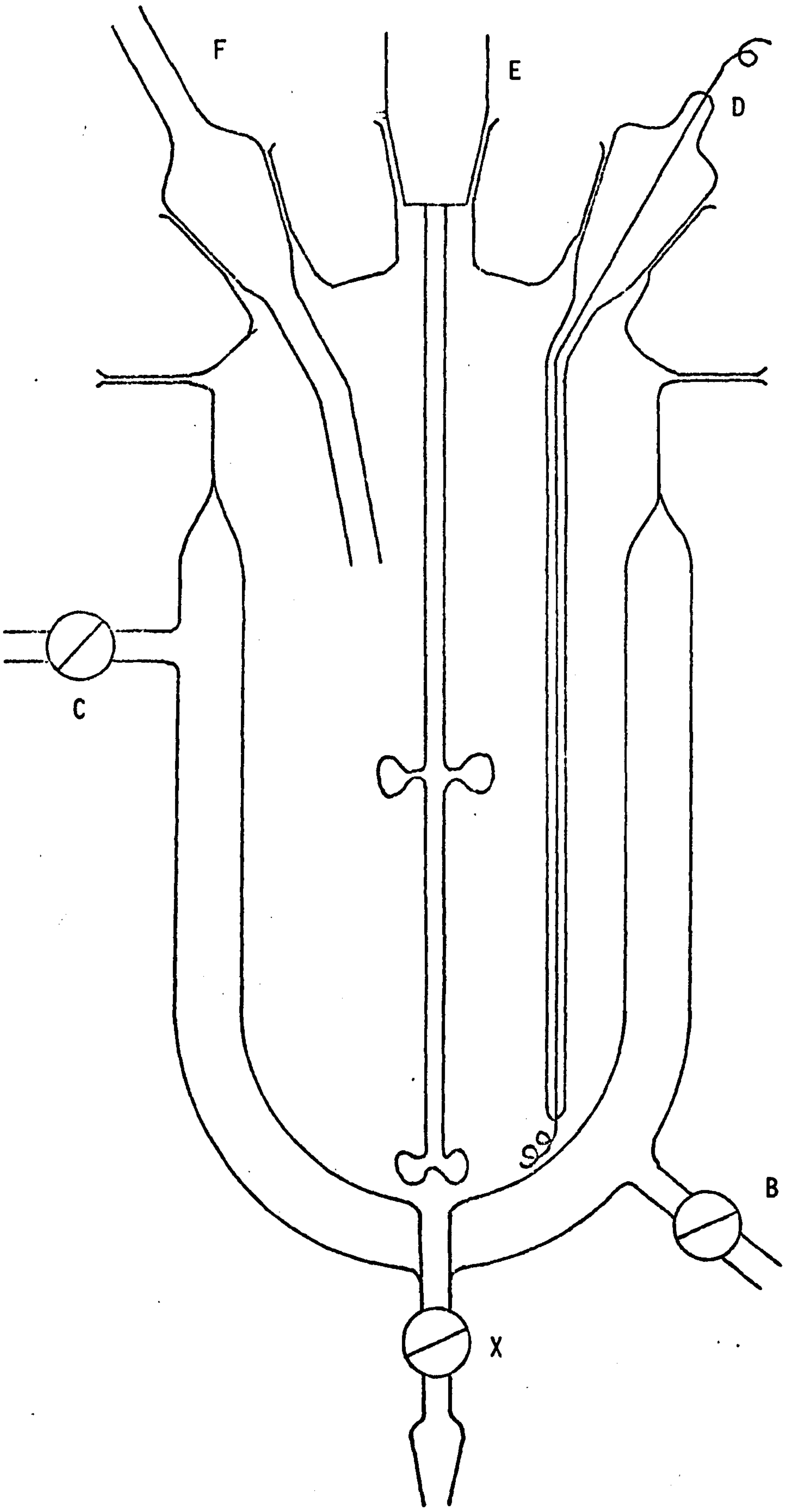
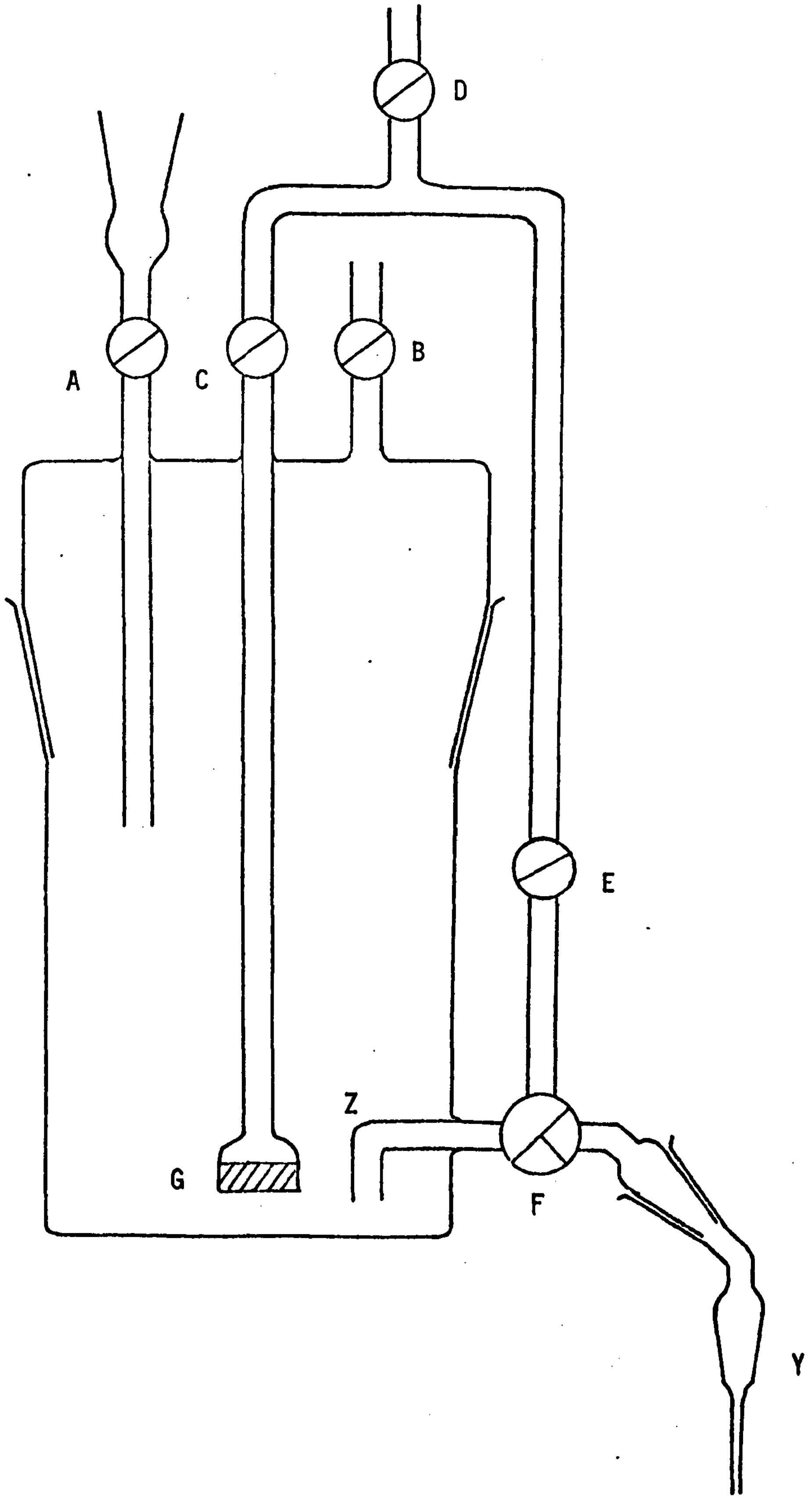


FIGURE 2.1.2 AMALGAM STORAGE/ DISPENSING VESSEL



thermal electrolytic type of electrode. This type of electrode was chosen since a fast response was not essential, but low bias potentials about a stable standard potential were required.

Nine electrodes were made in a batch in the following manner: a 30 mm length of 26 gauge platinum wire was spot welded to copper wire of a slightly thicker gauge. The platinum wire was sealed into a glass tube so that nearly 20 mm of wire protruded from the sealed end. This wire was coiled into three turns of a spiral about 1.5 mm diameter. The platinum spiral was cleaned by boiling briefly in concentrated HNO_3, washing with distilled water and finally boiling for 15 min in conductivity water. Pure Ag_2O in the form of a water paste was applied to the platinum spiral with a clean spatula so as to completely fill and cover the spiral giving a 3.5 mm diameter ball of paste suspended from the Pt/glass seal by about 4 mm of uncoated wire.

The silver oxide was thermally reduced to silver by suspending the electrodes in a vertical loading furnace. The furnace temperature was slowly raised to 90-95^{o}C and was held at this temperature for 1 hour to prevent spluttering caused by rapid water vapourisation. The temperature was then slowly raised to 450^{o}C and held at this for 40 minutes. The electrodes were cooled within the furnace to avoid thermal shock. A second coat of Ag_2O was applied by dipping the electrode into an aqueous slurry of silver oxide. This gave an even coating about 0.25 mm thick. Thermal reduction was carried out as before. "Araldite" was poured down each electrode to prevent mechanical stress at either the spot weld or Pt/glass seal.

The electrodes were chloridised in 0.05 N KCl solution. A parallel arrangement of silver electrodes was used, equidistant from a large central platinum cathode. It was thought that a parallel assembly of electrodes would give a more consistent percentage conversion of silver to silver chloride than a series arrangement, if the silver spheres were of significantly different size. The platinum cathode was a cylinder of platinum foil about 15 mm high and about 15 mm diameter. This was suspended by means of two platinum wires, spot welded to the cylinder and also to a thick copper wire above the surface of the chloridising solution. Ives and Janz (21) suggest that between 10% and 20% of the silver is converted to the chloride, though the figure presented on p. 217 of reference 21 indicates that about 20% conversion should give stable potentials with the correct E^{o} value after a short ageing period of 10 hours. Chloridisation in excess of 20% is not recommended due to poorer stability of potential and sluggish response. The percentage chloridisation could not be accurately estimated since the weight of silver was not known with any precision. This was estimated by assuming 4 mm spheres of silver, 40% of the volume being attributed to porosity and 10% to the Pt spiral. A total current of 30 m.a. was passed through the 9 electrodes for a time calculated to chloridise 15% ±5% of the silver on each electrode. After ageing overnight in the KCl solution used for chloridising, bias potentials were found to be 5 μv or less. The electrodes were washed with distilled water and stored in $CaCl_2$ solution. Bias potentials were remeasured after a further 7 days and found to be 10 μv or less.

2.1.12 Calcium responsive electrode

An Orion 92-20 membrane electrode was used. A diagram showing the internal construction of this electrode is given in Figure 2.1.3. The electrode case is constructed from P.T.F.E., and the ion exchange liquid is a solution of 0.1 molar calcium didecylphosphate in dioctylphenylphosphonate. This solution is supported on a hydrophobic membrane which separates the external test solution and internal reference solution. For the latter, a solution of 0.033 molal $CaCl_2$ was used. The solubility of calcium didecylphosphate in water is sufficiently low for the response of the electrode to be Nernstian down to concentrations of 10^{-5} molal $CaCl_2$ (38).

2.1.13 Nitrogen

"White spot" nitrogen was passed through a tube of copper turnings maintained at about 520°C in order to remove any remaining traces of oxygen. Nitrogen used to degas the test solutions was first passed through two water bubblers and also through a bubbler containing the same solution as that in the cells. All connections were made with Portex thick walled tubing.

2.1.14 Cells

The design of cells used for measuring calcium sulphate activity is shown in Figure 2.1.4. Separate compartments were employed for the calcium responsive and sulphate responsive electrodes. This was primarily because this design enabled oxygen to be excluded from the sulphate compartment at all times, but had the additional advantage that lead ions could be excluded from the calcium compartment if this was desired.

Cells used for measuring calcium chloride activity, both as reference cells and in the preliminary experiments, were essentially similar to those shown in Figure 2.1.4 except that the central sulphate compartment was omitted. The cleaning procedure used was to thoroughly wash out the cells with concentrated nitric acid, followed by water, and finally to twice boil water in the cells for 15 minute periods.

2.1.15 Lead sulphate slurry transfer apparatus

This apparatus is shown in Figure 2.1.5. It was used initially to prepare a slurry of lead sulphate crystals in an aqueous phase of the same composition as that to be used in the cell. This was achieved by transferring a portion of the slurry in pure water to the apparatus and filtering off excess water through a No. 3 porosity sintered glass filter at H. Transfer tube K was not used at this stage and was replaced by a stopper. A portion of the most dilute of the solutions to be investigated was shaken with the lead sulphate, and after settling, the supernatant liquor was filtered off. This procedure was repeated about 8 times using a volume ratio of fresh solution to settled slurry of about 5 to 1. The transfer tube was inserted and the apparatus connected to the

FIGURE 2.1.3 CALCIUM ION REVERSIBLE MEMBRANE ELECTRODE

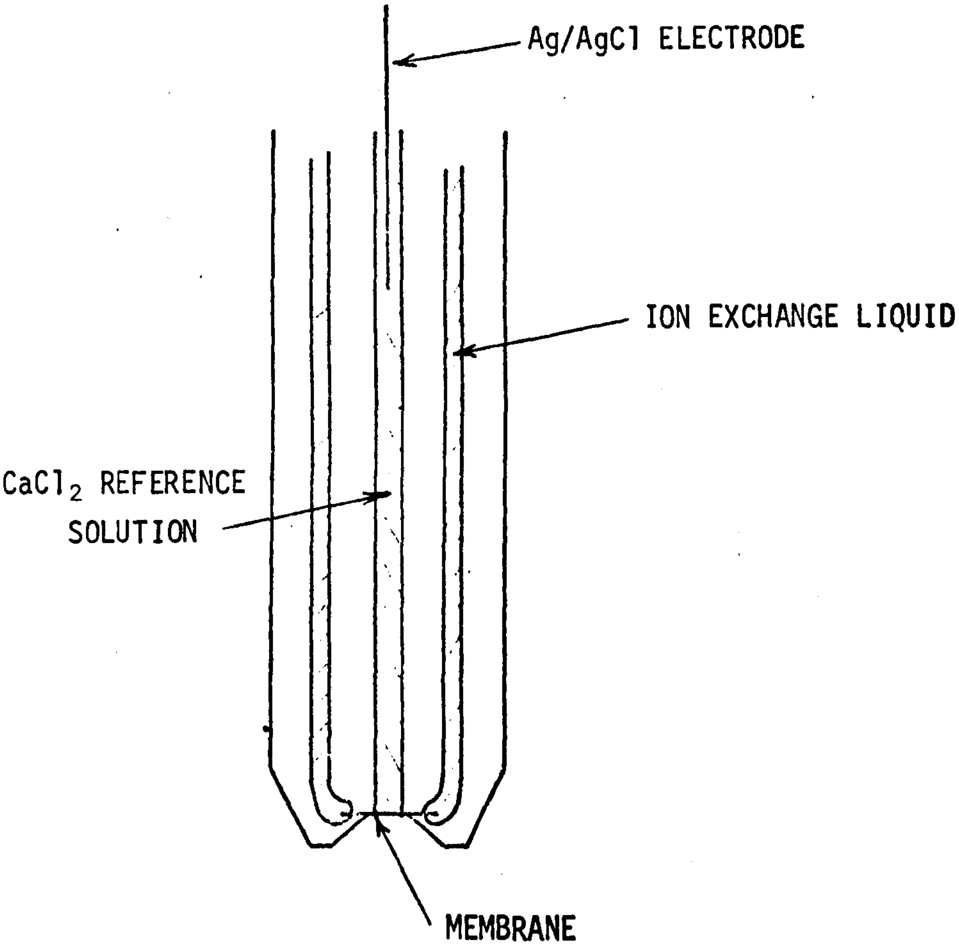


FIGURE 2.1.4 TEST CELLS

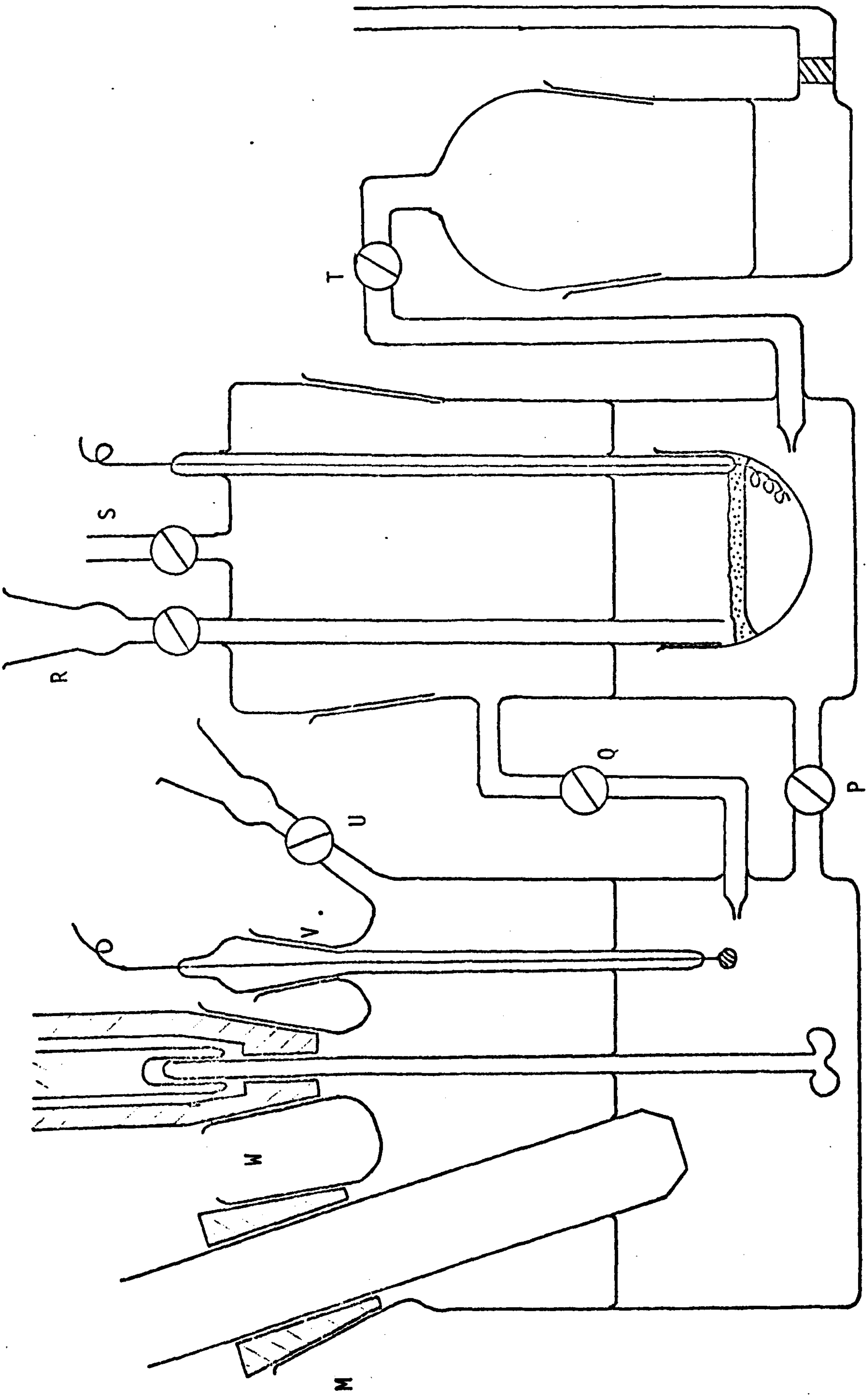
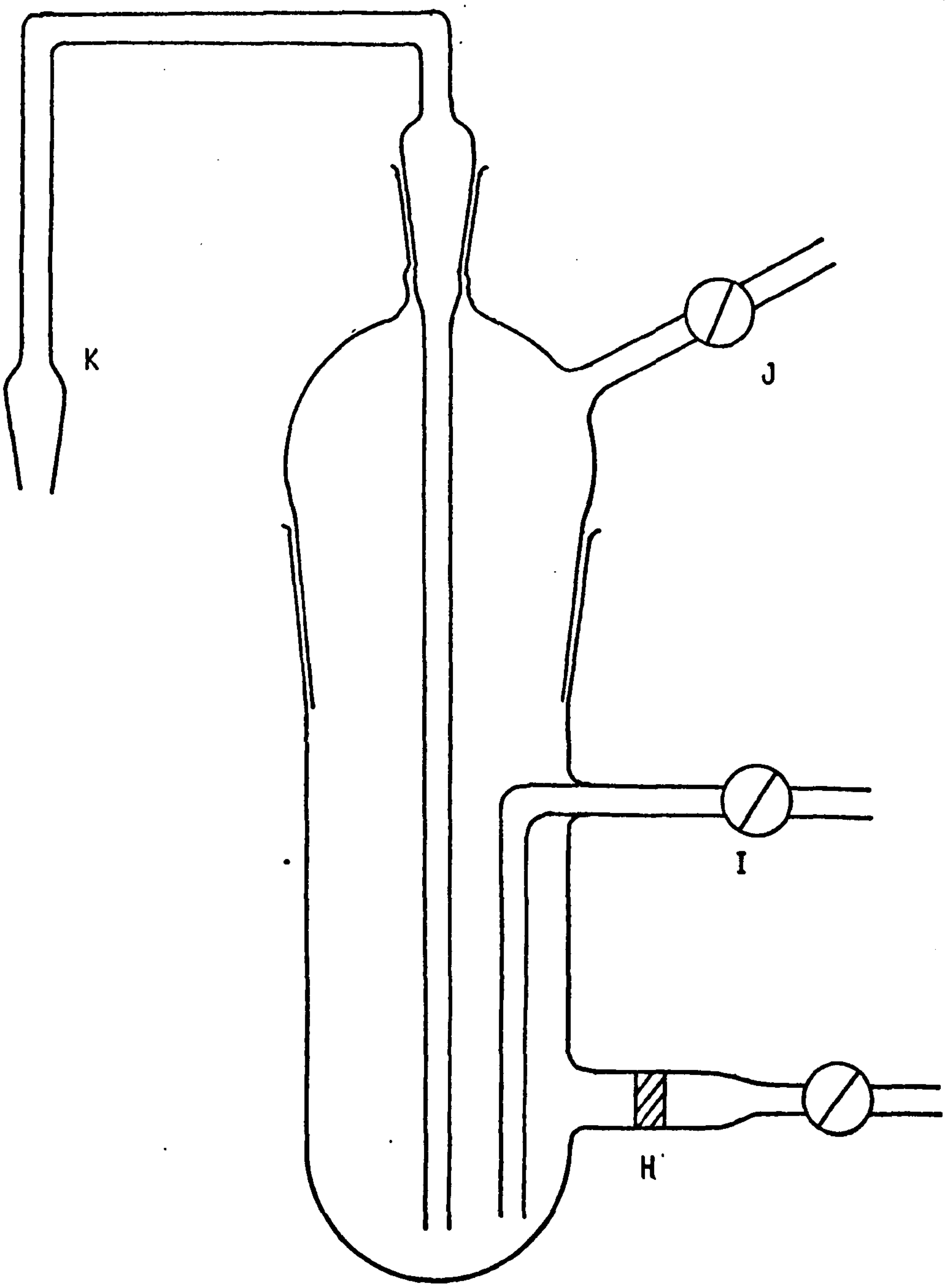


FIGURE 2.1.5 SLURRY TRANSFER APPARATUS



cell at R. The slurry was deoxygenated by passing oxygen free nitrogen in through both I and K and out through J. By closing tap J, the slurry was forced through K and into the cell at R.

This procedure could then be repeated using the next most concentrated solution without the necessity of cleaning out the apparatus. A new transfer tube was however required each time.

2.1.16 Measuring circuit

The calcium electrode had a very high resistance and consequently a measuring circuit was required with a high imput impedence. An E. I. L. "Vibron" electrometer (model 33B) was used. The most sensitive scale on the instrument was always used by backing off the major part of any potential greater than 10 mv with a Tinsley 5590A vernier potentiometer. The output from the electrometer was recorded on a Honeywell-Brown chart recorder. With a suitable capacitance across the imput to the recorder, the residual noise of about 0.1 mv amplitude from the electrometer was smoothed out enabling the potential to be measured to within ±0.02 mv. The potentiometer was standardised using a Tinsley (type 152B) Weston standard cell. Two similar cells were used to check that the standard potential was correct. High quality screened cable was used for all connections between electrodes, electrometer, and potentiometer. A mains water pipe was the only earth connection used.

2.1.17 pH measurement

A Radiometer PHM26c pH meter was used in conjunction with a Radiometer K401 calomel reference electrode, filled with saturated KCl solution, and a Radiometer G202C glass electrode. The instrument was standardised using a double buffering technique and was very stable. An expanded scale enabled results to be measured to within 0.01 pH units.

2.1.18 Temperature control

The room used for the experiments could be thermostatted above ambient temperatures, but no cooling facility was available, and room temperature occasionally rose above 25°C. The cells were therefore placed in an insulated air box. This had the added advantage that the cells could be screened from electrical disturbances by earthing the aluminium foil lining of the box. Heating was provided by four 15 watt red light bulbs. Coloured bulbs were used since it was noticed that the cell e.m.f. showed a small reversible response to light from the fluorescent strip lights in the room, presumably due to the Ag/AgCl electrode (21). Water cooled copper coils were installed around two fans used for air circulation, and thermostatic control was achieved by utilising a mercury contact thermometer to control the heating circuit. The cells were placed on an aluminium plate 20 mm thick, the latter acting as a heat reservoir. The temperature was initially set (and occasionally rechecked) with a Hewlett Packard 2801A quartz crystal thermometer which had itself been checked using a platinum resistance thermometer. When the centre of the box was set at 25°C the bottom was found to be at 25.03°C. A mercury thermometer sensitive to changes of 0.1°C, showed no significant temperature variation over the course of the experiments.

2.1.19 Stirrer

An Electrothermal IE5502 mini-stirrer was used, with a glass paddle having blades about 4 mm in diameter. A 12 v d.c. output mains transformer/rectifier was used to give continuously variable speed control.

2.2 PRELIMINARY EXPERIMENTS

The effect of controllable variables was initially investigated using two of the reference cells filled with calcium chloride solutions. A change in the immersion depth of the calcium electrode from 5 mm to 20 mm did not lead to a significant change in cell e.m.f. This is consistent with the results of Rechnitz and Lin (39) who found that a change in immersion depth from 10 mm to 60 mm produced an increase in cell e.m.f. of 0.1 mv. The depth of immersion in subsequent experiments was maintained at 10 mm ±3mm. The effect of bubbling nitrogen through the solutions, was also found to be without significant effect. This was not unexpected from the viewpoint of dissolved oxygen affecting the Ag/AgCl electrode, since this problem is restricted to acid media rather than to neutral or nearly neutral solutions (21). Some change would have resulted if sufficient CO_2 was initially present in the solutions to lead to a measurable hydrogen ion response by the calcium electrode (38). The two solutions used were found to have pH values of about 5.9. Addition of small quantities of NaOH solutions did not produce a measurable change in cell e.m.f. until the pH was raised above 10. Above this pH, the e.m.f. began to fall, possibly due to the formation of $CaOH^+$ ion pairs.

During these preliminary experiments, stirring rate was found to be a significant factor. Absence of any stirring resulted in a slow drift of potential. Very fast stirring rates gave rapid response times, but the terminal e.m.f. was rather unstable. The difference in cell e.m.f. between a fast rate of stirring and unstirred solution was about 0.2 mv. Rechnitz and Lin (39) stated that an increase in stir rate from 200 r.p.m. to 400 r.p.m. resulted in an increase of 0.3 mv in cell potential. The most reproducible results were obtained using slow stirring rates of 40 to 100 r.p.m. The steady state e.m.f. was found to be insensitive to changes in stirring rate within this range, and for the preliminary experiments a standard stir rate of about 70 r.p.m. was adopted.

After these initial experiments were completed, six calcium chloride solutions were used having the molalities shown in Table 3.1.2. The electrode was always transferred to the solution next higher or next lower in concentration. In the latter case, the electrode was washed with water from a wash bottle, and in both cases excess liquid was removed from the tip of the electrode by carefully wiping with clean cellulose tissue. The cell e.m.f. generally reached a constant value 5 to 10 minutes after placing in the solution, but if a slow drift was still discernable the potential was taken after 15 minutes. Since cell transfers were made in both directions, any overall drift in the standard potential of the calcium electrode should be eliminated on averaging the results.

Measurements were made initially at the natural pH of each solution. Nitrogen was not bubbled through the solutions so that the pH would have a tendency to be lower than the "correct" value. The pH of each solution was measured, one drop of 0.25 molar NaOH added to each and the pH was re-measured. Transfer potentials were measured the following day but unfortunately one cell was left unstoppered overnight and appreciable evaporation losses resulted. The solution pH was re-measured immediately after carrying out the transfer e.m.f. measurements.

The cells were rinsed and refilled with fresh solution, and cell potentials and solution pH values were re-measured. One drop of 0.1 molar NaOH was added to each solution, and pH measurements were made immediately before and after the next set of e.m.f. measurements. This emphasis on the effect of solution pH was thought necessary in view of the reported (38) anomalous minima in cell potential which occurs at pH 4 for 0.1 molar $CaCl_2$ and pH 6 for 0.0001 molar $CaCl_2$.

2.3 PREPARATION OF CELLS FOR MEASUREMENT OF CALCIUM SULPHATE ACTIVITY

The amalgam storage reservoir was attached to the cell at R using a connector of the design illustrated in Fig. 2.1.2 at Y. The purpose of the connector was to allow the amalgam to be transferred to the cell without leaving any excess amalgam above the tap R. It was therefore necessary that the orifice of the connector was smaller than the bore of tap R, and that when in position, the tip of the connector was virtually touching the P.T.F.E. tap. Nitrogen was bubbled through the presaturaters for a period of at least one hour. Tap T was then closed, and the cell flushed with nitrogen via R. The three way tap at F was closed to the passage of amalgam but was clearly open to the passage of nitrogen between E and Y. Taps P and Q were closed and the system up to taps D and C evacuated via S. After checking the ability of the system to hold a vacuum, it was alternately flushed with nitrogen and evacuated, finally leaving an excess pressure of N_2 in the cell and closing tap E. The amalgam was heated to about 65°C using a hot plate covered with a sheet of asbestos. Agitation was provided by bubbling N_2 through the sintered glass filter at G. By alternating this with evacuation via B, the amalgam in the outlet tube Z was partially discharged and refilled. When all traces of the solid phase $HgPb_2$ disappeared, the pressure above the amalgam was increased to about two atmospheres and tap C closed. The cell (Fig. 2.1.4) was once again flushed with N_2 by opening taps E and Q. A pressure slightly in excess of atmospheric was produced by closing tap Q and about 1 second later tap E. Amalgam was run into the electrode cup by turning the three way tap F clockwise through 90° until the cup was about one third full. With tap F in its original position, any excess amalgam left in the connection between F and R was forced into the cell by opening tap E. This was closed together with tap R, the storage reservoir was disconnected, and replaced by the slurry transfer apparatus (Fig. 2.1.5). Taps T and Q were opened, allowing N_2 to flow through the cell while the amalgam cooled. An excess pressure of about half an atmosphere was allowed to build up by closing Q, and was released by opening R. Since this forced air in the transfer tube through the slurry, it was necessary to deoxygenate the slurry vigorously for about 30 minutes, using both K and I as inlets. The slurry was transferred by opening tap Q and closing tap J. Nitrogen entering at I served the dual purpose of preventing the slurry from settling, and providing the pressure necessary to transfer the slurry. When sufficient lead sulphate was transferred to give a settled layer 2 to 3 mm thick, tap J was opened, tap R of the cell closed, and the transfer apparatus disconnected.

Sufficient solution to fill both cell compartments to a level above the top of the electrode bowl was poured in the calcium electrode compartment. This solution was deoxygenated for at least one hour by bubbling N_2 in through both Q and P and out through U, with stoppers at M, W and V. Part of the deoxygenated solution was then transferred into the lead amalgam-lead sulphate compartment. This was carried out by applying an excess pressure of N_2 on the solution at U, closing Q, opening S, and alternately opening and closing tap P until the level of solution was equal in both compartments. The fast flow rates of solution produced by this procedure, forced any N_2 bubbles out of the connecting tube P. (The presence of bubbles in P apparently gave rise to instability in the measuring circuit.) Taps P and S were closed, O was opened, and the source of N_2 removed from U. Tap T was open throughout the slurry transfer and solution transfer stages.

Since the filling operations were performed at approximately 25°C in the temperature controlled room, thermal equilibrium was quickly achieved in the thermostatted air box, and the first potential reading was made between 15 and 30 minutes after solution was transferred to the lead amalgam-lead sulphate compartment.

2.4 E.M.F. MEASUREMENTS

Two reference cells containing pure $CaCl_2$, and four test cells were used for each run. Three runs were made using pure $CaSO_4$ solutions in the test cells, and one run with saturated $CaSO_4$ in $CaCl_2$ solutions. One of the reference cells was chosen to be used in transfer experiments with the test cells, the other was used to check that the calcium electrode was responding in a Nernstian manner. This check was made at least twice daily. Measurements were made on each test cell about 20 minutes after placing it in the thermostatted air box. Subsequent measurements were made at gradually increasing intervals of time over the following few days.

2.4.1 Experimental conditions

The major differences in technique between these measurements and the preliminary work were as follows:

(i) nitrogen was bubbled continuously through both compartments, but when potential measurements were made, the gas was normally allowed to escape through tap S, rather than be forced through the calcium compartment via tap Q. This procedure was followed in order to avoid pressure differences across tap P. This connecting tap was kept closed to avoid any significant diffusion of lead ions into the calcium compartment. The input impedence of the electrometer was sufficiently high to make this procedure feasible.

(ii) Rather than remove excess liquid from the tip of the calcium electrode with cellulose tissue between transfers, the electrode was washed with the solution on which measurements were about to be made. As before, if the previous solution was more concentrated than the new in any solute, a preliminary wash with deionised water was given. This technique gave shorter, more shallow, transient e.m.f. curves.

(iii) Use of the stirrer was discontinued except under the special circumstances referred to later. This was simply because stirring gave much less marked effects than in the preliminary work.

2.4.2 Pressure effects

When measurements were first taken, N_2 was allowed to bubble through both cells, and it was noticed that the observed e.m.f. increased and decreased in sequence with bubble formation in the calcium compartment. Also when the pressure in the lead sulphate compartment was released by opening tap S, the observed e.m.f. decreased. Both these results were more evident as the concentration of $CaSO_4$ decreased. The magnitude of these effects as a function of applied pressure was measured by connecting a water manometer to S. The manometer design was such that the tube joining it to S could be flushed with nitrogen before any measurements were taken. Further checks were made by (i) monitoring the effect of overall pressure due to changes in atmospheric pressure; (ii) increasing the pressure in the calcium compartment alone and (iii) by increasing the pressure on both compartments simultaneously.

2.4.3 Effect of oxygen

At the end of the first run, the cells were left for 13 days and it was found that the lead amalgam-lead sulphate electrode potentials had drifted to more negative values. Oxygen was bubbled through the sulphate compartment of one of the cells, and the cell e.m.f. was monitored. A steady change in cell potential of 0.3 mv per minute resulted. The direction of this change was again to more negative lead amalgam potentials. When the oxygen supply was replaced by nitrogen, the amalgam potential continued to fall for 15 minutes, but then gradually increased and eventually rose above the value prevailing before oxygen was admitted. It would have been very interesting to have continued the nitrogen flow to check if the cell potential would reach the value found when the cell was first prepared. This would have answered the question of whether the electrode was truly reversible to oxygen impurities, but unfortunately measurements were terminated prematurely.

2.4.4 Introduction of lead sulphate into calcium compartment

Under normal operating conditions the calcium compartment of the cell was maintained free of dissolved lead sulphate. This procedure necessitated a correction for liquid junction potential between the two compartments, but obviated the need for a correction due to response of the calcium electrode to lead ions. Calculations in section 3.2.3 show that the latter correction is more important, and that both corrections increase in magnitude as the $CaSO_4$ concentration falls. In order to test the accuracy of the calculated corrections, $PbSO_4$ was added to the calcium compartments of two of the cells and the change in cell potential monitored. The lead sulphate was added in the form of a slurry, the aqueous phase being of the same $CaSO_4$ concentration as that of the test solution. Rapid equilibrium was reached by dispersing the $PbSO_4$ using the mini-stirrer. The change in potential was taken as the mean difference between four transfer potentials before the addition and four results taken after the addition.

2.4.5 The most dilute solutions

At the lowest concentration of calcium sulphate used (0.000658 molal), a steady drift in cell potential was always present unless the solution was stirred. The direction of the drift was consistent with a build-up of calcium ions in the solution from dissolved ion exchange molecules. When the stirrer was switched on, a small jump in potential resulted, regardless of whether the paddle was turning or not. Measurements were therefore taken immediately after the stirrer was switched off. This technique gave very consistent results.

The solution of next highest calcium concentration (0.00111 molal) gave a discernable drift, but the magnitude of this drift was not significant.

2.4.6 Single ion activities

Although the activities of single ions are indeterminate, it was thought worthwhile to measure the changes in calcium and sulphate ion "activities" in order to compare the results with other workers (18) and (19). Measurements were made on four of the $CaSO_4$ solutions and on the two $CaCl_2$ solutions. The calomel electrode used in the pH measurements was used as a reference electrode, in conjunction with the calcium and silver-silver chloride electrodes in the $CaCl_2$ solutions, and with the calcium and sulphate responsive electrode in the other solutions.

2.4.7 pH measurement

Solution pH measurements were made at the end of each run. These were taken when nitrogen had been bubbling through the solutions for a minimum of three hours. During the measurements, the calcium compartment was flushed with nitrogen from tap U to avoid any CO_2 absorption.

2.4.8 Mixed $CaSO_4$-$CaCl_2$ solutions

In addition to measuring calcium sulphate activities, a silver/silver chloride electrode was placed in the calcium compartment of the test cells, and calcium chloride activities were measured. For the most concentrated $CaCl_2$ solution (0.97 molal), the observed transfer potential using the chloride responsive electrode was close to the theoretical value. This showed that the calcium electrode was still responding in an approximately Nernstian manner at the high $CaCl_2$ concentration. The transfer potential using the sulphate electrode was however in error by about 35 mv, even after taking account of the change in water activity. The most obvious explanation was that some change in the $PbSO_4$ solid phase occurred at the high concentration of calcium chloride. The next section gives experimental details of how this hypothesis was investigated.

2.5 X-RAY DIFFRACTION STUDIES

The question of whether solid $PbSO_4$ suffered a phase change in the solution of high $CaCl_2$ concentration, was complicated by the possibility that removal of the solid phase from its aqueous environment would destroy the new phase. This problem was overcome by studying slurries of high solids content by powder X-ray diffraction.

A Phillips powder X-ray diffractometer was used with a copper anode. Copper $K\beta$ radiation was cut off using a nickel filter and samples were generally scanned over the range $5^{0}2\theta$ to $70^{0}2\theta$. In order to prevent evaporation losses during measurements the surface of the sample was covered with "Sellotape". This resulted in loss in intensity and also gave rise to a broad peak in the region $8^{0}2\theta$ to $15^{0}2\theta$. A number of slurry samples were run both covered and uncovered. Details of the samples studied are given below.

X 1: A slurry of $PbSO_4$ in water as originally prepared.

X 2: Slurry from the most concentrated $CaCl_2$ solutions (0.97 m), which remained in the slurry transfer apparatus and was assumed to be identical to that giving an anomalous cell e.m.f.

X 3: A portion of X2 was filtered, washed with acetone and vacuum dried.

X 4: Analar $CaCl_2 \cdot 6H_2O$ was dissolved in a portion of X2.

X 5: To check reproducibility, freshly prepared $PbSO_4$ was equilibrated with the 0.97 molal $CaCl_2$ solution using a multiple "agitation followed by decantation" technique.

X 6: Lead sulphate was equilibrated with the next most concentrated solution (0.317 molal $CaCl_2$).

In all the above samples the calcium chloride solutions were presaturated with calcium sulphate and contained small quantities of solid phase gypsum. In the three samples below, pure $CaCl_2$ solutions were used.

X 7, X 8 and X 9: Lead sulphate was equilibrated with calcium chloride solutions of concentration 0.97, 0.78 and 0.50 molal, respectively.

When the solids density of settled slurries was low, the samples were partially filtered using a "Millipore" membrane before examination on the diffractometer.

3. RESULTS AND DISCUSSION

3.1 PRELIMINARY WORK

3.1.1 Results

The observed transfer potentials are given in Table 3.1.1. This is split into four sections primarily on the basis of solution pH. The reason for the large discrepancy in pH values in the two columns of Table 3.1.1B is that the initial readings were made on the previous day, allowing considerable time for CO_2 pick-up.

3.1.2 Calculation of theoretical transfer potentials

The cells may be represented by:

$$\mathrm{Ag\ /\ AgCl\ /\ CaCl_2\ (m_R)}\ \overset{x}{\underset{x}{/}}\ \mathrm{CaCl_2\ (m_X)\ /\ AgCl\ /\ Ag}$$

calcium electrode

where x - x represents the liquid ion exchange membrane which is impermeable to water and anions. The observed cell potential will be the sum of the potential developed at the membrane and the difference in the individual electrode potentials. If the concentration of $CaCl_2$ is higher in the reference solution than the test solution, a process of ion exchange will occur at both surfaces of the membrane with the nett effect that Ca^{2+} ions cross from the reference to the test solution. This will quickly result in an equilibrium potential developing across the membrane, such that the test solution is positively charged with respect to the reference solution. In the absence of other cations, the membrane potential (E_M) should be given by (8),

$$E_M = \frac{RT}{2F} \ln \frac{(a_{Ca^{2+}})_R}{(a_{Ca^{2+}})_X} + E_A = E_{MX} - E_{MR} \qquad \text{(E.3.1.1)}$$

where R and X refer to reference and test solutions, E_{MX} and E_{MR} are the potentials on either side of the membrane and E_A is an asymmetry potential which should ideally be independent of the nature of the test solution.

Silver/silver chloride electrodes respond to chloride ion activity in a Nernstian manner, consequently the difference in chloride concentrations leads to a potential difference given by

$$E_{EX} - E_{ER} = E^0_{AgCl/Ag} - \frac{RT}{F} \ln (a_{Cl^-})_X - E^0_{AgCl/Ag} + \frac{RT}{F} \ln (a_{Cl^-})_R$$

or

$$E_E = \frac{RT}{F} \ln \frac{(a_{Cl^-})_R}{(a_{Cl^-})_X} \qquad \text{(E.3.1.2)}$$

where E_{EX} and E_{ER} are the electrode potentials measured with respect to adjacent solution, and $E^0_{AgCl/Ag}$ is the standard reduction potential of the silver/silver chloride electrode on the

TABLE 3.1.1 RESPONSE OF THE CALCIUM RESPONSIVE ELECTRODE IN CALCIUM CHLORIDE SOLUTIONS

(A) 30/6/1971: Solutions at "natural" pH

Solution	pH	E.m.f. differences between adjacent solutions /absolute millivolts				Mean e.m.f. differences /m.v.
A	5.92					
		41.1	40.95	41.1		41.05
B	5.93					
		39.3	39.5	39.6		39.47
C	5.92					
		39.3	39.0	39.1		39.13
D	5.96					
		36.2	36.0	35.85		36.02
E	5.96					
		36.9	37.0	37.25	37.1	37.08
F	6.42					

(B) 2/7/1971: After adding 1 drop of 0.25 N sodium hydroxide

Solution	pH Initially	pH Finally	E.m.f. differences between adjacent solutions				Mean e.m.f. differences
A	9.46	8.33					
			41.25	41.17	41.2	41.2	41.20
B	8.96	7.11					
			39.15	39.23	39.2	39.25	39.21
C	9.00	7.08					
			39.05	38.95	39.05	39.0	39.01
D	9.00	7.28					
			72.7	72.55	72.75	72.65	72.66
F	7.83	6.85					

(C) 19/7/1971: Fresh solutions at "natural" pH

Solution	pH	E.m.f. differences between adjacent solutions				Mean e.m.f. differences
A	5.82					
		41.1	40.08	41.2	40.75	40.98
B	5.88					
		39.55	39.5	39.45	39.45	39.49
C	6.02					
		39.12	39.2	39.05		39.09
D	5.75					
		35.43	35.7	35.45		35.52
E	5.87					
		36.6	37.1	37.05		36.91
F	6.38					

(D) 21/7/1971: After adding 1 drop of 0.1 N sodium hydroxide

Solution	pH Initially	pH Finally	E.m.f. differences between adjacent solutions				Mean e.m.f. differences
A	7.74	6.67					
			41.25	41.0	40.95		41.07
B	7.66	6.53					
			39.15	39.35	39.4		39.30
C	8.18	6.65					
			38.85	38.9	39.1		38.95
D	7.43	6.51					
			35.5	35.5	35.5		35.50
E	7.68	6.60					
			36.75	37.0	36.85	37.05	36.91
F	7.33	6.78					

TABLE 3.1.2 CALCULATED ACTIVITY COEFFICIENTS AND TRANSFER E.M.F. VALUES FOR $CaCl_2$ SOLUTIONS

Solution	$CaCl_2$ molality	$\gamma_\pm$	$Log_{10} (m\gamma_\pm)$	Theoretical Transfer e.m.f./m.v.	
A	0.0010275	0.8877	-3.0399	41.32	
B	0.0032519	0.8197	-2.5742	39.38	
C	0.010650	0.7286	-2.1304	39.16	
D	0.033081	0.6185	-1.6891	35.68	72.67
E	0.099104	0.5211	-1.2870	36.99	
F	0.295890	0.4559	-0.8700		

TABLE 3.1.3 STATISTICAL ANALYSIS OF TRANSFER E.M.F. RESULTS

Solution	Mean transfer e.m.f./m.v.	Standard Deviation /m.v.	No. of results	Theoretical - mean /m.v.	Student's t	t (P = 0.05)
A	41.073	0.161	14	+0.147	5.74	2.16
B	39.363	0.151	14	+0.027	0.42	2.16
C	39.052	0.120	13	+0.108	3.24	2.18
D	35.681	0.277	9	-0.001	0.01	2.51
E	36.960	0.189	10	+0.030	0.501	2.26
F						

arbitrary scale such that $E^{o}_{H^+/H_2} = 0$. The sign convention used is that of the I.U.P.A.C. (40). The theoretical potential of the cell is obtained by adding equations 3.1.2 and 3.1.1:

$$E_C = E_X - E_R = \frac{RT}{2F} \ln \frac{(a_{Ca^{2+}} a^2_{Cl^-})_R}{(a_{Ca^{2+}} a^2_{Cl^-})_X} + E_A \qquad (E.3.1.2)$$

If E_A can be neglected, the cell potential will be positive.

If the calcium electrode is transferred to a second test solution, the difference between the second cell potential and the first will be given by

$$E_T = E_{C2} - E_{CI} = \frac{RT}{2F} \ln \frac{(a_{Ca^{2+}} a^2_{Cl^-})_{XI}}{(a_{Ca^{2+}} a^2_{Cl^-})_{X2}} \qquad (E.3.1.4)$$

where E_T is referred to as the transfer potential. This assumes that the asymmetry potential is the same in both test solutions. The calcium chloride activities may be represented as

$$a_{CaCl_2} = a_{Ca^{2+}} a^2_{Cl^-} = 4m^3 \gamma^3_{\pm}$$

where m is the stoichiometric molality of $CaCl_2$ and $\gamma_{\pm}$ is the mean molal activity coefficient. Values of $\gamma_{\pm}$ at the required concentrations were calculated using the parameters given by Lietzke and Stoughton (41) for the equation

$$\ln\gamma_{\pm} = -\frac{|Z_+Z_-|\, S\sqrt{I}}{1 + A\sqrt{I}} + 2BI + \frac{3}{2}CI^2 + \frac{4}{3}DI^3 \qquad (E.3.1.5)$$

The authors computed best fit values of A, B, C and D to the corresponding osmotic coefficient equation, using experimental osmotic coefficients in the concentration range 0.002 to 6.0 molal.

Theoretical values for the transfer potentials were calculated using

$$E_T = \frac{3}{2}\frac{RT}{F} \ln \frac{(m\gamma_{\pm})_{XI}}{(m\gamma_{\pm})_{X2}} \qquad (E.3.1.6)$$

with RT/F taken as 25.692 to give values in absolute millivolts. The results are given in Table 3.1.2.

3.1.3 Statistical analysis

Since no systematic trend was observed, either with time or solution pH, the results were treated as a single population and Student's t test applied:

$$t_{n-1} = \frac{|\bar{x} - \mu|}{s(\bar{x})}$$

where n = number of observations,

$\bar{x}$ = arithmetic mean

μ = theoretical value

$s(\overline{x})$ = standard error of mean = $s(x)/\ n^{\frac{1}{2}}$

$s(x)$ = standard deviation of observations

$$= \sqrt{\frac{\sum_{i} (x_i - \overline{x})^2}{n - 1}}$$

Values of t_{n-1} were calculated and compared with tabulated values of t_{n-1} corresponding to a 5% probability level. The results are given in Table 3.1.3. If $|\overline{x} - \mu|/s(\overline{x})$ is greater than t_{n-1} $(p = 0.05)$ then it can be said with 95 per cent confidence that $\overline{x}$ is significantly different to μ. At this probability level, two out of the five results are significantly different in the statistical sense.

3.1.4 Discussion

A factor of equal if not greater importance than the above statistical test, is the magnitude of the differences between experimental and theoretical results. All the differences in mean values are within 0.15 mv. These discrepancies should be compared with tolerable errors in $\gamma_{\pm}$ for the calcium sulphate measurements. At the solubility limit of gypsum an error of 0.25 mv in transfer e.m.f. corresponds to an error of 1% in $\gamma_{\pm}$. It should be recognised that the computed $CaCl_2$ activity coefficients are subject to uncertainty arising from a number of sources: errors in the experimental osmotic coefficients, errors in the analytical Gibbs-Duhem integration to give activity coefficients (arising both from experimental error and from the use of imperfect equations for ϕ and $\gamma_{\pm}$) and finally, errors in interpolation. It was therefore concluded that in the relevant concentration range the response of the calcium electrode was generally consistent with the Nernst equation, and that observed deviations from this ideal behaviour were within acceptable limits. The precision of the results however, was such that a single determination did not give satisfactory accuracy.

3.2 PURE CALCIUM SULPHATE SOLUTIONS

3.2.1 Results and statistics

The cells may be represented as

$$(Hg)Pb\ /\ PbSO_4\ /\ \begin{matrix} CaSO_4(m_1) \\ PbSO_4(m_2) \end{matrix}\ /\ \begin{matrix} CaSO_4 \\ (m_1) \end{matrix}\ /\ \text{Calcium electrode} \qquad \text{Cell II}$$

and

$$Ag\ /\ AgCl\ /\ CaCl_2\ (m_3)\ /\ \text{Calcium electrode} \qquad \text{Cell III}$$

If m_2 is assumed to be zero, the e.m.f. of cell II is given by

$$E_{II} = \text{"}E^{o}_{Ca}\text{"} + \frac{RT}{2F} \ln a_{Ca^{2+}} - E^{o}_{Pb^{2+}/Pb(Hg)} - \frac{RT}{2F} \ln \left(\frac{a_{Pb^{2+}}}{a_{Pb(Hg)}} \right)$$

The activity of lead ions is controlled by the activity of sulphate ions through the solubility product of $PbSO_4$, and in a two phase amalgam $a_{Pb(Hg)}$ is a constant. Consequently the e.m.f. of cell II may be re-written as

$$E_{II} = "E^o_{Ca}" - E^o_{PbSO_4/Pb(Hg)} + \frac{RT}{2F} \ln a_{Ca^{2+}} a_{SO_4^{2-}} \qquad (E.3.2.1.1)$$

The e.m.f. of cell III may be written in a similar manner as

$$E_{III} = "E^o_{Ca}" + \frac{RT}{2F} \ln a_{Ca^{2+}} - E^o_{Ag^+/Ag} - \frac{RT}{F} \ln a_{Ag^+}$$

or as

$$E_{III} = "E^o_{Ca}" - E^o_{AgCl/Ag} + \frac{RT}{2F} \ln a_{Ca^{2+}} a^2_{Cl^-} \qquad (E.3.2.1.2)$$

The transfer potential is given by subtracting E.3.2.1.2 from E.3.2.1.1 giving:

$$E_T = E^o_{AgCl/Ag} - E^o_{PbSO_4/Pb(Hg)} + \frac{RT}{F} \ln m_1 \gamma_{\pm CaSO_4} - \frac{3RT}{2F} \ln 4^{1/3} m_3 \gamma_{\pm CaCl_2} \qquad (E.3.2.1.3)$$

In the presence of dissolved $PbSO_4$, the transfer potentials are modified as discussed in section 3.2.3. When $PbSO_4$ is restricted to the lead amalgam compartment, the transfer potential is given by

$$E^*_T = E^o_{AgCl/Ag} - E^o_{PbSO_4/Pb(Hg)} + \frac{RT}{2F} \ln m_1 (m_1 + m_2) \gamma^2_{\pm CaSO_4}$$

$$- \frac{3RT}{2F} \ln 4^{1/3} m_3 \gamma_{\pm CaCl_2} - |E_j| \qquad (E.3.2.1.4)$$

where E_j is the liquid junction potential between the two compartments.

The observed values of E^*_T for each cell are given in Table 3.2.1 in chronological order. No significant trends were observed as a function of time so mean values, and 95% confidence limits for the means, were calculated for each cell. Where more than one cell was used for a given solution, differences were less than 0.3 mv. Overall values were calculated for each solution and these results are summarised in Table 3.2.2.

3.2.2 Effect of pressure differences

It was found that the observed cell e.m.f. was unchanged when the overall pressure was increased on both compartments. A pressure increase on one compartment alone gave rise to a change in potential the sign of which was dependent on the direction of the pressure difference. The magnitude of the change was found to be proportional to the pressure difference, and approximately inversely proportional to the concentration of $CaSO_4$. These results which are shown graphically in

TABLE 3.2.1 OBSERVED TRANSFER POTENTIALS

Cell No. and Solution No.	Date of Measurements	Observed Transfer Potentials /(absolute millivolts)	Solution pH
	25/8/71	564.46	
1	26/8/71	564.71	
H	27/8/71	564.56, 564.21	
	28/8/71	564.23, 564.20, 564.20	6.09
2	27/8/71	571.63	
G	28/8/71	571.65, 571.55, 571.55, 571.7	5.97
3	27/8/71	544.57, 544.43	
J	28/8/71	544.75, 544.75, 544.8	5.99
	pH of calcium chloride reference solution (D) on 28th August =		6.05
	29/9/71	564.51, 564.45, 564.33	
4	30/9/71	564.35, 564.43	
H	1/10/71	564.30, 564.48	
	2/10/71	564.50	
	4/10/71	564.24	6.14
	30/9/71	522.68, 522.80, 522.87, 522.8	
5	1/10/71	522.70, 532.68	
L	2/10/71	522.75	
	4/10/71	522.33, 522.89	6.32
	30/9/71	544.48, 544.40, 544.43, 544.48	
6	1/10/71	544.45, 544.53	
J	2/10/71	544.45	
	4/10/71	544.46, 544.49	6.59
7	1/10/71	571.24, 571.42, 571.46, 571.30, 571.35, 571.38	
G	2/10/71	571.55, 571.57	
	4/10/71	571.85	6.24
	pH of calcium chloride reference solution (D) on 4th October =		6.23
	26/10/71	512.30, 512.30, 512.30, 512.35, 512.30, 512.30, 512.00	
8	27/10/71	512.64, 512.37, 512.32	
M	28/10/71	512.16, 512.16, 512.15, 512.00	
	29/10/71	512.43, 512.22, 512.20, 511.91, 511.98	5.65
9	27/10/71	535.05, 535.06, 534.82	
K	28/10/71	535.06, 535.00, 534.65	
	29/10/71	535.04, 534.98, 534.66, 534.70, 534.58, 534.43	6.01
10	27/10/71	555.30, 555.30	
I	28/10/71	555.65, 555.56, 555.49, 555.30, 555.05	
	29/10/71	555.64, 555.58, 555.32, 555.20, 555.13, 555.08	6.39
11	28/10/71	571.70, 571.68, 571.70, 571.71, 571.67, 571.85, 571.85	
G	29/10/71	571.86, 571.75, 571.70, 571.83, 571.73	6.49
	pH of calcium chloride reference solution (D) on 29th October =		6.38

TABLE 3.2.2 SUMMARY OF TRANSFER POTENTIAL RESULTS

Solution	$CaSO_4$ molality /mol. kg^{-1}	Cell No.	No. of Results	Mean value of E_T^*/m.v.	95% Confidence limits of mean/m.v.
G	0.01518	2	5	571.62	± 0.08
		7	9	571.46	± 0.14
		11	12	571.75	± 0.05
		OVERALL	26	571.62	± 0.07
H	0.009980	1	6	564.33	± 0.08
		4	9	564.40	± 0.03
		OVERALL	15	564.37	± 0.08
I	0.005997	10	13	555.35	± 0.13
J	0.00336	3	5	544.66	± 0.19
		6	9	544.46	± 0.03
		OVERALL	14	544.53	± 0.08
K	0.002003	9	12	534.84	± 0.14
L	0.001109	5	9	522.72	± 0.13
M	0.0006576	8	19	512.23	± 0.04

Figure 3.2.1 may be explained by assuming that the pressure differences cause solution to flow through tap P (Figure 2.1.4) even though the tap is nominally closed.

When a dilute electrolyte solution is forced through a fine capillary by an applied pressure difference, a potential known as the streaming potential (45) is set up between the ends of the capillary. The potential difference should only be referred to as the streaming potential (E_{SP}) when zero electrical current flows through the capillary. Under these conditions

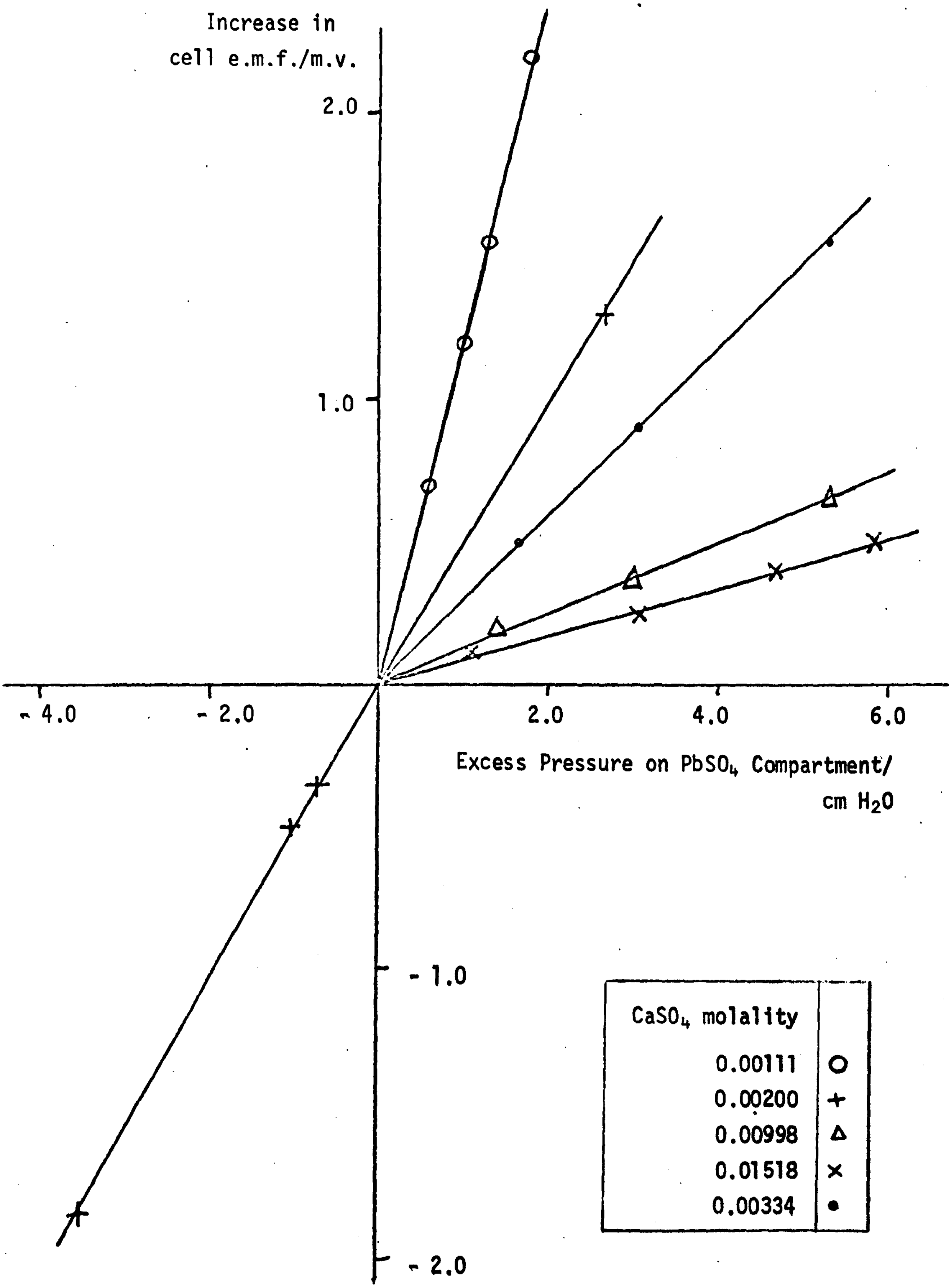
$$E_{SP} = -\frac{L_{12}}{L_{11}} \Delta P \qquad \text{(E.3.2.2.1)}$$

where ΔP is the pressure difference.

This equation derives from the phenomenological equation for the electrical current density (J), when J is set equal to zero.

$$J = L_{11} E + L_{12} P \qquad \text{(E.3.2.2.2)}$$

FIGURE 3.2.1 EFFECT OF PRESSURE DIFFERENCES BETWEEN CELL COMPARTMENTS



where E is the electrical potential gradient and P is the pressure gradient. L_{11} and L_{12} are the appropriate proportionality constants. In the absence of a pressure gradient L_{11} is simply interpreted as the electrical conductivity. Table 3.2.3 gives the gradients, equivalent conductivities (λ), and values of L_{12} calculated from

$$L_{12} = \frac{E_{SP}\,\lambda m}{\Delta P} \qquad \text{(E.3.2.2.2)}$$

Equivalent conductivities were assumed to have a similar concentration dependence as $ZnSO_4$ and $CuSO_4$ solutions. Values were interpolated graphically from the data given in Harned and Owen (47). With the exception of the lowest concentration L_{12} is seen to be approximately independent of concentration. It can be shown (45) that provided the capillary is not too small, or the concentration too low,

$$L_{12} = \frac{\zeta\,\varepsilon}{4\pi\,\eta}$$

where ζ is the zeta potential, ε is the permittivity and η is the solution viscosity. In dilute solution ε and η can be taken as concentration independent, and ζ has been found experimentally to increase only slightly with electrolyte concentration. Reference 42 gives results for potassium chloride.

It was therefore concluded that the pressure dependence and the concentration dependence of the results could be satisfactorily explained by the phenomenon of streaming potential.

TABLE 3.2.3 CONCENTRATION DEPENDENCE OF THE STREAMING POTENTIAL

m_{CaSO_4} /mol. kg^{-1}	$E_{SP} / \Delta P$ /m.v. $(mm\ H_2O)^{-1}$	λ /(ohm. equiv.)$^{-1}$ cm^2	L_{12} arbitrary units
0.01518	0.88	64	0.85
0.00998	1.24	74	0.92
0.00333	2.92	91	0.88
0.00200	4.94	98	0.97
0.00111	11.9	107	1.41

3.2.3 Effect of lead sulphate solubility

The cells were generally used in such a manner that the calcium electrode compartment was maintained free of dissolved $PbSO_4$. Under these conditions the cell e.m.f. is modified by the presence of dissolved lead sulphate in the lead amalgam compartment because:

(i) the additional sulphate present gives rise to a correction term at the amalgam electrode of magnitude $\frac{RT}{2F} \ln \frac{m_1 + m_2}{m_1}$ where m_1 is the $CaSO_4$ molality and m_2 is the $PbSO_4$ molality.

(ii) The activity coefficient of sulphate ions in the amalgam compartment is changed by the presence of dissolved $PbSO_4$. The correction required to compensate for this effect is small compared to (i), and was consequently neglected.

(iii) A liquid junction potential (E_j) is set up between the two compartments. The magnitude of liquid junction potentials are difficult to predict. If activity coefficients are neglected the diffusion potential (E_d) may be estimated by using the Henderson equation (42)

$$E_d = \frac{RT}{F} \frac{\sum_i \frac{u_i}{z_i}\left(c_i'' - c_i'\right)}{\sum_i u_i \left(c_i'' - c_i'\right)} \ln \left[\frac{\sum_i c_i' u_i}{\sum_i c_i'' u_i}\right] \qquad (E.3.2.3.1)$$

Provided E_d is small, the approximation $E_j = E_d$ should be adequate. u_i is the ionic mobility of the i'th ionic species and c_i'', c_i' are limiting concentrations at either side of the liquid junction. If the double prime is taken to refer to the amalgam compartment, then

$$E_d = \frac{RT}{F}\left[\frac{\frac{1}{2} U_{Pb^{2+}} m_2 - \frac{1}{2} U_{SO_4^{2-}} m_2}{U_{Pb^{2+}} m_2 + U_{SO_4^{2-}} m_2}\right] \ln \left[\frac{U_{SO_4^{2-}} m_1 + U_{Ca^{2+}} m_1}{U_{SO_4^{2-}} (m_1 + m_2) + U_{Ca^{2+}} m_1 + U_{Pb^{2+}} m_2}\right]$$

$$= -\frac{RT}{2F}\left[\frac{\lambda_{Pb^{2+}} - \lambda_{SO_4^{2-}}}{\lambda_{Pb^{2+}} + \lambda_{SO_4^{2-}}}\right] \ln \left[1 + \frac{(\lambda_{Pb^{2+}} + \lambda_{SO_4^{2-}})\, m_2}{(\lambda_{Ca^{2+}} + \lambda_{SO_4^{2-}})\, m_1}\right] \qquad (E.3.2.3.2)$$

Differences in molal and molar concentration scales are ignored.

In the logarithmic term, the use of equivalent conductivities at infinite dilution (λ_i^0) should not lead to a significant error, but a correction for concentration was made to the pre-logarithmic term using the theoretical equation (43)

$$t_+ = \frac{\lambda_+}{\Lambda} = \frac{\lambda_+^0 - \frac{1}{2} z_+ B \sqrt{I}/(1 + A\sqrt{I})}{\Lambda^0 - \frac{1}{2}(z_+ + |z_-|) B \sqrt{I}/(1 + A\sqrt{I})} \qquad (E.3.2.3.3)$$

for the transport number of the cation (t_+) and the corresponding equation for t_-.

The value of A was taken as 1.3, and the values of B and λ^0 were taken from reference (43). The pre-logarithmic term of equation (E.3.2.3.2) now reduces to $- \frac{RT}{2F} (t_+ - t_-)$.

When cell potentials were measured with both compartments saturated with $PbSO_4$, a liquid junction potential is no longer present, but two additional corrections are necessary.

(iv) The activity coefficient of calcium ions will be modified but this effect was neglected for the same reasons as (ii).

(v) The calcium electrode will respond to the presence of Pb^{2+} ions in the test solution. The response may be estimated by using the semi-empirical equation (38):

$$E = \text{constant} + \frac{RT}{2F} \ln \left[a_A + \sum_{i \neq A} k_i \, a_i^{z_i/z_A} \right] \qquad (E.3.2.3.4)$$

where k_i are selectivity constants which are determined experimentally. The selectivity constant for Pb^{2+} ions in the present system is quoted by Ross (38) as 0.63; but k values are concentration dependent and equation (E.3.2.3.4) is not recommended for correcting cell potentials when the level of impurity ion is high. If equation (E.3.2.3.4) is assumed to be adequate, and activities are replaced by molalities, the magnitude of the correction term is given by

$$\frac{RT}{2F} \ln \frac{m_1 + 0.63\, m_2}{m_1}$$

The importance of these various effects can only be calculated if the solubility of lead sulphate in calcium sulphate solutions is known. Unfortunately, no experimental determinations could be found in the literature and the solubility was estimated in the following manner. The mean of four results (44) determined between 1930 and 1934 for the solubility of $PbSO_4$ in water at 25° is 0.0452 g per litre or 0.000149 molal. The solubility product of lead sulphate is therefore given by

$$K_{sp}^{25^0}(PbSO_4) = (0.000149\, \gamma_\pm)^2 \qquad (E.3.2.3.5)$$

In the presence of $CaSO_4$ (m_1) the solubility of lead sulphate (m_2) is given by

$$K_{sp}^{25^0}(PbSO_4) = m_2(m_1 + m_2)\, \gamma_\pm^2 \qquad (E.3.2.3.6)$$

The problem to be resolved is therefore one of estimating $\gamma_\pm$ for $PbSO_4$ in the pure solution and in the mixed solutions with $CaSO_4$. Fortunately, absolute values are unnecessary provided the variation of $\gamma_\pm$ with ionic strength is known with reasonable accuracy. Gardner and Glueckauf (2) in their treatment of freezing point data for 2:2 sulphates found that the variation of $\gamma_{\pm}$ with concentration was largely independent of the metal ion. It was decided to use their values for $\gamma_{\pm}$ ($CaSO_4$) as an estimate for $\gamma_{\pm}$ ($PbSO_4$) on the grounds that:

(a) of the divalent metal ions whose sulphates have been studied, the Ca^{2+} ion has the largest ionic radius and is therefore most comparable with Pb^{2+};

(b) in the mixed solutions the ionic medium is essentially that of $CaSO_4$, since the concentration of lead ions is always small.

Table 3.2.4 shows the values of $\gamma_{\pm}$ interpolated graphically from reference (2), together with the estimated solubilities of $PbSO_4$ calculated using equations (3.2.3.5) and (3.2.3.6). Also shown are the estimated corrections to the cell e.m.f. required to compensate for the dissolved lead sulphate. At the three lowest concentrations of $CaSO_4$, these corrections are of significant magnitude. Fortunately the percentage error in estimating the solubility of $PbSO_4$ is least under these conditions. An attempt was made to estimate the 95% confidence limits for the solubilities and e.m.f. corrections and these are also given in the table. The reason for choosing to measure cell e.m.f. values with the calcium compartment free of lead sulphate is now apparent. The uncertainty in potential caused by the liquid junction potential is well within experimental error at all the concentrations of $CaSO_4$, but the uncertainty in the correction required to compensate for response of the calcium electrode to lead ions would have been significant at the lowest $CaSO_4$ concentrations.

The sign of the liquid junction potential was deduced from the equivalent conductivities of Pb^{2+} and SO_4^{2-} ions. The mobility of sulphate ions is higher than that of lead ions, so that an equilibrium liquid junction is set up such that the calcium compartment becomes negatively charged relative to the compartment containing dissolved $PbSO_4$. Since experimentally it was found that the calcium electrode was the positive electrode, the effect of the liquid junction was to reduce the observed cell e.m.f. and transfer potential from the ideal values given by equations (3.2.1.2) and (3.2.1.3). The effect of additional sulphate ions on the response of the sulphate electrode increases the transfer potential over that given by equation (3.2.1.3). Saturating the calcium compartment with $PbSO_4$ removes the liquid junction potential, and introduces an additional response by the calcium electrode to Pb^{2+} ions. Both these effects serve to increase the e.m.f. of cell I. For solutions K and M, the changes in transfer potential on adding $PbSO_4$ to the calcium compartment were determined experimentally.

TABLE 3.2.4 LEAD SULPHATE SOLUBILITY

Solution	$CaSO_4$ molality /mol. kg^{-1}	Estimated $\gamma_\pm$	Estimated Solubility of $PbSO_4$ ($10^5 \times$ molality) /mol. kg^{-1}	Correction for liquid junction potential /m.v.	Correction for Ca Electrode /m.v.	Correction for SO_4 Electrode /m.v.
G	0.01518	0.33	1.03 ± 0.5	< 0.005	0.01 ± 0.005	0.010 ± 0.005
H	0.009980	0.385	1.15 ± 0.5	< 0.005	0.01 ± 0.005	0.015 ± 0.005
I	0.005997	0.453	1.39 ± 0.5	< 0.005	0.02 + 0.01	0.03 ± 0.01
J	0.003336	0.528	1.83 ± 0.6	< 0.005	0.05 ± 0.02	0.07 ± 0.02
K	0.002003	0.610	2.27 ± 0.7	0.01 ± 0.01	0.09 ± 0.04	0.14 ± 0.04
L	0.001109	0.676	3.28 ± 0.9	0.03 ± 0.02	0.23 ± 0.10	0.37 ± 0.10
M	0.0006576	0.751	4.29 ± 1.0	0.06 ± 0.03	0.52 ± 0.20	0.81 ± 0.20
PURE $PbSO_4$		0.879	14.9 ± 1.0			

Changes of + 0.08 m.v. and + 0.45 m.v. resulted. The calculated values are + 0.10 ±0.05 m.v. and + 0.58 ±0.23 m.v. respectively. In view of the errors in both experimental and calculated changes, this is considered to be reasonable agreement.

3.2.3.A Single ion activities

The precision of the measurements described in section 2.4.6 was poor. This was presumably due to variability of the liquid junction potential at the reference electrode. In view of this problem and since the objectives of this section were of limited importance, the results will not be discussed further.

3.2.4 Initial treatment of results

Equation (3.2.1.4) may be reexpressed as

$$E_T' = E_T^* - E^0_{AgCl/Ag} - \frac{RT}{2F} \ln m_1(m_1 + m_2) + \frac{3RT}{2F} \ln 4^{1/3} m_3 \gamma_{\pm CaCl_2} + |E_j|$$

$$= \frac{RT}{F} \ln \gamma_{\pm CaSO_4} - E^0_{PbSO_4/Pb(Hg)} \qquad (E.3.2.4.1)$$

A plot of E_T' against some function of concentration, should give the standard electrode potential of the lead amalgam electrode as the zero concentration intercept. This must always be so, regardless of the suitability of the extrapolation function, provided accurate results are available to sufficiently low concentrations. If the square root of concentration is used in the extrapolation function, the limiting slope at zero concentration must be given by the Debye-Hückel limiting law constant multiplied by $|z_+ z_-|RT/F$.

This procedure was followed in order to check if the present results were consistent with literature values for $E^0_{PbSO_4/Pb(Hg)}$. The standard potential of the silver-silver chloride electrode was taken as + 222.4 m.v. This is the mean of three results at 25°C spanning a range of 0.12 m.v. (21). The activity of the calcium chloride reference solution was calculated in the same manner as given in section 3.1.2. Values of E_T' are given in Table 3.2.5 and are plotted in Figure 3.2.2. as a function of $m_1^{\frac{1}{2}}$. The results are shown extrapolated to a value of E^0 which was deduced subsequently using more sophisticated methods of treatment. Also shown are the values of $E^0_{PbSO_4/Pb(Hg)}$ quoted by Shrawder and Cowperthwaite (29) and by Baumstark (34), and the Debye-Hückel limiting law gradient.

The experimental points do not extend to sufficiently low concentrations to enable the limiting law to be sensibly utilised. As a consequence, the extrapolation could not have been made with any accuracy if it was based solely on the present treatment. Even so, it is difficult to reconcile any extrapolation of the present results having the correct theoretical slope at the origin, with Shrawder's value of - 350.52 m.v. This point will be discussed again later.

The estimated maximum error limits shown in Table 3.2.5 were obtained by adding the 95% confidence limits calculated for the precision of the transfer potentials, to the estimated maximum errors in the estimated corrections made for lead sulphate solubility. To this total, a constant contribution of ±0.15 m.v. was added to account for errors in $E^0_{AgCl/Ag}$, calcium sulphate molality, calcium chloride activity, and any other systematic errors present. This total is greater than the overall 95% confidence limits for E_T', since all sources of error would need to be in the same direction for an error of this magnitude to occur.

FIGURE 3.2.2 PRELIMINARY TREATMENT OF RESULTS

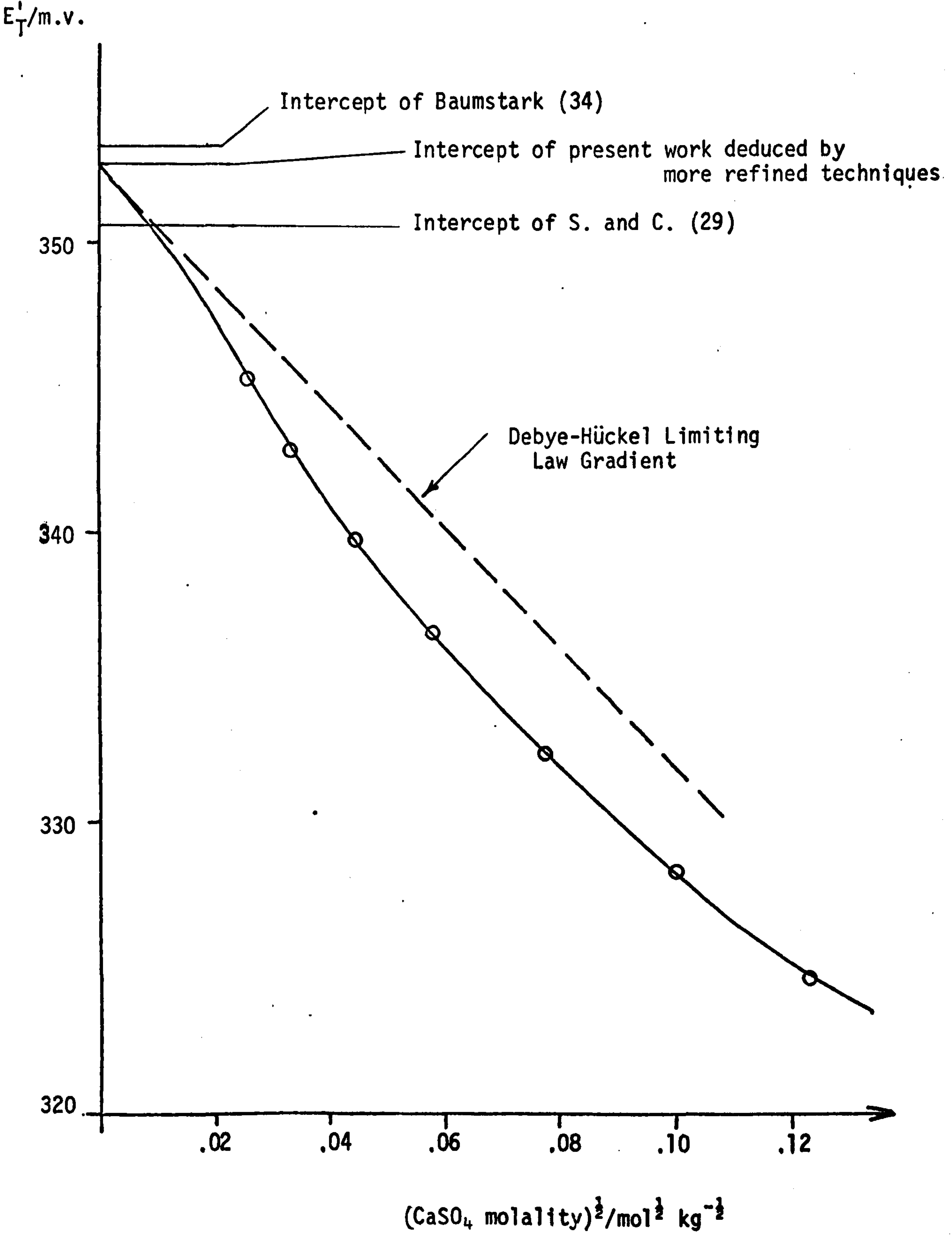


TABLE 3.2.5 PRELIMINARY TREATMENT OF RESULTS

Solution	Cell No.	E_T/m.v.	E'_T/m.v.	Estimated maximum error limits in E'_T/m.v.
G	2	571.61	324.73	± 0.24
	7	571.45	324.57	± 0.30
	11	571.74	324.86	± 0.21
	OVERALL	571.61	324.73	± 0.23
H	1	564.31	328.21	± 0.24
	4	564.39	328.28	± 0.18
	OVERALL	564.35	328.25	± 0.24
I	10	555.32	332.30	± 0.29
J	3	544.59	336.64	± 0.36
	6	544.39	336.44	± 0.20
	OVERALL	544.46	336.51	± 0.25
K	9	534.71	339.87	± 0.34
L	5	522.37	342.72	± 0.40
M	8	511.48	345.25	± 0.42

3.2.5 Extrapolations for a model system

It is clear from the previous section, that if an accurate value of $E^o_{PbSO_4/Pb(Hg)}$ is to be obtained, a different extrapolation function must be used. An adequate function must give a reasonably accurate prediction of the concentration dependence of the activity coefficient, from zero concentration up to the highest concentration used. One of the objects of this section is to determine the tolerable limits within which the "adequate function" can differ from the "perfect function".

As discussed earlier, the activity coefficients of 2:2 sulphates may be approximated to reasonably high concentrations by using either a non-linearised solution of the Poisson-Boltzmann equation, or a linearised D-H solution in conjunction with an assumed equilibrium between free ions and ion-pairs. The latter treatment is used in this section, since it is more amenable to computation.

Consider a hypothetical 2:2 electrolyte MX, which has a dissociation constant for the equilibrium between ion pairs and free ions,

$$\left[M^{2+}\,X^{2-}\right] \rightleftharpoons M^{2+} + X^{2-}$$

of $$K_D = \frac{a_{M^{2+}}\,a_{X^{2-}}}{a_{MX^0}} = 0.005 \text{ mol kg}^{-1} \qquad (E.3.2.5.1)$$

This value for K_D was chosen in order to be consistent with literature values for $CaSO_4$ (5).

An ion pair was defined in the Bjerrum sense as any pair of oppositely charged ions which are closer than some arbitrary distance q. Ions within this distance are considered to make no contribution to the ionic strength of the solution, while so called free ions, outside this distance contribute to the electrostatic non-ideality of the system in a Debye-Hückel manner. The equation chosen for the mean activity coefficient of free ions was

$$\ln \gamma_f = \frac{-\,|Z_+Z_-|\,S\,\sqrt{I}}{1 + (q/a_0)\,\sqrt{I}} \qquad (E.3.2.5.2)$$

a_0 is a constant in the Debye-Hückel equation, dependent only on temperature and the dielectric constant. The distance of closest approach of free ions (the distance defining association) q, was taken as 0.714 nm which is half the Bjerrum distance (q_B) for a 2:2 electrolyte at 25°C. In the original Bjerrum treatment q was fixed for any electrolyte by

$$q_B = \frac{|Z_+Z_-|\,e^2}{2\,\varepsilon\,kT} \qquad (E.3.2.5.3)$$

where e is the electronic charge, and k is the Boltzmann constant. This is the distance at which the mutual electrical potential energy of two ions is equal to 2kT, and according to the Bjerrum model, is the distance at which the number of negatively charged ions in a thin spherical shell around a central positive ion is a minimum. Guggenheim (48) has suggested that for 2:2 electrolytes the use of q distances less than about 1.0 nm is unsuitable in a linearised D-H equation. This is of no consequence in the present treatment since we are defining the exact properties of a model system.

Consider the hypothetical cell

$$M \,/\, M^{2+}\,X^{2-}\,(m) \,/\, NX_{(s)} \,/\, N \qquad \text{Cell IV}$$

where NX is a very sparingly soluble electrolyte salt of the metal N. The cell potential is given by

$$E = E^0_{NX/N} - E^0_{M^{2+}/M} - \frac{RT}{2F}\ln\left(a_{M^{2+}}\,a_{X^{2-}}\right) \qquad (E.3.2.5.4)$$

The standard cell potential E^0 was arbitrarily set at 100 m.v., and the equation re-written as

$$E = E^0 - \frac{RT}{F}\ln m_f\,\gamma_f \qquad (E.3.2.5.5)$$

The subscript f indicates that the properties of free ions are referred to. If the activity coefficient of ion pairs is assumed to be unity, equation (3.2.5.1) may be re-expressed as

$$K_D = \frac{(m_f \gamma_f)^2}{m - m_f} \qquad (E.3.2.5.6)$$

Cell potentials were calculated as a function of stoichiometric molality (m) by solving equations (3.2.5.2) and (3.2.5.6) by an iterative procedure for m_f and γ_f. The molality of free ions was initially set at the arbitrary value of 0.75 m. Equation (3.2.5.2) was solved for γ_f using $I = 4\,m_f$, and equation (3.2.5.6) solved to give a new value of m_f. The cycle was repeated until the new value of m_f was within 0.01 per cent of the old value. Using equation (E.3.2.5.5), cell potentials were calculated for concentrations of MX up to 0.1 molal. The results can be considered as experimental cell potentials having zero error.

The effect of using incorrect values of K_D or q was found by using equation (3.2.5.5) to calculate E^0 for each concentration. Values of m_f and γ_f under these new conditions, were found by the same iterative procedure as described above. Dissociation constants of 0.0035, 0.0045, 0.006 and 0.007 mol kg^{-1}, and distances of closes approach of 1.071 nm ($3q_B/4$) and 0.476 nm ($q_B/3$) were used.

The results are shown plotted against ionic strength in Figures 3.2.3 and 3.2.4. Ionic strength was chosen as the abscissa, since in a real system, the contributions of non-electrostatic terms to $\ln\gamma$ are linear in I at low concentration, and because a small error in the distance of closest approach can normally be compensated for by a suitable addition term to $\ln\gamma$ which is again linear in I. This latter relationship is modified by the ion-pair dissociation equilibrium, since the concentration of free ions also varies.

The model system was also used to check the effect of using incorrect values of E^0 and q on the value of K_D obtained by a similar extrapolation procedure.

For each concentration, the value of $m_f\gamma_f$ was calculated using equation (3.2.5.5), and by assuming an initial value of K_D, an approximate value of m_f was found from equation (3.2.5.6). This was used to calculate a value for γ_f using equation (3.2.5.2) and a new value of m_f was found using the fixed value of $m_f\gamma_f$. The last cycle was continued until the new value of m_f was within 0.01% of the old value and K_D was calculated from equation (3.2.5.5).

The results are given in Figures 3.2.5, 3.2.6 and 3.2.7 where log K_D is plotted against I. This choice of functions was made on the grounds that if errors linear in I are expected for $\ln\gamma$, linear errors in I should also be expected in log K_D rather than K_D. The effect of an error in q is shown in Figure 3.2.5, where results for $q = q_B/3$ and $q = 3q_B/4$ are seen to exhibit increasing curvature towards the "correct" value of log K_D at low concentrations, but do not extrapolate to this value. This was not unexpected since K_D (unlike E^0), is not a true thermodynamic constant. Figure 3.2.6 shows that an error in E^0 leads to K_D values which diverge from the "correct K_D" as I approaches zero. This divergence does not become marked, however, until quite low concentrations are reached. Figure 3.2.7 shows the effect of partially compensating errors in E^0 and q. For one pair of values, an almost constant value for K_D results for all concentrations between 0.006 I and

FIGURE 3.2.3 MODEL CALCULATIONS FOR A HYPOTHETICAL 2:2 ELECTROLYTE. EFFECT OF INCORRECT VALUES FOR K_D

$$q = 0.5 \times q_B \left(= 0.714 \text{ nm}\right)$$

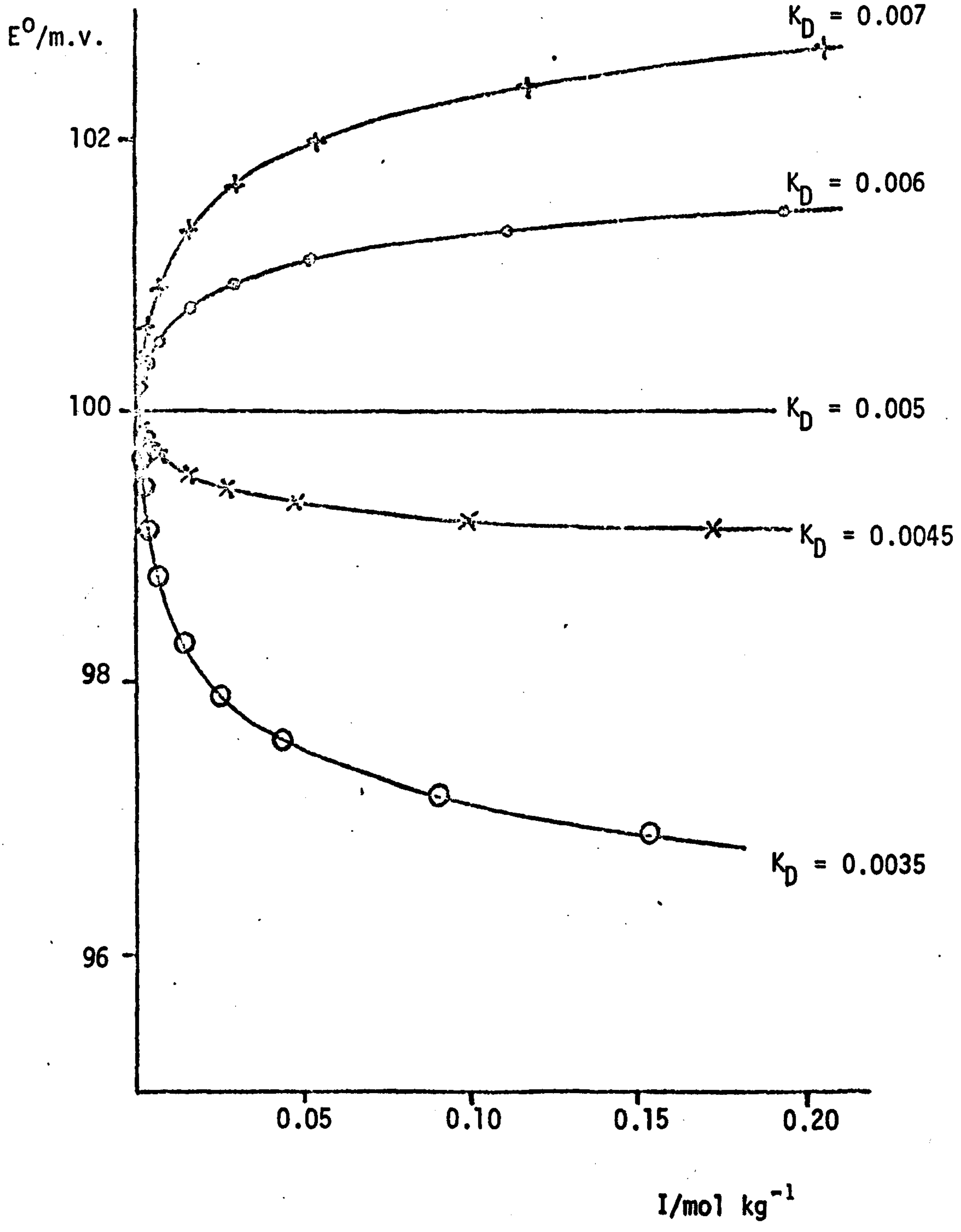


FIGURE 3.2.4 MODEL CALCULATIONS FOR A HYPOTHETICAL 2:2 ELECTROLYTE. EFFECT OF INCORRECT VALUES FOR q

$K_D = 0.005 \text{ mol kg}^{-1}$

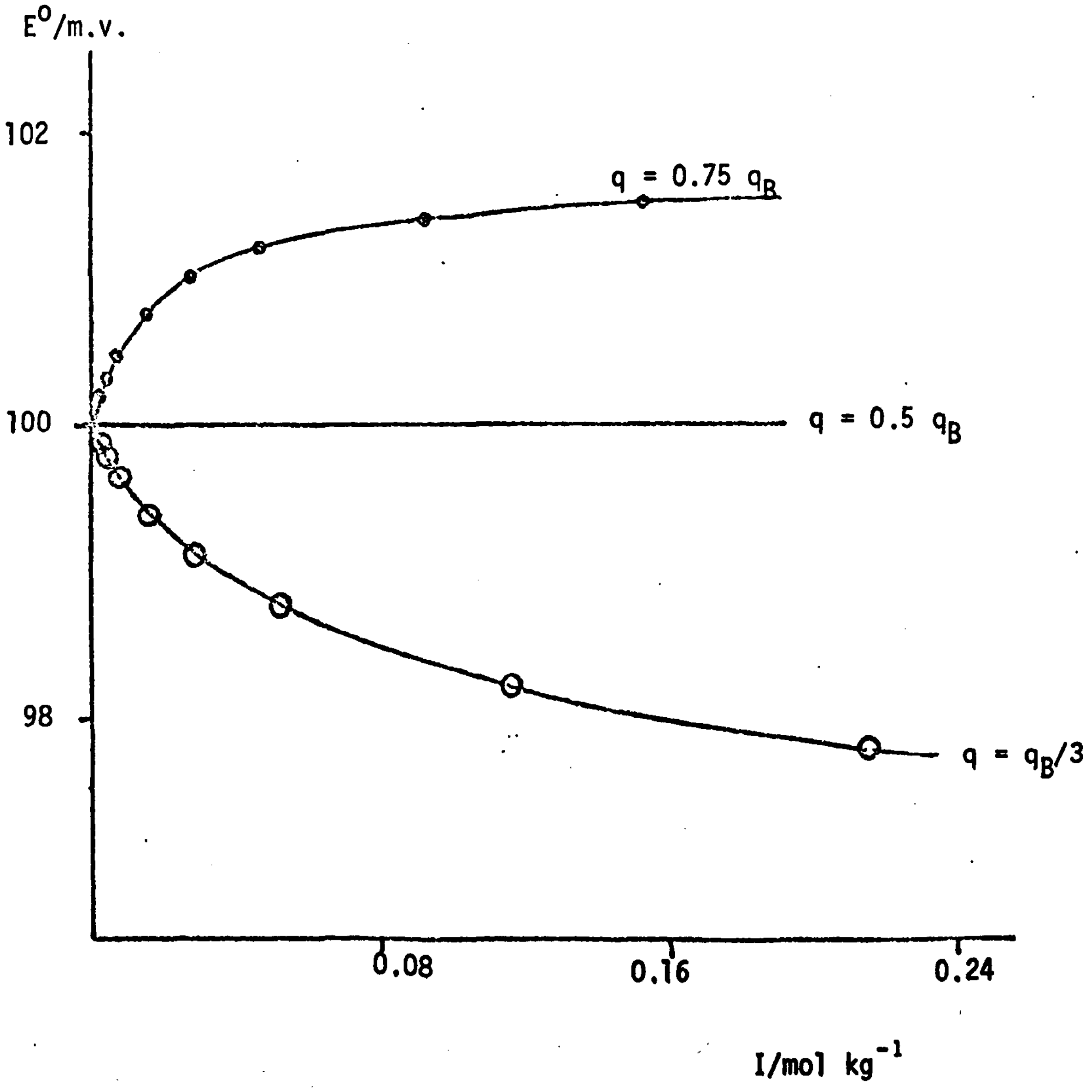


FIGURE 3.2.5 MODEL CALCULATIONS FOR A HYPOTHETICAL 2:2 ELECTROLYTE. EFFECT OF INCORRECT VALUE OF q

$E^o = 100$ m.v.

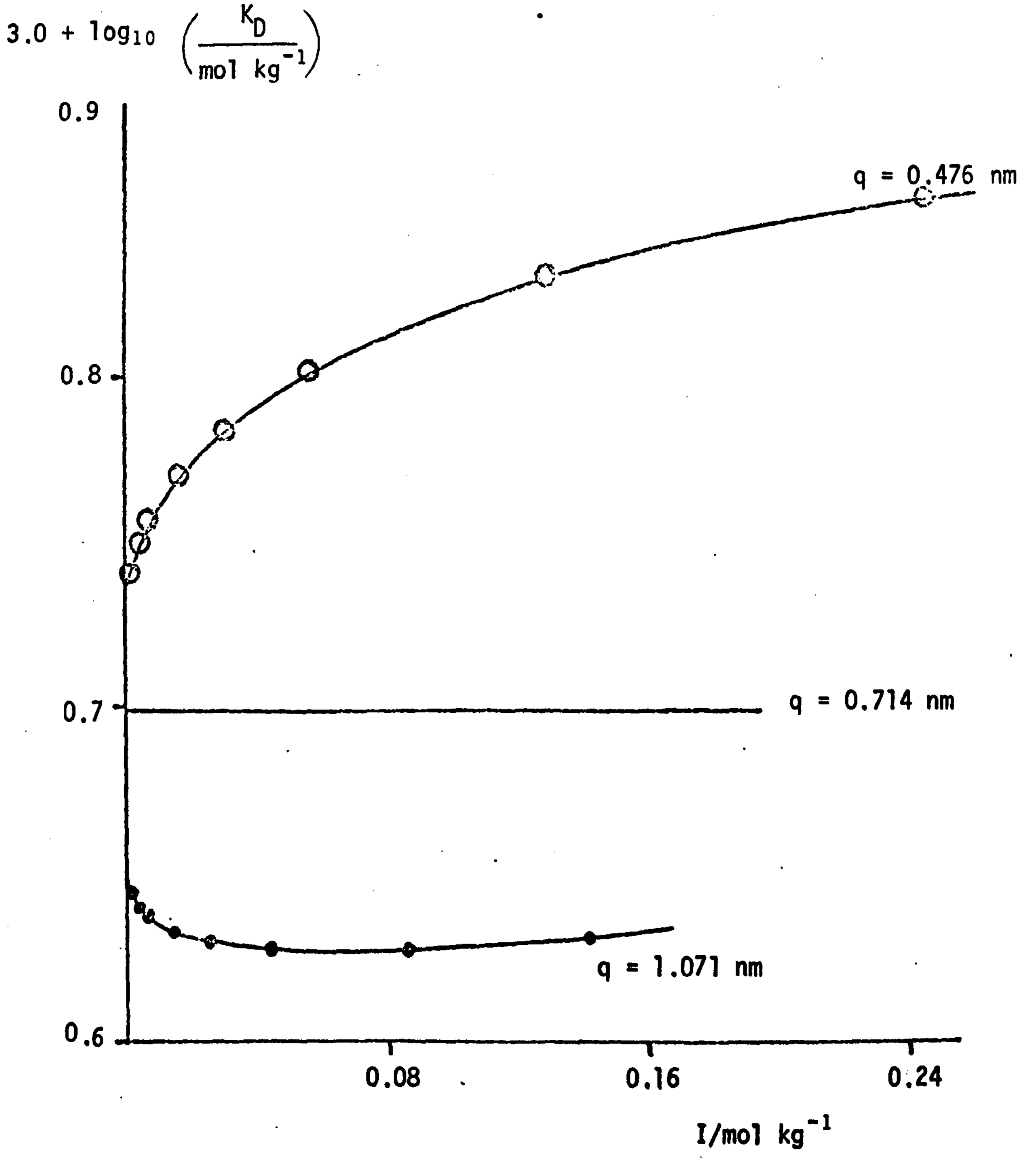


FIGURE 3.2.6 MODEL CALCULATIONS FOR A HYPOTHETICAL 2:2 ELECTROLYTE. EFFECT OF INCORRECT VALUES OF E^o

$q = 0.714$ nm

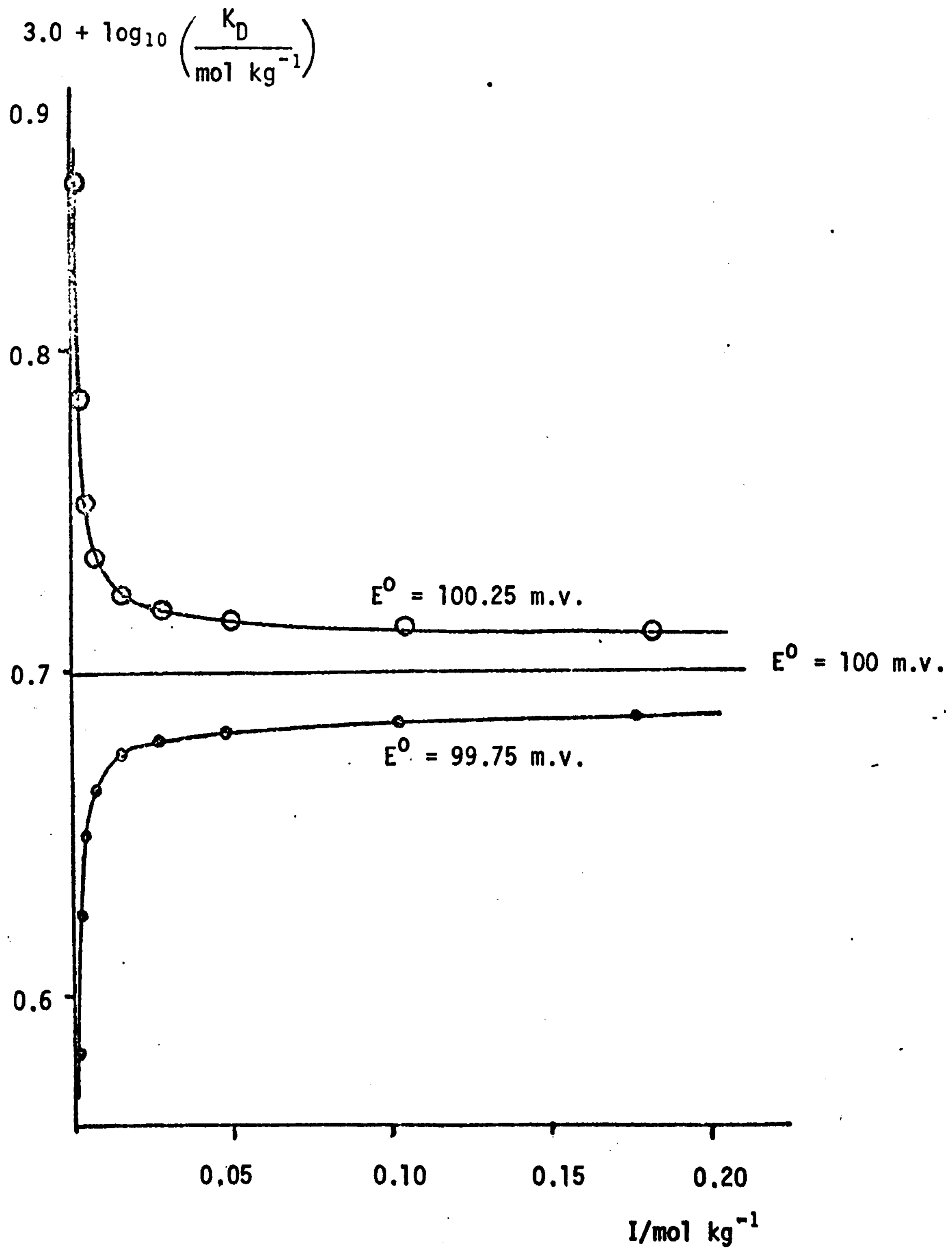
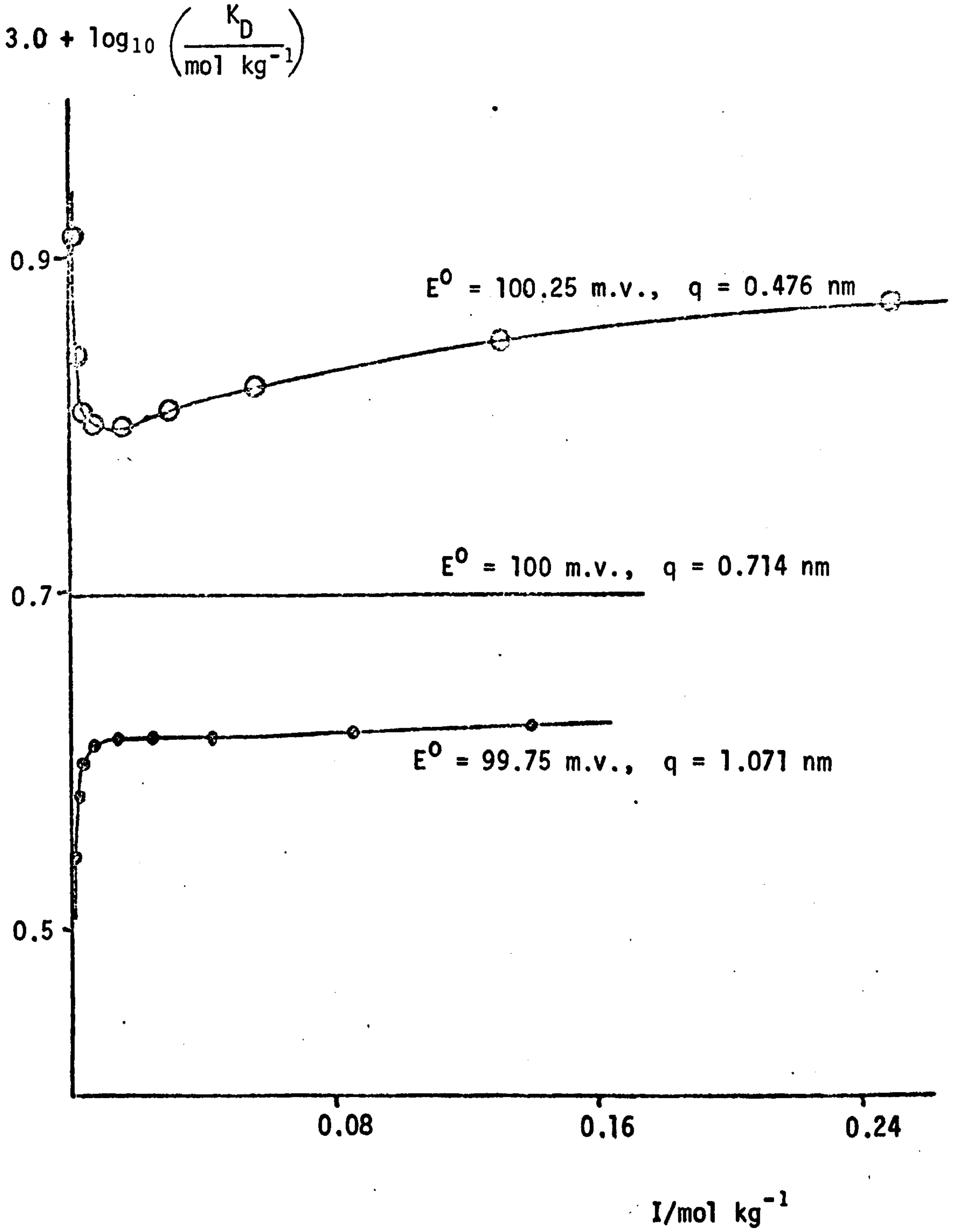


FIGURE 3.2.7 MODEL CALCULATIONS FOR A HYPOTHETICAL 2:2 ELECTROLYTE. EFFECT OF INCORRECT VALUES FOR E^0 AND q



0.14 I. It follows that if this pair of K_D and q values were used in a determination of E^o, a value close to 99.75 m.v. would result over this same concentration range. The error in E^o would only become apparent if accurate cell potentials were available below 0.006 I.

Experimental cell potentials cannot be measured to indefinitely low concentrations, and errors increase as the concentration is reduced. This is the main point to remember when considering the implications these model calculations have for real systems. A number of points arise:

(i) in the determination of E^o small errors in K_D or q could lead to results being incorrectly interpreted as linear in I, giving an error in the intercept;

(ii) if distinct curvature is present, a better value of E^o can be obtained by drawing a best curve through the points, rather than by forcing a linear fit;

(iii) the most effective way of ensuring an accurate extrapolated value for E^o is to vary the parameters around reasonable values, and take advantage of the knowledge that all the sets of points must extrapolate through the same intercept. Most weight should be given to the set of points giving an apparently linear extrapolation;

(iv) the question put at the beginning of this section concerning the tolerable difference between an "adequate function" and the "perfect function" is seen to be unanswerable without a knowledge of the concentration range and accuracy of the results. A more sensible question is "Do the results extend to sufficiently low concentrations with the accuracy required to distinguish an "adequate function" from functions leading to significant error?" If the answer to the latter question is affirmative, then errors in the parameters are unimportant, since they can be detected and eliminated by the procedure outlined above;

(v) in the determination of K_D values, the intercept is not expected to be independent of q and E^o;

(vi) if any doubt exists as to the value of the standard cell potential given in the literature, it is advisable to check that the results are compatible with this value, otherwise the K_D values obtained may be meaningless. Only an E^o value compatible with the results should be used to determine K_D;

(vii) the determination of a "correct" pair of K_D and q values is a difficult task, and the best procedure is probably to choose a reasonable range of q values and give corresponding K_D values for each.

Similar considerations would apply if any other method of representing the activity coefficients were used. The suitability of an equation or set of equations for representing the concentration dependence of the activity coefficient may be judged by ability to predict a linear dependence of E^o with I. In addition the gradient required should not be unreasonably high.

3.2.6 Treatment of results using ion-pair concept

The results for $CaSO_4$ were treated in the same manner as for the model system. An arbitrary value of $K_D = 0.004$ mol kg^{-1} was chosen and used in conjunction with values of q between q_B and $q_B/4$. An arbitrary value of $q = q_B/2$ was also used with values of K_D between 0.003 and 0.007 mol kg^{-1}.

For each pair of K_D and q values, equations

$$K_D = \frac{(m_f\ \gamma_f)^2}{m_1 - m_f} \qquad (E.3.2.5.6)$$

and

$$\ln \gamma_f = \frac{-|Z_+Z_-|\ S\ \sqrt{I}}{1 + (q/a_0)\ \sqrt{I}} \qquad (E.3.2.6.1)$$

were solved by an iterative procedure to give self consistent values of m_f and γ_f. Values of $E^{o\prime}_{PbSO_4/Pb(Hg)}$ were calculated at each concentration using

$$E^{o\prime}_{PbSO_4/Pb(Hg)} = E^{o}_{AgCl/Ag} - E_T + \frac{RT}{F} \ln (m_f\ \gamma_f) - {}^3/_2\ \frac{RT}{F} \ln\left(4^{1/3}\ m_3\ \gamma_{\pm CaCl_2}\right) \qquad (E.3.2.6.2)$$

where E_T is the transfer e.m.f. corrected for errors introduced by the solubility of $PbSO_4$. The additional superscript to the cell potential denotes that $E^{o\prime}$ will only be equal to E^o when I equals zero, due to imperfections in the equations used to calculate calcium sulphate activities.

The results of this treatment are given in Figures 3.2.8 and 3.2.9. Provided non-linearity is permitted, smooth curves can be drawn through all the sets of points to a common intercept of -352.6 m.v. Other pairs of K_D and q values were used which gave apparent linearity of $E^{o\prime}$ with ionic strength. These latter results were analysed by the method of least squares assuming a linear regression between $E^{o\prime}$ and I. All the intercepts were within ±0.15 m.v. of -352.6 m.v., and the standard error of the intercept (46) led to 95% confidence limits of ±0.16 m.v. This does not of course take into account systematic errors, which were estimated at a maximum of ±0.15 m.v. It is clear that these results are quite incompatible with the value deduced by Shrawder and Cowperthwaite (29) of -350.52 m.v.

By utilising the value of $E^o = -352.6$ m.v. the results were analysed to give values of K_D for q values in the range $q = q_B$ to $q = q_B/4$. The value of $m_f\gamma_f$ was calculated from equation (3.2.6.2) and the individual values of m_f and γ_f calculated in the same manner as for the model calculations. Finally K_D was deduced using equation (3.2.5.6).

The results are shown for the two extreme values of q in Figure 3.2.10. No significant deviations from linearity were discernable, so the points were fitted to straight lines using the least squares principle. Dissociation constants obtained from the intercepts are shown in Table

FIGURE 3.2.8 · TREATMENT OF CaSO DATA USING ION-PAIR CONCEPT.

EFFECT OF VARIATION IN K_D WITH $q = 0.5\ q_B$.

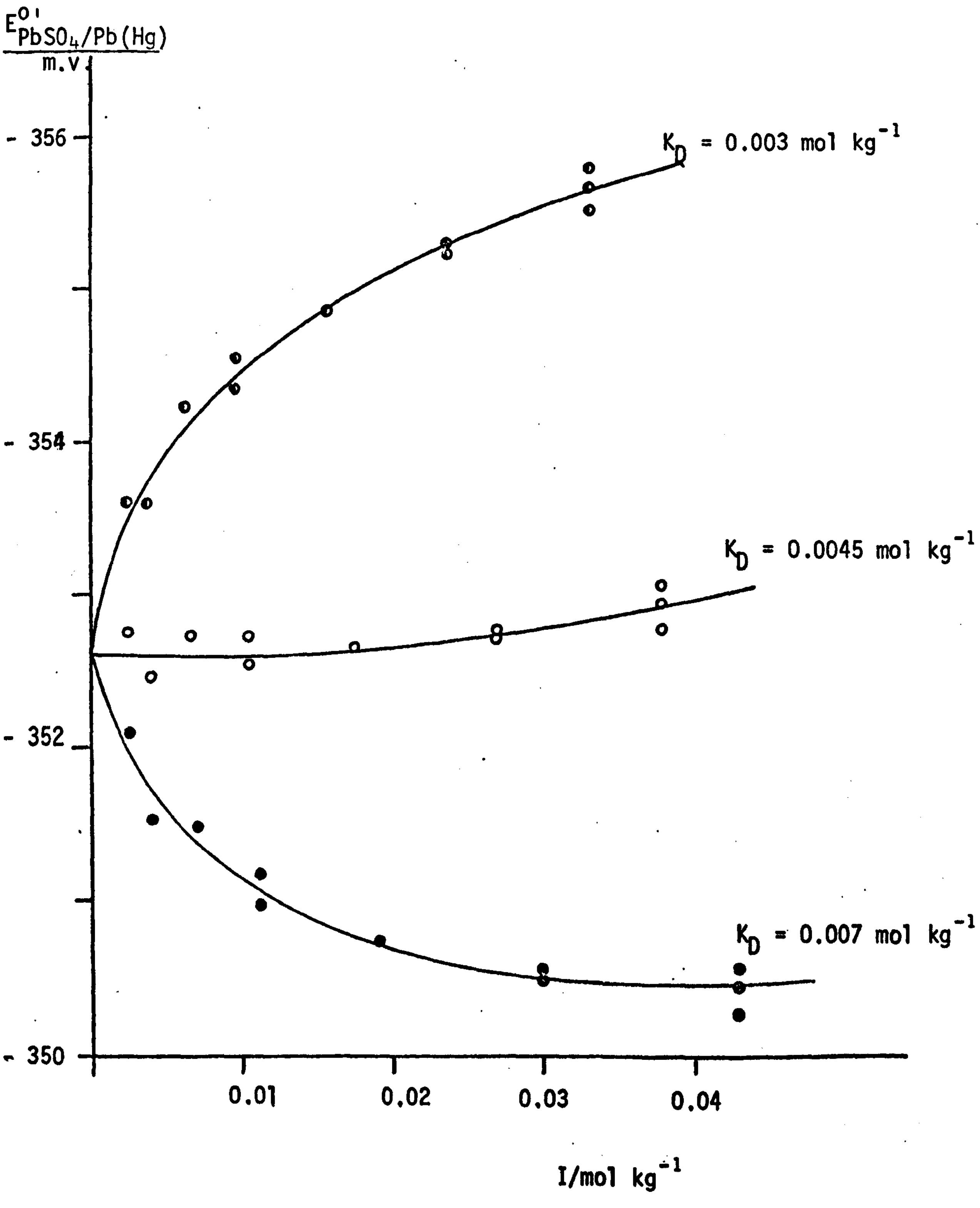


FIGURE 3.2.9 TREATMENT OF $CaSO_4$ DATA USING ION-PAIR CONCEPT.

EFFECT OF VARIATION IN q WITH K_D = 0.004 mol kg^{-1}

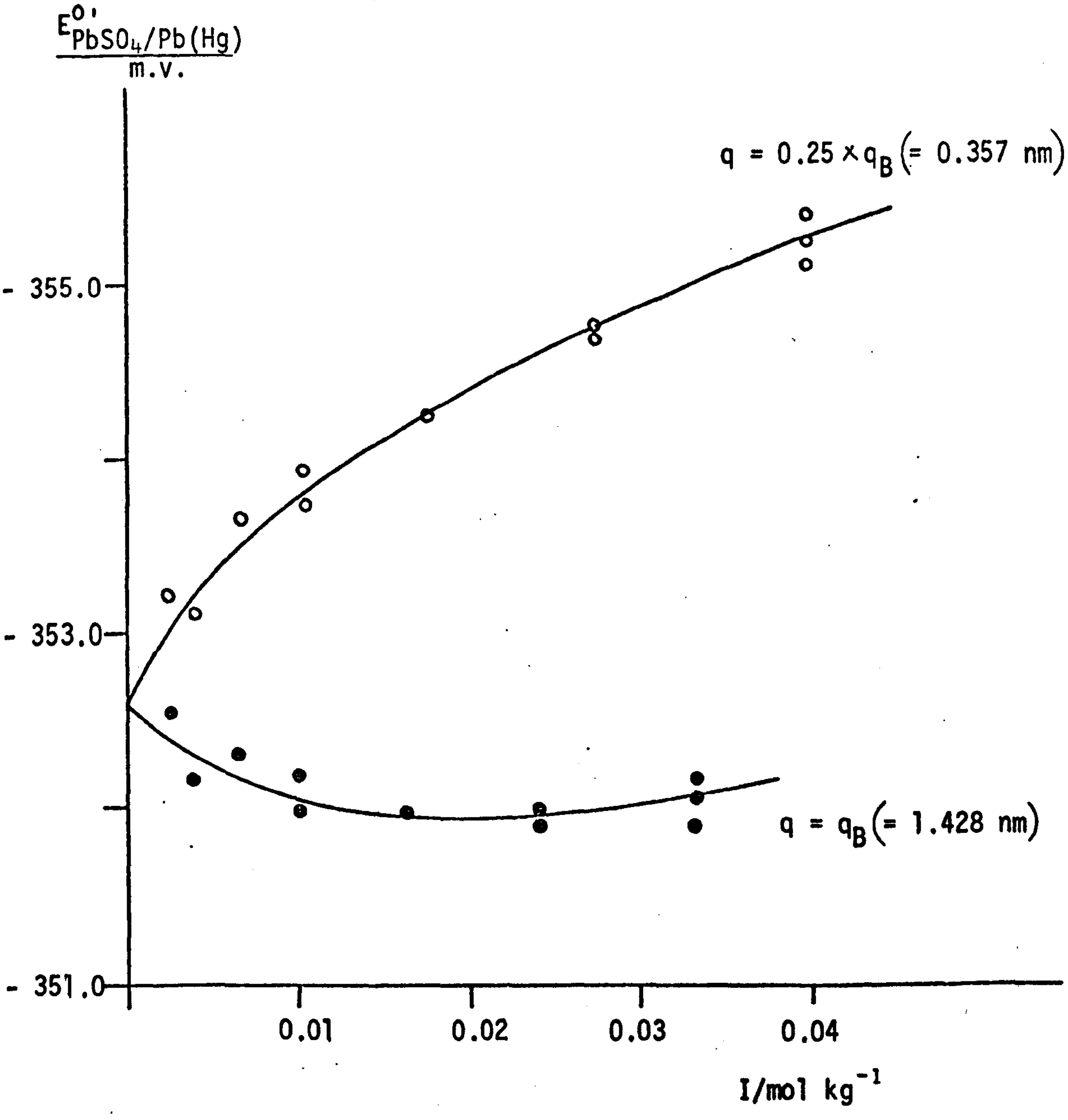
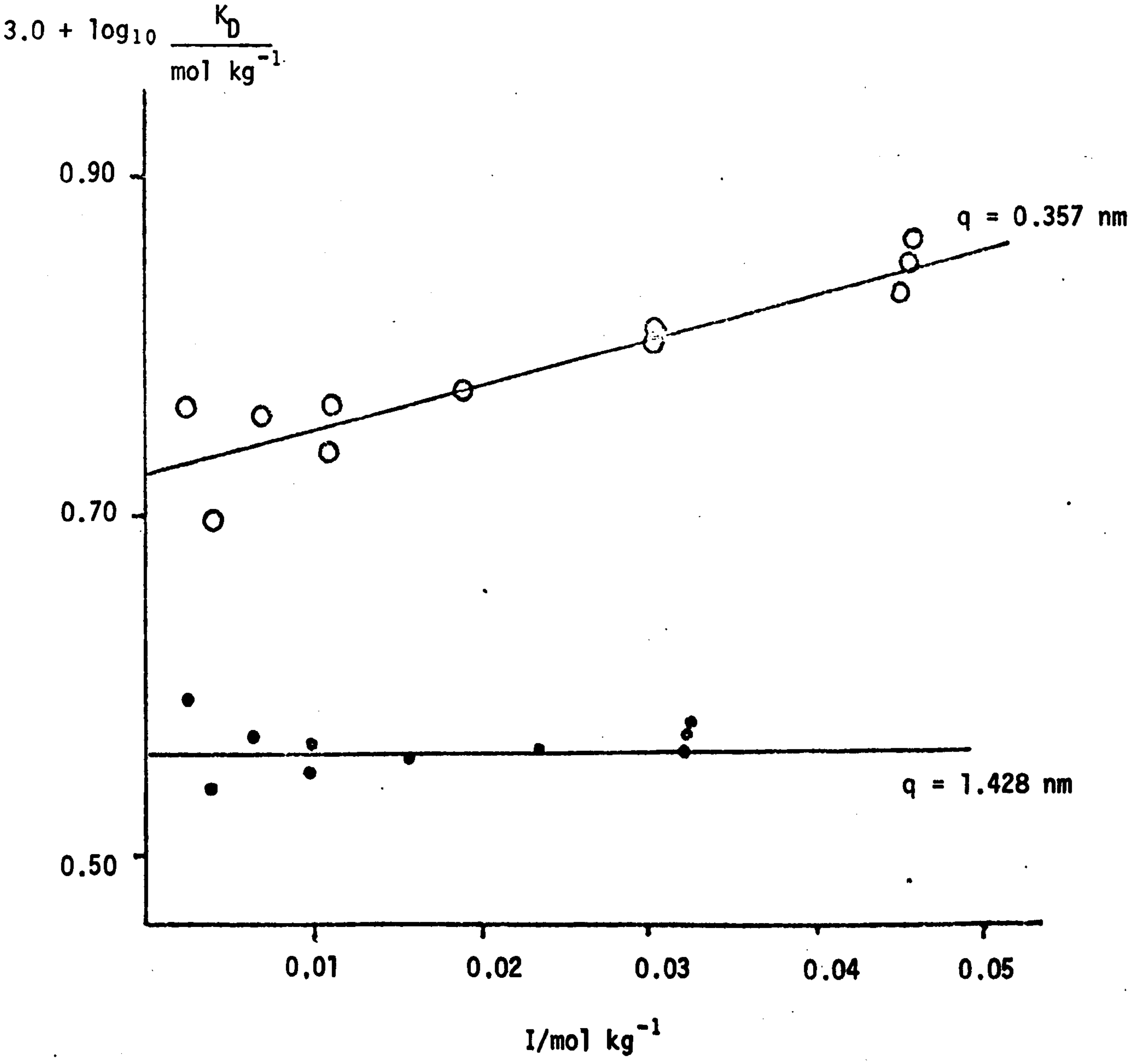


FIGURE 3.2.10 TREATMENT OF $CaSO_4$ DATA USING ION-PAIR CONCEPT. EFFECT OF VARIATION IN q USING E^0 = -352.6 m.v.



3.2.6 together with the standard errors of the intercepts. Corresponding values of K_D were also calculated using E^0 = -352.4 m.v. and -352.8 m.v. These results are also given in Table 3.2.6.

If the Bjerrum treatment is applied to these results, values may be calculated for the distance of closest approach (a) of ions within the ion pair. The degree of association, or the fraction of negatively charged ions within the distance a to q of a positively charged ion is given by (43)

$$1 - \alpha \quad = \quad \frac{4\,\pi\,m\,L}{1000}\,(2q_B)^3 \int_{2q_B/q}^{2q_B/a} x^{-4}\,e^x\,dx \qquad \text{(E.3.2.6.3)}$$

where α is the degree of dissociation, L is Avogadro's constant, $x = -\,z_+ z_-\,e^2/\epsilon kTr$ and r is the distance between ion centres. The dissociation constant may be written as

$$K_D \quad = \quad \frac{\alpha^2\,m\,\gamma_f^2}{1 - \alpha} \qquad \text{(E.3.2.6.4)}$$

so that the association constant is given by

$$K_D^{-1} \quad = \quad \frac{4\,\pi\,L}{1000\,\alpha^2\gamma_f^2}\,(2q_B)^3\,Q \qquad \text{(E.3.2.6.5)}$$

where $$Q \quad = \quad \int_{2q_B/q}^{2q_B/a} x^{-4}\,e^x\,dx$$

As the concentration approaches zero, both α and γ_f approach unity, giving a limiting value for the association constant of

$$K_D^{-1} \quad = \quad \frac{4\,\pi\,L}{1000}\,(2q_B)^3\,Q \qquad \text{(E.3.2.6.6)}$$

For any pair of K_D and q values, the only unknown in equation (3.2.6.6) is the distance of closest approach (a). Robinson and Stokes (43) tabulate values of

$$Q(b) \quad = \quad \int_2^b x^{-4}\,e^x\,dx$$

as a function of b at 25°C. Equation (3.2.6.6) may be written in the form

$$\int_2^{2q_B/a} x^{-4}\,e^x\,dx \quad = \quad \int_2^{2q_B/q} x^{-4}\,e^x\,dx \quad + \quad \frac{1000}{4\,\pi\,L\,(2q_B)^3\,K_D} \qquad \text{(E.3.2.6.7)}$$

This equation was solved for 'a' using graphical interpolation of the tabulated Q(b) values. The results are given in Table 3.2.7 together with the results obtained by Brown and Prue (5) from a comparable analysis of their freezing point data. The error limits shown for the distance of closest approach correspond to changes in E^0 of ±0.2 m.v. A smaller value of $|E^0|$ leads to a larger value of 'a'. Values of q in the range 0.5 q_B to q_B give an almost invariant distance of closest approach of about 0.38 nm. This is precisely the value predicted from the relevant bond lengths, (4), but this exact agreement is probably fortuitous. As would be expected, smaller values

TABLE 3.2.6 ION PAIR DISSOCIATION CONSTANTS FOR $CaSO_4$

q/nm	K_D / (mole kg^{-1})			
	E^o = -352.6 m.v.	Standard error in K_D	E^o = -352.4 m.v.	E^o = -352.8 m.v.
0.357 (¼ q_B)	0.00530	± 0.00014	0.00585	0.00484
0.476 (⅓ q_B)	0.00501	± 0.00012	0.00550	0.00460
0.714 (½ q_B)	0.00453	± 0.00010	0.00492	0.00418
1.071 (¾ q_B)	0.00400	± 0.00008	0.00431	0.00373
1.428 (q_B)	0.00364	± 0.00007	0.00390	0.00341

TABLE 3.2.7 COMPARISON WITH RESULTS BASED ON FREEZING POINT MEASUREMENTS

PRESENT WORK (25°C)			BROWN AND PRUE (5) (0°C)		
q/nm	K_D /(mole kg^{-1})	a/nm	q/nm	K_D /(mole kg^{-1})	a/nm
1.428 (q_B)	0.00364	0.393 ±0.01	1.387 (q_B)	0.0033	0.356
1.071 (¾ q_B)	0.00400	0.381 ±0.01			
0.714 (½ q_B)	0.00453	0.371 ±0.009	0.694 (½ q_B)	0.0043	0.348
			0.50	0.0050	0.341
0.476 (⅓ q_B)	0.00501	0.348 ±0.009			
			0.40	0.0054	0.326

for q lead to smaller values for 'a'. Use of q values lower than the physically reasonable 0.38 nm can only give absurdly small 'a' values, and q = $q_B/2$ is probably the lowest value which can sensibly be used. This restriction is also consistent with Guggenheim's view (48) that small q values are not suitable for use in the linearised D-H equation.

Comparison with results obtained by Brown and Prue (5) is slightly complicated by the temperature difference. This should not have any effect on the distance of closest approach, but K_D would be expected to be lower at 25°C than at 0°C by about 0.0004 mole kg^{-1} (49). The present analysis gives values of K_D and 'a' which are both higher than the corresponding figures at 0°C. The descrepancy is not excessively large, a standard cell potential of about -353.2 m.v. would give good agreement between the two sets of results. Other workers (2,3,49) have analysed the data of Brown and Prue assuming further association of ions into triplets. Although this assumption should not have a marked effect at these low concentrations, the results are more concordant with the present analysis. Using $q = q_B$, Pitzer (49) found $K_D = 0.0036$ mole kg^{-1} at 0^oC; and Gardner and Glueckauf (2) using $q = 2q_B/3$ found $K_D = 0.00428$ mole kg^{-1} and $a = 0.362$ nm at 0^oC. The dissociation constant has also been estimated from solubility data of calcium iodate in potassium sulphate by Bell and George (50), and from conductivity data at low concentrations by Money and Davies (51). Bell and George (50) used the Davies equation (E.1.2.2) to represent all activity coefficients. This is approximately equivalent to using $q = 0.38$ nm (at $I = 0.01$ m), and leads to a value for K_D of 0.0049 mole kg^{-1} at 25^oC. The value of "a" quoted by Bell and George (50) (4.43 Å) is almost certainly a misprint, since it is inconsistent with a statement made by the authors in their discussion. Even if this were not so, the result would be meaningless due to the inconsistency of using "$q = 0.38$ nm" in the activity coefficient expression to give K_D, and then using $q = q_B$ (1.43 nm) in the Bjerrum treatment to obtain "a" from K_D. Money and Davies treated their data using the D-H limiting law which is equivalent to setting q equal to zero. This is not of great importance however due to the low concentrations used. A value of $K_D = 0.0053$ mole kg^{-1} was obtained at 18^oC.

Summarising this section, the application of Bjerrum's concept of ion pairing has enabled activity coefficients of calcium sulphate to be determined as a function of concentration. It was necessary to make an arbitrary choice of two parameters, but provided reasonable values were assigned to these, a unique value for the standard electrode potential was obtained. This potential was used in conjunction with physically realistic association distances, to give ion-pair dissociation constants and corresponding distances of closest approach which were in good agreement with literature results.

The apparent success of the method does not preclude the possibility that the concentration dependence of the calculated activity coefficients was sufficiently in error to give a significantly incorrect intercept. This possibility is investigated in the next section, by dispensing with the ion-pair concept. More direct calculations of activity coefficients were made in order to test whether the same intercept for the standard electrode potential was obtained.

3.2.7 Treatment of results using numerical solutions of Poisson's equation

Historically the most fruitful approach in the calculation of activity coefficients in dilute solution has been via calculations of the mean electrostatic potential for a single fixed ion. Poisson's equation connecting the electrostatic potential at a central ion (i) with the average distribution of surrounding charge may be written as

$$\nabla^2 \psi = -\frac{4\pi}{\varepsilon} \sum_i e z_i \rho_i \exp\left(-W_i/kT\right) \qquad \text{(E.3.2.7.1)}$$

where ψ is the mean electrostatic potential,

ρ_i is the average density of i-type ions

and W_i is potential of mean force.

This equation is exact as written, but Debye and Hückel substituted $z_i e\psi$ for W_i, an approximation which is only valid when the distribution of charge is spherically symmetrical at all times. This is only true for extremely dilute solutions. Frank and Thompson (65) found that significant deviation from spherical symmetry was present for 1:1 electrolytes at concentrations as low as 10^{-4} molal. For 2:2 electrolytes the problem arises at still lower concentrations. Debye and Hückel made a further approximation by linearising equation (3.2.7.1) giving

$$\nabla^2 \psi = -\frac{4\pi}{\varepsilon} \sum_i \frac{e^2 z_i^2}{kT} \rho_i \psi \qquad \text{(E.3.2.7.2)}$$

This approximation re-introduces a degree of physical self consistency, but results in large errors due to the neglect of higher order terms, especially for electrolytes of valency types higher than 1:1. Müller (10), Gronwall *et al* (11) Guggenheim (66) and Glueckauf (4) have retained the higher order terms in treatments of 2:2 electrolytes, but have all used the approximation that $W_i = z_i e\psi$. Gronwall (11) used an analytical solution, while the other authors resorted to numerical solutions. Outhwaite (67,68) has used a more sophisticated procedure by expressing (E.3.2.7.1) as

$$\nabla^2 \psi = -\frac{4\pi}{\varepsilon} \sum_i e z_i \rho_i V \exp\left[- e z_i (\psi + \delta)/kT\right] \qquad \text{(E.3.2.7.3)}$$

where V is the excluded volume term and δ is called the fluctuation term. Both of these concepts were introduced by Kirkwood (71) who used a statistical mechanical approach. The deviation of V from unity is unimportant for dilute solutions, but the δ term is of significant magnitude at the lowest concentrations used in this study. δ may be evaluated using different closure approximations depending upon the number of fixed ions for which the potential is calculated. For a single fixed ion δ = zero and (E.3.2.7.3) is the normal Poisson-Boltzmann equation (if V = 1). Outhwaite has evaluated δ for two fixed ions in linearised (67), and also in non-linearised numerical solutions (68,69). The computations were carried out using both the Debye and the Güntelberg charging processes. In the former, ions in fixed positions are reversibly charged from zero to $z_i e$, while in the latter, ions of charge $z_i e$ are brought from infinity to their final positions relative to the fixed central ion.

The results were compared with the recent Monte-Carlo calculations of Card and Valleau (70), and were found to give better agreement than activity coefficients calculated using the unmodified Poisson-Boltzmann equation. The self consistency of the results was checked by using the "second moment condition" of Stillinger and Lovett (73), and also by testing the agreement between Debye and Güntelberg charging processes. Both tests indicated that the modifications were in general an improvement, but self consistency varied with concentration and with electrolyte charge type. The modifications were also judged to be an improvement, since they correctly predicted oscillations in the radial distribution function above a critical value of κa (κ is the reciprocal of the effective radius of the ionic atmosphere).

Outhwaite (69) has tabulated values of $\ln\gamma_\pm$ as a function of concentration and distance of closest approach. He gives results for the Debye charging process using the normal Poisson-Boltzmann equation (PBD), his modified equation (MPBD), and for his modified equation using the Güntelberg charging process (MPBG). Results are not given for the unmodified equation using a Güntelberg charging process (PBG), but these are given by Gardner and Glueckauf (4). Unfortunately Outhwaite gives values of $\ln\gamma_\pm$ at only three s/a ratios, and at κa values which are too widely separated for accurate interpolation.

$$s = \frac{z_i^2 e^2}{\varepsilon kT} = 2q_B \qquad (E.3.2.7.4)$$

and $$\kappa = \left(\frac{8\pi L e^2}{1000\,\varepsilon kT}\right)^{\frac{1}{2}}\sqrt{I} = b\sqrt{I} \qquad (E.3.2.7.5)$$

Dr. Outhwaite generously agreed to compute values of $\ln\gamma_\pm$ using the MPBG treatment at three values of s/a, and at values of κa corresponding to the $CaSO_4$ concentrations used in this study. The values of s/a chosen were 8.0, 7.6 and 7.2 corresponding at 25°C to distances of closest approach of 0.356, 0.375 and 0.396 nm. Using these values of $\ln\gamma_\pm$, the standard electrode potential of the lead amalgam electrode was calculated at each concentration using equation (3.2.4.1), and a best estimate was obtained by extrapolating to I = 0. The results of this analysis are shown in Figure 3.2.11. It is apparent that the treatment is consistent with a unique intercept of $E^0 = -352.6$ m.v. If linearity of $E^{0'}$ with concentration is chosen as the criterion with which to judge the most appropriate distance of closest approach, then a value of a = 0.38 - 0.39 nm results. This treatment is consequently entirely consistent with the previously described Bjerrum treatment, provided q distances greater than $\frac{1}{2}q_B$ are used in the latter.

Values of $\ln\gamma_\pm$ were deduced for the MPBD and the PBD treatments at s/a = 7.2 by plotting $\ln\gamma_\pm$ (PBD) - $\ln\gamma_\pm$ (MPBG) and $\ln\gamma_\pm$ (MPBD) - $\ln\gamma_\pm$ (MPBG) against κa using the values tabulated by Outhwaite at s/a = 7.0. The differences were interpolated at the pertinent concentrations, and were added to the $\ln\gamma_\pm$ (MPBG) values evaluated above at s/a = 7.2. This treatment involves the assumption that the differences between the different $\ln\gamma_\pm$ values are independent of s/a over the range 7.0 to 7.2. E^0 values calculated using these activity coefficients in equation (3.2.4.1) are shown in Figure 3.2.12. The results corresponding to $\ln\gamma_\pm$ (MPBG) are shown again for comparison. The differences between the treatments are clearly significant, but best curves drawn through all the sets of points are once again consistent with a unique intercept of -352.6 m.v. for E^0. The precision of the intercept is difficult to assess due to the marked non-linearity of the curves. It is evident that the distance of closest approach required to give linearity, decreases in the order MPBG, MPBD, PBD.

Values of $\ln\gamma_\pm$ using the PBG treatment were evaluated with the aid of Gardner and Glueckauf's (4) tabulated values of $\ln\gamma_M$. These authors defined $\ln\gamma_M$ as

FIGURE 3.2.11 USE OF MODIFIED P-B EQUATION WITH GÜNTELBURG CHARGING PROCESS

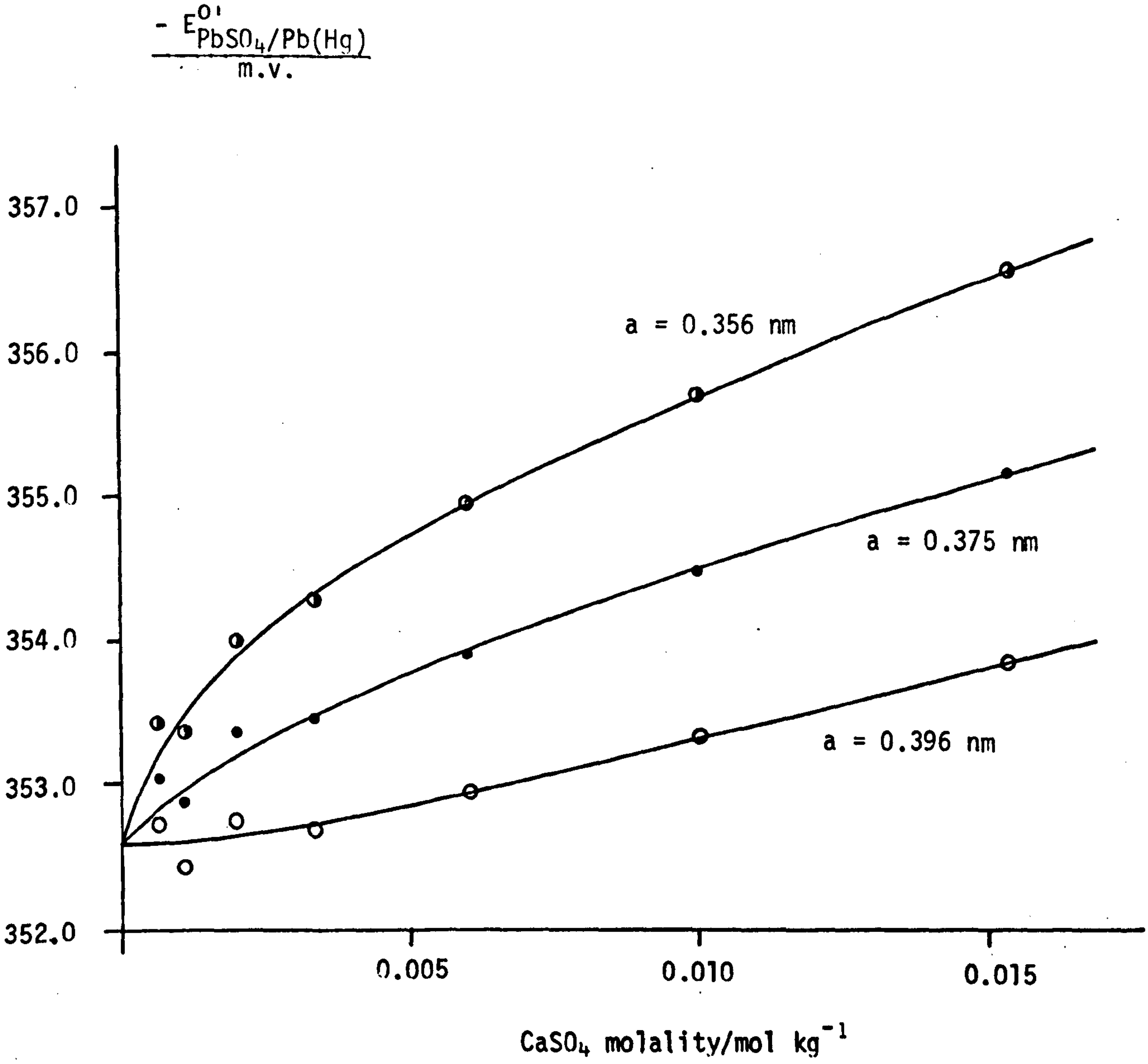
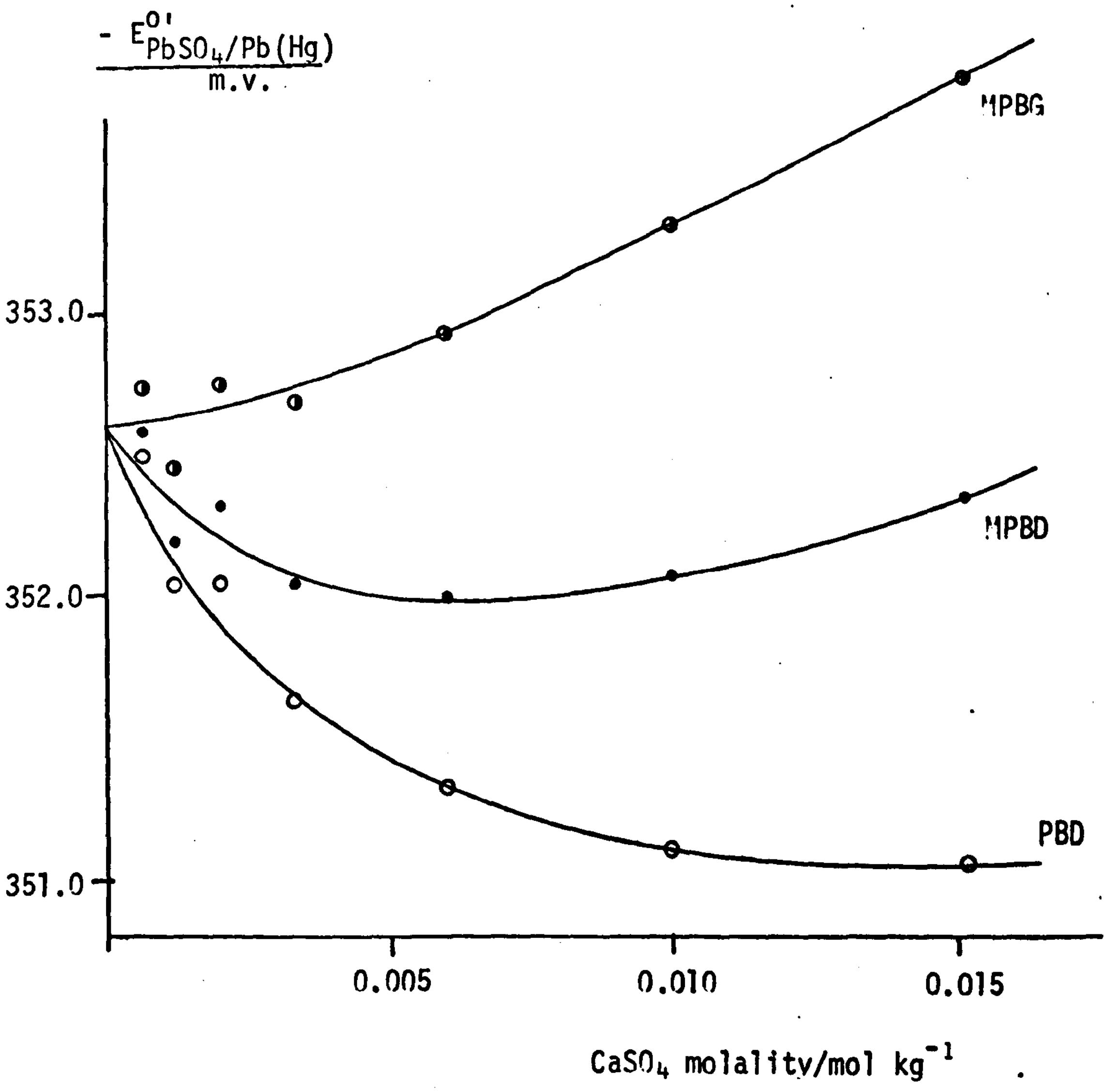


FIGURE 3.2.12 EFFECT OF DIFFERENT ASSUMPTIONS IN EVALUATING $\gamma_{\pm}$, ALL WITH a = 0.396 nm



$$\ln\gamma_{\pm} = \ln\gamma_{DH} + \ln\gamma_{M} \qquad (E.3.2.7.6)$$

where γ_{DH} is the Debye-Hückel activity coefficient defined by

$$\ln\gamma_{DH} = -\tfrac{1}{2}\, s \,\frac{\kappa}{1 + \kappa a} \qquad (E.3.2.7.7)$$

Consequently $\ln\gamma_M$, the Müller extension term, is equivalent to Gronwall's extension terms (11) except that the latter gave only the third and fifth order terms, while $\ln\gamma_M$ includes terms up to the 19th order. Glueckauf's tables are sufficiently extensive to enable accurate graphical interpolation of $\ln\gamma_M$. Values of $\ln\gamma_M/\kappa a$ were plotted against $\sqrt{\kappa a}$ at s/a values of 8.0, 7.6 and 7.2. Interpolated values of $\ln {}_M$ were added to calculated values of $\ln\gamma_{DH}$. $E^{0'}_{PbSO_4/Pb(Hg)}$ was once again evaluated using equation (3.2.4.1) and was plotted against molality of $CaSO_4$ in Figure 3.2.12A. The extrapolated values were consistent with an intercept of $E^0 = -352.8$ m.v.

Glueckauf (4) prefers a modification of (E.3.2.7.6) in which $\ln\gamma_{DH}$ is replaced by the following activity coefficient expression:

$$\ln\gamma_{KG} = -\frac{s\,\kappa}{2}\left(\frac{1 + 0.5\,\kappa a}{1 + \kappa a}\right)^2 \qquad (E.3.2.7.8)$$

This equation was proposed by Glueckauf (6) in an effort to correct for the approximations in $\ln\gamma_{DH}$. It is based on the work of Kirkwood (12) in that it closely approximates Kirkwood's equation for concentrations up to $\kappa a = 1.0$. Values of $\ln\gamma_{KG}$ were calculated and used to give new values of E^0, but the differences in γ_{DH} and γ_{KG} were negligible at low concentrations, and the extrapolated value of E^0 was unchanged by this analysis.

Values of $-\ln\gamma_{\pm}$ are compared in Table 3.2.8 for all the various treatments outlined above using a ratio of s/a of 7.2. The discrepancies between the Güntelberg and Debye charging processes, for both the unmodified and modified P-B treatments shows that both treatments are imperfect. Values based on Outhwaite's work (69) should be preferred on the grounds outlined previously, but a decision as to which set of activity coefficients are best is unnecessary for the present purpose. This is because all the treatments give good agreement when used to obtain extrapolated E^0 values. The difference between the value derived using the PBG treatment (-352.8 m.v.) and that derived from all the other treatments, including the ion-pair concept of Bjerrum (-352.6 m.v.), is small compared with the sum of the experimental precision and the possible systematic errors. This result is strong evidence that all these methods of obtaining E^0 are adequate. Compared with the semi-empirical method discussed in section 3.2.4, of plotting E_T' against $\sqrt{m}$ and extrapolating to zero concentration, any of the methods used in this or the preceeding section results in a negligible uncertainty in $E^0_{PbSO_4/Pb(Hg)}$.

FIGURE 3.2.12A UNMODIFIED P-B TREATMENT WITH GÜNTELBERG CHARGING PROCESS

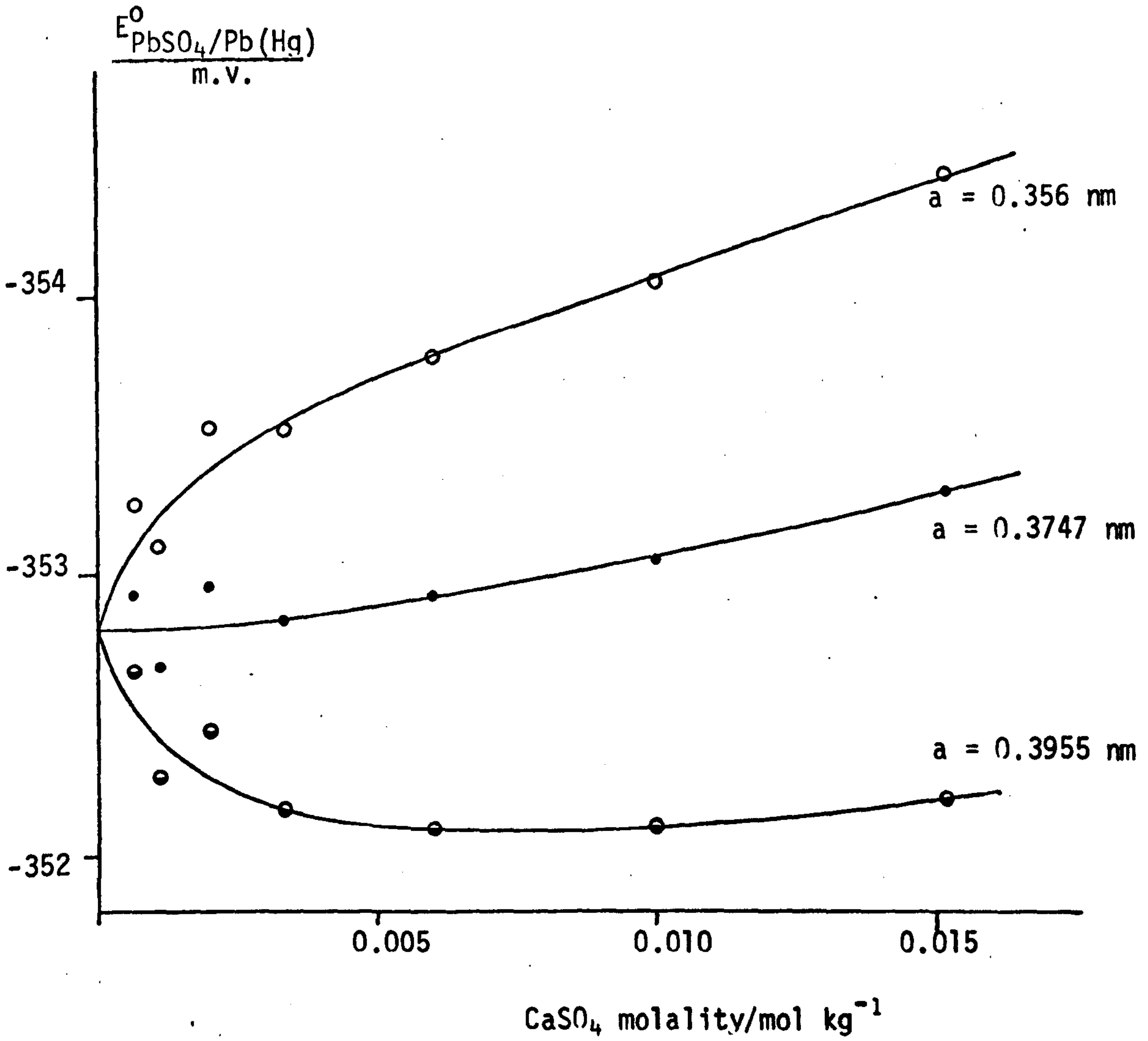


TABLE 3.2.8 CALCULATED VALUES OF THE ELECTROSTATIC CONTRIBUTION TO $-\ln\gamma_\pm$ FOR A 2:2 ELECTROLYTE WITH s/a = 7.2

Solution	κa	$-\ln\gamma_\pm^{elec.}$					
		D-H	PBD	MPBD	PBG (DH)	PBG (KG)	MPBG
G	0.3199	0.8725	1.0246	1.0748	1.0689	1.0858	1.1326
H	0.2594	0.7415	0.8896	0.9271	0.9285	0.9383	0.9756
I	0.2011	0.6027	0.7399	0.7656	0.7702	0.7752	0.8029
J	0.1500	0.4695	0.5881	0.6043	0.6091	0.6113	0.6296
K	0.1162	0.3748	0.4739	0.4842	0.4891	0.4903	0.5014
L	0.08647	0.2865	0.3626	0.3684	0.3721	0.3726	0.3786
M	0.06658	0.2247	0.2819	0.2852	0.2880	0.2882	0.2914

3.2.8 Re-analysis of e.m.f. data for sulphuric acid

A large discrepancy exists between the standard electrode potential for the lead sulphate two phase lead amalgam electrode required to fit the present data, and the value deduced by Shrawder and Cowperthwaite (S and C) (29) from results on the cell

$$\text{Pt, } H_2 \;/\; H_2SO_4\,(m) \;/\; PbSO_{4\,(s)} \;/\; Pb(Hg) \qquad \text{Cell I}$$

It was decided to re-analyse the raw data of the above authors and those of Baumstark (34) for the same cell, in order to determine whether this discrepancy was due to the observed cell potentials, or to the extrapolation procedures used.

The cell potential is given by

$$E = E^0_{PbSO_4/Pb(Hg)} - \frac{RT}{2F} \ln a_{SO_4^{2-}} a^2_{H^+} \qquad (E.3.2.8.1)$$

Baumstark expressed his results in the form

$$E^{0''} = E + \frac{RT}{2F} \ln 4m^3 = E^0 - \frac{RT}{2F} \ln\gamma_\pm^3 \qquad (E.3.2.8.2)$$

He plotted $E^{0''}$ against $m^{\frac{1}{2}}$ and used a linear extrapolation of the data, giving for the intercept E^0 = -352.17 m.v. This procedure is open to many obvious criticisms, but the neglect of both ion association, and deviations from the D-H limiting law, coincidentally resulted in a linear relationship over almost the whole concentration range studied, and the intercept gives a reasonable value for E^o. Shrawder (29) assumed that the first dissociation of sulphuric acid was complete, but that only a fraction α of the resulting bisulphate ions were dissociated.

The dissociation constant of the bisulphate ion, given by

$$K_2 \quad = \quad \frac{a_{H^+}\, a_{SO_4^{2-}}}{a_{HSO_4^-}} \quad = \quad \frac{(1 + \alpha)m\ (\alpha m + Z)}{(1 - \alpha)m\ \gamma_{HSO_4^-}}\ \gamma_{H^+}\, \gamma_{SO_4^{2-}} \qquad \text{(E.3.2.8.3)}$$

was taken as 0.0120 mole kg^{-1}. This is the value deduced by Hamer (52). More recent determinations by both e.m.f. and spectrophotometric methods point to a lower value in the region of 0.0104 ±0.0004 (43,53). In equation (3.2.8.3) the activity coefficients refer to free ions, and Z is the solubility of $PbSO_4$ in the given sulphuric acid solution. Using this nomenclature, equation (3.2.8.1) was expressed as

$$E \quad = \quad E^o_{PbSO_4/Pb(Hg)} \ - \ \frac{RT}{2F} \ln\ (\alpha m + Z)(1 + \alpha)^2 m^2 \ - \ \frac{RT}{2F} \ln\ \gamma_{SO_4^{2-}}\, \gamma^2_{H^+} \qquad \text{(E.3.2.8.4)}$$

and was re-arranged in the usual way to give

$$E^{o*} \quad = \quad E \ + \ \frac{RT}{2F} \ln\ (\alpha m + Z)(1 + \alpha)^2 m^2 \qquad \text{(E.3.2.8.5)}$$

In order to calculate the degree of dissociation of the bisulphate ion, S and C assumed that for any solution γ_{H^+} and $\gamma_{HSO_4^-}$ were equal. Equation (3.2.8.3) was then solved by making the additional assumption that $\gamma_{SO_4^{2-}}$ was given by the Gronwall, LaMer and Sandved extension (11) of the D-H equation. An ion size of 0.364nm was employed. This was the distance giving best agreement with e.m.f. data for cadmium sulphate and zinc sulphate. The standard cell potential was determined by plotting E^{o*} against $m^{\frac{1}{2}}$. Shrawder (29) stated that E^{o*} approached the Debye-Hückel limiting slope as the concentration decreased, and that E^o was evaluated by taking values of E^{o*} which fell on the limiting slope and adding to them appropriate values of $3RT/nF \ln\gamma$ computed with the aid of the limiting law. These statements will be referred to again shortly.

The method used by S and C is open to a number of criticisms. The most obvious is that Hamer's value (52) of K_2 is no longer considered to be correct. The assumption that $\gamma_{H^+} = \gamma_{HSO_4^-}$ may introduce some error, but this or some equivalent assumption is difficult to avoid. Use of the Gronwall, LaMer and Sandved expression (11) for the single ion activity coefficient of SO_4^{2-} is difficult to justify. Estimating single ion activity coefficients is always best avoided if possible, but in this case $\gamma_{SO_4^{2-}}$ may be used in equation (3.2.8.3) without significant error provided the value of K_2 has been determined from a similar equation using the same expression for $\gamma_{SO_4^{2-}}$ and the same assumption that $\gamma_{H^+} = \gamma_{HSO_4^-}$. Hamer (52) used the D-H limiting law expression, while later workers used D-H expressions of the form of equation (3.2.6.1). It is clearly inconsistent to determine a value of K_2 using $\gamma_{SO_4^{2-}}$ given by a D-H expression, and then to use this value of K_2 to calculate $\gamma_{SO_4^{2-}}$ values using a different expression, even if the only change is in the distance of closest approach parameter in the same D-H equation. Use of a Gronwall, LaMer and

Sandved expression is particularly inappropriate, since this extended form of the D-H equation was designed as an alternative to the use of dissociation constants. The activity coefficients given by this equation are therefore stoichiometric rather than for free ions.

Literature values for the solubility of $PbSO_4$ in H_2SO_4 solutions used by S and C are generally in good agreement with more recent values (54,55 and 56) except at the lowest concentrations. The error in the earlier values is not of great importance with Shrawder's own results, but is of significance at the lower concentrations used by Baumstark (34). Equations (3.2.8.4) and (3.2.8.5) are slightly different to those given in reference 29 in that the former equations assume complete dissociation of all dissolved lead sulphate, while S and C assume the same degree of dissociation as that of the HSO_4^- ion. Calculations using a dissociation constant of 0.0045 mol kg^{-1} for $PbSO_4$ ion pairs shows that the real situation is closer to that given by equations (3.2.8.4) and (3.2.8.5), but that both assumptions are adequate.

At a low enough ionic strength, the concentration dependence of E^{o*} must be given by the D-H limiting law:

$$\ln\gamma_{\pm} = -|Z_+Z_-|\, A \sqrt{m} \qquad \text{(E.3.2.8.6)}$$

where A is a constant closely related to the previously defined constant S. At the concentrations used by Shrawder (29), a more refined equation of the form given by (E.3.2.6.1) should be required, where m is replaced by ionic strength calculated on the basis that only free ions contribute, and the denominator $1 + \rho\sqrt{I}$ is introduced. If ρ is arbitrarily set at unity, the denominator is significantly different to unity (1.055) even at the lowest concentration used by S and C (0.001 molal).

In view of these various criticisms of the procedure used in reference 29, it was thought rather odd that the three experimental points of lowest concentration should all fall on the limiting slope when plotted against $\sqrt{m}$. This assertion, made by the authors, was checked by measuring the gradient of the D.H.L.L. curve given in their Figure 3. A value of 0.129 V $kg^{\frac{1}{2}}$ $mol^{-\frac{1}{2}}$ resulted. A more accurate assessment of this gradient was made by dividing (E^{o*} - E^o) by $m^{\frac{1}{2}}$, for the three points of lowest ionic strength. The authors' value of E^o was used (-350.52 m.v.) and values of E^{o*} were taken from their Table III. This method gave gradients of 0.128, 0.127 and 0.127 V $kg^{\frac{1}{2}}$ $mol^{-\frac{1}{2}}$ at concentrations of 0.001, 0.002 and 0.005 molal. The theoretical gradient using modern values for RT/F and the D-H limiting slope is given by

$$\frac{\partial E^{o'}}{\partial\sqrt{m}} = \frac{3}{2}\frac{RT}{F}\left(-S|Z_+Z_-|\sqrt{3}\right) = 0.1564 \text{ V kg}^{\frac{1}{2}} \text{ mol}^{-\frac{1}{2}}$$

This large discrepancy cannot be accounted for by changes in the values assigned to constants. Values used by the LaMer school at the time of reference 29, lead to a gradient of 0.155 V $kg^{\frac{1}{2}}$ $mol^{-\frac{1}{2}}$. It follows that the extrapolation used by Shrawder (29) was merely an arbitrary straight line passing through the three points of lowest concentration. This means that the extrapolated value of $E^o_{PbSO_4/Pb(Hg)}$ cannot be relied upon to give an accurate result and the value of S and C should not be given any greater weight than Baumstark's value (34).

The present analysis of the data was carried out on the same basis as that for $CaSO_4$. Equation (3.2.8.3) was solved for α by setting γ_{H^+} equal to $\gamma_{HSO_4^-}$ and by calculating the activity coefficient of free sulphate ions using

$$\ln\gamma_f = -\frac{4\,S\,\sqrt{I}}{1 + (q/a_0)\,\sqrt{I}} \qquad \text{(E.3.2.8.7)}$$

where I is given by $m(1 + 2\alpha) + 4Z$. Estimated values of Z at each H_2SO_4 concentration were made from a best curve of solubility data used by S and C and from the later results of references 54, 55 and 56. The same type of iterative procedure was utilised and an arbitrary value of $K_2 = 0.011$ was used in combination with distances of closest approach for free ions of 0.714, 0.536, 0.357 and 0.236 nm. For sulphuric acid these distances correspond to q_B, 0.75 q_B, 0.5 q_B, and $q_B/3$, respectively. The equations were also solved for α using an arbitrary q distance of 0.536 nm in conjunction with dissociation constants of 0.009, 0.010, 0.012 and 0.013 mol kg^{-1}. The raw data of both Baumstark (34) and of S and C were treated in the same manner, and $E^{0'}_{PbSO_4/Pb(Hg)}$ was calculated by substituting the results into

$$E^{0'}_{PbSO_4/Pb(Hg)} = E_{cell} + \frac{RT}{2F}\ln(\alpha m + Z)(1 - \alpha)^2 m^2 - \frac{3RT}{F}\,\frac{S\,\sqrt{I}}{(1 + q\,\sqrt{I}/a_0)} \qquad \text{(E.3.2.8.8)}$$

Once again if optimum values are chosen for K_2 and q, a linear dependence of $E^{0'}$ on ionic strength is expected.

Figures 3.2.13 and 3.2.14 show results based on Shrawder's data plotted against I, and Figure 3.2.15 gives results for both sets of data on the same graph. It is apparent that Shrawder's (29) results show less scatter, but that both sets of data are compatible with a common intercept at I = 0 of -351.6 m.v. Errors were estimated as ±0.2 m.v. for systematic errors, ±0.1 m.v. for uncertainty in the adequacy of the extrapolation technique, and ±0.3 m.v. as the 95% confidence limits of the intercept. The latter is a function of scatter in the combined data. This analysis indicates that about half the discrepancy between Shrawder and Cowperthwaite's (29) value for E^0 and that deduced from the $CaSO_4$ data was due to differences in extrapolation procedure. This still leaves a difference of 1 m.v. to be accounted for. A number of explanations are possible:

(i) the difference could have arisen by chance due to random experimental errors in the results;

(ii) differences in the chemical purity of the amalgam used, or possibly differences in the physical nature of the solid phase Pb_2Hg or $PbSO_4$;

(iii) errors due to incomplete exclusion of oxygen; though the direction of the difference necessitates that oxygen was present in the $CaSO_4$ solutions to a greater extent than in the H_2SO_4 solutions. This is thought to be unlikely in view of the reproducibility and stability of the $CaSO_4$ results, which indicate that the comprehensive precautions taken to prevent oxygen contaminating the amalgam were successful.

FIGURE 3.2.13 REANALYSIS OF SHRAWDER AND COWPERTHWAITE'S RESULTS FOR CELL I

EFFECT OF VARYING K_2 WITH q SET AT $0.75\ q_B$

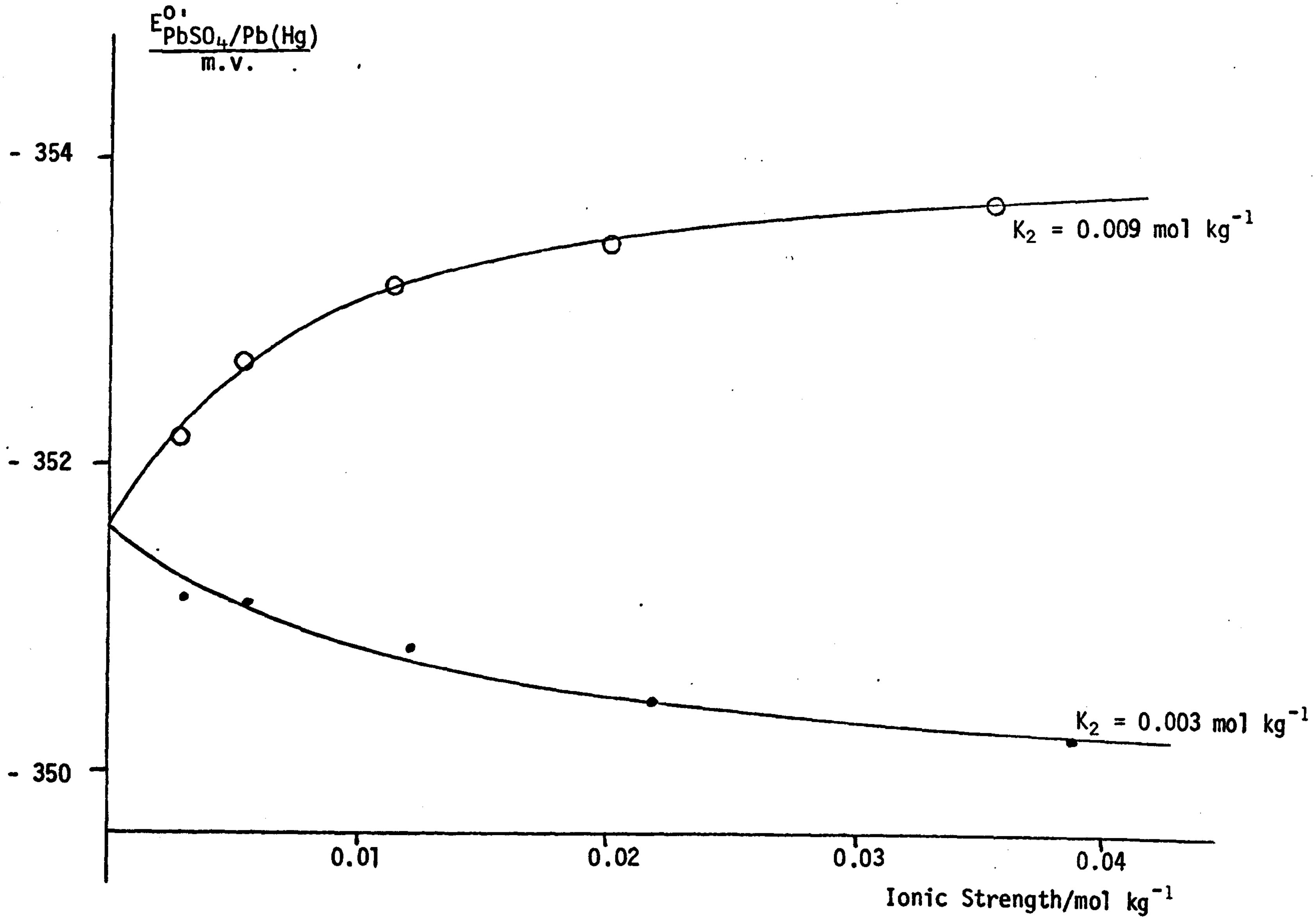


FIGURE 3.2.14 REANALYSIS OF SHRAWDER AND COWPERTHWAITE'S RESULTS FOR CELL I

EFFECT OF VARYING q WITH K_2 SET AT 0.011 mol kg^{-1}

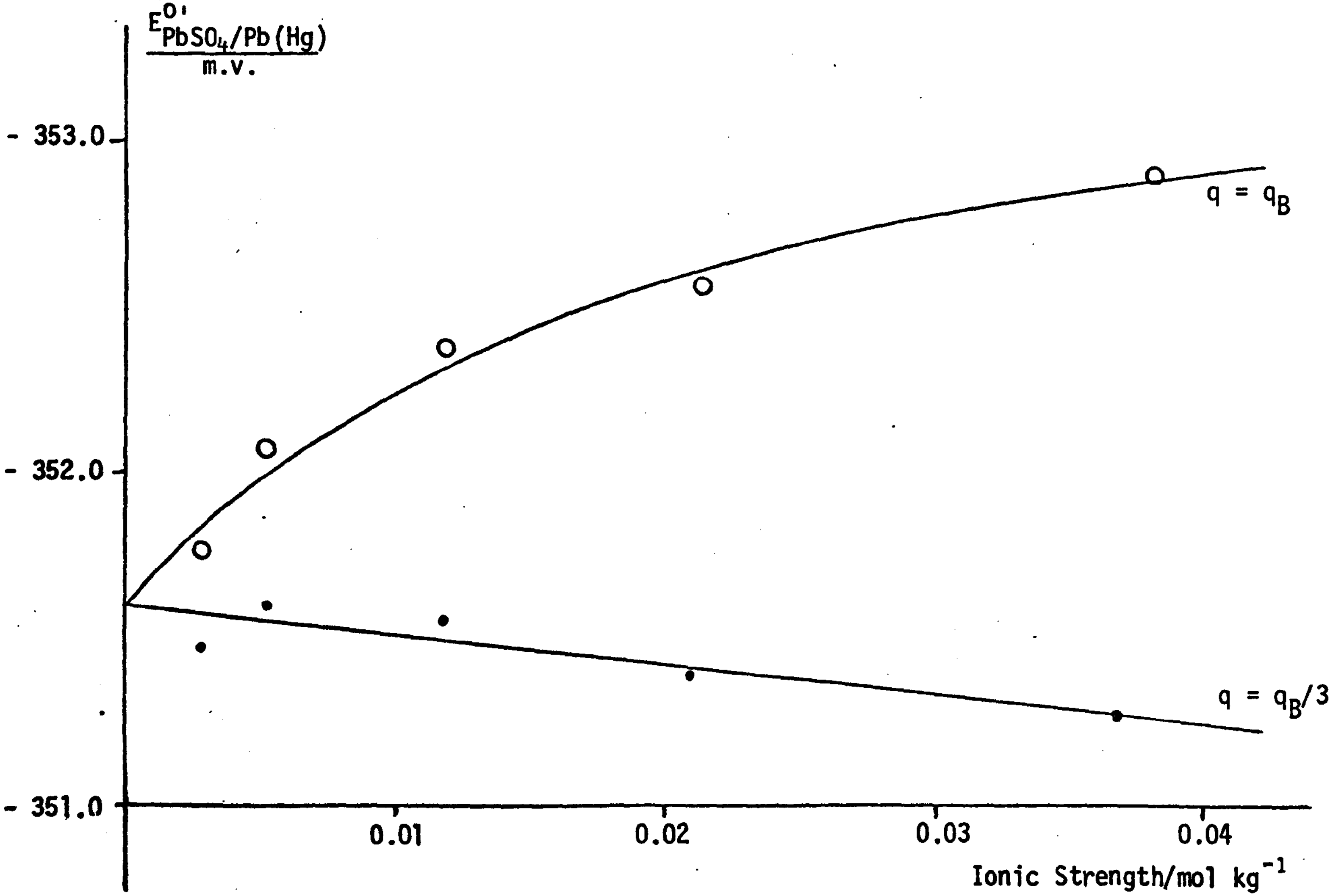
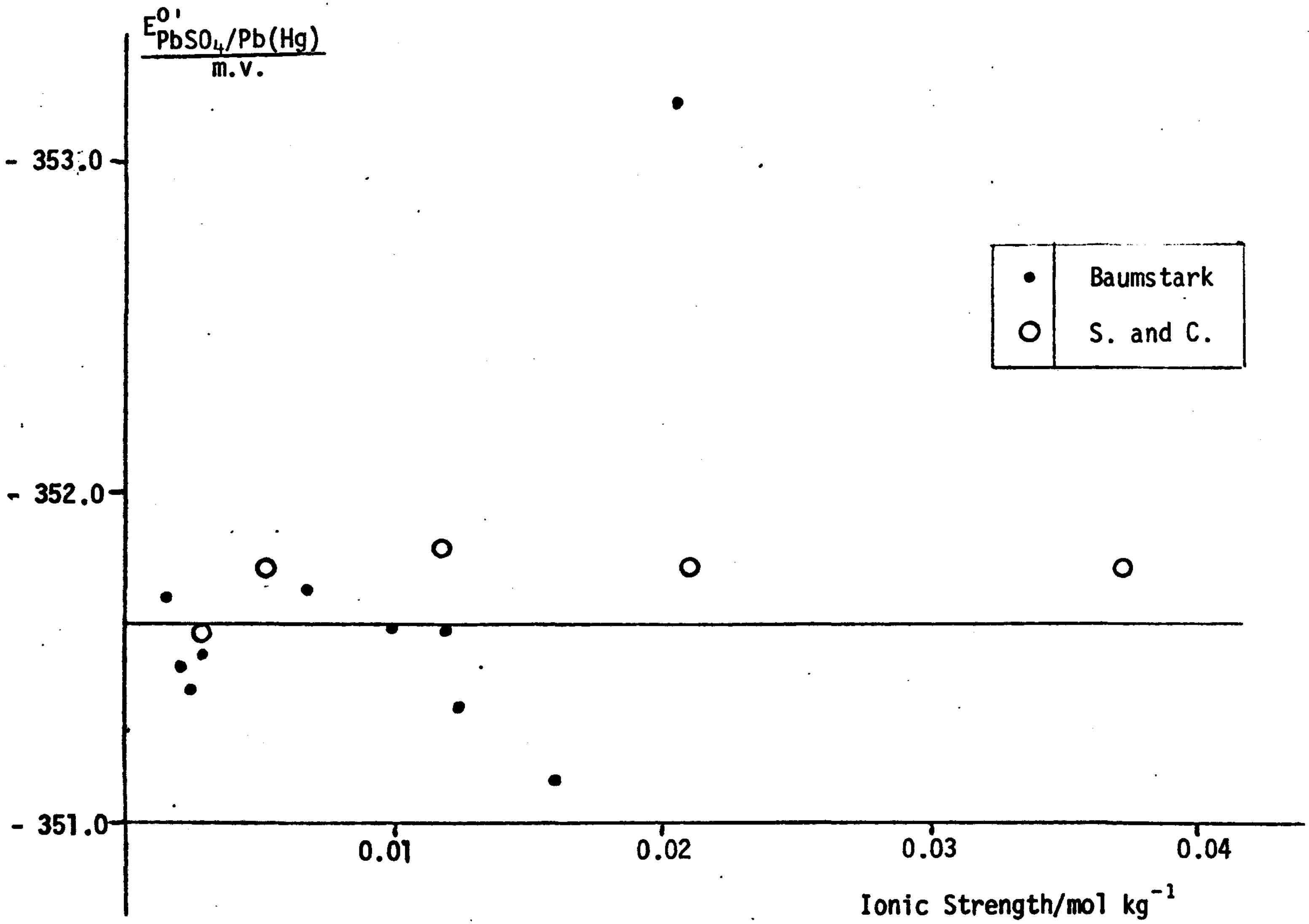


FIGURE 3.2.15

REANALYSIS OF RESULTS FOR CELL I

q SET AT 0.75 q_B, K_2 SET AT 0.011 mol kg^{-1}



3.2.9 Stoichiometric activity coefficients of H_2SO_4

The availability of accurate stoichiometric activity coefficients for sulphuric acid would enable a choice to be made between the two E^o values. Numerous investigations of the stoichiometric activity coefficients of sulphuric acid are present in the literature. Cell e.m.f. measurements have been the most frequent source of data, but freezing point and vapour pressure methods have also been used. The range of values is as great as 20% at a concentration of 0.02 molal. This is unfortunate since H_2SO_4 is often used as a primary standard in isopiestic work. Until recently the accepted results were those of Harned and Hamer (62), for cells IV and V. These were put on an absolute scale by extrapolation of Hamer's results (63) for the cell

$$\mathrm{Pt,\ H_2\ /\ H_2SO_4\ (m)\ /\ PbSO_4\ /\ PbO_2\ /\ Pt} \qquad \text{Cell V}$$

Hamer's value (52) for the dissociation constant of the bisulphate ion was used in the extrapolation. Covington *et al* (64) concluded that Hamer's results for cell V were in error, particularly at low concentrations. Covington found consistent results for cell V and for

$$\mathrm{Pt,\ H_2\ /\ H_2SO_4\ (m)\ /\ Hg_2SO_4/\ Hg} \qquad \text{Cell VI}$$

These results are considered the most reliable, but some uncertainty was attached to the values, due to uncertainty in the bisulphate ion dissociation constant and the distance of closest approach parameter. The results did not extend to sufficiently low concentrations to enable non-linear extrapolations to be of use. This led to an uncertainty in the E^o values of ±0.4 m.v.

The results of Shrawder and Cowperthwaite (29) and of Baumstark (34) using the two phase lead amalgam electrode have been largely disregarded by recent authors, possibly because of the disparity between sulphuric acid activity coefficients quoted in references 29 and 34, but also because of the adverse opinion of the reliability of the electrode in acid solution formed by Harned and Hamer (32). The present analysis of both sets of data has shown that these objections are largely invalid, and the uncertainty in the extrapolated value of E^o is comparable with that of E^o for other electrodes. The difference between E^o derived from the H_2SO_4 results and that derived from the $CaSO_4$ results is not of importance, provided this reflects a true difference in standard electrode potential due for example, to a different physical nature of the lead amalgam.

Stoichiometric activity coefficients were calculated by re-expressing equation (3.2.8.1) as

$$3/2\ \frac{RT}{F}\ln\gamma_\pm = E^o_{PbSO_4/Pb(Hg)} - E - \frac{RT}{2F}\ln 4\,m^2\,(m + Z) \qquad \text{(E.3.2.8.9)}$$

and taking E^o as -351.6 m.v. The resulting values for Shrawder and Cowperthwaite's data are shown in Table 3.2.9. The positive and negative error limits correspond to E^o values of -352.0 m.v. and -351.2 m.v. respectively. Also shown are values of $\gamma_\pm$ given by Harned and Hamer (62) and values calculated from the results of Covington *et al* (64). It is seen that the present results fall at intermediate values. An E^o value of -352.6 m.v. forces exact agreement with the results of Covington. The concurrence of this value with E^o derived from the $CaSO_4$ e.m.f. data is thought to

TABLE 3.2.9 COMPARISON OF STOICHIOMETRIC MEAN MOLAL ACTIVITY COEFFICIENTS FOR H_2SO_4

Molality of H_2SO_4	Stoichiometric Activity Coefficients		
	Present analysis of S and C data	Harned and Hamer (ref. 62)	C, D and W-J (ref. 64, cell II)
0.001	0.818 ±0.008	0.830	
0.002	0.749 ±0.007	0.757	
0.005	0.630 ±0.006	0.639	
0.010	0.529 ±0.005	0.544	0.516
0.020	0.433 ±0.005	0.453	0.420

be coincidental, but does indicate that the "true" standard potential of the two phase lead amalgam electrode may be closer to -352.6 than -351.6 m.v. Consideration of the uncertainty in the present results and those of Covington leads to the conclusion that the stoichiometric activity coefficients calculated from these two sources of data are, within experimental error, the same.

3.2.10 Evaluation of bisulphate ion dissociation constants

Since a more reliable extrapolation of the cell e.m.f. data had been carried out, it was considered worthwhile to continue this treatment of H_2SO_4 by evaluating values of K_D and the distance of closest approach of H^+ and SO_4^{2-} ions.

Sulphuric acid activities given by

$$a_{SO_4^{2-}}\, a_{H^+}^2 = (\alpha m + Z)(1 + \alpha)^2 m^2\, \gamma_{SO_4^{2-}}\, \gamma_{H^+}^2 \qquad (E.3.2.10.1)$$

were calculated from equation (3.2.8.4). For any given value of q, values of $\gamma_{SO_4^{2-}}$ and γ_{H^+} were estimated using (E.3.2.6.1) by choosing an initial value of α in order to calculate a value for I. Substituting values into (E.3.2.10.1) gave a cubic equation in α which was solved iteratively and the physically reasonable root chosen. This enabled better estimates of the free ion activity coefficients to be calculated, and the cycle was continued until self consistent values of α and γ were obtained. These values were then substituted into (E.3.2.8.3) to give a value of K_2. This procedure was carried out using q values of ⅓, ½, ¾ and 1 times q_B in conjunction with $E^0 = -351.6$ m.v., and with $q = ¾\, q_B$ in conjunction with $E^0 = -352.0$ and -351.2 m.v.

Values of log K_2 for Shrawder and Cowperthwaite's data (29) are shown plotted against ionic strength in Figures 3.2.16 and 3.2.17. Figure 3.2.18 presents the data of both S and C and of Baumstark (34), for $E^0 = -351.6$ m.v. and $q = ¾\, q_B$. For all pairs of E^0 and q values, the points

FIGURE 3.2.16 EVALUATION OF K_2 FOR SULPHURIC ACID FROM THE DATA OF S. AND C.

EFFECT OF VARIATION IN q WITH E^O SET AT - 351.6 m.v.

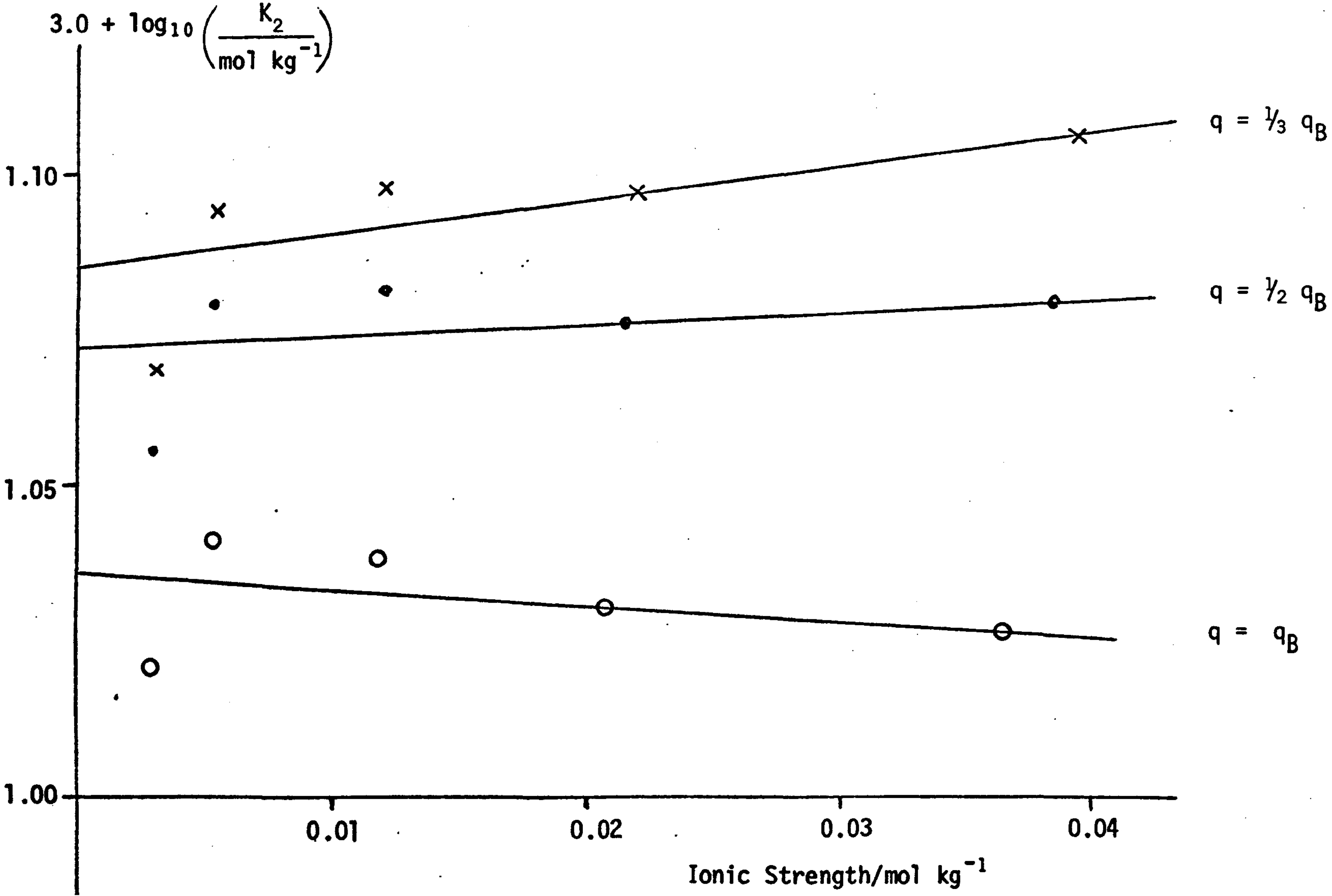


FIGURE 3.2.17 EVALUATION OF K_2 FOR SULPHURIC ACID FROM THE DATA OF S. AND C.

EFFECT OF VARIATION IN E^0 WITH q SET AT 0.75 q_B = 0.536 nm

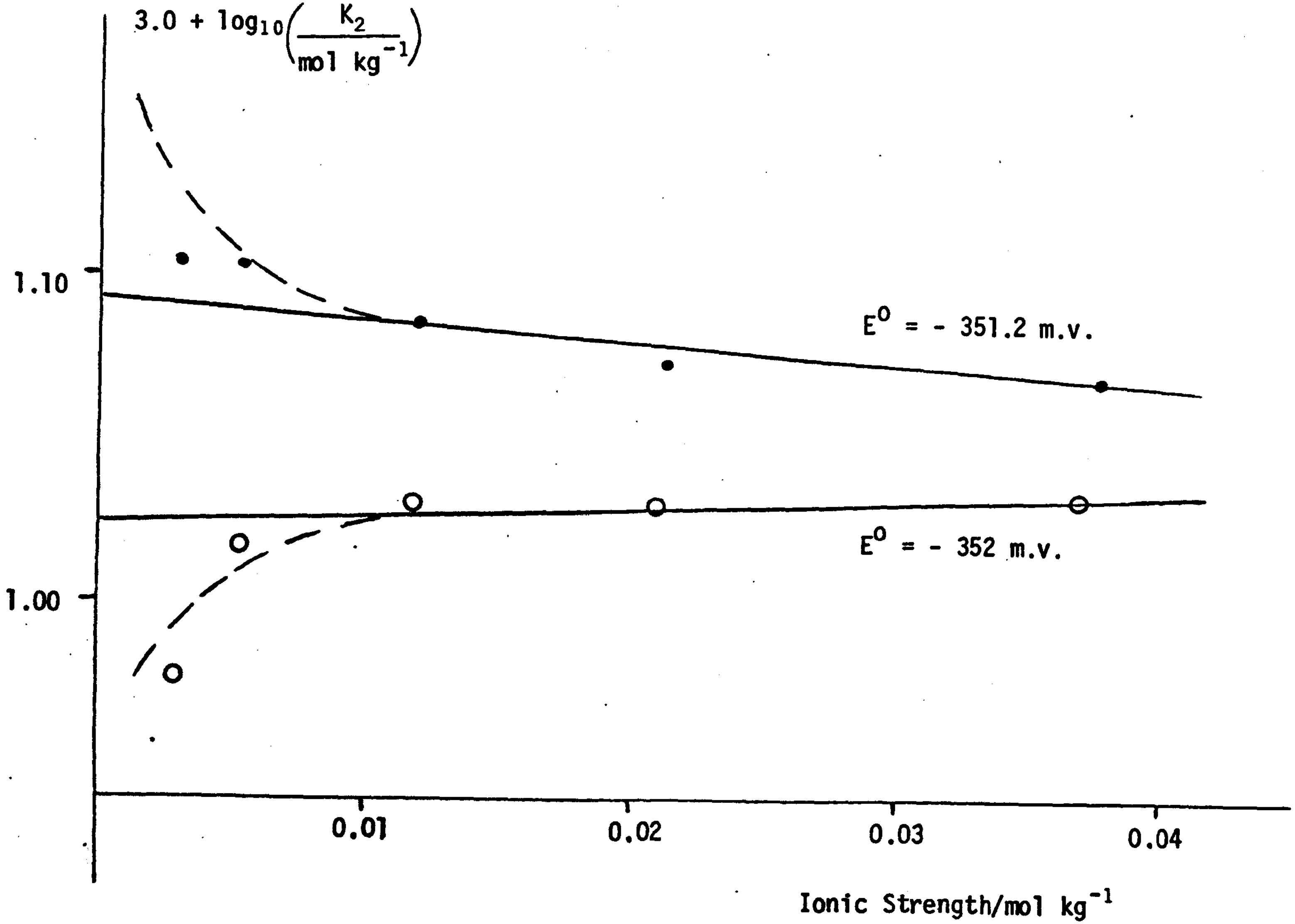
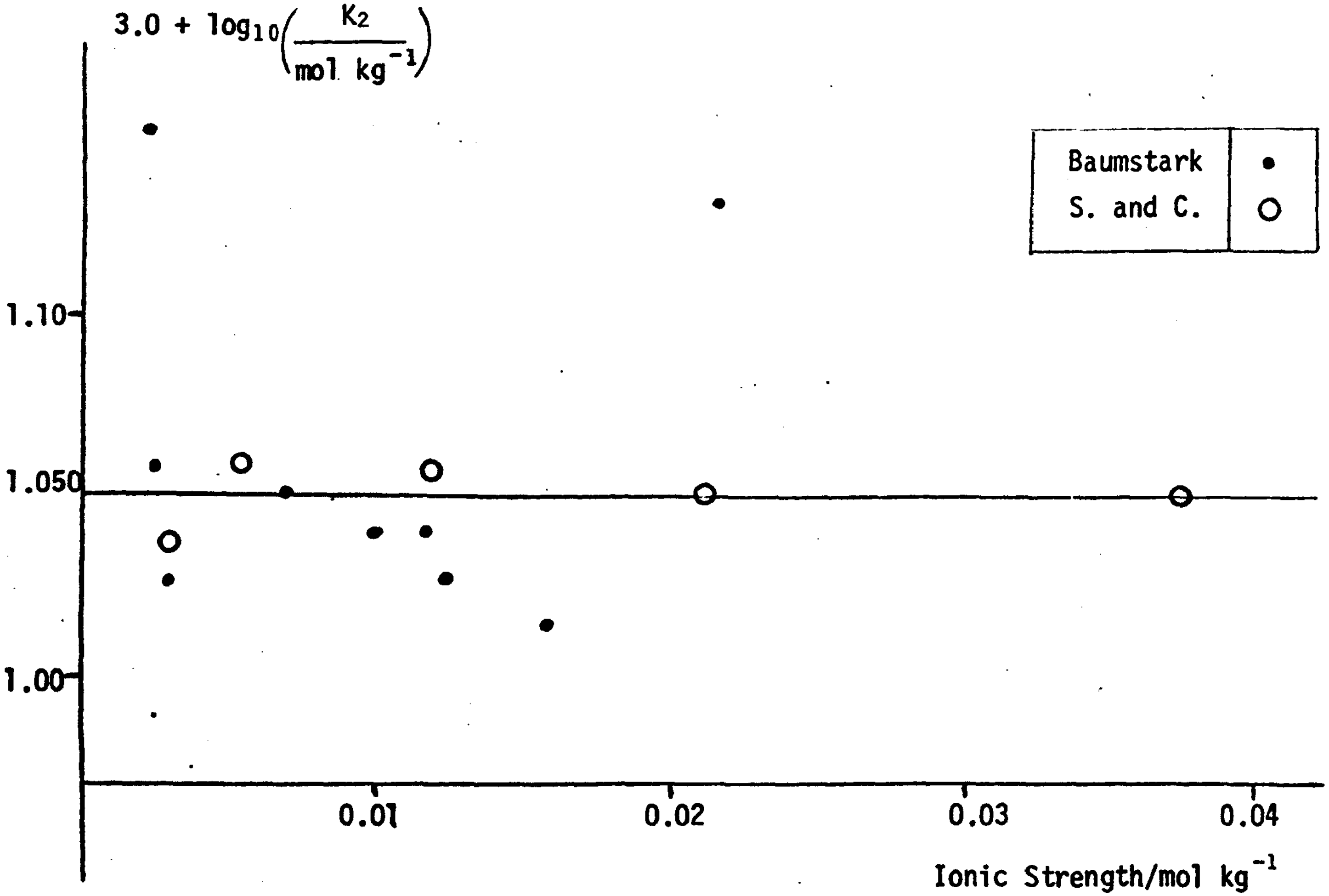


FIGURE 3.2.18 EVALUATION OF K_2 FOR SULPHURIC ACID FROM DATA ON CELL I

E^0 SET AT - 351.6 m.v., q SET AT 0.75 q_B



are shown extrapolated to I = zero, in a linear manner giving rather more weight to the data at high concentrations. This is because as the concentration approaches zero, small experimental errors, or a small error in E^0 result in wildly divergent values for the dissociation constant. Consequently, the precision of the intercept is not high and the resulting values of K_2 must be given rather wide error limits. The values of the ion pair dissociation constant of HSO_4^- are summarised in Table 3.2.10. It is seen that an uncertainty of about ±0.008 mol kg^{-1} arises from imprecise knowledge of E^0, and that for a given E^0 value an uncertainty of ±0.004 mol kg^{-1} remains due to doubt as to the suitability of the extrapolation. The variation of K_2 with the distance defining ion pairing should not be judged as representing the same type of uncertainty, since a relationship between the two is physically necessary. Whether the observed numerical relationship is physically reasonable is perhaps best judged by using the Bjerrum treatment to test whether the distance of closest approach is effectively constant over a range of q values where the theory should be expected to hold. It is clear from the results that this system is unsuited to precise determinations of K_2, due to the nature of the cell used. Table 3.2.10 also gives values derived by Covington *et al* (53) using the cell

Pt, H_2 / $NaHSO_4$ (m_1), Na_2SO_4 (m_2) / $HgSO_4$ / Hg Cell VII

This and other buffered cells discussed in reference 53 should give more reliable values for K_2. The present results are higher than those obtained using Cell VII, but the differences are probably within experimental error.

3.2.11 The distance of closest approach of H^+ and SO_4^{2-} ions in the HSO_4^- ion-pair

For an unsymmetrical electrolyte, derivation of the relationship between K_D and 'a' using the Bjerrum treatment is not as straightforward as that given for 2:2 electrolytes. Since this does not appear in any of the standard texts, it is outlined below.

If a central SO_4^{2-} ion is considered, the number of H^+ ions (N_{H^+}) within the distance $a \rightarrow q$ of the central ion is given according to Bjerrum's treatment by $N_{H^+} = 4\pi\, n_{H^+}\, (2q_B)^3 Q$, where n_{H^+} is the total concentration of H^+ ions per c.c. (assuming q_B is expressed in cm) and the other symbols have been previously defined. If the total concentration of SO_4^{2-} ions is m (the stoichiometric concentration of H_2SO_4), then the concentration of ion pairs is given by

$$m\, N_{H^+} = 4\pi \frac{2m^2\, L}{1000} (2q_B)^3\, Q \qquad (E.3.2.11.1)$$

where L is Avogadro's constant.

If a central H^+ ion is considered, the number of SO_4^{2-} ions within $a \rightarrow q$ of the central ion is only half N_{H^+}, but since the total concentration of H^+ ions is 2m, the concentration of ion-pairs is again given by equation (3.2.11.1).

TABLE 3.2.10 ION PAIR DISSOCIATION CONSTANTS FOR THE BISULPHATE ION

Present analysis of S and C's results (ref. 29)				Covington et al (ref. 53)	
q/nm	E^0 = -352.0 m.v.	E^0 = -351.6 m.v.	E^0 = -351.2 m.v.	q/nm	
0.714 (q_B)	0.0106	0.0108 ±0.0004	0.0123		
0.536 (¾ q_B)		0.0112 ±0.0004			
0.357 (½ q_B)		0.0118 ±0.0004		0.517	0.0105
0.236 (⅓ q_B)		0.0122 ±0.0004		0.304	0.0116

TABLE 3.2.11 THE DISTANCE OF CLOSEST APPROACH OF H^+ AND SO_4^{2-} IN THE HSO_4^- ION PAIR ACCORDING TO THE BJERRUM TREATMENT AND USING E^0 = -351.6 m.v. FOR CELL I

Distance defining ion pair (q)/nm	Distance of closest approach (a)/nm
0.714 (q_B)	0.155
0.536 (¾ q_B)	0.154
0.357 (½ q_B)	0.153
0.236 (⅓ q_B)	0.149

Defining the degree of dissociation α as

$$\alpha = \frac{m_{SO_4^{2-}}}{m_{SO_4^{2-}} + m_{HSO_4^-}} = \frac{m_{SO_4^{2-}}}{m}$$

the ion pair dissociation constant K_D may be expressed as

$$K_D = \frac{\alpha m\ (1 + \alpha)\ m}{(1 - \alpha)\ m} \quad \frac{\gamma_{SO_4^{2-}}\ \gamma_{H^+}}{\gamma_{HSO_4^-}} \qquad \text{(E.3.2.11.2)}$$

but (1 - α)m is the concentration of ion pairs given by (E.3.2.11.1) so that

$$K_D^{-1} = \frac{4\pi\ 2L\ (2q_B)^3\ Q}{1000\ \alpha\ (1 + \alpha)} \cdot \frac{\gamma_{HSO_4^-}}{\gamma_{SO_4^{2-}}\ \gamma_{H^+}} \qquad \text{(E.3.2.11.3)}$$

but as m → 0, α → 1 and all the activity coefficients also approach unity. Under these conditions,

$$K_D^{-1} = \frac{4\ \pi\ L}{1000}\ (2q_B)^3\ Q \qquad \text{(E.3.2.11.4)}$$

This equation is identical to (E.3.2.6.6), derived for $CaSO_4$ ion-pairs, except that q_B for a 2:1 electrolyte is only half the size of q_B for a 2:2 electrolyte. The relationship between K_D and å is therefore given as before by equation (3.2.6.7).

Pairs of K_D and q values, calculated in the previous section using E^0 = -351.6 m.v., were used in equation (3.2.6.7) and the resulting value of å are shown in Table 3.2.11. It is apparent that å is insensitive to change in q over the range $\frac{1}{2}q_B$ to q_B, a distance of 0.154 nm being required to fit the dissociation constants over this range. The question of whether this distance is physically reasonable is obscured by the unsuitability of the Bjerrum model to represent the two stage process (72) involved:

$$HSO_4^- + H_2O \rightleftharpoons \left[H_3O^+\ SO_4^{2-}\right]^- \rightleftharpoons H_3O^+ + SO_4^{2-}\ .$$

3.2.12 Stoichiometric activity coefficients for $CaSO_4$

The evaluation of $\gamma_\pm$ for the calcium sulphate solutions rests primarily on the value taken for the standard potential of the two phase lead amalgam. It is important to distinguish between the "true" and "experimental" values of this potential. As a consequence of the unresolved discrepancy of 1 m.v. between the E^0 values derived from $CaSO_4$ and H_2SO_4 cells and the uncertainty in each, the "true" standard potential is not known to better than ±1 m.v. The relevant potential required in the evaluation of stoichiometric activity coefficients, is the effective E^0 value of the electrodes used. This may differ from the "true" potential due to impurities or due to solid phases being in metastable states (e.g. small or strained crystals). Since all the methods of extrapolating the $CaSO_4$ results give consistent values for the "experimental" standard electrode potential within the precision of the measurements, it is this value of -352.6 m.v. which should be used to evaluate $\gamma_\pm$ for $CaSO_4$. This concept also means that any difference between the value taken for the standard potential of the Ag/AgCl electrode and the experimentally effective value would also be automatically allowed for by the present analysis. The only restriction in using this distinction between "true" and "experimental" standard potentials is that all the electrodes used must have the *same* standard potential. Bias potential checks showed that this was true for the Ag/AgCl electrodes, and the observed reproducibility of transfer potentials from different cells of the same $CaSO_4$ concentration indicated that this was also the case for the lead amalgam electrodes.

Activity coefficients were calculated for the seven calcium sulphate solutions using equation (3.2.4.1) viz.

$$E_T' = \frac{RT}{F} \ln \gamma_\pm - E^0_{PbSO_4/Pb(Hg)}$$

The resulting values are given in Table 3.2.12 using E^0 = -352.6 m.v. Values of $\gamma_\pm$ derived by Gardner and Glueckauf (3) to fit Brown and Prue's (5) freezing point data, were interpolated as a function of temperature and concentration from the data in Table 3 of reference 3. These are also presented in Table 3.2.12. Activity coefficients derived by Pitzer (49) from the same freezing point data and using a similar analysis to that of Glueckauf are almost identical to Glueckauf's values at low concentrations, but are slightly higher than his at the two highest concentrations.

The error limits shown in Table 3.2.12 were calculated by adding the error limits given in Table 3.2.5 for E_T' to the estimated error in the "experimental" value of E^0. The latter was taken to be the sum of the 95% confidence limits calculated from the standard error of the intercept (±0.16 m.v.), the uncertainty in the validity of the activity coefficient expressions used in the extrapolation (±0.1 m.v.), and the systematic errors (±0.15 m.v.), giving a total of ±0.41 m.v. The systematic errors are already included in the estimated error limits of E_T', so that the pertinent uncertainty in E^0 is ±0.26 m.v. Part or all of the systematic error in E_T' should also be discounted when estimating $\gamma_\pm$, since the method of estimating the "experimental" value of $E^0_{PbSO_4/Pb(Hg)}$ should be, in part, self-compensating. This fact was disregarded.

Comparison of the present results with those of Glueckauf (3), shows that at the two lowest concentrations, the values are within experimental error the same. At higher concentrations the two sets of values deviate, but inclusion of error limits for Glueckauf's results would probably enable the differences to be reconciled.

3.2.13 Osmotic coefficients of calcium sulphate solutions

Osmotic coefficients were calculated by utilising the relationship

$$\phi = \frac{1 - \alpha}{2} + \alpha \phi^f \qquad \text{(E.3.2.13.1)}$$

in which α is the fraction of free calcium ions and ϕ^f is the osmotic coefficient of free ions.

TABLE 3.2.12 STOICHIOMETRIC MEAN MOLAL IONIC ACTIVITY COEFFICIENTS OF $CaSO_4$ IN AQUEOUS SOLUTION AT 25°C

$CaSO_4$ molality /mol kg^{-1}	Stoichiometric activity coefficients of $CaSO_4$	
	Present results	G and G ref. (3)
0.01518	0.338 ±0.006	0.317
0.00998	0.388 ±0.008	0.369
0.005997	0.454 ±0.009	0.436
0.003336	0.535 ±0.010	0.519
0.002003	0.609 ±0.014	0.591
0.001109	0.681 ±0.017	0.675
0.0006576	0.751 ±0.020	0.739

The equation implies the assumption that ion-pairs behave ideally. It would have been preferable to use stoichiometric activity coefficients in a direct Gibbs-Duhem integration:

$$\phi = 1 + \frac{1}{m}\int_{m'=o}^{m'=m} m'd\ \ln \gamma_{\pm} \qquad (E.3.2.13.2)$$

Unfortunately the integration from m' = zero up to the lowest experimental concentration is difficult without an accurate analytical expression for $\ln\gamma_{\pm}$.

In order to calculate ϕ^f it was convenient to use a pair of K_D and q values which gave a linear relationship between $E^{0'}$ and I. Such a pair are K_D = 0.0043 and q = 0.714 nm, which gave (using a least squares fit) the relationship

$$E^{0'} = -352.67 - 54.8\ m^f_{SO_4} \quad (m.v.) \qquad (E.3.2.13.3)$$

Combining equations (3.2.6.1) and (3.2.6.2) and adding a term kI to $\ln\gamma_f$ to account for the linear dependence gives

$$E^{0'} = 354.47 - E_T + 25.692\left[\ln m_f - \frac{4 \times 1.172\ \sqrt{I}}{1 + 7.14 \times 0.3291\ \sqrt{I}} + kI\right] \qquad (E.3.2.13.4)$$

Using this equation with k = zero, gave equation (3.2.13.3). It follows that the correct value of k, required to make $E^{0'}$ independent of I is given by

$$k = \frac{+\,54.8}{25.692 \times 4} = 0.533 \text{ kg mol}^{-1}$$

The usual Gibbs-Duhem relationship between activity and osmotic coefficients then gives

$$\phi^f = 1 - \frac{4\,s}{\rho^3 I}\left(R - 2 \ln R - \frac{1}{R}\right) + \frac{k}{2} I \qquad \text{(E.3.2.13.5)}$$

where $\rho = q/a_0$ and $R = 1 + \rho \sqrt{I}$

Osmotic coefficients calculated in this manner are shown in Fig. 3.2.19 plotted against molality of calcium sulphate. The experimental results of Brown and Prue (5) are given for comparison. These are seen to be within experimental error of the present results, except perhaps at the highest concentration. A correction for the temperature difference between the two sets of data would exacerbate this difference, since Pitzer (49) suggests that for divalent sulphates

$$\phi_{25^\circ C} - \phi_{0^\circ C} = -\,0.008 \pm 0.008 \ .$$

3.2.14 The thermodynamic solubility product

This may be calculated directly from Equation (1.1.1), viz.

$$K_{sp} = m_s^2\, \gamma_\pm^2\, a_w^2$$

where m_s = 0.01518 mol kg^{-1} (see Part II of this thesis)

$\gamma_\pm$ = 0.338 ±0.006

and $a_w = \exp\left(-\,0.036\, m_s\, \phi_s\right) = 0.9995$.

The result is

$$K_{sp}\ (25^\circ C) = \underline{(2.63 \pm 0.09) \times 10^{-5} \text{ mol}^2 \text{ kg}^{-2}}$$

Any error in the measured solubility of gypsum (m_s) is irrelevant, since its prior use in calculating $\gamma_\pm$ exactly compensates for any error present. The solubility product could have been calculated directly from the results without any knowledge of m_s, except for its use in calculating the corrections arising from $PbSO_4$ solubility.

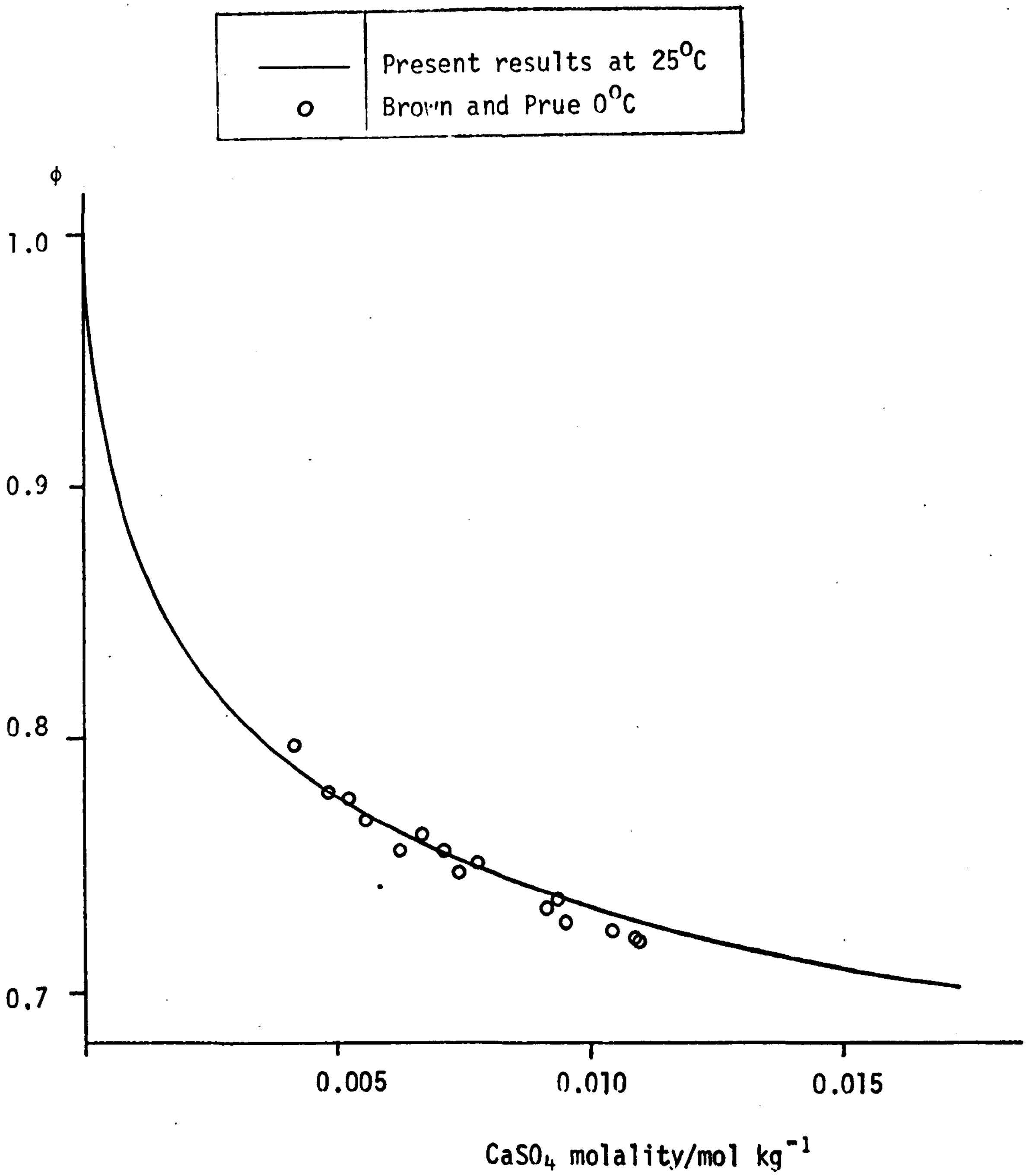
This value for the solubility product lies at the centre of the literature results discussed in the introduction, but the error limits are much smaller than those estimated for the literature values.

3.3 MIXED $CaSO_4$ - $CaCl_2$ SOLUTIONS

3.3.1 Experimental transfer potentials

Using the lead amalgam electrode, the test cells may be represented as

FIGURE 3.2.19 OSMOTIC COEFFICIENTS OF AQUEOUS CALCIUM SULPHATE SOLUTIONS



$$(\mathrm{Hg})\ \mathrm{Pb}\ /\ \mathrm{PbSO_4}\ /\ \begin{array}{l} \mathrm{CaSO_4}\ (\mathrm{sat} - m_1) \\ \mathrm{CaCl_2}\ \ (m_4) \end{array}\ /\ \text{calcium electrode} \qquad \text{Cell IV A}$$

Since the solutions were all saturated with gypsum, the effect of dissolved $PbSO_4$ was always negligible and has been ignored in the representation of Cell IV. The potential of cell IVA is given by Equation (3.2.1.1), and if the potential of cell III is subtracted, the transfer potential is given by

$$E_T\ (A) = E^o_{AgCl/Ag} - E^o_{PbSO_4/Pb(Hg)} + \frac{RT}{2F} \ln a_{Ca^{2+}}\, a_{SO_4^{2-}} - \frac{3RT}{2F} \ln 4^{1/3}\, m_3\, \gamma_{\pm CaCl_2(ref)} \qquad (E.3.3.1.1)$$

Alternatively, if the silver-silver chloride electrode is used, the test cell may be represented as

$$\mathrm{Ag}\ /\ \mathrm{AgCl}\ /\ \begin{array}{l} \mathrm{CaSO_4}\ (\mathrm{sat} - m_1) \\ \mathrm{CaCl_2}\ \ (m_4) \end{array}\ /\ \text{calcium electrode} \qquad \text{Cell IV B}$$

The cell potential of which is given by

$$E_{IVB} = \text{"}E^o_{Ca}\text{"} - E^o_{AgCl/Ag} + \frac{RT}{2F} \ln \left(a_{Ca^{2+}}\, a^2_{Cl^-}\right)_{IVB}$$

Subtraction of the potential of the pure $CaCl_2$ reference cell leads to a transfer potential of

$$E_T\ (B) = \frac{RT}{2F} \ln \left(a_{Ca^{2+}}\, a^2_{Cl^-}\right)_{IVB} - \frac{3RT}{2F} \ln 4^{1/3}\, m_3 \gamma_{\pm CaCl_2(ref)} \qquad (E.3.3.1.2)$$

Transfer potentials are given for the four test cells in Table 3.3.1. Mean values are given in Table 3.3.2 together with 95% confidence limits calculated from the standard error of each mean. The solution pH values were within acceptable limits.

3.3.2 Theoretical transfer potentials

Since all the solutions were saturated with gypsum, $E_T(A)$ should be dependent only upon the water activity as influenced by the presence of calcium chloride. From equation (1.1.1) we have for any solution

$$a_{Ca^{2+}}\, a_{SO_4^{2-}} = K_{sp} / a_w^2$$

If the present test solutions are denoted by X and water saturated with pure gypsum is denoted by G, then

$$\frac{\left(a_{Ca^{2+}}\, a_{SO_4^{2-}}\right)_X}{\left(a_{Ca^{2+}}\, a_{SO_4^{2-}}\right)_G} = \frac{\left(a_w^2\right)_G}{\left(a_w^2\right)_X}$$

TABLE 3.3.1

TRANSFER POTENTIALS FOR $CaSO_4$ - $CaCl_2$ TEST CELLS

Solution No. and $CaCl_2$ molality /mol kg^{-1}	Date	Observed Transfer Potentials/m.v.		Solution pH
		E_T (A)	E_T (B)	
N 0.005090	15/11/71	571.71, 571.61, 571.68, 571.70	NEGATIVE VALUES	6.68
		571.68, 571.63, 571.63, 571.68	55.58, 55.57, 55.59	
	16/11/71	572.03, 571.92, 571.93,	55.59, 55.54, 55.53	
		571.82, 571.88, 571.71	55.55, 55.59, 55.68	
	17/11/71	571.80, 571.97, 571.97	65.62, 55.59, 55.60	
	18/11/71	571.87, 571.64, 571.54, 571.36	55.62, 55.54, 55.56,	
			55.53	
	19/11/71	571.61, 571.40	55.54, 55.55	
	25/11/71	571.56,	55.48	
	26/11/71	571.53	55.52	
O 0.03347			POSITIVE VALUES	6.41
	16/11/71	571.91, 571.89, 572.06, 571.84	0.88, 0.72	
	17/11/71	571.94, 571.73, 571.90, 571.94	0.73, 0.71, 0.87, 0.77	
	18/11/71	572.01, 571.89, 571.84	0.78, 0.75, 0.78, 0.72	
	19/11/71	571.75	0.69	
	25/11/71	572.71	0.79	
	26/11/71	572.20		
P 0.31735	16/11/71	572.30, 572.27		6.85
	17/11/71	572.23, 572.28, 572.29, 572.30		
	18/11/71	572.40, 572.46, 572.44, 572.47	75.23, 75.24, 75.27,	
		572.49	75.27	
	19/11/71	572.33, 572.43	75.24, 75.16	
	25/11/71	572.34, 572.22	75.00, 74.93	
	26/11/71	572.23, 572.41	75.13, 75.30	
Q 0.97043	17/11/71	607.19, 607.29, 607.52, 607.56		6.83
		607.56		
	18/11/71	607.68, 607.72, 607.77, 607.74	123.13, 123.22, 123.22	
			123.24	
	19/11/71	607.70, 607.50, 607.57	123.22, 123.03, 123.02	
	25/11/71	607.03, 607.18	122.47, 122.55	
	26/11/71	606.55, 606.80	121.97, 122.20	
pH of calcium chloride reference solution (D) on 18/11/71				6.49

TABLE 3.3.2 MEAN TRANSFER POTENTIALS AND CONFIDENCE LIMITS

$CaCl_2$ molality	$CaSO_4$ molality /mol kg^{-1}	Mean Transfer Potentials/m.v.			
		E_T (A)	95% confidence limits	E_T (B)	95% confidence limits
0.005090	0.01345	571.68	± 0.08	- 55.57	± 0.02
0.03347	0.01005	571.91	± 0.08	0.77	± 0.04
0.31735	0.00772	572.35	± 0.05	75.18	± 0.09
0.9704*	0.0059*	607.40	± 0.20	122.84	± 0.31

* Nominal values - see text

TABLE 3.3.3 THEORETICAL EFFECT OF WATER ACTIVITY ON E_T (A)

Solution	$CaCl_2$ molality /mol kg^{-1}	Water activity	Change in Transfer potential /m.v.	Expected Transfer potential /m.v.
G	0.000	0.9995	-	571.62
N	0.00509	0.9992	0.006	571.63
O	0.03347	0.998	0.041	571.66
P	0.3174	0.985	0.38	572.00
Q	0.9704	0.947	1.39	573.01

and

$$E_T\,(A)_X - E_{T\,G} = \frac{RT}{F}\ln\,(a_w)_G - \frac{RT}{F}\ln\,(a_w)_X$$

Water activities were interpolated graphically using the data given for calcium chloride by Robinson and Stokes (43). The molality of calcium chloride was taken to be $m_4 + m_1$, but the correction for $CaSO_4$ solubility was almost negligible. The calculated transfer potentials are given in Table 3.3.2 based on the mean observed value for solutions saturated with gypsum alone. The solution of lowest $CaCl_2$ concentration has almost exactly the predicted transfer potential and the next two solutions are probably within experimental error of the expected value. These results provide excellent confirmation that cell IVA measures $CaSO_4$ activity. The transfer potentials of the most concentrated solution are clearly in error, and it is evident from the magnitude of the differences that some factor other than experimental error is involved.

One possible explanation for this anomaly was that the calcium electrode was responding in a non-Nernstian manner at the highest $CaCl_2$ concentration. This suggestion was checked for solutions P and Q by making the reasonable assumption that the concentration of dissolved $CaSO_4$ had a negligible effect on the $CaCl_2$ activity. Theoretical transfer potentials ($E_T(B)$) were calculated using equation (E.3.3.1.2) and stoichiometric activity coefficients of $CaCl_2$ obtained as before from equation (E.3.3.1.5) using the parameters of reference (41). The calculated values were 75.19 m.v. and 121.77 m.v. for solutions P and Q, respectively. The agreement is excellent for solution P, but is in error by more than 1 m.v. for solution Q. This result is in accord with the results of Huston and Butler (57) who found deviations from a Nernstian response when the external test solution had a much higher calcium ion activity than the internal reference solution. After taking account of this error in the response of the calcium electrode, a discrepancy of 30 m.v. still remained unexplained.

3.3.3 Investigation of "$PbSO_4$" solid phase

The only remaining source of error was the sulphate responsive electrode, and the most obvious possibility was that the lead sulphate suffered some modification at high $CaCl_2$ concentrations which altered the equilibrium Pb^{2+} ion concentration adjacent to the amalgam. Either solid solution or the formation of new compounds could produce this result, and X-ray diffraction should be capable of detecting either type of phase change. In preparing samples for study by this technique a number of observations were made. The pure lead sulphate crystals were too small for their shape to be distinguished by the unaided eye, and settled slurry had a high density. On adding $CaCl_2$ solutions of concentration higher than about 0.5 molal, crystal growth occurred overnight giving needle shaped crystals up to 3 mm in length. After shaking the mixture to break up the interlocked crystals, the slurry settled to only about a fifth of the original settled density. These changes did not occur when dilute $CaCl_2$ solutions were used, and therefore indicated formation of a new compound rather than solid solution in the lead sulphate crystals.

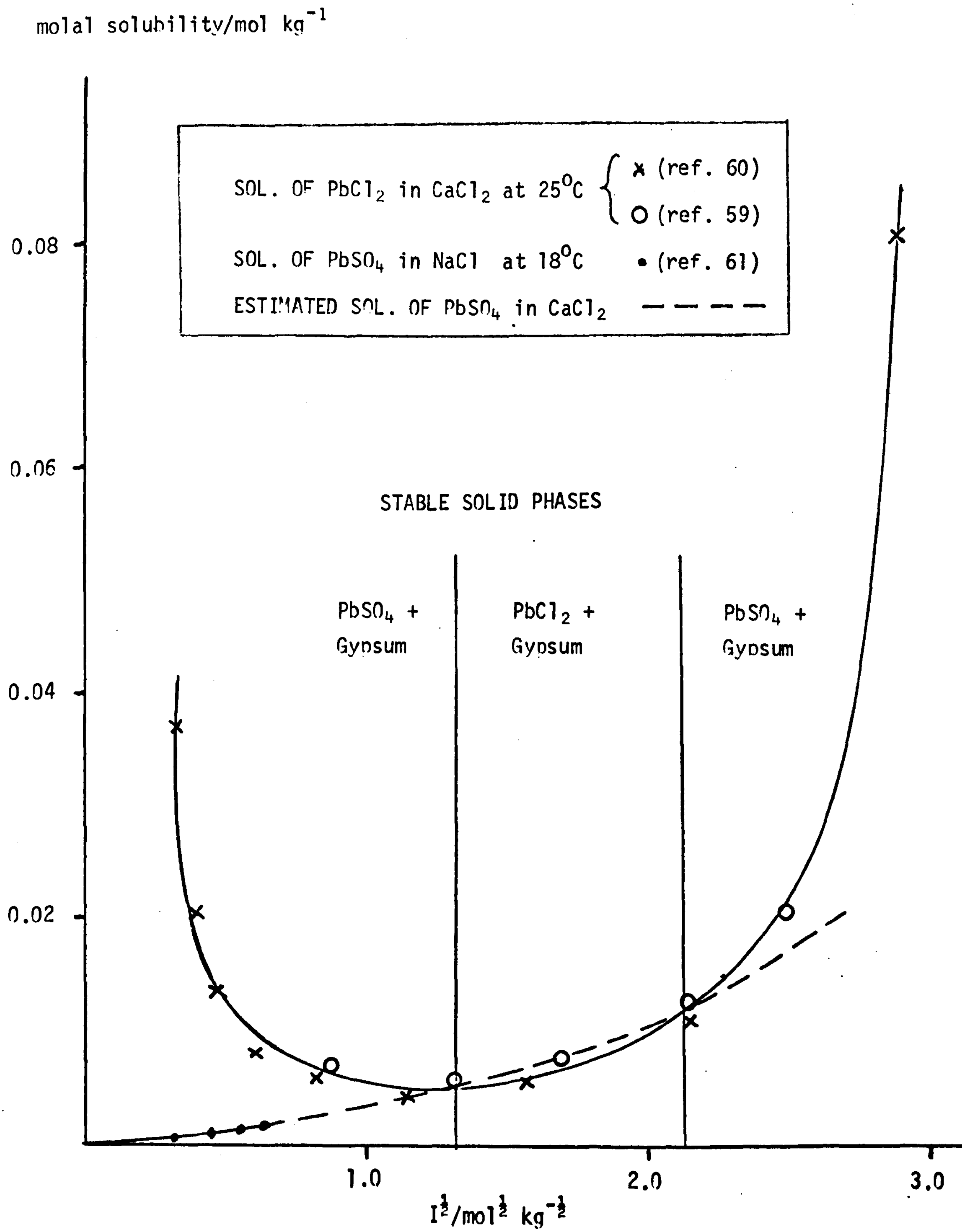
The results of the X-ray diffraction studies showed quite clearly that samples X1, X4, X6 and X9 were all pure $PbSO_4$. All major peaks predicted by the A.S.T.M. index (58) were present at the correct angles and with about the expected intensity ratios. No spurious peaks of significant intensity were observed. For samples X2, X3, X5, X7 and X8, all traces of $PbSO_4$ were absent. The peak patterns could be completely explained, both in position and intensity, by a 1:1 mole ratio of $PbCl_2$ and $CaSO_4.2H_2O$. Slurries having $CaCl_2$ concentrations of 0.97 or 0.78 molal were used for all these samples. For the samples having a pure $PbSO_4$ solid phase, $CaCl_2$ concentrations of 0.0, 3.2, 5.0 and >1.0 molal were used. These results imply that at high and low concentrations of

$CaCl_2$, the stable phase is pure $PbSO_4$, but that for intermediate concentrations in the very approximate concentration range 0.6 to 1.5 molal, the reaction

$$CaCl_2 + PbSO_{4(s)} + 2H_2O \rightarrow PbCl_{2(s)} + CaSO_4.2H_2O_{(s)}$$

proceeds until all the solid $PbSO_4$ has reacted. This rather odd conclusion may be explained by considering the solubilities of $PbSO_4$ and $PbCl_2$ in $CaCl_2$ solutions. Figure 3.3.1 shows the data of Hertz and Hellebrandt (59) and Tschischikoff and Schachoff (60) for the solubility of $PbCl_2$ in $CaCl_2$ plotted as a function of $\sqrt{I}$. On the same figure, the data of Beck and Stegmuller (61) for the solubility of $PbSO_4$ in NaCl is also plotted against $\sqrt{I}$. Literature solubilities of $PbSO_4$ in $CaCl_2$ could not be found, but at low concentrations, the solubility in NaCl should be approximately the same function of ionic strength as the solubility in $CaCl_2$ since no common ions are involved. The dashed line shows the estimated solubility of $PbSO_4$ at higher ionic strengths than are experimentally available. This line was drawn so as to be consistent with the X-ray diffraction results. The diagram demonstrates that the experimental results are not unreasonable. The region of instability of solid $PbSO_4$ being a consequence of the pronounced minimum in the $PbCl_2$ solubility curve.

FIGURE 3.3.1 SOLUBILITIES OF $PbCl_2$ AND $PbSO_4$ IN $CaCl_2$ SOLUTIONS



4. SUMMARY OF CONCLUSIONS

The following conclusions were derived from the work described in Part I.

(i) It was shown that accurate activity coefficients for a 2:2 electrolyte can be obtained by an electromotive force method.

(ii) The standard reduction potential of the lead sulphate-two phase lead amalgam electrodes used in this work was found to be - 352.6 ±0.4 mV.

(iii) The thermodynamic solubility product of gypsum in aqueous solution at 25°C was found to be $(2.63 \pm 0.09) \times 10^{-5}$ mol kg^{-2}.

(iv) Calculated osmotic coefficients of aqueous calcium sulphate solutions were found to be in good agreement with literature values derived directly from freezing point measurements.

(v) Two alternative treatments of the results, one using the Bjerrum concept of ion association and the second employing non-linear solutions of the Poisson-Boltzmann equation, both suggested that the distance of closest approach of calcium and sulphate ions in aqueous solution is 0.38 ±0.1 nm. This distance is compatible with ionic dimensions.

(vi) Reanalysis of literature electromotive force data obtained in sulphuric acid solutions, led to a value of - 351.6 mV for the standard reduction potential of the lead sulphate-two phase lead amalgam electrodes. The reason for the discrepancy of 1 mV between this result and that obtained in the present work is not known. Sulphuric acid activity coefficients were found to be within experimental error of modern values.

PART II

SOLUBILITY OF CALCIUM SULPHATE DIHYDRATE
IN THE SYSTEM $Ca^{2+} - Na^{+} - SO_4^{2-} - Cl^{-} - H_2O$
AT 25°C

5. INTRODUCTION

5.1 "THE SEA WATER MAGNESIA PROCESS"

The Steetley Company operate a large scale process (120) in which magnesium hydroxide is precipitated from sea water by the addition of calcium hydroxide. The supernatant liquor, normally referred to as "spent sea water", corresponds essentially to the system $Na^+ - Ca^{2+} - Cl^- - SO_4^{2-} - H_2O$ with minor impurities of K^+, Sr^{2+}, Br^-, CO_3^{2-} and BO_3^{3-}. One of the many technical problems associated with this process is that precipitation of more than about 73% (121) of the stoichiometric amount of $Mg(OH)_2$ results in saturation of the solution with reference to gypsum. Operation at higher extraction percentages than this is fortunately possible due to the formation of relatively stable saturated solutions, but the concentration of deleterious impurities of calcium and sulphate in the product are increased, and the sudden precipitation of vast quantities of gypsum is not unknown. This is clearly an extremely complicated problem involving many aspects of physical chemistry. The three areas primarily concerned are (i) the kinetics of crystallisation; (ii) the surface chemistry of non-stoichiometric, high surface area precipitates in aqueous electrolyte solutions; (iii) the thermodynamics of mixed electrolyte solutions. It is with the third aspect of this problem with which Part II of this thesis is concerned. The primary objective from this viewpoint, was therefore to derive soundly based equations which accurately predicted osmotic coefficients and calcium sulphate activity coefficients in the system referred to above. Such equations, together with the thermodynamic solubility product, would enable the equilibrium solubility of gypsum to be predicted for any composition of solutes in the system. In addition, these equations would enable the magnitude of the thermodynamic driving force for crystallisation to be evaluated for any solution composition which was supersaturated with respect to gypsum. Achievement of this objective would then facilitate investigations of aspects (i) and (ii) of the problem in a more rigorous manner.

This technical problem motivated the choice of the system studied, but having defined this, the aims of the work were widened to include the general problem of the thermodynamics of mixed electrolytes at moderate and high concentrations.

5.2 REVIEW OF PERTINENT MIXED ELECTROLYTE SOLUTION THEORY

The simplest theory of mixed electrolyte solutions is the "ionic strength principle" of Lewis and Randall (95). This states, "In *dilute* solutions the activity coefficient of a given *strong* electrolyte is the same in all solutions of the same ionic strength". This theory is perfectly adequate provided the italicised restrictions in the statement are satisfied. In concentrated solutions, this principle breaks down due to the importance of "specific interactions" between groups of two or more ions. These interactions have been treated using two assumptions. In the first, they are formally represented using equilibrium constants for the formation of associated species, with a consequent reduction in the effective ionic strength. In the second, the interactions are considered to modify the free energy of the solution, but the ions involved retain separate identities. At high concentrations, it is sometimes advantageous to treat certain systems using a combination of these two assumptions. For aqueous solutions containing "strong" electrolytes of 1:1 and 2:1 charge types, the second method of treatment is clearly preferable; for mixtures containing weak electrolytes, such as acetic acid, the first method is more suitable; but for the system involved in this study, it is unclear which method of treatment is to be preferred. This is because calcium sulphate solutions can be treated as associated or unassociated depending upon the manner in which electrostatic contributions are evaluated (see Part I of this thesis).

Some of the most pertinent treatments of mixed electrolyte solutions are briefly discussed below under author headings.

Tanji

The paper by Tanji (19) was discussed in the introduction to Part I. The author treated specific interactions between sulphate ions, and calcium, magnesium and sodium ions, using the ion pairing concept. All other specific interactions in the systems he studied were assumed to be negligible. The activity coefficients of all free ions, and charged ion pairs, were assumed to be given by the Davies (74) equation (E.1.2.2). Tanji used literature values for the solubility product of gypsum, and ion pair dissociation constants of $CaSO_4^0$, $MgSO_4^0$ and $NaSO_4^-$, to predict solubilities of gypsum. Experimental and calculated solubilities in single and mixed solutions of $NaCl$, $MgCl_2$, $CaCl_2$, Na_2SO_4 and $MgSO_4$ were compared. For solutions of ionic strength up to 0.15 molar, Tanji considered that the two sets of solubilities were in close agreement.

This method of analysis is very useful for low ionic strength solutions, since it gives reasonable estimates of activity coefficients from information generally available in the literature. Treatment of higher ionic strength solutions by this approach, would require additional terms in the activity coefficient expression to account for specific interactions not represented by ion pairing.

Gardner and Glueckauf

These authors (4) have treated mixtures of 2:2 and 1:1 charge type electrolyte solutions. Numerical solutions of the unlinearised Poisson-Boltzman equation were used to calculate the electrostatic contribution to the non-ideality of the solutions. The experimental solubility measurements (7) of gypsum in sodium chloride solutions were treated by this approach. The electrostatic non-ideality was split into two terms: a Debye-Hückel leading term, and a term referred to as a "Müller extension term" (see E.3.2.7.6). Glueckauf (4) represented the statistical contribution to the calcium sulphate activity coefficient by an expression of the form

$$\ln \gamma^{\text{stat}} = K_2 m_2 + K_{12} m_1 + K_{112} m_1^2 \qquad \text{(E.5.2.1)}$$

m_2 is the molality of calcium sulphate and m_1 the molality of sodium chloride. The unimportant constant K_2 was obtained by comparison with results in reference (2), and the constants K_{12} and K_{112} were given values required to give a good fit to the experimental solubilities. Equation (5.2.1) was found to be an inadequate expression for $\ln\gamma^{stat}$ unless the D-H term in (E.3.2.7.6) was replaced by an alternative expression (E.3.2.7.8) proposed by Glueckauf (6). With this modification calculated values of $\ln\gamma_{\pm}$ for $CaSO_4$ in the mixture, could be fitted to within ±1.5% of the experimental values, for ionic strengths up to 6 molal.

Glueckauf has not published any more general treatments of mixed electrolytes. Logical modifications to his approach would be extension of the electrostatic terms to include mixtures of asymmetric charge types, and replacement of his expression (4) for the statistical contributions (E.5.2.1) by expressions of the type used by Scatchard *et al* (98) for "non-Debye-Hückel" contributions.

Reilly, Wood and Robinson

Reilly and Wood (103) have developed an equation for the free energy of a general mixture of electrolytes. The equation, based on the work of Friedman (94), enables predictions to be made of the properties of mixed electrolyte solutions from a knowledge of the properties of single electrolytes and common ion mixtures. Reilly, Wood and Robinson (117) have derived corresponding equations for the osmotic and activity coefficients of multicomponent electrolyte solutions. The equations allow for interactions between pairs of ions, but triplet interactions are only accounted for under special circumstances. The two main restrictions of the method are that strong ion association is not adequately accounted for, and the equations give no information concerning the concentration dependence of the properties. For systems in which strong ion association and triplet (and higher) interactions can be neglected, these equations are of great utility. They offer a major advantage over all other treatments in that a standard electrostatic contribution, of some arbitrarily assumed form, is not required. At low ionic strengths, when specific interactions between like-charged ions may be neglected, the equations are capable of good approximations for the properties of mixtures, based on the properties of single electrolyte solutions alone. The major problem involved in applying these equations to the present system is that, except under special conditions, certain properties are required which can never be measured. The equations require knowledge of the osmotic and activity coefficients of all the pure electrolyte solutions which make up the mixture *at the same ionic strength as the mixture*. Such properties can only be hypothetical for calcium sulphate solutions at concentrations above the solubility limit.

Scatchard

Equations were derived by Scatchard (92) for the excess free energy, activity coefficient and osmotic coefficient of general mixed electrolyte solutions. In many respects these equations are similar to those developed by Reilly, Wood and Robinson (103,117). Excess free energies of the mixture were expressed using properties of component single electrolyte solutions at the same ionic strength, and additional terms involving the concentration products of pairs of solute ionic strength fractions and further terms to account for asymmetry. Concentration dependence of the equations was introduced by using analytical expressions for the properties of single electrolyte solutions and also for the proportionality parameters involved in the additional terms. Debye-Hückel type equations were proposed for the single electrolyte solutions, extended by semi-empirical terms, in linear and higher powers of ionic strength.

Scatchard (97,98) has modified this treatment by using ions rather than neutral electrolytes as components. This greatly improves the predictive power of the equations. The new equations provide better estimates of activity and osmotic coefficients when data on only single salt systems are available. In addition, data on binary electrolyte solutions with a common ion can be used in conjunction with single salt data, to calculate the properties of solutions containing more than three different ion types. This was not possible with the earlier treatment of reference 92.

In the context of the system involved in this investigation, the approach of Scatchard (97,98) suffers from the same problem as the method of Reilly *et al* (103,117) in that properties of pure calcium sulphate solutions above the solubility limit are required. A second problem, is that the analytical expressions used for activity and osmotic coefficients of single electrolyte solutions are not suitable to express the concentration dependence of these properties for aqueous 2:2 sulphates.

5.3 OBJECTIVES

The objectives of this section were as follows.

(i) To measure gypsum solubilities in aqueous solutions of the single electrolytes NaCl, $CaCl_2$ and Na_2SO_4, and the binary electrolytes Na_2SO_4 - NaCl and $CaCl_2$ - NaCl.

(ii) To calculate stoichiometric mean ionic activity coefficients of $CaSO_4$ in the solutions.

(iii) To check if a reasonable value for the solubility product of gypsum could be obtained from the solubility measurements.

(iv) To develop equations which are capable of fitting the experimental solubilities over the whole concentration range.

(v) To predict the experimental $CaSO_4$ activity coefficients using (a) only the properties of single electrolyte solutions; (b) the properties of solutions of single electrolytes and binary electrolytes with a common ion.

(vi) To predict gypsum solubilities in the binary electrolyte solutions from the experimental solubilities in the single electrolytes.

(vii) To develop general equations capable of predicting calcium sulphate activities and gypsum solubilities for any mixture in the Ca^{2+} - Na^{+} - SO_4^{2-} - Cl^{-} - H_2O system.

6. EXPERIMENTAL

6.1 MATERIALS AND APPARATUS

6.1.1 Water and calcium chloride

As for Part I.

6.1.2 Sodium chloride

Analar material was dried for two days at 180°C and stored in a desiccator.

6.1.3 Sodium sulphate

The Analar anhydrous salt was dried for two days at 240°C and stored in a desiccator.

6.1.4 Calcium sulphate dihydrate

Two samples of Analar "calcium sulphate dihydrate" were used. Material supplied by British Drug Houses Limited was used almost exclusively for solutions in which gypsum solubilities were determined by calcium analysis. Material supplied by Hopkin and Williams Limited was used for solutions in which gypsum solubilities were determined by a gravimetric technique. The B.D.H. material was unsuitable for this method of analysis due to impurities of calcium sulphate phases other than the dihydrate. Investigations of the chemical and physical states of these two samples are discussed in Appendix II.1.

The suitability of the H. & W. material for the gravimetric method of analysis was tested by checking the loss in weight on conversion to the anhydrous salt; and by comparing calcium ion concentrations determined volumetrically, with those computed from the weights used in preparing solutions. It was found that the material stored in a desiccator as received gave acceptable (within 0.3% of theoretical) figures over the period during which measurements were made.

6.1.5 E.D.T.A. (0.01 M solution)

Analar E.D.T.A. (di-sodium salt dihydrate) was dried for one week at 80°C. Five litres of 0.01 M solution were prepared using a calibrated volumetric flask at 25°C. The solution was stored in thick-walled polyethylene containers rather than glassware, in order to avoid any possible slow reaction with calcium ions present in the glass.

6.1.6 Calcium chloride (0.01 M solution)

Analar calcium carbonate was dried at 150°C for two days, and was carefully dissolved in a minimum of dilute Analar hydrochloric acid. The solution was boiled for two minutes and a drop of methyl red indicator solution added. The solution was neutralised with dilute Analar sodium hydroxide solution and was made up to the appropriate volume.

6.1.7 Zinc chloride (0.01 M solution)

This was prepared from Analar zinc granules and dilute Analar hydrochloric acid. Details of the procedure used are given in Wilson and Wilson (75).

6.1.8 Buffer solutions

pH 10.0 and pH 10.8 buffer solutions were prepared by dissolving appropriate quantities of Analar ammonium chloride in Analar aqueous ammonia solution. pH 12 → 13 buffer solutions were prepared using fresh Analar sodium hydroxide pellets to give a 2 M solution. All buffer solutions were stored in thick walled polyethylene bottles.

6.1.9 Indicators

Erichrome Black T (76, p. 33): one part of dye was ground with 300 parts of NaCl, and the mixture stored in an airtight container.

o-Cresolphthalein Complexone: this indicator is known under five other names, see Welcher (76, p. 47). The indicator (16 mg) and naphthol green (4 mg) were dissolved in 2 ml of pH 10.8 buffer and 30 ml of water. Fresh solutions were prepared each day, though the indicator did not deteriorate seriously for up to three days.

Patton and Reeder's Indicator (76, p. 39): this was used in its commercial form, Cal. Red, which is a 1:100 mixture with sodium chloride.

Murexide (76, p. 61): this was used as a ground mixture of 0.5 g in 20 g of NaCl.

6.1.10 Magnesium - E.D.T.A. complex

A solution of 0.1 molar Analar $MgSO_4 \cdot 7H_2O$ was prepared, and to 30 ml of this solution, 10 ml of pH 10 buffer was added. A little Erichrome Black T was added, and the solution titrated using 0.01 M E.D.T.A. until the red solution had almost changed to a stable blue (i.e. just a trace of red remained).

6.1.11 Volumetric glassware

All pipettes and burettes were grade A standard, but were calibrated at 25°C by weight titrations using deionised water. It was found necessary to calibrate the 50 ml burette at 5 ml intervals and to use a correction curve. A 10 ml burette used for "pendulum" end points was found to be of adequate accuracy, but corrections were necessary for two pipettes. All the burettes used were of the automatic filling type.

6.1.12 Sample bottles

Two types of bottles were used for equilibration of gypsum with the various solutions. Bottles having a capacity of 50 cm^3 were used when the method of solubility determination was by volumetric analysis of equilibrated solution. When a gravimetric method was used, 500 cm^3 bottles were used. The latter were designed with round bottoms, and with smooth curves of large radius between the neck and main body in order that all solid gypsum could be easily washed out. All the bottles were sealed with P.T.F.E. sleeves and socket stoppers.

6.1.13 Sample equilibration

Samples were given a preliminary equilibration at room temperature (generally within 1° of 25°C) by attaching the bottles to a large wheel. This was rotated at about 30 revolutions per minute. Final equilibration was achieved by completely submerging the bottles in a water bath. Regular checks with the quartz crystal thermometer indicated that the bath maintained a temperature of 25 ±0.02°C. The bottles were removed from the bath and shaken manually at least three times per day.

6.1.14 Sampling for volumetric analysis

The apparatus used is illustrated in Figure 6.1.1. Suction was provided by a water pump connected via two water traps to A. B is an air bleed, C is a preweighed 250 cc Quick Fit flask, D is a No. 4 porosity sintered glass filter stick and E and F are taps.

Each bottle was sampled twice using the same filter stick and connection piece, but clean glassware was used for each sample bottle. Aliquots were transferred to collection flasks in about 4 to 8 seconds. The latter were immediately stoppered ready for reweighing.

The magnitude of evaporation losses during filtration were checked as follows. Water at 25°C was transferred to a collection flask. The flask was stoppered, weighed and replaced on the apparatus. With a stopper at G, the system was partially evacuated in the usual manner for 60 seconds. The flask was then removed, stoppered and weighed. The loss in weight was less than 0.01 g, which on the basis of the smallest aliquot (> 9 g) for a transfer time of 6 sec, corresponds to a negligible error of less than 0.01%.

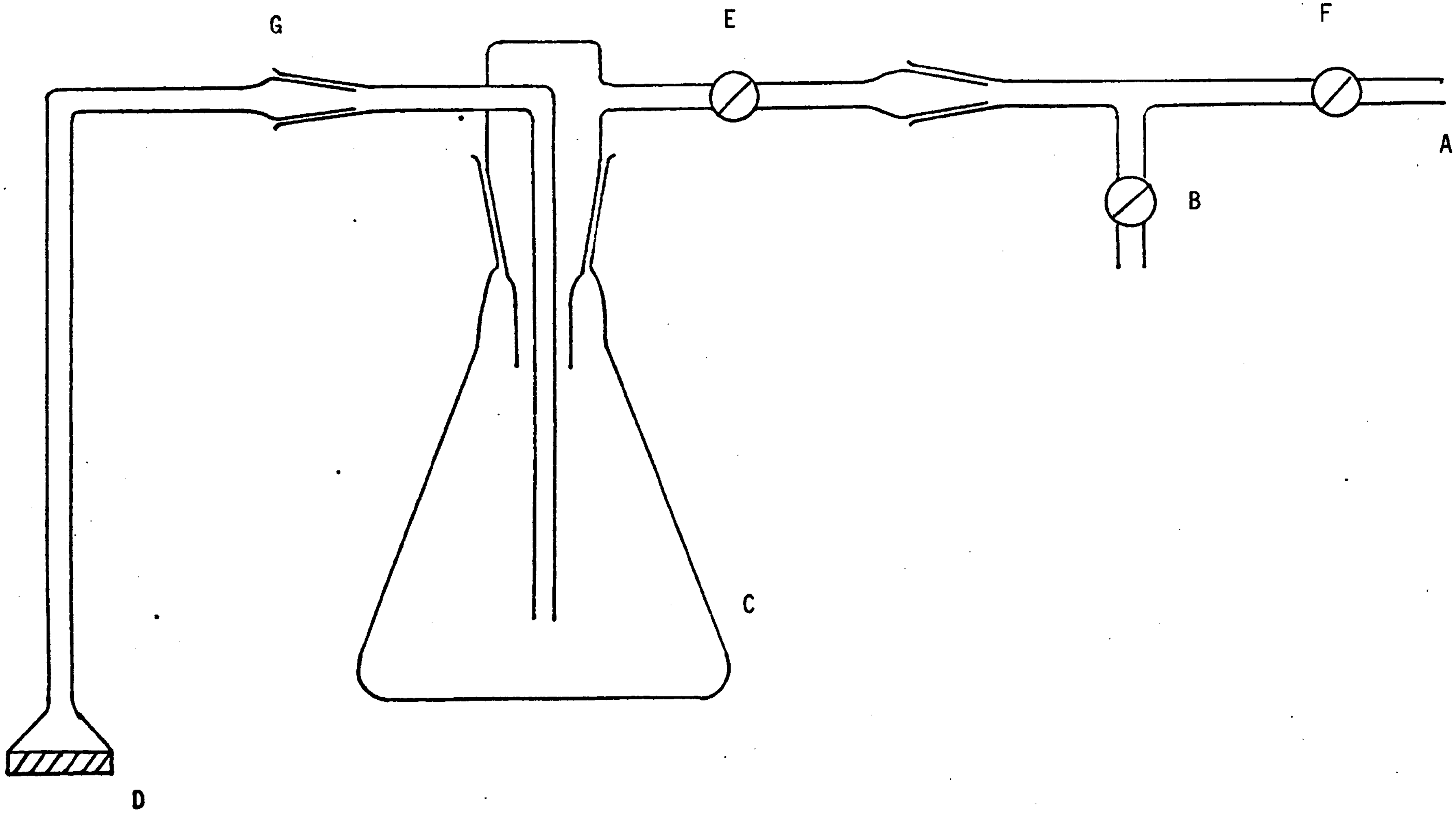
6.2 METHOD OF ANALYSIS OF SOLUTIONS CONTAINING ZERO, OR LOW $CaCl_2$ CONCENTRATIONS

6.2.1 Choice of analysis method

It was decided that the most suitable method of determining gypsum solubilities in sodium chloride and sodium sulphate solutions was by volumetric analysis for calcium using E.D.T.A. This technique is applicable to solutions containing calcium chloride, but the precision of results decreases as the ratio of concentrations of $CaCl_2$ to $CaSO_4$ increases. Other methods of calcium analysis such as precipitation of calcium oxalate would be

FIGURE 6.1.1

SAMPLING APPARATUS



subject to coprecipitation of sodium and sulphate ions (79). Instrumental methods suffer from a variety of problems and offer no improvement in accuracy. Sulphate analysis is clearly inappropriate for solutions containing sodium sulphate, and is also unsuitable for accurate work at high concentrations of sodium chloride or calcium chloride. Methods of sulphate analysis are discussed in section 6.7.1.

Details of possible titrimetric determinations of calcium using E.D.T.A. are given in the standard texts (75,76,77,78). Since sodium ions are the only other cations present, and these show no interference, the main question to be answered was which of the available procedures gave the most precise end-point. Four indicators were used in titrations with 0.01 m E.D.T.A. and 0.01 m $CaCl_2$ solutions:

(i) Murexide

The $CaCl_2$ solution was run into 4 cc of 2 N sodium hydroxide in 40 cc of E.D.T.A.. The end-point was very imprecise and could not be improved by using Naphthol Green as a screening agent.

(ii) Erichrome Black T

Conditions used were 20 cc water, 25 cc 0.01 m $CaCl_2$, 5 cc pH 10 buffer, 10 cc magnesium E.D.T.A. complex, a little KCN to mask traces of metal ions which may block the indicator, and a little ascorbic acid to avoid oxidation of the indicator. The titration was carried out at 60°C to a red → blue end-point which was considerably better than for Murexide, but was not particularly sharp.

(iii) Cal-Red

This indicator was used in 25 cc of the $CaCl_2$ solution with 5 cc of 2 N sodium hydroxide. The end-point, from wine red to pure blue, was quite sharp.

(iv) o-Cresolphthalein Complexone

At the pH of the titration (10.8) the calcium-indicator complex is an intense red. The free indicator is normally colourless but becomes faintly pink if the pH is too high. The end-point was improved by adding sufficient Naphthol Green to give a faint green colouration to the calcium free solution. 25 cc of calcium chloride solution, with 2 cc of pH 10.8 buffer and 5 drops of indicator solution gave an end-point which was very sharp. Half a drop of E.D.T.A. solution being sufficient to change the colour from clear red to a clear pale green. This indicator was consequently chosen for subsequent work, but Cal-Red would probably have been adequate. The suitability of the indicator for use at very high concentrations of NaCl and Na_2SO_4 was checked by adding a large volume of concentrated ($I \approx 6$) solution of each salt to solutions previously titrated just to the faint green end-point. The solution changed to a pale green-pink-blue colour in each case, presumably due to traces of calcium ions in the salts and the high ionic strength. Addition of one drop of E.D.T.A. removed the pink colouration but the colour change was not as sharp as for dilute solutions. Dilution of the solution to an ionic strength of unity improved the sharpness of the end-point to that originally observed.

6.2.2 Details of analysis procedure

An aliquot of equilibrated solution, estimated to contain about $(3.5 \pm 1) \times 10^{-4}$ g ions of calcium, was transferred to a 250 cc collection flask. After re-weighing the flask, water was added to give a volume of 25 cc, or for concentrated solutions sufficient water to bring the ionic strength below unity. Three cc of pH 10.8 buffer solution and 6 drops of indicator were added and E.D.T.A. solution was run into the flask from a 50 cc burette until the end-point was just passed. The sides of the flask were rinsed with water, and $CaCl_2$ from a 10 cc burette was run in until the pink colour was just restored. The end-point was finally taken by adding the small quantity of E.D.T.A. solution required to just remove the pink colouration leaving a faint green. This could be judged to within less than a drop by "contact transfer" of partially formed drops from the burette to the flask. Both burettes were read to the nearest 0.01 cc. About 1 cc of $CaCl_2$ solution was then added and a second pendulum end-point measured. This was repeated again and the mean result calculated. If any of the three readings differed by more than 0.03 cc from this mean, a fourth pendulum end-point was measured and a new mean of the four results calculated. The acceptance or rejection of the deviant result depended upon whether or not it was within ±0.03 cc of this new mean. Since two aliquots of solution were removed from each sample bottle, the results are averages of at least 6 end-point determinations.

6.2.3 Checks on standard solutions

Analar grade of the disodium salt of E.D.T.A. dihydrate is normally used as a primary standard, but in view of the accuracy desired, the solution was checked against standard calcium chloride and standard zinc chloride solutions. Comparison of the solubility of gypsum measured by calcium analysis and by the gravimetric technique discussed later, served as a further post mortem check. The titrations against standard zinc chloride were carried out using 45 cc of $ZnCl_2$ solution, Erichrome Black T as indicator, 4 ml pH 10 buffer and a little Methyl-Red as screening agent. End-points, from red to blue-green, were very sharp.

The results were self consistent to within 0.3%. The greatest differences being between E.D.T.A. and $CaCl_2$ solutions; consequently the zinc solution was taken to be the primary standard. On this basis, the mean solubilities of gypsum in pure water measured by the volumetric and gravimetric methods differed by only 0.1%.

6.3 DETERMINATION OF THE TIME REQUIRED TO REACH EQUILIBRIUM, AND OF THE SOLUBILITY OF GYPSUM IN PURE WATER

After completing preliminary experiments to standardise techniques, a number of sample bottles were filled with water and excess gypsum at individually noted times. The bottles were placed on the revolving wheel immediately after filling, and were removed and sampled in pairs. Equilibrium times up to three days were used, and the remaining unsampled bottles were placed in the water bath. The results were unexpected, and to check their reliability, the experiment was repeated. Room temperature was 24°C ±2°C over the duration of both experiments. The equilibrium concentration of gypsum was determined by measurements on five samples from the second run, after a total equilibration time of 7 days, and ten samples from the first run after 21 days.

On the basis of the results, minimum equilibration times of 2 days on the wheel, followed by 6 days in the water bath were used in subsequent work.

6.4 SOLUBILITY OF GYPSUM IN NaCl AND IN Na_2SO_4 SOLUTIONS

Salt and water were weighed directly into the sample bottle, and excess gypsum was added. Concentrations of sodium chloride up to 5.5 molal, and of sodium sulphate up to 1.7 molal were used. A few of the bottles were reweighed after two days equilibration on the wheel. Zero weight losses were recorded. Equilibration time in the sodium chloride solutions was checked by measuring solubilities after 8, 12 and 14 days. Samples covering a wide range of NaCl concentration were checked at each stage. In this and all subsequent work, a sample of gypsum in pure water was included in each set of determinations to ensure that all conditions were consistent.

6.5 SOLUBILITY OF GYPSUM IN NaCl - Na_2SO_4 SOLUTIONS

Three stock solutions were prepared by weight having a total ionic strength of about 5. Ionic strength ratios of NaCl : Na_2SO_4 of 2:1, 1:1 and 1:2 were used. Aliquots of stock solution were transferred to the sample bottles by pipette, but measurements were made by weight. Sufficient water was added to bring the total volume to about 50 cc, and excess gypsum was added.

6.6 SOLUBILITY OF GYPSUM IN DILUTE $CaCl_2$ SOLUTIONS

A stock $CaCl_2$ solution was prepared of concentration about 1.8 molal (Soln. A). Further stock solutions, having concentrations approximately 0.18 m (A1) and 0.018 m (A2), were prepared by weight dilution. The most dilute solution was analysed for calcium using the standard E.D.T.A. procedure, and the concentrations of the other stocks calculated from this analysis. Solutions of $CaCl_2$ for equilibration with gypsum were prepared from A1 and A2 up to a maximum concentration of 0.087 molal. Equilibrated samples were analysed for calcium in the usual manner.

6.7 METHOD OF ANALYSIS FOR SOLUTIONS CONTAINING $CaCl_2$

6.7.1 Choice of analysis method

Analysis of total calcium content by E.D.T.A. titrations is clearly inappropriate for solutions containing high concentrations of calcium chloride. The accuracy of sulphate analyses is also limited by this same factor. The most common method of sulphate analysis is by precipitation using barium chloride solution. Numerous titrimetric and gravimetric techniques depend on this precipitation, but all are subject to co-precipitation problems which are aggravated by the presence of other electrolytes (79,80,81). Calcium chloride in the solution could be converted to other electrolytes (e.g. HCl by ion exchange, or NaCl by ion exchange followed by neutralisation with NaOH) which do not co-precipitate to the same extent; but at the highest concentrations of $CaCl_2$ to be used, any substituted electrolyte would give rise to serious error. Various other methods of sulphate analysis were considered, but all were rejected on the basis of poor accuracy.

Having rejected all methods relying on analysis of filtered solutions, only two other possible procedures remained:

(a) use a known quantity of gypsum and determine the amount remaining as solid phase after equilibration;

(b) determine the weight of gypsum required to exactly saturate a known quantity of solution by using a trial and error technique.

The former procedure clearly involves problems of complete transfer of residue to filter, and of contamination of the filtered residue by the remaining liquid phase. The latter procedure, however, would be extremely time consuming and would require vast quantities of recrystallised calcium chloride solution. A compromise solution was reached; preliminary small scale experiments were carried out using procedure (a). This was to give approximate gypsum solubilities. The measurements were then repeated, again using procedure (a), but using 500 cc volumes of solution with initial weights of gypsum calculated to be about 5% in excess of that required for saturation. This enabled any errors incurred at the filtration and washing stages to be reduced to acceptable values.

Two methods of solving the problems of complete transfer of residue, and of contamination of the filter cake with concentrated electrolyte solution were considered. The first was to use recycled filtrate to transfer any gypsum remaining in the sample bottle, and to weigh the unwashed filter crucible after calcining at such a temperature that all salts were converted to the anhydrous state. The amount of $CaCl_2$ or mixed $CaCl_2$ and NaCl (in known proportion) could then be determined by chloride analysis. The second method was to use water which was presaturated with gypsum at 25°C both for transferring the residue and for washing the filter cake. Of these two methods, the latter was chosen, partly on the grounds of convenience, but also because of problems with filtrate recycling and with weighing deliquescent calcium chloride which would be associated with the former. Washed gypsum residues were thermally decomposed and weighed as the anhydrous salt. It was thought doubtful that accuracy could be improved by dissolving the residue and analysing for calcium by E.D.T.A. titrations.

6.7.2 Investigation of the composition of two Analar samples of "$CaSO_4\cdot 2H_2O$"

When using a direct gravimetric technique of the type chosen, it is of obvious importance that the material used is either exactly $CaSO_4\cdot 2H_2O$ with insignificant impurities, or if impurities such as moisture are present, the whole sample should be homogeneous and of a known unchanging composition. The percentage loss in weight of the British Drug Houses (B.D.H.) material, used for the solubility measurements in NaCl and Na_2SO_4 solutions, was determined for ignition temperatures up to 470°C. It was found that the weight loss was considerably below the theoretical value and was rather variable. It was therefore necessary to investigate the composition of this sample to ensure that the measurements already made using the material were not in error. A sample of Hopkin and Williams (H. & W.) Analar $CaSO_4\cdot 2H_2O$ was also examined to ascertain whether it would be suitable for the proposed direct gravimetric method.

Details of this investigation are presented in Appendix II.1 since they are subsidiary to the main work, but the important conclusions are presented here:

(i) Crystalline phases, other than $CaSO_4\cdot 2H_2O$, were not detected in the H. & W. sample and the weight loss figures on ignition to 240°C were within 0.7% of theoretical and were constant to within ±0.1%. Consequently the material was considered adequate for the proposed solubility measurements in calcium chloride solutions.

(ii) The B.D.H. sample contained gypsum as the major phase, with about 30 mole per cent natural anhydrite ($CaSO_4$) and small quantities of $CaSO_4\cdot \frac{1}{2}H_2O$ or soluble anhydrite (γ-$CaSO_4$), or possibly both of the latter phases. Other impurities were not detected.

(iii) Equilibration of B.D.H. material with water gave a solid phase in which only gypsum could be detected. It was therefore judged that the measurements made in NaCl and Na_2SO_4 solutions were not invalidated by the initial presence of phases other than $CaSO_4\cdot 2H_2O$.

6.7.3 Details of analysis procedure

Gypsum, stock solution and water were all weighed into a sample bottle, and the mixtures equilibrated in the normal manner. After removing a sample bottle from the water bath, its outer surface was quickly dried, and the contents filtered through a No. 4 porosity sintered glass crucible. The latter had previously been dried at 240°C, cooled in a desiccator and weighed. By shaking the sample bottle and contents before, and two or three times during filtration, virtually all the residual gypsum could be transferred to the crucible. Any remaining crystals were washed into the filter crucible by holding the sample bottle at a suitable angle and using a jet of saturated calcium sulphate solution. The solution used for this purpose was stored in a large flask and maintained at 25°C by immersion in a water bath. When air was pumped into the flask, solution was forced through a No. 4 porosity filter stick to the jet used for washing. After transferring all the gypsum to the crucible, the filter cake was washed until the filtrate was essentially free of chloride ions. This was checked by testing the washings with silver nitrate solution. The crucible and contents were then calcined for two days at 240°C, cooled in a desiccator containing phosphorus pentoxide, and weighed as quickly as possible. Speed was necessary, since the anhydrite was hygroscopic; but since the approximate weight was known, weighing required only a few seconds and the estimated moisture pick-up was negligible.

Errors due to solution or precipitation of gypsum during the washing procedure depend primarily on the contact time of the residue with solutions of composition significantly different to either the original filtrate or the wash liquor. The time required for washing was generally less than 20 seconds, and tests with $AgNO_3$ solution showed that the washings were essentially pure $CaSO_4$ solution after only 5 seconds. The other important factor is the ratio of $CaSO_4(H_2O)_2$ activity in solutions of intermediate composition, to the activity of $CaSO_4(H_2O)_2$ in solutions in equilibrium with gypsum. This determines the driving force for precipitation or solution, and consequently affects the rate of either process. Since the activity of $CaSO_4(H_2O)_2$ in both end solutions is identical, the activity in the mixtures should not be markedly different.

6.8 PRELIMINARY WORK USING SMALL SAMPLE BOTTLES

The first experiments were made with calcium chloride solutions prepared from stocks A1 and A2 up to concentrations of 0.053 molal. This was essentially a trial run to gain experience of the method, and to standardise the transfer and washing procedures. Measurements were then made in the absence of added electrolytes to ensure that accuracy and precision were adequate. The effect of high concentrations of foreign salt was tested by making measurements in sodium chloride solutions from 0.26 molal to 4.34 molal and comparing the results with those obtained by the volumetric method. These initial experiments showed that measurements made using 50 cc volumes of solution were suitable for the limited purpose of giving approximate solubilities, but that for precise work, larger volumes were required.

Two further stock solutions of $CaCl_2$ were prepared by weight dilution from solution A having concentrations 0.166 m (A3) and 0.0166 m (A4). The concentration of solution A4 was checked by volumetric analysis and found to be within 0.06% of the expected value. Using these three stock solutions, 24 solubility determinations were made for $CaCl_2$ concentrations up to 1.48 molal. Literature values (82,83,84,85) for the solubility of gypsum in calcium chloride solutions were used as a guide to the quantity of gypsum required.

Large volumes of sodium chloride (B) and calcium chloride (C) stock solution were prepared having ionic strengths of about 6. The concentration of $CaCl_2$ was determined by calcium analysis of solutions prepared by weight dilution. As usual, the concentration of NaCl stock was calculated from the weights used in its preparation. Mixed stock solutions of ionic strength ratios ($NaCl:CaCl_2$) of 3:1, 1:1 and 1:2 were prepared from B and C. Further mixed stock solutions were prepared by weight dilution. For each ionic strength ratio, twelve solubility measurements were made for concentrations up to $I \sim 6$. The quantity of gypsum required at the higher concentrations of added electrolytes was guided by prior knowledge of the solubilities in pure NaCl, pure $CaCl_2$ and in mixed solutions of lower concentration.

6.9 MEASUREMENTS USING LARGE SAMPLE BOTTLES

With the aid of results from the previous section, quantities of gypsum required to give a small excess after equilibration could be estimated with reasonable accuracy. New stock solutions of calcium chloride were prepared by weight dilution from C and the concentration of the most dilute checked by volumetric analysis. New mixed stock solutions were prepared in the same manner as was described in the previous section. Measurements were made in pure $CaCl_2$ and the three mixed NaCl/ $CaCl_2$ solutions up to ionic strengths of about 6. One measurement was made in pure sodium chloride solution, to give an additional comparative check with the volumetric analysis results. A bottle containing only gypsum and water was included in each run to check that equilibrium was reached. These "blanks" were used to estimate the precision of the method, and in combination with the volumetric results, were used to give a best estimate of gypsum solubility in pure water.

7. RESULTS AND DISCUSSION

7.1 EQUILIBRATION TIME

The results of the experiments designed to estimate the minimum time required to reach equilibrium are illustrated in Fig. 7.1.1. The two sets of results show essentially the same trend: measured calcium concentrations increased to a maximum of about 0.0162 molal after about 4 hours agitation with water, and subsequently decreased to about 0.0152 m after 70 hours. Statistical analysis (discussed in section 7.1.2) of results obtained using equilibration times of 7 and 21 days indicated that both sets of samples were at equilibrium. Similar conclusions were drawn from the absence of any discernable time dependence of calcium sulphate solubilities measured after 8, 12 and 14 days in sodium chloride solutions.

The maximum in the solubility curve is almost certainty due to the presence of phases other than gypsum in the B.D.H. material used in this work (see Appendix II.1). W. M. Power *et al* (86) showed that when soluble anhydrite or $CaSO_4 \cdot \frac{1}{2}H_2O$ is dissolved in water, a maximum in the solubility versus time curve normally results. This is because gypsum is the stable phase at 25°C (i.e. has the lowest solubility). The magnitude of this effect depends upon the relative rates of solution of the more soluble phase and crystallisation of stable phase. The small crystallite size of gypsum in the original material would also have contributed to the higher initial solubility. The smallest mean crystallite dimension (~0.05 μm in the 200 direction - see Appendix II.1) was not especially small, so that this factor was not of major importance unless the size distribution was exceptionally wide.

Consideration of all the results obtained in this study suggests that the minimum equilibration times of 2 days on the rotating wheel at room temperature, followed by 6 days in a water bath, were adequate because scatter in the results was no greater than could be expected from random errors in analysis.

7.2 SOLUBILITY OF GYPSUM IN PURE WATER

Gypsum solubilities, measured by both techniques, are presented in Table 7.2.1. The first two columns of results are for measurements which were initially made to determine the minimum time required for equilibration. The statistical significance of the difference in the two samples means was tested using Student's t test. The value of

$$t_{(n_1 + n_2 - 2)} = \frac{|\bar{x}_1 - \bar{x}_2| - 0}{\sqrt{s^2\left(\frac{1}{n_1} + \frac{1}{n_2}\right)}} \qquad \text{(E.7.2.1)}$$

was calculated as $t_{13} = 1.00$. Subscripts 1 and 2 refer to the two sets of results, and s^2 the pooled estimate of variance is given by

FIGURE 7.1.1

EFFECT OF EQUILIBRATION TIME

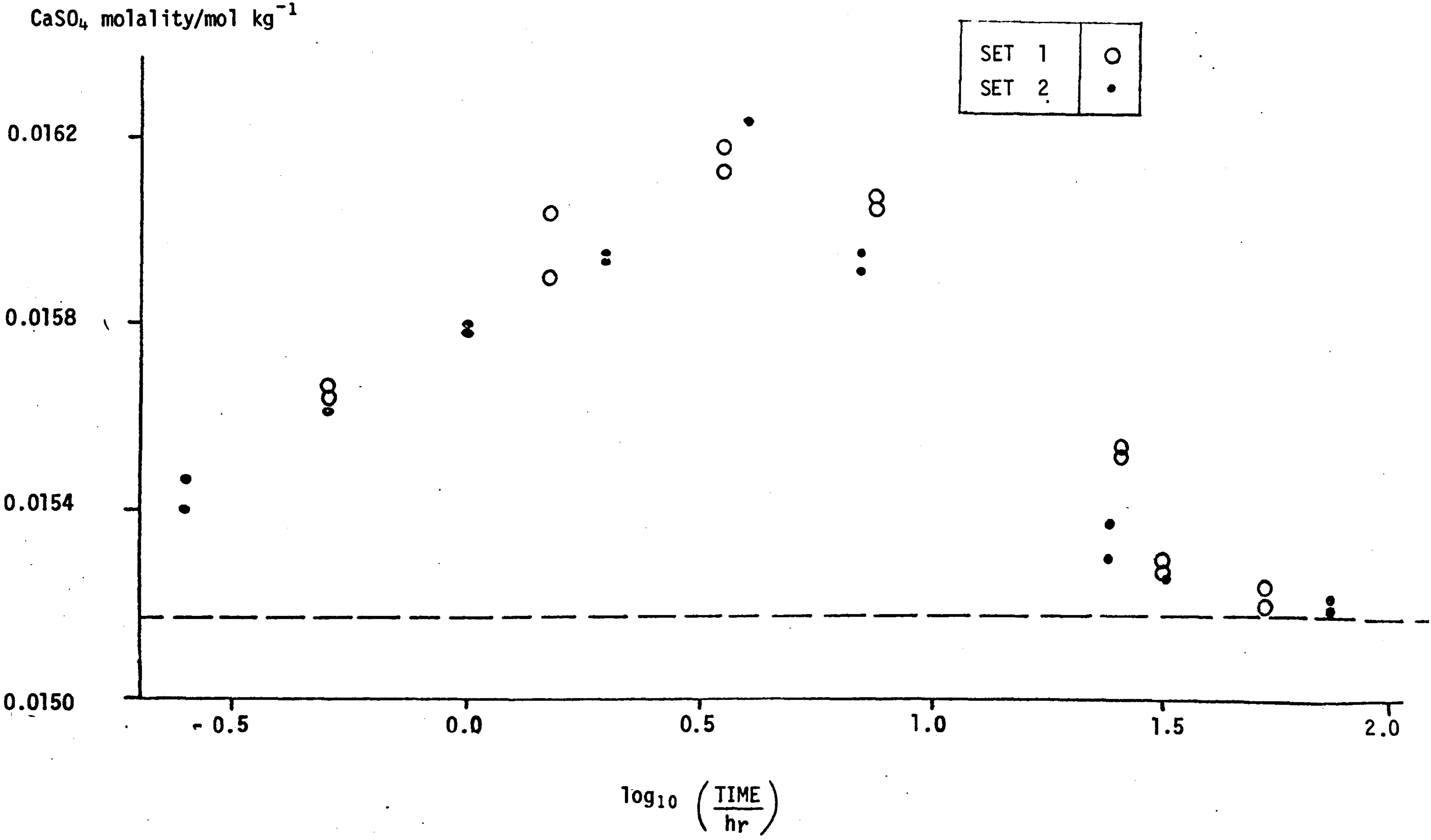


TABLE 7.2.1 MOLAL SOLUBILITY OF GYPSUM IN WATER AT 25°C

	Determined by Volumetric Analysis			Determined by L. S. Gravimetric Analysis
	Set of measurements after 7 days	Set of measurements after 21 days	Single measurements from various sets	Single measurements from various sets
	0.015176	0.015179	0.015219	0.015171
	0.015185	0.015192	0.015182	0.015206
	0.015165	0.015163	0.015188	0.015183
	0.015148	0.015159	0.015211	0.015202
	0.015147	0.015163	0.015198	0.015206
		0.015162	0.015196	0.015162
		0.015175	0.015189	0.015172
		0.015179		
		0.015165		
		0.015172		
mean	0.015164	0.015171	0.015197	0.015186
s(x)	1.65×10^{-5}	1.04×10^{-5}	1.32×10^{-5}	1.85×10^{-5}

$$s^2 = \frac{(n_1 - 1)\left[s(x_1)\right]^2 + (n_2 - 1)\left[s(x_2)\right]^2}{n_1 + n_2 - 2} \qquad \text{(E.7.2.2)}$$

otherwise the nomenclature is as given in section 3.1.3. Reference to tabulated values of t_n at various percentage probability levels showed that the difference in sample means was not significant at the 95% probability level since t_{13} $(P = 0.05) = 2.16$. It was on this basis that both sets of samples were considered to be in equilibrium, but this conclusion was supported by the higher mean solubility of the second set. If equilibrium was not reached in 7 days, measured solubilities for the second set should have been lower, not higher, than the first set since equilibrium is approached from supersaturated solutions.

Treating the results obtained by volumetric analysis as a single population, gave a mean of 0.015178 molal and a standard deviation of 1.86×10^{-5} molal. Comparing this mean with the results obtained by the gravimetric method, showed that the two methods of measuring gypsum solubility gave results which were not significantly different at the 95% probability level. t_{27} was calculated to be 0.99, while t_{27} ($P = 0.05$) = 2.05.

Consequently, all the results presented in Table 7.2.1 were treated as a single population giving the following results:

mean solubility = 0.015180 mol kg^{-1}
standard deviation = 0.0000186 mol kg^{-1}
standard error of mean = 0.0000035 mol kg^{-1}
95% confidence limits of mean: ± 0.0000071 mol kg^{-1}
95% confidence limits for a single determination: ± 0.000038 mol kg^{-1}

The magnitude of possible systematic errors is difficult to estimate. The good agreement between results obtained by two different methods of analysis on two different samples of gypsum suggests that systematic errors were small in both instances. The possibility of errors in both methods having the same magnitude and direction cannot be discounted, but the probability of this must be low. Systematic errors were estimated rather arbitrarily at ±0.00003 molal, making the present estimate for solubility of gypsum at 25°C in pure water to be 0.01518 ±0.00004 molal.

Comparison of this result with literature values is not particularly useful, due to the wide range and uncertain accuracy of the latter. Twenty one results, taken mainly from reference 44, cover a range from 0.0150 to 0.0159 molal with a mean between 0.0152 and 0.0153 molal. Consequently the literature values neither support nor refute the present result. The wide range of values implies that either some of the experimental work was not of a high standard, or the solubility of gypsum is dependent on the particular sample of gypsum used. The second hypothesis is not supported by any literature evidence for metastable states of gypsum, but if this was so, the limits suggested for maximum systematic error in this study would require revision to give a greater possible range.

7.3 SOLUBILITY OF GYPSUM IN SOLUTIONS OF PURE NaCl and PURE Na_2SO_4

The results obtained by volumetric analysis of filtered solutions are presented in Table 7.3.1 and Table 7.3.2, together with values of other thermodynamic quantities calculated in sections 7.8 and 7.9. Concentrations of added salt were corrected for the small amount of additional water present as a consequence of the solution of gypsum, but the correction was generally negligible. The results are presented in pairs, corresponding to the two aliquots which were analysed from each bottle. It is evident from these results, that the analysis procedure was very precise. The results are also shown in Figures 7.3.1 and 7.3.2 where molal solubilities are plotted against the function: $I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$.

Literature values of Hill and Wills (87) and Cameron and Breazeale (88) for the solubility of gypsum in sodium sulphate solutions are given in Figure 7.3.2. In general the present results indicate lower solubilites than those obtained by earlier workers, but at the highest concentrations

FIGURE 7.3.1 SOLUBILITY OF GYPSUM IN SODIUM CHLORIDE SOLUTIONS

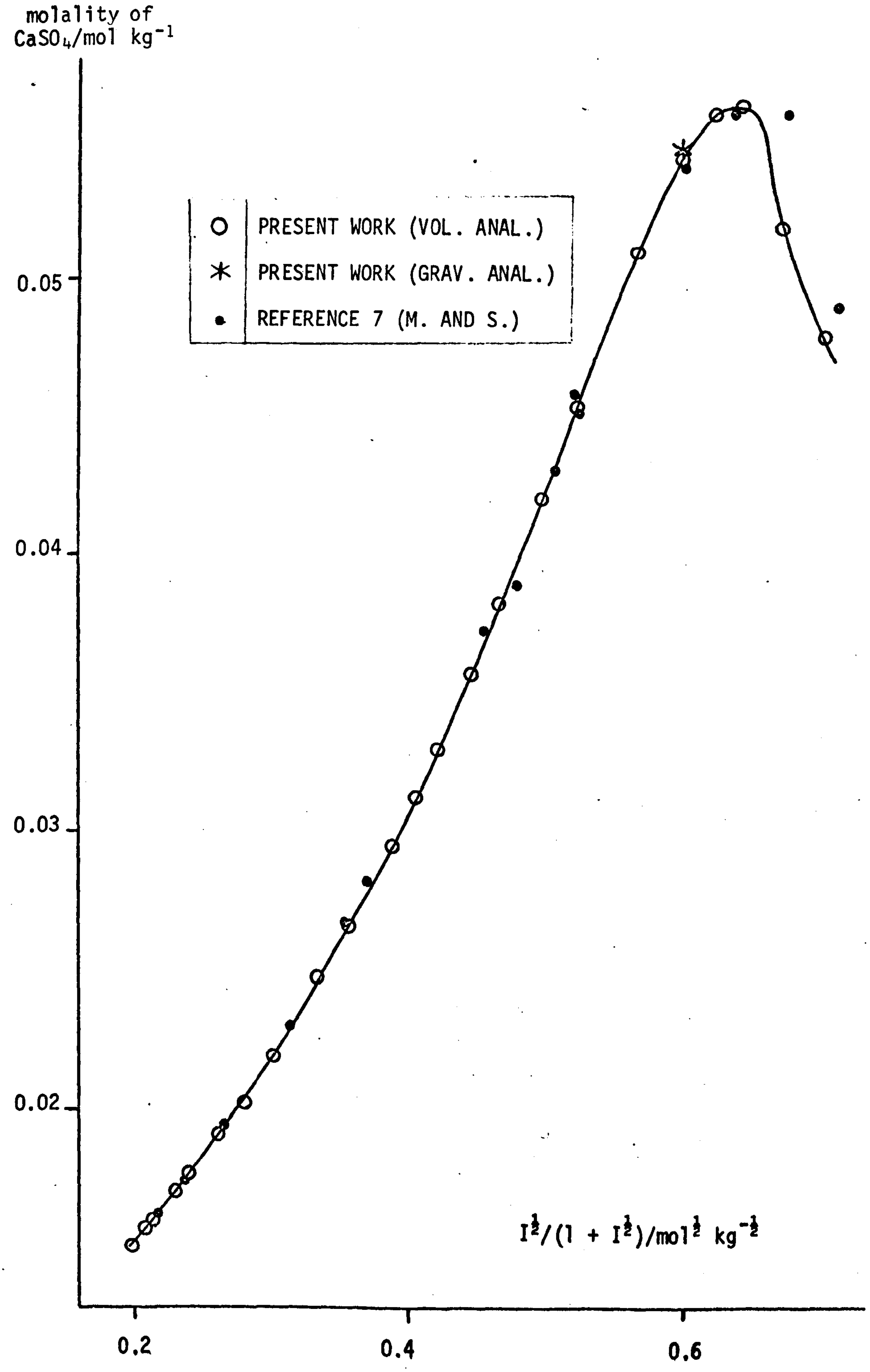


FIGURE 7.3.2 SOLUBILITY OF GYPSUM IN SODIUM SULPHATE SOLUTIONS

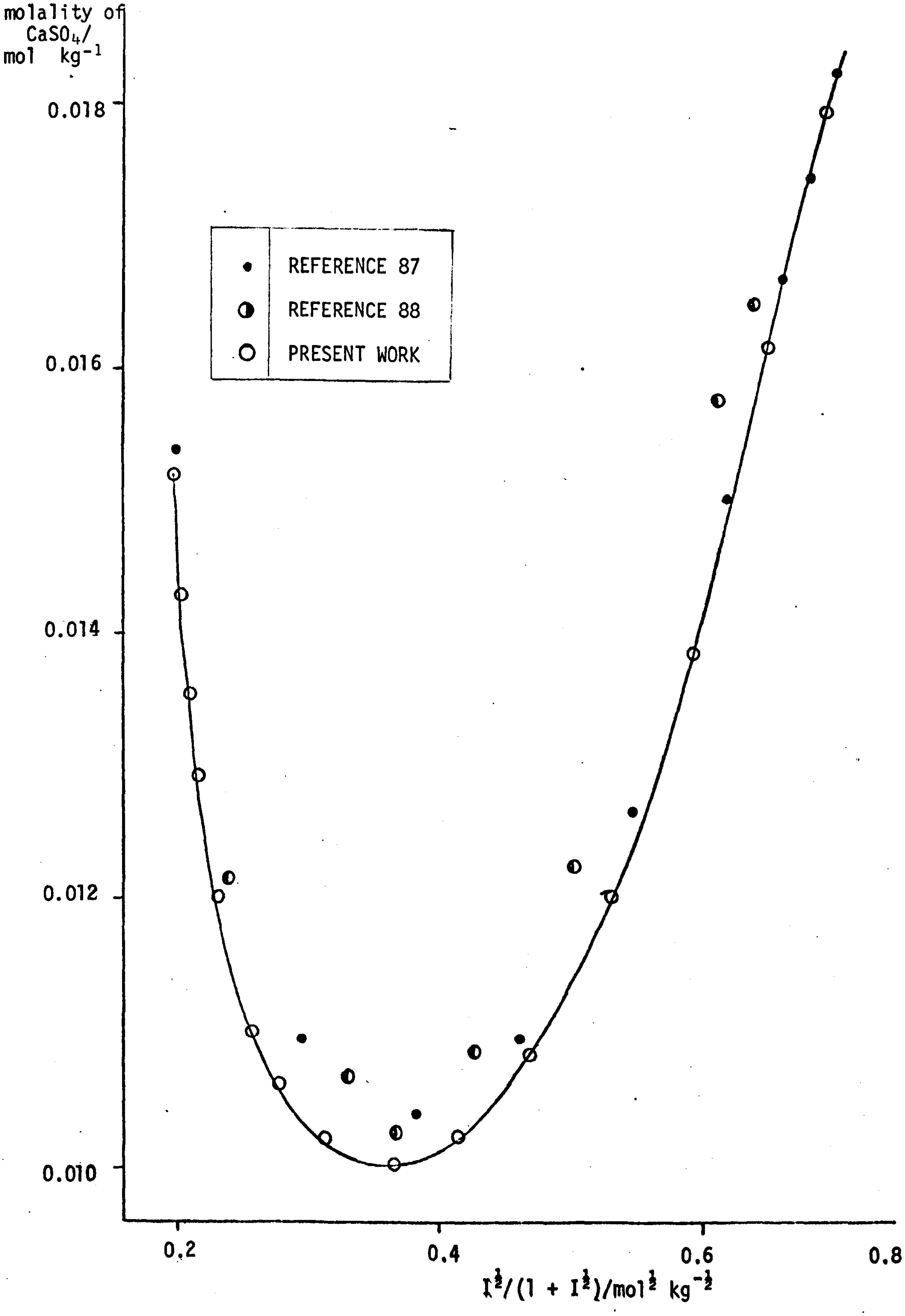


TABLE 7.3.1

PROPERTIES OF $CaSO_4$-NaCl SOLUTIONS IN EQUILIBRIUM WITH GYPSUM

NaCl molality /mol kg^{-1}	$CaSO_4$ molality /mol kg^{-1}	Molal Ionic Strength	Osmotic Coefficient	Water Activity	$\gamma_{\pm CaSO_4}$	R
0.005653	0.015760	0.068693	0.93898	0.99927	0.32563	1.094
0.005653	0.015763	0.068705	0.93897	0.99927	0.32557	1.094
0.008874	0.016086	0.073218	0.93794	0.99915	0.31907	1.096
0.008874	0.016057	0.073102	0.93797	0.99915	0.31965	1.095
0.020220	0.017082	0.088548	0.93491	0.99874	0.30059	1.099
0.020220	0.017084	0.088556	0.93491	0.99874	0.30056	1.099
0.028090	0.017676	0.098794	0.93321	0.99846	0.29057	1.099
0.028090	0.017653	0.098701	0.93322	0.99846	0.29095	1.098
0.049290	0.019134	0.125826	0.92965	0.99771	0.26863	1.096
0.049290	0.019159	0.125926	0.92964	0.99770	0.26828	1.097
0.069400	0.020415	0.151060	0.92719	0.99700	0.25195	1.094
0.069400	0.020400	0.151000	0.92719	0.99700	0.25214	1.094
0.098030	0.021950	0.185830	0.92472	0.99601	0.23457	1.086
0.098030	0.021944	0.185806	0.92473	0.99601	0.23463	1.086
0.155980	0.024728	0.254892	0.92185	0.99401	0.20863	1.074
0.155980	0.024735	0.254920	0.92185	0.99401	0.20858	1.074
0.200000	0.026491	0.305964	0.92081	0.99251	0.19504	1.062
0.200000	0.026511	0.306044	0.92081	0.99251	0.19490	1.063
0.281290	0.029441	0.399054	0.92039	0.98974	0.17599	1.045
0.281290	0.029441	0.399054	0.92039	0.98974	0.17599	1.045
0.334940	0.031112	0.459388	0.92079	0.98792	0.16684	1.032
0.334940	0.031185	0.459680	0.92079	0.98792	0.16645	1.034
0.395750	0.032927	0.527458	0.92171	0.98586	0.15798	1.021
0.395750	0.032907	0.527378	0.92170	0.98586	0.15807	1.020
0.503590	0.035660	0.646230	0.92415	0.98220	0.14641	0.998
0.503590	0.035704	0.646406	0.92415	0.98220	0.14623	0.999
0.610880	0.038123	0.763371	0.92733	0.97854	0.13747	0.979
0.610880	0.038140	0.763440	0.92733	0.97854	0.13740	0.980
0.807100	0.041957	0.974928	0.93446	0.97181	0.12577	0.947
0.807100	0.041964	0.974956	0.93446	0.97181	0.12575	0.947
1.025600	0.045337	1.206948	0.94376	0.96423	0.11731	0.914
1.025600	0.045326	1.206904	0.94376	0.96423	0.11733	0.914
1.520600	0.050960	1.724440	0.96845	0.94663	0.10630	0.859
1.520600	0.050880	1.724120	0.96843	0.94664	0.10647	0.858
2.020200	0.054328	2.237511	0.99699	0.92818	0.10169	0.823
2.020200	0.054311	2.237444	0.99699	0.92818	0.10173	0.823
2.536200	0.056017	2.760268	1.02933	0.90833	0.10078	0.803
2.536200	0.055993	2.760172	1.02932	0.90834	0.10083	0.803
3.018600	0.056140	3.243160	1.06159	0.88904	0.10274	0.795
3.018600	0.056142	3.243168	1.06159	0.88904	0.10274	0.795
4.011400	0.051682	4.218128	1.13202	0.84728	0.11711	0.779
4.011400	0.051675	4.218100	1.13202	0.84728	0.11713	0.779
5.487700	0.047830	5.679020	1.24513	0.78009	0.13744	0.889
5.487700	0.047764	5.678756	1.24511	0.78010	0.13763	0.888
0.000000	0.015150	0.060600	0.94103	0.99948	0.33867	1.090
0.000000	0.015177	0.060708	0.94100	0.99948	0.33807	1.091

TABLE 7.3.2 PROPERTIES OF $CaSO_4$-Na_2SO_4 SOLUTIONS IN EQUILIBRIUM WITH GYPSUM

Na_2SO_4 molality /mol kg^{-1}	$CaSO_4$ molality /mol kg^{-1}	Molal Ionic Strength	Osmotic Coefficient	Water Activity	$\gamma_{\pm CaSO_4}$	R
0.000000	0.015193	0.060772	0.86763	0.99952	0.33770	1.092
0.000000	0.015181	0.060724	0.86767	0.99952	0.33797	1.091
0.002825	0.014282	0.065603	0.86417	0.99942	0.32828	1.095
0.002825	0.014266	0.065539	0.86421	0.99942	0.32861	1.094
0.005481	0.013532	0.070571	0.86082	0.99932	0.31993	1.095
0.005481	0.013533	0.070575	0.86082	0.99932	0.31991	1.095
0.008589	0.012922	0.077455	0.85650	0.99920	0.30784	1.099
0.008589	0.012900	0.077367	0.85655	0.99920	0.30826	1.098
0.014608	0.012002	0.091832	0.84843	0.99896	0.28726	1.101
0.014608	0.012003	0.091836	0.84843	0.99896	0.28724	1.101
0.025346	0.011091	0.120402	0.83523	0.99852	0.25548	1.102
0.025346	0.011129	0.120550	0.83517	0.99852	0.25492	1.104
0.036635	0.010781	0.153029	0.82322	0.99805	0.22726	1.108
0.036636	0.010628	0.152420	0.82342	0.99805	0.22926	1.101
0.056459	0.010222	0.210265	0.80691	0.99724	0.19697	1.091
0.056459	0.010218	0.210249	0.80691	0.99724	0.19701	1.091
0.098211	0.010028	0.334745	0.78234	0.99557	0.15635	1.070
0.098211	0.010035	0.334773	0.78233	0.99557	0.15629	1.070
0.154910	0.010240	0.505690	0.75972	0.99338	0.12553	1.054
0.154910	0.010227	0.505638	0.75973	0.99338	0.12562	1.053
0.250855	0.010829	0.795881	0.73342	0.98982	0.09732	1.043
0.250855	0.010814	0.795821	0.73343	0.98982	0.09739	1.042
0.000000	0.015193	0.060772	0.86763	0.99952	0.33770	1.092
0.000000	0.015183	0.060732	0.86766	0.99952	0.33792	1.091
0.419521	0.012011	1.306607	0.70184	0.98391	0.07239	1.047
0.419521	0.012005	1.306583	0.70184	0.98391	0.07241	1.047
0.702531	0.013846	2.162977	0.66618	0.97469	0.05282	1.052
0.702532	0.013830	2.162916	0.66618	0.97469	0.05286	1.051
1.129123	0.016155	3.481988	0.63341	0.96140	0.03904	1.008
1.139123	0.016158	3.482000	0.63341	0.96140	0.03904	1.008
1.691879	0.017932	5.147365	0.61856	0.94463	0.03100	0.932
1.691878	0.017957	5.147461	0.61856	0.94463	0.03098	0.933

(I = 3.0 to 5.4) the data of reference 87 are in good agreement with this work. The solubilities given in reference 88 appear to be of poor precision since a smooth curve cannot be drawn through all the points. Other solubility data on this system are present in the literature, but the precision is worse than in reference 88, and the results were not considered further.

It is peculiar that the results given in reference 87 should be in good agreement with the present results at high Na_2SO_4 concentrations, but higher by as much as 4% at lower concentrations. Impurities in either sample of sodium sulphate would exacerbate any differences as the concentration of added salt was increased. The reason for these discrepancies most probably lies in the different methods of analysis used. Hill and Wills precipitated calcium as the oxalate. They commented on the problem of occlusion of impurities in the precipitate, leading to high results, and mentioned a method of removing these impurities by volatilisation. It is possible that only the precipitates from solutions having high Na_2SO_4 concentrations were treated in this way. Regardless of such speculation, the method of analysis used in this study is considered superior to methods in the literature, and the present results are thought to be the most reliable.

The data of Marshall and Slusher (7) for the solubility of gypsum in sodium chloride solutions at 25°C is presented in Fig. 7.3.1. With the exception of the two highest concentrations, these data are seen to be in good agreement with the present results. This system has been studied by many other groups of workers. Marshall and Slusher graphically compared their results with data from five other investigations. They found that all six sets of solubilities were in good agreement at low concentrations, but that deviations of up to 0.01 molal were present at the highest concentrations. Work on this system since reference 7 (1966) has generally been at higher temperatures or at low concentrations. The results of reference 7 were therefore taken to represent literature results in general, with the scatter of other results around those of (7), an estimate of the uncertainty. On this basis it was concluded that the present solubility measurements in sodium chloride solutions were in good agreement with literature data.

The single result on this system obtained by the large scale gravimetric technique is also shown in Fig. 7.3.1. This is seen to be concordant with the other results. Measurements made using the small sample bottles were of low precision and are not shown. The results were however quite compatible with those in Fig. 7.3.1.

7.4 SOLUBILITY OF GYPSUM IN PURE $CaCl_2$ SOLUTIONS

Results obtained using the large scale gravimetric method are shown in Table 7.4.1. These results, together with those obtained using the volumetric method, are plotted against $I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$ in Figure 7.4.1. Since the method of calculating concentrations for the volumetric method was not straightforward in the presence of $CaCl_2$, the procedure used is outlined in Appendix II.2.

Inspection of Figure 7.4.1 shows that with the exception of the two volumetric results at the highest $CaCl_2$ concentrations, the two methods of analysis give concordant results. The ratio of $CaCl_2$ to $CaSO_4$ molalities for these errant results is about 10 to 1. It is therefore not surprising that significant differences between the two methods should arise due to poor precision of the volumetric method.

In order to avoid confusion between present and literature results, the latter are shown displaced by 0.005 molal concentration units. The smooth curve passing through all the present

FIGURE 7.4.1 SOLUBILITY OF GYPSUM IN CALCIUM CHLORIDE SOLUTIONS

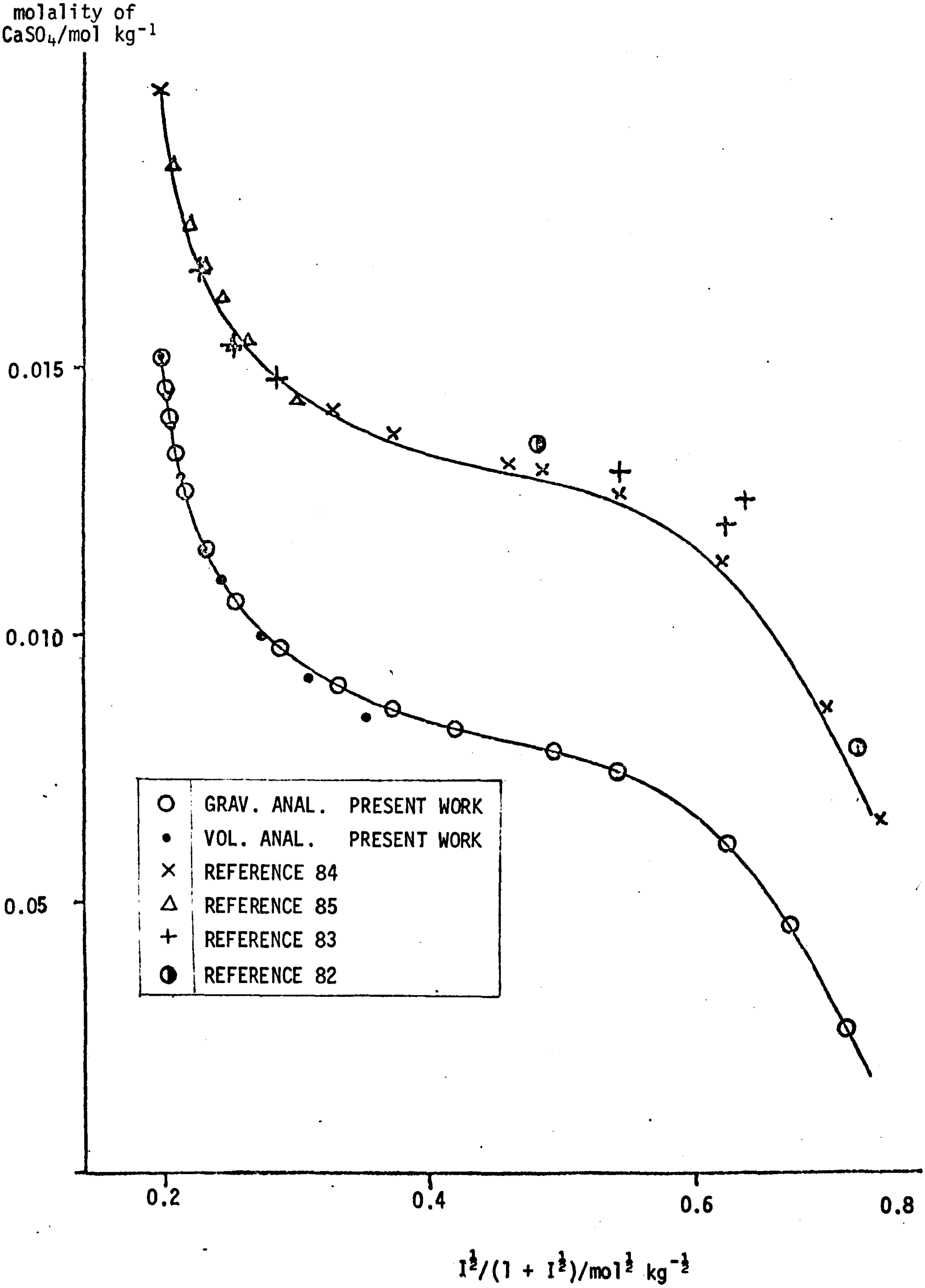


TABLE 7.4.1 PROPERTIES OF $CaSO_4$-$CaCl_2$ SOLUTIONS IN EQUILIBRIUM WITH GYPSUM

$CaCl_2$ molality /mol kg^{-1}	$CaSO_4$ molality /mol kg^{-1}	Molal Ionic Strength	Osmotic Coefficient	Water Activity	$\gamma_{\pm CaSO_4}$	R
0.000000	0.015206	0.060824	0.88717	0.99951	0.33742	1.092
0.000000	0.015172	0.060688	0.88724	0.99951	0.33817	1.091
0.000000	0.015162	0.060648	0.88726	0.99951	0.33840	1.091
0.001401	0.014629	0.062719	0.88627	0.99946	0.33507	1.092
0.003148	0.014059	0.065679	0.88492	0.99940	0.32991	1.095
0.005413	0.013382	0.069767	0.88317	0.99931	0.32358	1.096
0.008512	0.012644	0.076112	0.88067	0.99919	0.31381	1.099
0.015227	0.011564	0.091937	0.87542	0.99891	0.29167	1.107
0.024549	0.010622	0.116135	0.86935	0.99851	0.26572	1.110
0.041313	0.009725	0.162838	0.86177	0.99777	0.23070	1.108
0.070736	0.009041	0.248372	0.85525	0.99645	0.19163	1.098
0.105420	0.008610	0.350700	0.85337	0.99488	0.16451	1.080
0.163465	0.008186	0.523139	0.85669	0.99220	0.13788	1.056
0.307506	0.007769	0.953594	0.87829	0.98526	0.10517	1.044
0.456570	0.007454	1.399526	0.90860	0.97759	0.08919	1.061
0.914620	0.006038	2.768012	1.02394	0.95043	0.07237	1.135
1.392030	0.004545	4.194269	1.16866	0.91565	0.07029	1.232
2.070300	0.002665	6.221560	1.40666	0.85425	0.08076	1.468

gravimetric results is also shown displaced by the same distance to facilitate comparison. The results of Cameron and Seidell (84) are slightly higher than the present data over the whole concentration range. Those of van Veldhuizen (85) are in good agreement but do not extend to high concentrations of $CaCl_2$. The results of D'Ans (83) are also in good agreement at low concentrations, but at high concentrations the solubilities show serious scatter and were disregarded. Sveshnikova (82) gives two results for high $CaCl_2$ molalities; these are a little higher than the present results. It was concluded from this comparison that the present gravimetric results were generally in good agreement with literature data, but were possibly a little low.

7.5 SOLUBILITY OF GYPSUM IN MIXED NaCl-Na_2SO_4 SOLUTIONS

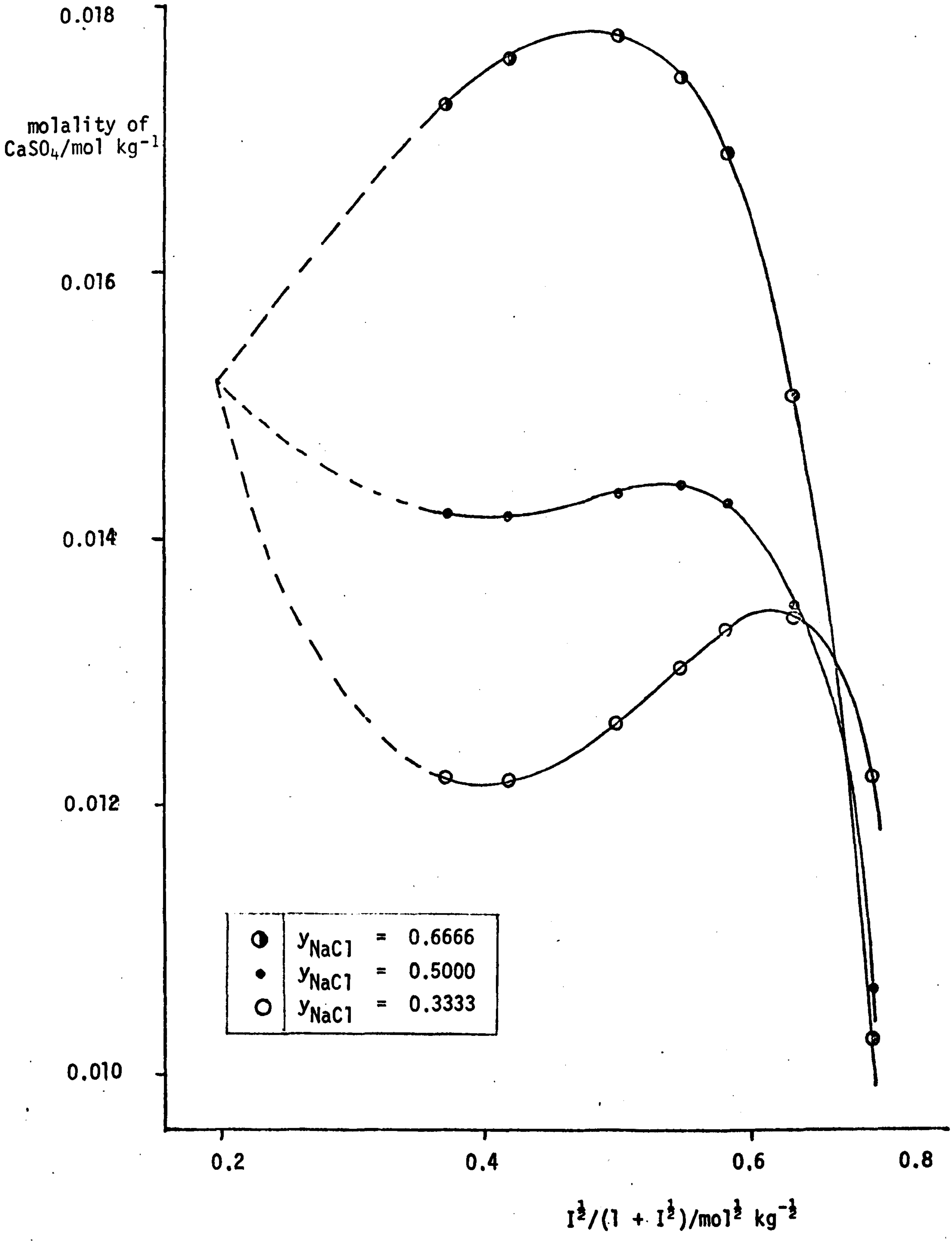
The results for this system are presented in Table 7.5.1 and in Figure 7.5.1. y_{NaCl} is the ionic strength fraction of sodium chloride when dissolved $CaSO_4$ is neglected. The measured solubilities for each concentration ratio of NaCl to Na_2SO_4 all lie on smooth curves, indicating once again the high precision of the volumetric analysis method. Other workers (14) and (89) have measured gypsum solubilities in this system at 25^{o}C, but intercomparison of the data was not attempted because of the different concentration ratios used.

TABLE 7.5.1 PROPERTIES OF $CaSO_4$-NaCl-Na_2SO_4 SOLUTIONS

IN EQUILIBRIUM WITH GYPSUM

NaCl molality /mol kg^{-1}	Na_2SO_4 molality /kg mol^{-1}	y_{NaCl}	$CaSO_4$ molality /kg mol^{-1}	Molal Ionic Strength	Osmotic Coefficient	Water Activity	$\gamma_{\pm CaSO_4}$	R
0.000000	0.000000	0.000000	0.015211	0.060844	1.00000	0.99945	0.33733	1.093
0.000000	0.000000	0.000000	0.015196	0.060784	1.00000	0.99945	0.33766	1.092
0.099568	0.066377	0.333338	0.012198	0.347490	0.84701	0.99357	0.16672	1.084
0.099568	0.066377	0.333338	0.012202	0.347506	0.84701	0.99357	0.16669	1.084
0.156499	0.104330	0.333339	0.012195	0.518269	0.83494	0.99026	0.13738	1.073
0.156499	0.104330	0.333339	0.012173	0.518181	0.83494	0.99026	0.13751	1.072
0.314386	0.209587	0.333337	0.012591	0.993511	0.81788	0.98127	0.09881	1.058
0.314386	0.209587	0.333337	0.012604	0.993563	0.81788	0.98127	0.09875	1.059
0.477132	0.318082	0.333337	0.013021	1.483461	0.81061	0.97214	0.08034	1.051
0.477132	0.318082	0.333337	0.013015	1.483431	0.81061	0.97214	0.08036	1.051
0.631098	0.420725	0.333337	0.013308	1.946504	0.80877	0.96351	0.07003	1.044
0.631099	0.420725	0.333337	0.013294	1.946449	0.80877	0.96351	0.07007	1.043
0.985790	0.657182	0.333337	0.013410	3.010976	0.81704	0.94324	0.05733	1.019
0.985790	0.657181	0.333337	0.013416	3.010996	0.81704	0.94324	0.05732	1.020
1.665989	1.110640	0.333337	0.012124	5.046404	0.86762	0.90074	0.04879	1.054
1.665991	1.110641	0.333337	0.012089	5.046270	0.86761	0.90074	0.04887	1.052
0.000000	0.000000	0.000000	0.015210	0.060840	1.00000	0.99945	0.33735	1.093
0.000000	0.000000	0.000000	0.015198	0.060792	1.00000	0.99945	0.33762	1.092
0.149664	0.049887	0.500005	0.014176	0.356028	0.86982	0.99254	0.17145	1.077
0.149664	0.049887	0.500005	0.014161	0.355969	0.86982	0.99254	0.17156	1.076
0.233191	0.077729	0.500004	0.014155	0.522998	0.86197	0.98876	0.14381	1.062
0.233192	0.077729	0.500005	0.014147	0.522967	0.86197	0.98876	0.14386	1.061
0.480908	0.160300	0.500004	0.014319	1.019084	0.85365	0.97762	0.10490	1.033
0.480908	0.160300	0.500004	0.014305	1.019028	0.85365	0.97762	0.10496	1.033
0.712383	0.237458	0.500003	0.014354	1.482173	0.85447	0.96720	0.08819	1.014
0.712383	0.237457	0.500004	0.014373	1.482246	0.85447	0.96720	0.08813	1.014
0.954042	0.318009	0.500003	0.014248	1.965061	0.86015	0.95619	0.07795	0.997
0.954043	0.318010	0.500003	0.014234	1.965009	0.86015	0.95619	0.07798	0.997
1.462602	0.487527	0.500003	0.013476	2.979087	0.88330	0.93216	0.06695	0.974
1.462601	0.487527	0.500003	0.013495	2.979162	0.88330	0.93215	0.06690	0.975
2.499032	0.832999	0.500003	0.010636	5.040573	0.96347	0.87766	0.06168	1.057
2.499033	0.833000	0.500003	0.010625	5.040532	0.96347	0.87766	0.06171	1.056
0.000000	0.000000	0.000000	0.015210	0.060840	1.00000	0.99945	0.33735	1.093
0.000000	0.000000	0.000000	0.015213	0.060852	1.00000	0.99945	0.33728	1.093
0.190363	0.031730	0.666646	0.017273	0.354645	0.88941	0.99185	0.17771	1.066
0.190363	0.031730	0.666646	0.017264	0.354609	0.88942	0.99185	0.17778	1.065
0.309373	0.051568	0.666641	0.017567	0.534345	0.88464	0.98719	0.14906	1.043
0.309373	0.051568	0.666641	0.017570	0.534357	0.88464	0.98719	0.14904	1.043
0.628015	0.104681	0.666641	0.017726	1.012962	0.88461	0.97473	0.11294	0.996
0.628014	0.104681	0.666641	0.017747	1.013044	0.88461	0.97473	0.11287	0.997
0.938408	0.156419	0.666641	0.017463	1.477517	0.89227	0.96245	0.09669	0.963
0.938408	0.156419	0.666641	0.017466	1.477529	0.89227	0.96245	0.09668	0.964
1.271108	0.211875	0.666641	0.016881	1.974256	0.90522	0.94897	0.08696	0.938
1.271108	0.211875	0.666641	0.016885	1.974272	0.90522	0.94897	0.08695	0.938
1.938385	0.323101	0.666641	0.015056	2.967911	0.94158	0.92061	0.07807	0.913
1.938384	0.323101	0.666641	0.015064	2.967943	0.94158	0.92061	0.07804	0.914
3.332097	0.555413	0.666641	0.010250	5.039335	1.04813	0.85412	0.07885	1.016
3.332092	0.555412	0.666641	0.010297	5.039516	1.04814	0.85411	0.07866	1.018

FIGURE 7.5.1 SOLUBILITY OF GYPSUM IN MIXED NaCl - Na_2SO_4 SOLUTIONS



7.6 SOLUBILITY OF GYPSUM IN MIXED $NaCl$-$CaCl_2$ SOLUTIONS

The results obtained are presented in Table 7.6.1 and Figure 7.6.1. No literature data could be found for solubilities in this system, so the only criterion available to test the results was the degree of scatter about the smooth curves drawn through data of the same y_{NaCl} value. Since this is clearly small, it was inferred that the gravimetric method gave reliable results for this system.

7.7 EVALUATION OF THE THERMODYNAMIC SOLUBILITY PRODUCT OF GYPSUM

7.7.1 Objectives

The solubility product of gypsum in aqueous solution at 25°C was determined in Part I of this thesis. It was not the aim of this section to question the value of K_{sp} obtained. The objectives were to test whether a reliable value of K_{sp} could be obtained using solubility measurements, and at the same time check that these measurements were compatible with the value of K_{sp} deduced in Part I.

7.7.2 Method of evaluation

The procedure used by Marshall and Slusher (7) to obtain K_{sp} from gypsum solubilities in sodium chloride solutions was briefly outlined in the introduction to Part I (section 1.2.3). This was taken as a basis for the present method, but ion pairing of calcium and sulphate ions was accounted for in a more realistic manner and solubilities in all three single salt solutions were used.

Activity coefficients of free ions were expressed as

$$\ln\gamma_{\pm}^{f} = \frac{-|Z_{+}Z_{-}|S\,(I')^{\frac{1}{2}}}{1 + A\,(I')^{\frac{1}{2}}} + BI' + C(I')^{2} \qquad (E.7.7.1)$$

The symbols are as in section 1.2.3 except that a/a_0 is replaced by A and $\gamma_{\pm}$ and I are given superscripts to indicate that they refer to properties of free ions. If K_{sp} is written as

$$K_{sp} = m^{f}_{Ca^{2+}}\, m^{f}_{SO_4^{2-}}\, (\gamma^{f}_{\pm})^{2}\, a^{2}_{H_2O} \qquad (E.7.7.2)$$

it may be re-expressed as either

$$\ln K_{sp} = \ln\,(m^{f}_{Ca^{2+}}\, m^{f}_{SO_4^{2-}}\, a^{2}_{H_2O}) - \frac{8S\,(I')^{\frac{1}{2}}}{1 + A\,(I')^{\frac{1}{2}}} + 2BI' + 2C(I')^{2} \qquad (E.7.7.3)$$

or as

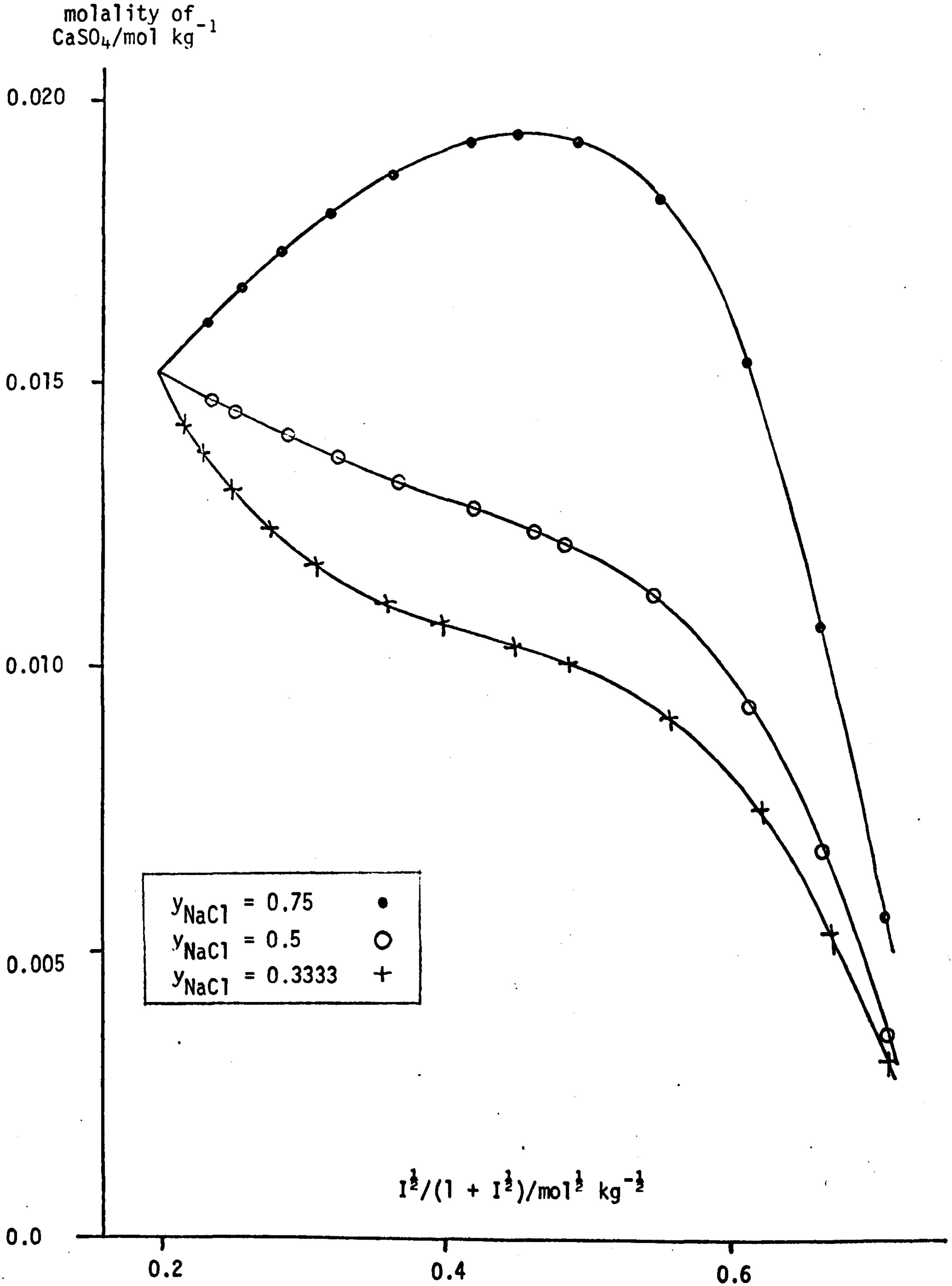
$$\ln K_{sp} = \ln\,(m^{f}_{Ca^{2+}}\, m^{f}_{SO_4^{2-}}) - \frac{8\,S\,(I')^{\frac{1}{2}}}{1 + A\,(I')^{\frac{1}{2}}} + 2B'I' + 2C'(I')^{2} \qquad (E.7.7.4)$$

TABLE 7.6.1

PROPERTIES OF $CaSO_4$-NaCl-$CaCl_2$ SOLUTIONS IN EQUILIBRIUM WITH GYPSUM

NaCl molality /mol kg^{-1}	$CaCl_2$ molality /mol kg^{-1}	y_{NaCl}	$CaSO_4$ molality /mol kg^{-1}	Molal Ionic Strength	Osmotic Coefficient	Water Activity	$\gamma_{\pm CaSO_4}$	R
0.038519	0.004289	0.749584	0.016709	0.118225	0.92220	0.99795	0.27434	1.098
0.019934	0.002219	0.749584	0.016093	0.090968	0.92645	0.99868	0.29911	1.097
0.000000	0.000000	0.000000	0.015203	0.060812	0.93353	0.99948	0.33749	1.092
0.064813	0.007217	0.749584	0.017362	0.155917	0.91825	0.99692	0.24900	1.096
0.110681	0.012325	0.749584	0.018025	0.219758	0.91445	0.99516	0.22032	1.084
0.184989	0.020599	0.749584	0.018721	0.321677	0.91231	0.99231	0.19047	1.067
0.329274	0.036667	0.749584	0.019279	0.516391	0.91425	0.98679	0.15824	1.036
0.447662	0.049850	0.749584	0.019407	0.674845	0.91860	0.98222	0.14241	1.013
0.651794	0.072582	0.749584	0.019286	0.946686	0.92900	0.97423	0.12505	0.980
1.084122	0.120724	0.749584	0.018287	1.519448	0.95754	0.95668	0.10631	0.927
2.934065	0.326729	0.749584	0.010760	3.957296	1.12598	0.86992	0.09782	0.886
4.524517	0.503837	0.749584	0.005654	6.058649	1.29854	0.78089	0.12235	1.140
1.831711	0.203974	0.749584	0.015391	2.505200	1.01872	0.92401	0.09551	0.874
0.000000	0.000000	0.000000	0.015171	0.060687	0.92358	0.99949	0.33818	1.091
0.054738	0.018250	0.499941	0.014065	0.165749	0.90583	0.99686	0.24130	1.101
0.089414	0.029811	0.499941	0.013660	0.233493	0.90219	0.99520	0.21145	1.093
0.142476	0.047503	0.499941	0.013272	0.338075	0.90079	0.99265	0.18190	1.082
0.237834	0.079296	0.499941	0.012796	0.526909	0.90416	0.98803	0.15120	1.063
0.348729	0.116270	0.499941	0.012388	0.747093	0.91241	0.98254	0.13073	1.044
0.028716	0.009574	0.499941	0.014442	0.115211	0.91138	0.99811	0.27587	1.100
0.017829	0.005944	0.499941	0.014689	0.094421	0.91493	0.99863	0.29496	1.100
0.421496	0.140531	0.499941	0.012186	0.891839	0.91919	0.97888	0.12143	1.035
0.706216	0.235460	0.499941	0.011256	1.457624	0.95136	0.96396	0.10095	1.003
1.244737	0.415009	0.499941	0.009304	2.526984	1.02612	0.93297	0.08748	0.965
1.954330	0.651595	0.499941	0.006720	3.935999	1.14151	0.88616	0.08700	0.971
3.046350	1.015686	0.499941	0.003561	6.107657	1.33860	0.80205	0.10612	1.254
0.019680	0.013122	0.333292	0.013104	0.111469	0.90197	0.99829	0.27708	1.104
0.011468	0.007647	0.333292	0.013737	0.089356	0.90635	0.99880	0.29958	1.100
0.006373	0.004249	0.333292	0.014263	0.076176	0.90972	0.99911	0.31587	1.096
0.000000	0.000000	0.000000	0.015207	0.060828	0.91466	0.99949	0.33740	1.092
0.032192	0.021465	0.333292	0.012463	0.146442	0.89720	0.99751	0.25001	1.105
0.050100	0.033406	0.333292	0.011830	0.197643	0.89310	0.99640	0.22248	1.101
0.089393	0.059606	0.333292	0.011184	0.312951	0.89015	0.99392	0.18336	1.093
0.131392	0.087611	0.333292	0.010816	0.437490	0.89163	0.99124	0.15856	1.083
0.205357	0.136929	0.333292	0.010378	0.657658	0.89940	0.98644	0.13296	1.068
0.000000	0.000000	0.000000	0.015183	0.060732	0.91470	0.99949	0.33793	1.091
0.286863	0.191277	0.333292	0.010067	0.900966	0.91170	0.98100	0.11611	1.059
0.518555	0.345766	0.333292	0.009120	1.592336	0.95616	0.96459	0.09345	1.040
0.896892	0.598038	0.333292	0.007515	2.721067	1.04438	0.93445	0.08135	1.028
1.387361	0.925077	0.333292	0.005386	4.184141	1.17653	0.88881	0.08150	1.050
2.043785	1.362774	0.333292	0.003082	6.144438	1.37147	0.71696	0.09674	1.304

FIGURE 7.6.1 SOLUBILITY OF GYPSUM IN MIXED NaCl - $CaCl_2$ SOLUTIONS



In the second equation the assumption is made that the water activity may be written with reasonable accuracy as

$$\ln a_{H_2O} \quad = \quad bI \; + \; cI^2$$

If the calcium sulphate ion pair dissociation constant is defined in the usual manner as

$$K_D \quad = \quad \frac{a_{Ca^{2+}} \, a_{SO_4^{2-}}}{a_{CaSO_4^0}} \tag{E.7.7.5}$$

and $\gamma_{CaSO_4^0}$ is taken to be unity, then the concentration of ion pairs may be expressed as

$$m_{CaSO_4^0} \quad = \quad \frac{K_{sp}}{K_D \, a_{H_2O}^2} \tag{E.7.7.6}$$

and the ionic strength as $I' \; = \; I \; - \; 4 \, m_{CaSO_4^0}$.

Equation (E.7.7.4) may then be written as

$$0.5 \ln \left[\left(m_{Ca^{2+}} \; - \; \frac{K_{sp}}{K_D a_{H_2O}^2} \right) \left(m_{SO_4^{2-}} \; - \; \frac{K_{sp}}{K_D a_{H_2O}^2} \right) \right] \; = \; \ln s_o \; + \; \frac{4S \, (I')^{\frac{1}{2}}}{1 + A(I')^{\frac{1}{2}}} \; - \; B'I' \; - \; C'(I')^2 \tag{E.7.7.7}$$

where s_o is $(K_{sp})^{\frac{1}{2}}$ and is therefore the hypothetical solubility of gypsum at zero ionic strength. Given a fixed arbitrary value of K_D, solubility data for one of the added salts could be used to obtain best fit values of s_o, A, B' and C'. This was carried out using a non-linear least squares procedure as follows:

(i) suitable initial values were chosen for K_{sp}, A, B' and C' (if these differed excessively from the unknown best fit values, the iteration diverged);

(ii) I was calculated for each solution;

(iii) the parameters of Lietzke and Stoughton (41) were used to calculate a value for the osmotic coefficient of each solution using

$$\phi \; = \; 1 \; - \; S \; \frac{|Z_+Z_-|}{A^3 \, I} \left[1 \; + \; A \, I^{\frac{1}{2}} \; - \; 2\ln(1 + A \, I^{\frac{1}{2}}) \; - \; \frac{1}{1 + A \, I^{\frac{1}{2}}} \right] + \; BI \; + \; CI^2 \; + \; DI^3 \tag{E.7.7.8}$$

(iv) water activities were evaluated using

$$\ln a_{H_2O} \quad = \quad - \, 0.018015 \, \phi \sum_i m_i \tag{E.7.7.9}$$

where m_i is the molality of all solute species. (At low concentrations of added salt, the calculated value of ϕ is too high, but the error in the water activity is negligible.);

(v) I' was calculated from

$$I' = I - \frac{4\,K_{sp}}{K_D\,a^2_{H_2O}}$$

and the value of the L.H.S. of (E.7.7.7) was computed for each solution;

(vi) best fit values of s_0, A, B' and C' were computed. The iteration procedure was terminated when the calculated shifts to each parameter were all less than one tenth of the respective standard deviations of the parameters;

(vii) the osmotic coefficients were re-computed, but substituting I' for I;

(viii) water activities were recomputed with better values of ϕ and $\sum_i m_i$;

(ix) the cycle from (v) to (ix) was repeated until the difference between the old and new K_{sp} values was less than 10^{-8} mol^2 kg^{-2}.

The original fixed value of K_D was then decreased by an arbitrary shift and the iteration procedure repeated, but this time starting at (v). It was necessary to start with a large value of K_D and gradually step down, due to oscillation and other problems which caused difficulties at low values of K_D. The calculations were carried out on an I.C.L. 1907 computer using double precision (about 22 significant figures) in order to ensure that accuracy was not lost at the matrix inversion stage. This precision was necessary when interparameter correlation coefficients were high.

7.7.3 Details of calculations carried out and results obtained

Initial computations were made with the assumption of zero ionic association. Best fit parameters for all three systems were evaluated using both (E.7.7.3) and (E.7.7.4). Calculations were carried out with the concentration range restricted to I less than unity using all four parameters, and also with C set at zero. These calculations were repeated using data for the whole concentration range using four parameters, and also with an additional term in $D(I')^3$ included in (E.7.7.1). When the high concentration data was included, difficulty was experienced obtaining convergent iterations. This was overcome by using an alternating iterative procedure. In one cycle parameter A was held constant. The problem was then linear and best fit values for the other parameters could be computed exactly.

In the next cycle, the shifts to all the parameters were computed by a non-linear method, but only a fraction of the calculated shifts were added to the parameters deduced in the preceding linear cycle. This reduced the speed of the process but avoided divergent solutions.

A synopsis of the results obtained is given in Tables 7.7.1 and 7.7.2. The symbol V represents the variance of fit of the experimental values of the L.H.S. of (E.7.7.7) (with K_D set at infinity) to values calculated using the best fit values of the parameters in the R.H.S. V is defined by

TABLE 7.7.1 RESULTS OF LEAST SQUARES FITTING USING DATA FOR THE WHOLE CONCENTRATION RANGE

Added Electrolyte	Quantity Tabulated in Columns 3 to 6	$\ln a^2_{H_2O}$ incorporated in B', C' and D'		$\ln a^2_{H_2O}$ calculated separately	
		4 Parameter Fit	5 Parameter Fit	4 Parameter Fit	5 Parameter Fit
Na_2SO_4	$\ln s_0$	- 5.0949	- 5.1027	- 5.0935	- 5.1016
	A	1.1111	1.1469	1.1765	1.0507
	B' or B	- 0.09057	- 0.00278	- 0.07078	0.02098
	C' or C	0.00488	- 0.02200	0.00491	- 0.02300
	D' or D	-	0.00280	-	0.002905
	$10^5 \times K_{sp}$	3.7554	3.6968	3.7658	3.7045
	$10^5 \times V$	2.799	1.802	2.8497	1.765
$CaCl_2$	$\ln s_0$	- 5.0766	- 5.0797	- 5.0749	- 5.0786
	A	1.2100	1.1852	1.2181	1.1887
	B' or B	0.01310	0.04210	0.03374	0.06795
	C' or C	0.00898	0.00111	0.01347	0.00417
	D' or D	-	0.00070	-	0.00082
	$10^5 \times K_{sp}$	3.8948	3.8710	3.9080	3.8797
	$10^5 \times V$	1.330	1.195	1.408	1.186
NaCl	$\ln s_0$	- 5.0362	- 5.0028	- 5.0332	- 5.0003
	A	1.5152	1.7742	1.5192	1.7747
	B' or B	- 0.02508	- 0.2332	0.02743	- 0.1773
	C' or C	0.01818	0.08409	0.02427	0.08916
	D' or D	-	- 0.00662	-	- 0.00652
	$10^5 \times K_{sp}$	4.2226	4.5141	4.248	4.537
	$10^5 \times V$	17.35	3.065	17.09	3.233

SYMBOL	A	B' or B	C' or C	D' or D	K_{sp}
UNITS	$kg^{\frac{1}{2}}\ mol^{-\frac{1}{2}}$	$kg\ mol^{-1}$	$kg^2\ mol^{-2}$	$kg^3\ mol^{-3}$	$mol^2\ kg^{-2}$

TABLE 7.7.2 RESULTS OF LEAST SQUARES FITTING USING ONLY DATA FOR WHICH I IS LESS THAN UNITY

Added Electrolyte	Quantity Tabulated in Columns 3 to 6	$\ln a^2_{H_2O}$ incorporated in B' and C'		$\ln a^2_{H_2O}$ calculated separately	
		3 Parameter Fit	4 Parameter Fit	3 Parameter Fit	4 Parameter Fit
Na_2SO_4	$\ln s_0$	- 5.1081	- 5.1081	- 5.1069	- 5.1258
	$\sigma (\ln s_0)$	0.00269	0.00319	0.00268	0.00321
	A	1.0131	0.7326	1.0183	0.7413
	B' or B	0.02831	0.6569	0.04874	0.6660
	C' or C	-	- 0.3002	-	- 0.2959
	$10^5 \times K_{sp}$	3.6574	3.5205	3.6660	3.5300
	$10^5 \times V$	1.327	0.4455	1.308	0.4473
$CaCl_2$	$\ln s_0$	- 5.0831	- 5.0936	- 5.0822	- 5.0922
	$\sigma (\ln s_0)$	0.00257	0.00484	0.00255	0.00492
	A	1.1567	1.0178	1.1565	1.0255
	B' or B	0.07552	0.32870	0.10765	0.34580
	C' or C	-	- 0.11799	-	- 0.1114
	$10^5 \times K_{sp}$	3.8450	3.7646	3.8515	3.7755
	$10^5 \times V$	0.8977	0.6324	0.8809	0.6531
NaCl	$\ln s_0$	- 5.0181	- 5.0056	- 5.0166	- 5.0035
	$\sigma (\ln s_0)$	0.00148	0.00137	0.00153	0.00137
	A	1.6178	1.7605	1.6076	1.7562
	B' or B	- 0.07182	- 0.2314	- 0.00473	- 0.1717
	C' or C	-	0.08434	-	0.08815
	$10^5 \times K_{sp}$	4.3785	4.4896	4.392	4.5078
	$10^5 \times V$	0.4522	0.0956	0.4847	0.0951

SYMBOL	A	B' or B	C' or C	K_{sp}
UNITS	$kg^{\frac{1}{2}}\ mol^{-\frac{1}{2}}$	$kg\ mol^{-1}$	$kg^2\ mol^{-2}$	$mol^2\ kg^{-2}$

$$V = \sum_i \Delta_i^2 / (N - M) \qquad (E.7.7.10)$$

where Δ is the difference between experimental and calculated values, N is the number of pairs of data points and M is the number of parameters. $\sigma(\ln s_0)$ is the standard deviation of $\ln s_0$. Standard deviations of the other parameters were calculated, but are not tabulated.

Following these initial calculations, the least squares fitting procedure was continued with various K_D values in the range 0.02 to 0.003 mol kg^{-1}. Results were obtained with the concentration range limited to I less than unity using 3 and 4 parameter fits, and with data for the whole concentration range using 4 parameter fits. Calcium chloride data covering the whole concentration range could not be treated unless values of K_D greater than 0.02 were used. Calculations were therefore carried out on this system with K_D set at 0.022 and 0.024 mol kg^{-1}. Water activities were included in the empirical extension terms, since the initial work had shown that independent calculation of water activities did not significantly affect any of the important parameters or variances.

The results of this work are summarised in Tables 7.7.3, 7.7.4 and 7.7.5.

7.7.4 Discussion

The results of the initial calculations, with K_D set at infinity, provide a number of points worthy of note.

(i) The best fit value of K_{sp} for a given salt was not markedly dependent on the concentration range used, the method of incorporation of water activities, or the number of empirical extension terms used.

(ii) The mean values of K_{sp} obtained for the three added electrolytes were 3.662×10^{-5}, 3.849×10^{-5} and 4.411×10^{-5} $mol^2\ kg^{-2}$ for Na_2SO_4, $CaCl_2$ and NaCl respectively. The differences between all three pairs of values were found to be statistically significant at the 95% confidence limit.

(iii) All the K_{sp} values are much higher than the result obtained in Part I (2.63×10^{-5} $mol^2\ kg^{-2}$).

(iv) Best fit values of parameter A were also quite different for the different salts. If the equations used were physically consistent with the properties of the solutions, such large differences in A would not be expected. The A parameter is intended to be directly proportional to the mean closest approach distance of calcium ions with all other ions in solution and of sulphate ions with all other ions in solution. The best fit values of A for Na_2SO_4 and NaCl, with 4 variable parameters and I restricted to less than unity, correspond to distances of closest approach of 0.22 nm and 0.54 nm. This large difference cannot be accounted for by the small difference in size between the effective ionic diameters of chloride and sulphate ions.

TABLE 7.7.3 EFFECT OF VARIATION IN K_D USING DATA FOR WHOLE CONCENTRATION RANGE

Added Electrolyte	K_D /mol kg^{-1}	$\ln s_o$	A /kg$^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$	B' /kg mol^{-1}	C' /kg^2 mol^{-2}	$10^5 \times K_{sp}$ /mol^2 kg^{-2}	$10^5 \times V$	σ ($\ln s_o$)
Na_2SO_4	0.018	- 5.1670	1.1714	- 0.1417	0.01001	3.232	1.457	0.00184
	0.016	- 5.1786	1.1798	- 0.1485	0.01071	3.176	1.353	0.00178
	0.014	- 5.1895	1.1905	- 0.1573	0.01160	3.108	1.252	0.00172
	0.012	- 5.2037	1.2054	- 0.1691	0.01281	3.021	1.177	0.00167
	0.010	- 5.2223	1.2264	- 0.1855	0.01450	2.910	1.201	0.00170
	0.008	- 5.2491	1.2599	- 0.2109	0.0174	2.759	1.561	0.00195
	0.006	- 5.2909	1.3216	- 0.2552	0.02180	2.538	3.274	0.00288
	0.004	- 5.3639	1.4683	- 0.3500	0.03200	2.193	12.509	0.00584
$CaCl_2$	0.024	- 5.1148	1.4564	- 0.1651	0.04572	3.6087	21.73	0.00908
	0.022	- 5.1112	1.5460	- 0.2313	- 0.05853	3.6345	46.09	0.01354
NaCl	0.018	- 5.1427	1.4099	- 0.00553	0.01788	3.413	1.629	0.00579
	0.016	- 5.1541	1.3984	- 0.00304	0.01781	3.336	1.612	0.00574
	0.014	- 5.1683	1.3841	- 0.00015	0.01772	3.242	1.591	0.00569
	0.012	- 5.1858	1.3664	0.00426	0.01758	3.131	1.564	0.00561
	0.010	- 5.2099	1.3417	0.01027	0.01737	2.983	1.523	0.00551
	0.008	- 5.2426	1.3083	0.01900	0.01701	2.795	1.464	0.00536
	0.006	- 5.3939	1.2563	0.03401	0.01633	2.527	1.368	0.00511

TABLE 7.7.4 EFFECT OF VARIATION IN K_D USING DATA FOR WHICH I IS LESS THAN UNITY WITH FOUR VARIABLE PARAMETERS

Added Electrolyte	K_D /mol kg^{-1}	$\ln s_o$	A /kg$^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$	B' /kg mol^{-1}	C' /kg^2 mol^{-2}	$10^5 \times K_{sp}$ /mol^2 kg^{-2}	$10^5 \times V$	σ ($\ln s_o$)
Na_2SO_4	0.020	- 5.1835	0.8608	0.4397	- 0.2511	3.145	0.535	0.00361
	0.018	- 5.1893	0.8763	0.4151	- 0.2451	3.109	0.522	0.00358
	0.016	- 5.1964	0.8960	0.3843	- 0.2375	3.065	0.539	0.00366
	0.014	- 5.2057	0.9228	0.3434	- 0.2272	3.009	0.588	0.00385
	0.012	- 5.2175	0.9589	0.2899	- 0.2136	2.938	0.607	0.00395
	0.010	- 5.2336	1.0118	0.2147	- 0.1941	2.845	0.678	0.00423
	0.008	- 5.2561	1.0944	0.1049	- 0.1649	2.720	0.814	0.00473
	0.006	- 5.2920	1.2506	- 0.0798	- 0.1149	2.532	1.161	0.00587
	0.004	- 5.3543	1.6333	- 0.4251	- 0.0251	2.235	2.541	0.00949
$CaCl_2$	0.020	- 5.1526	1.656	0.2024	- 0.0834	3.346	0.468	0.00432
	0.018	- 5.1586	1.1833	0.1890	- 0.0795	3.306	0.415	0.00409
	0.016	- 5.1660	1.2060	0.1724	- 0.0748	3.258	0.392	0.00400
	0.014	- 5.1756	1.2369	0.1508	- 0.0685	3.195	0.412	0.00413
	0.012	- 5.1879	1.2785	0.1238	- 0.0605	3.118	0.327	0.00372
	0.010	- 5.2046	1.3393	0.0879	- 0.0499	3.017	0.286	0.00353
	0.008	- 5.2277	1.4337	0.0414	- 0.0359	2.879	0.247	0.00336
	0.006	- 5.2646	1.6100	- 0.0159	- 0.0188	2.674	0.272	0.00368
	0.004	- 5.3280	2.0082	0.0074	- 0.0230	2.356	0.394	0.01526

TABLE 7.7.4 (Continued)

Added Electrolyte	K_D /mol kg^{-1}	$\ln s_o$	A /kg$^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$	B' /kg mol^{-1}	C' /kg^2 mol^{-2}	$10^5 \times K_{sp}$ /mol^2 kg^{-2}	$10^5 \times V$	σ ($\ln s_o$)
NaCl	0.020	- 5.1127	1.6166	- 0.1974	0.0799	3.624	0.113	0.00144
	0.018	- 5.1233	1.6013	- 0.1923	0.0789	3.547	0.114	0.00146
	0.016	- 5.1359	1.5831	- 0.1860	0.0775	3.460	0.117	0.00145
	0.014	- 5.1508	1.5610	- 0.1777	0.0757	3.358	0.119	0.00146
	0.012	- 5.1701	1.5321	- 0.1659	0.0729	3.231	0.122	0.00147
	0.010	- 5.1966	1.4907	- 0.1476	0.0682	3.064	0.127	0.00148
	0.008	- 5.2323	1.4336	- 0.1186	0.0605	2.853	0.132	0.00149
	0.006	- 5.2856	1.3440	- 0.0647	0.0452	2.564	0.140	0.00150

TABLE 7.7.5 EFFECT OF VARIATION IN K_D USING DATA FOR WHICH I IS LESS THAN UNITY WITH THREE VARIABLE PARAMETERS

Added Electrolyte	K_D /mol kg^{-1}	$\ln s_o$	A /k$^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$	B' /kg mol^{-1}	$10^5 \times K_{sp}$ /mol^2 kg^{-2}	$10^5 \times V$	σ ($\ln s_o$)
Na_2SO_4	0.014	- 5.1935	1.1402	- 0.0919	3.083	1.174	0.00263
	0.012	- 5.2066	1.1655	- 0.1142	3.003	1.159	0.00263
	0.010	- 5.2241	1.2022	- 0.1458	2.900	1.153	0.00265
	0.008	- 5.2480	1.2597	- 0.1932	2.764	1.175	0.00272
	0.005	- 5.3149	1.4761	- 0.3510	2.419	1.637	0.00339
	0.004	- 5.3532	1.6651	- 0.4664	2.240	2.452	0.00434
	0.003	- 5.4055	2.1041	- 0.6748	2.018	5.331	0.00785
$CaCl_2$	0.014	- 5.1703	1.3225	0.0148	3.229	0.455	0.00192
	0.012	- 5.1836	1.3559	0.0047	3.145	0.397	0.00180
	0.010	- 5.2011	1.4091	- 0.0085	3.036	0.330	0.00167
	0.008	- 5.2253	1.4826	- 0.0263	2.893	0.263	0.00152
	0.005	- 5.2897	1.7786	- 0.0573	2.543	0.372	0.00194
	0.004	- 5.3272	2.0482	- 0.0290	2.350	0.891	0.00320
NaCl	0.014	- 5.1578	1.4530	- 0.0339	3.311	0.402	0.00134
	0.012	- 5.1765	1.4301	- 0.0272	3.190	0.384	0.00136
	0.010	- 5.2020	1.3984	- 0.0173	3.031	0.355	0.00125
	0.008	- 5.2358	1.3559	- 0.0029	2.833	0.314	0.00115
	0.005	- 5.3255	1.2398	0.0438	2.368	0.186	0.00087
	0.004	- 5.3752	1.1735	0.0758	2.144	0.147	0.00076

(v) Comparison of the results obtained by Marshall and Slusher (7) for NaCl at 25°C with present results obtained under the same conditions (Table 7.7.1, column 3), shows that agreement is very good. Marshall's results for K_{sp}, A, B' and C' were 4.231×10^{-5}, 1.50, 0.0194 and 0.0134 in the same units. The different sign of B' arises from arbitrary choice of signs in his equation (6) in order to give positive signs to all best fit parameters.

(vi) As expected, increasing the number of variable parameters, always reduced the variance of fit (V). This was not so with the standard deviations of the parameters. When the number of parameters was increased from 3 to 4, σ ($\ln s_0$) for example, was only reduced for NaCl solutions. The mathematical reason for this is that the correlation coefficients between parameters were high, so that increasing the number of parameters allowed greater compensating variations in their values without significantly affecting the variance of the fit. This consequently led to a greater uncertainty in the values of the parameters.

The main conclusion of this initial work was that the criticisms of this procedure as a method of obtaining a value for K_{sp} which were made in section 1.2.4, were fully justified. The question which naturally arises is whether the introduction of a "suitable" dissociation constant for $CaSO_4$ ion pairs enables a reliable value for K_{sp} to be derived. The criteria which are available for choosing a "suitable" value for K_D are as follows.

(i) It should lead to best fit values of K_{sp} for the three salts which are not significantly different.

(ii) It should give best fit values of A for the three salts which are not unreasonably different.

(iii) It should give the best overall fit to the data.

(iv) It should give the lowest overall standard deviation of K_{sp}.

(v) It should not be unreasonably different to literature values for K_D.

If a value can be found which satisfies all or most of these criteria, and the corresponding mean value of K_{sp} is compared with that obtained in Part I, the question posed above may then be answered. The criteria given above were tested by constructing graphs (with K_D as abscissa) of $\ln s_0$, A, the sum of V for the three salts and the sum of σ ($\ln s_0$) for the three salts. These are presented in Figures 7.7.1, 7.7.2, 7.7.3 and 7.7.4, respectively. It is evident that to satisfy criteria (iii) and (iv), K_D must lie in the range 0.0055 to 0.008 with a most probable value of 0.0065 mol kg^{-1}. This is a little higher than literature values, but is certainly not untenable. With K_D fixed at this value, the range of A values for the three salts is also at a minimum with a mean of 1.39 kg$^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$. This corresponds to a "distance of closest approach" of 0.42 nm. A precise physical interpretation of this distance is difficult when the concept of ion-pairing is introduced for mixed electrolyte solutions. Consequently, the only comment which can sensibly be made concerning the A values is that they are not unreasonable either in range or magnitude. The range of $\ln s_0$ values is also at a shallow minimum in the region of K_D = 0.0065 mol kg^{-1}. Corresponding values of K_{sp} are (2.58, 2.64 and 2.73) $\times$ 10^{-5} mol^2 kg^{-2} for Na_2SO_4, NaCl and $CaCl_2$ solutions. A suitable value of K_D has therefore been found which not only satisfies the five criteria, but also leads to values of K_{sp} which are in excellent agreement with that derived in Part I.

Two criticisms of Marshall and Slusher's method of obtaining K_{sp} were made in section 1.2.4.

FIGURE 7.7.2

BEST FIT VALUES OF Å USING ONLY DATA FOR WHICH I IS LESS THAN UNITY

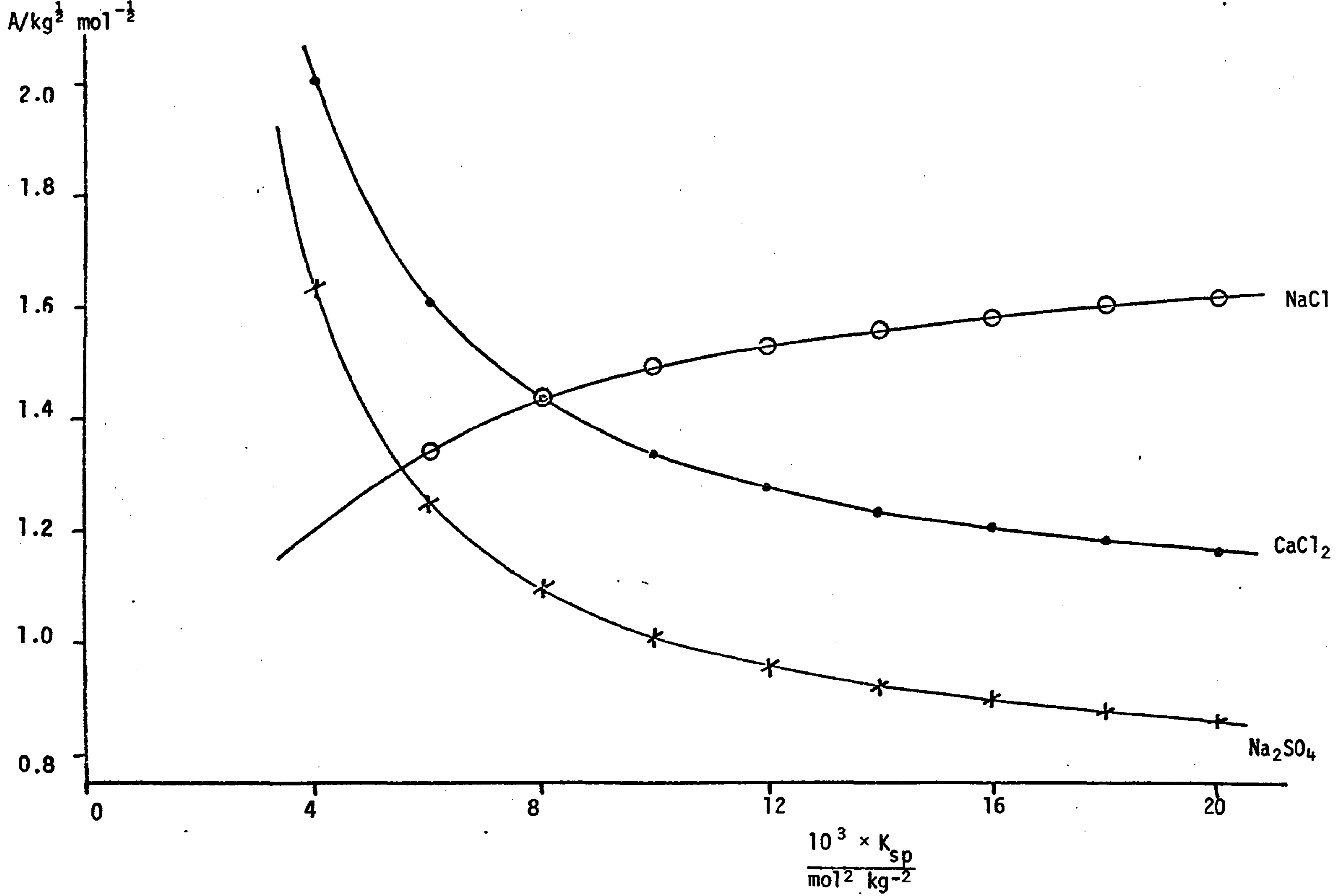


FIGURE 7.7.3 SUMMATION OF VARIANCE OF FIT FOR NaCl, $CaCl_2$ AND Na_2SO_4 SOLUTIONS USING ONLY DATA FOR WHICH I IS LESS THAN UNITY

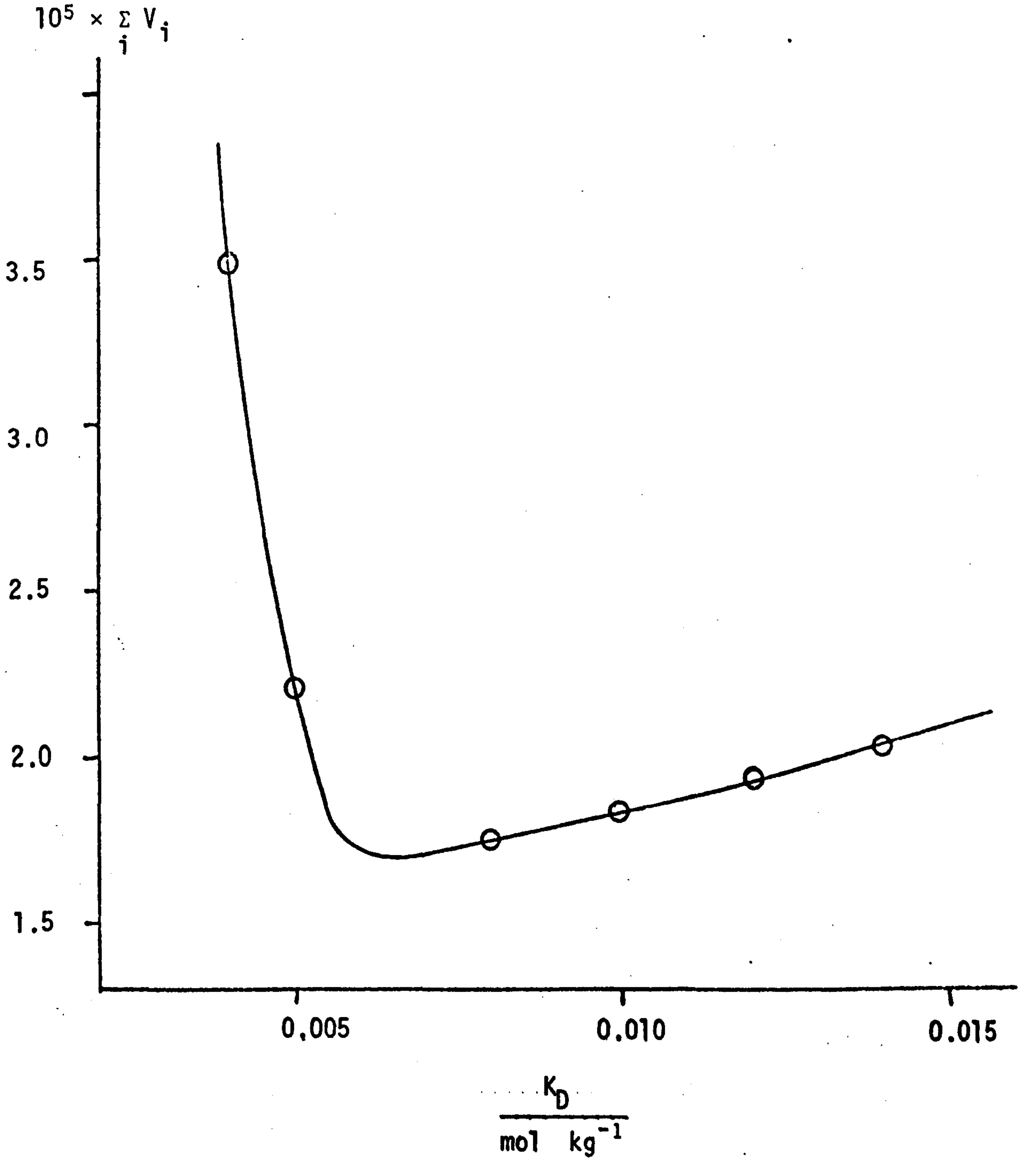
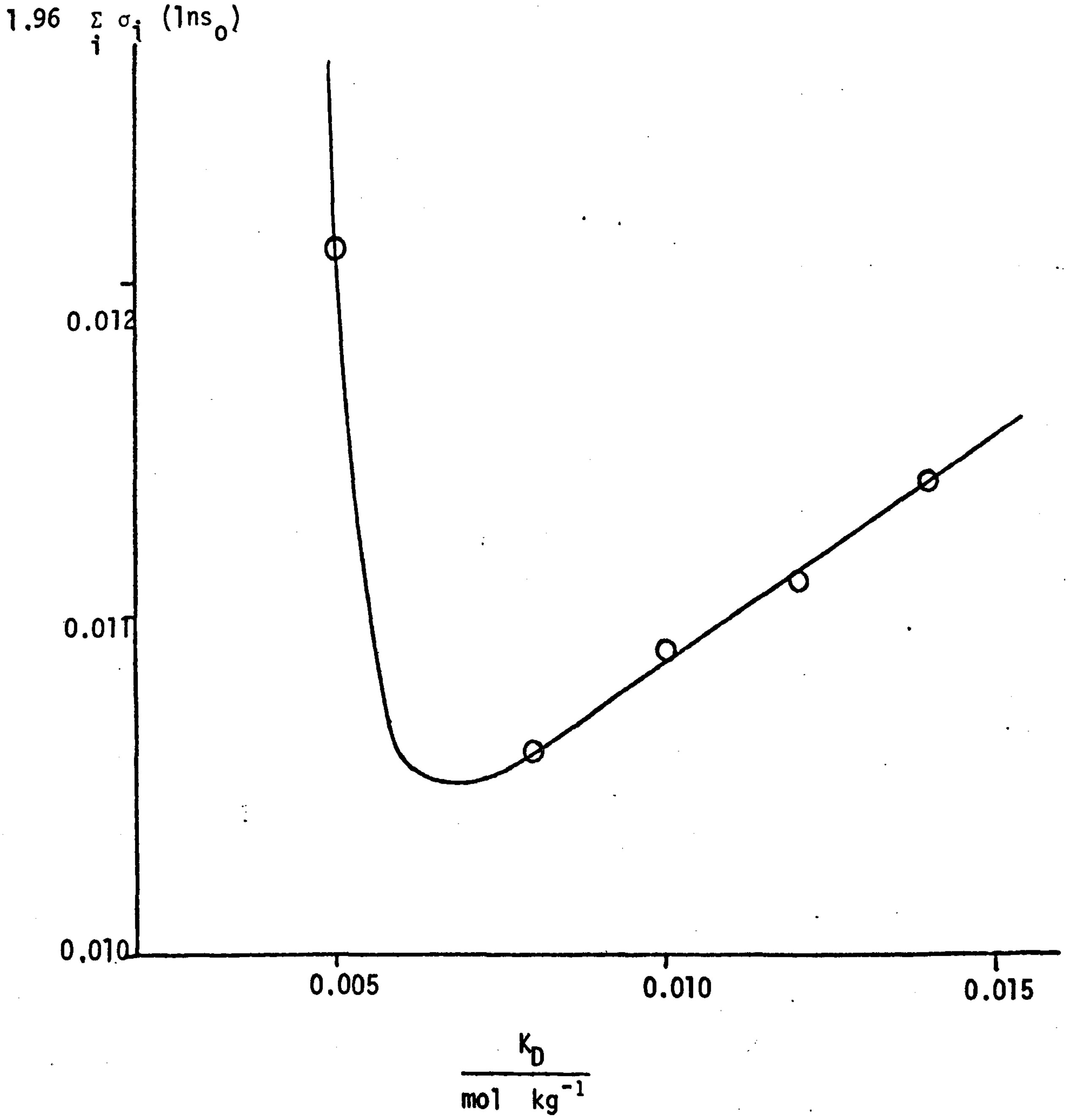


FIGURE 7.7.4 SUMMATION OF 95% CONFIDENCE LIMITS ON $\ln s_0$ FOR $NaCl$, $CaCl_2$ AND Na_2SO_4 SOLUTIONS USING ONLY DATA FOR WHICH I IS LESS THAN UNITY



The present procedure effectively compensates for Marshall's inadequate treatment of ion association, but does not tackle the second criticism. This was that the ionic strength dependence of $CaSO_4$ activity coefficients below the solubility limit, must be different to that above the limit where the major contribution to a change in ionic strength is a change in foreign electrolyte concentration. The small range of K_{sp} values for the three added salts when K_D was fixed at 0.0065 mol kg^{-1} suggests that this problem may not be of great importance. It was therefore concluded that a reliable value for the thermodynamic solubility product of gypsum may be obtained from solubility measurements, provided ion association is adequately treated, and measurements are made in a minimum of three foreign electrolytes. The uncertainty in the value deduced is however greater than that of the method used in Part I, and the treatment is less thermodynamically sound. The best estimate of K_{sp} determined in this section is $(2.65 \pm 0.3) \times 10^{-5}$ mol^2 kg^{-2}.

7.7.5 Treatment for the whole concentration range

One aspect of the previous section which caused concern was the inability of the treatment to fit the $CaCl_2$ data over the whole concentration range. If data for the most concentrated $CaCl_2$ solution is considered, the reason for this becomes apparent. The solubility of gypsum was found to be 0.002665 molal and the water activity of the solution was calculated as 0.854. It is evident that the concentration of $CaSO_4$ ion pairs cannot be greater than 0.002665 molal and consequently if equation (7.7.6) is to be satisfied, a minimum value of K_D may be calculated from

$$K_D\ (\text{min}) \quad = \quad \frac{K_{sp}}{0.002665 \times 0.854^2}$$

Taking K_{sp} to be 2.63×10^{-5} mol^2 kg^{-2} gives K_D (min) as 0.0135 mol kg^{-1}. The failure of the least squares procedure to fit the $CaCl_2$ data for K_D values lower than 0.022 mol kg^{-1} is a result of necessity of working from high to low K_D values for all the salts. The higher the value of K_D, the higher is the value of K_{sp} required to give a best fit to the data, and consequently the minimum value of K_D is higher under these conditions.

It is clear that the gypsum solubility data in concentrated calcium chloride solutions, is inconsistent with the equations defined in section 7.7.2 when K_D is fixed at the best fit value of 0.0065 mol kg^{-1}. This unsatisfactory situation would only be exacerbated by the introduction of higher associations for calcium and sulphate ions. There are two alternative ways of rationalising this problem:

(i) assume that K_D is not concentration independent;

(ii) assume that $\gamma_{CaSO_4^0}$ deviates from unity at high $CaCl_2$ concentrations.

K_D is defined by

$$K_D \quad = \quad \exp\left[\frac{\overset{o}{\mu}_{CaSO_4^0} - \overset{o}{\mu}_{Ca^{2+}} - \overset{o}{\mu}_{SO_4^{2-}}}{RT}\right] \quad = \quad \frac{a_{Ca^{2+}}\, a_{SO_4^{2-}}}{a_{CaSO_4^0}}$$

Definition of standard chemical potential terms in the usual manner, with pure solvent defined as the reference state, requires that K_D is invariant. If the reference state "solvent" is chosen as the particular calcium chloride solution concerned, K_D is then a function of calcium chloride concentration. This assumption does not provide a suitable method of obviating the problem, since no independent guide to the expected functional dependence of K_D is available.

The activity coefficient of ion pairs, $\gamma_{CaSO_4^0}$ may be related to experimental activity coefficients of non electrolytes (n.e.) in electrolyte solutions. A linear relationship between log $\gamma_{n.e.}$ and the molality m_e of added electrolyte is expected from theory (90, p. 585). Pitzer and Brewer (90) tabulate k values satisfying the equation

$$\log_{10} \gamma_{n.e.} = k\, m_e \qquad \text{(E.7.7.11)}$$

for a number of non electrolytes in a variety of one molal salt solutions. The tabulated values of k are generally in the range 0.1 ±0.1 mol^{-1}. These positive values correspond to "salting out" of non electrolyte by the added electrolyte.

A minimum value of $\gamma_{CaSO_4^0}$ can be calculated such that all sulphate ions in the most concentrated $CaCl_2$ solution are present as ion-pairs. This gives

$$\gamma_{CaSO_4^0} \text{ (min)} = \frac{2.63 \times 10^{-5}}{0.0065 \times (0.854)^2 \times 0.002665} = 2.08$$

Using this result in (E.7.7.11) together with the concentration of $CaCl_2$ (2.07 molal) shows that the minimum value of k compatible with the observed gypsum solubility is +0.154 mol^{-1}. This result is seen to be quite consistent with the experimental values of k given in reference 90.

Assumption (ii) was therefore chosen as being the more suitable, and the solubility data was treated using the assumption that

$$\log_{10}\gamma_{CaSO_4^0} = 0.1\ I' \qquad \text{(E.7.7.12)}$$

for all three added salts. This is approximately equivalent to a k value of twice the minimum value for calcium chloride solutions; a choice made so as to give a reasonable safety margin during the iterative calculations. Equation (7.7.12) was incorporated into the original treatment by replacing the factor

$$\frac{K_{sp}}{K_D\, a^2_{H_2O}} \quad \text{by} \quad \frac{K_{sp}}{K_D\, a^2_{H_2O} \exp\,(0.2303\ I')}$$

in equations (7.7.6) and (7.7.7).

These modifications enabled all three sets of data to be fitted over the whole concentration range using K_D values down to 0.004 mol kg^{-1}. Since the introduction of (E.7.7.12) was only of importance at high concentrations of added salt and the magnitude of K_{sp} and A were essentially controlled by the low concentration data, the new method of treatment gave almost unchanged values for these parameters. The conclusions which may be drawn from this modified analysis are:

(i) introduction of non-ideality for ion-pairs allowed all the data to be sensibly treated;

(ii) the best fit value of K_{sp} was essentially unchanged from that deduced in the original treatment.

7.7.6 Solubility data in ternary electrolyte solutions

Treatment of gypsum solubilities in mixed electrolyte solutions would probably have enabled a slightly more reliable value of K_{sp} to be obtained. These additional results were not analysed however since the limited objectives of this section were already satisfactorily achieved.

7.8 CALCULATION OF STOICHIOMETRIC MEAN MOLAL IONIC ACTIVITY COEFFICIENTS FOR CALCIUM SULPHATE IN THE GYPSUM SATURATED SOLUTIONS

Experimental solubilities of gypsum in the various single and mixed electrolyte solutions, together with the reliable value for K_{sp} obtained in Part I, enabled stoichiometric activity coefficients for calcium sulphate to be calculated from equation (1.1.1)

$$K_{sp} = m_{Ca^{2+}} m_{SO_4^{2-}} \gamma^2_{\pm CaSO_4} a^2_{H_2O} \qquad \text{(E.1.1.1)}$$

The only additional information required was the water activity. This was calculated using equation (7.7.9) with the same assumptions that dissolved gypsum was included in the summation of m_i, but that the osmotic coefficient was that associated with a solution of the added electrolytes only; except that the presence of dissolved gypsum was taken into account when evaluating the ionic strength.

When only a single foreign electrolyte was involved, osmotic coefficients were evaluated using the parameters of Lietzke and Stoughton (41) in equation (7.7.8).

Osmotic coefficients for the ternary system Na_2SO_4-$NaCl$-H_2O were calculated from isopiestic measurements at 25°C by Wu, Rush and Scatchard (91). The same authors treated this data utilising the equations developed by Scatchard (92). The equation used by Wu to express the osmotic coefficient was

$$\phi = 1 + \frac{I}{\nu_A m_A + \nu_B m_B} \Big[\alpha_A + (\alpha_B - \alpha_A) y_B + \beta^0_{AB} y_B (1 - y_B) + \beta'_{AB} y_B (1 - y_B)(1 - 2y_B) \Big] \qquad \text{(E.7.8.1)}$$

where

$$\alpha_J = \frac{2S}{(a^0_J)^3 I} \left[1 + a_J I^{\frac{1}{2}} - \frac{1}{1 + a_J I^{\frac{1}{2}}} - 2 \ln (1 + a_J I^{\frac{1}{2}}) \right] + a'_J I + a^2_J I^2 + a^3_J I^3 \qquad \text{(E.7.8.2)}$$

$$\beta^{0}_{AB} = b^{0,1}_{AB}\, I + b^{0,2}_{AB}\, I^2 + b^{0,3}_{AB}\, I^3 \qquad (E.7.8.3)$$

$$\beta'_{AB} = b^{1,2}_{AB}\, I^2 + b^{1,3}_{AB}\, I^3 \qquad (E.7.8.4)$$

y_J = ionic strength fraction of electrolyte J,

ν_J = number of moles of ions per mole of solute J,

m_J = molality electrolyte J,

a^n_J are best fit parameters to osmotic coefficients for pure electrolyte solutions,

$b^{m,n}_{AB}$ are best fit parameters required to account for additional interactions in the mixed (A-B) electrolyte solution,

and S = - 1.17202 (note the changed sign for the D-H limiting slope from that used previously).

The a^n_J parameters are closely related to the parameters compiled by Lietzke and Stoughton (41). a^0_J is the distance of closest approach parameter (A), and a'_J, a^2_J, a^3_J were evaluated by multiplying Lietzke's B, C and D respectively by the factor $-2/(Z_+Z_-)_J$ (N.B. Z_- taken to be negative). Wu found that for the system under consideration the standard deviation of fit to the osmotic coefficients was not significantly reduced by the inclusion of terms involving β'_{AB} or $b^{0,2}_{AB}$. The least squares fit using $b^{0,1}_{AB}$ and $b^{0,3}_{AB}$ was consequently taken as adequate, and the best fit values of these parameters were tabulated in (91).

Osmotic coefficients for the solutions used in the solubility measurements were therefore calculated using (7.8.1) and the values of a^n_J and $b^{0,n}_{AB}$ referred to above.

The system $NaCl$-$CaCl_2$-H_2O was investigated at 25°C by Robinson and Bower (93) using the isopiestic method. These workers analysed their data primarily from the view point of evaluating activity coefficients. In Part III of this thesis, the raw experimental data was treated using the theoretical approach of Friedman (94) based on cluster expansion methods. Values of ω_0 were obtained for each solution studied by Robinson, using the equation

$$y_A y_B\, I\, \omega_0 = 2y_A\,(\phi_{mix} - \phi^0_A) + y_B\,(\phi_{mix} - \phi^0_B) \qquad (E.7.8.5)$$

where A and B refer to the 1:1 and 2:1 salts respectively and ϕ^0_J is the osmotic coefficient of a pure solution of J at the same ionic strength as the mixed solution. ω_0 is a mixing parameter defined in Part III where equation (E.7.8.5) is derived. The values of ϕ^0_A, ϕ^0_B and also ϕ_{ref} for the NaCl reference solutions used in the isopiestic measurements were calculated using equation (7.7.8). For sodium chloride solutions, the parameters of Lietzke and Stoughton (41) were used, but for calcium chloride solutions the parameters used were determined independently by the same non-linear least squares procedure as in (41) but using different data. Osmotic coefficients in the mixed solutions were evaluated from the equation

$$\phi_{mix} = \frac{2\ m_{ref}\ \phi_{ref}}{2\ m_A + 3\ m_B} \qquad (E.7.8.6)$$

which derives directly from the equality of water activities in the reference and mixed electrolyte solutions.

In Figure 12.2 the calculated ω_o values are shown plotted against ionic strength. A detailed inspection of this figure shows that the large scatter in the data is primarily a result of neglect of asymmetry in the treatment used. For the present purpose, a better procedure would have been to replace ω_o in equation (7.8.1) by $\omega_o + \omega_1\ (y_A - y_B)$ and to obtain best fit values of parameters in

$$\begin{aligned} \omega_o &= A + BI + CI^2 \\ \omega_1 &= D + EI + FI^2 \end{aligned} \qquad (E.7.8.7)$$

A much simpler treatment was however used to account for the asymmetry, and its adequacy was subsequently checked by comparison with results in which asymmetry was neglected. The method adopted, was to assume a linear dependence of ω_o on ionic strength and obtain a best fit line of the form

$$\omega_o = 0.049 - 0.0045\ I\ \text{kg mol}^{-1} \qquad (E.7.8.8)$$

This was taken to be a satisfactory expression for the data having y_A equal to 0.5. Inspection of the deviations from (E.7.8.8) suggested, that for the remaining data, the relationship

$$\omega_o = 0.049 + D - 0.0045\ I \qquad (E.7.8.9)$$

with $D = +\ 0.01$ for $y_A = 0.333$ and $D = -\ 0.01$ for $y = 0.75$ would probably be of sufficient accuracy.

The results of all these computations are given in Tables 7.3.1, 7.3.2, 7.4.1, 7.5.1 and 7.6.1. In addition, values of $\ln\gamma_\pm$ ($CaSO_4$) are plotted against the function $I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$ in Figures 7.8.1, 7.8.2 and 7.8.3.

The effect of neglecting asymmetry in the NaCl-$CaCl_2$ results by using equation (7.8.8) for all the data, was to produce a negligible change in the 5th significant figure of $\ln\gamma_\pm$. This implies that non-asymmetry errors in ω_o were also negligible since it is unlikely that experimental errors in the isopiestic measurements would lead to ω_o values which were incorrect by amounts much greater than 0.01 kg mol^{-1}. Similar considerations apply to data for the other systems studied.

Possible errors in the individual activity coefficients arising from various sources were estimated as follows:

(i) ±3.4% in K_{sp} (see section 3.2.14);

(ii) ±0.26% in $m_{Ca^{2+}}$ and $m_{SO_4^{2-}}$. This is an estimate of the random errors in these molalities and was calculated directly from the 95% confidence limits for a single determination of gypsum solubility (see section 7.2);

FIGURE 7.8.1 CONCENTRATION DEPENDENCE OF $CaSO_4$ ACTIVITY COEFFICIENTS BELOW SATURATION AND AT SATURATION IN THE PRESENCE OF SINGLE ADDED ELECTROLYTES

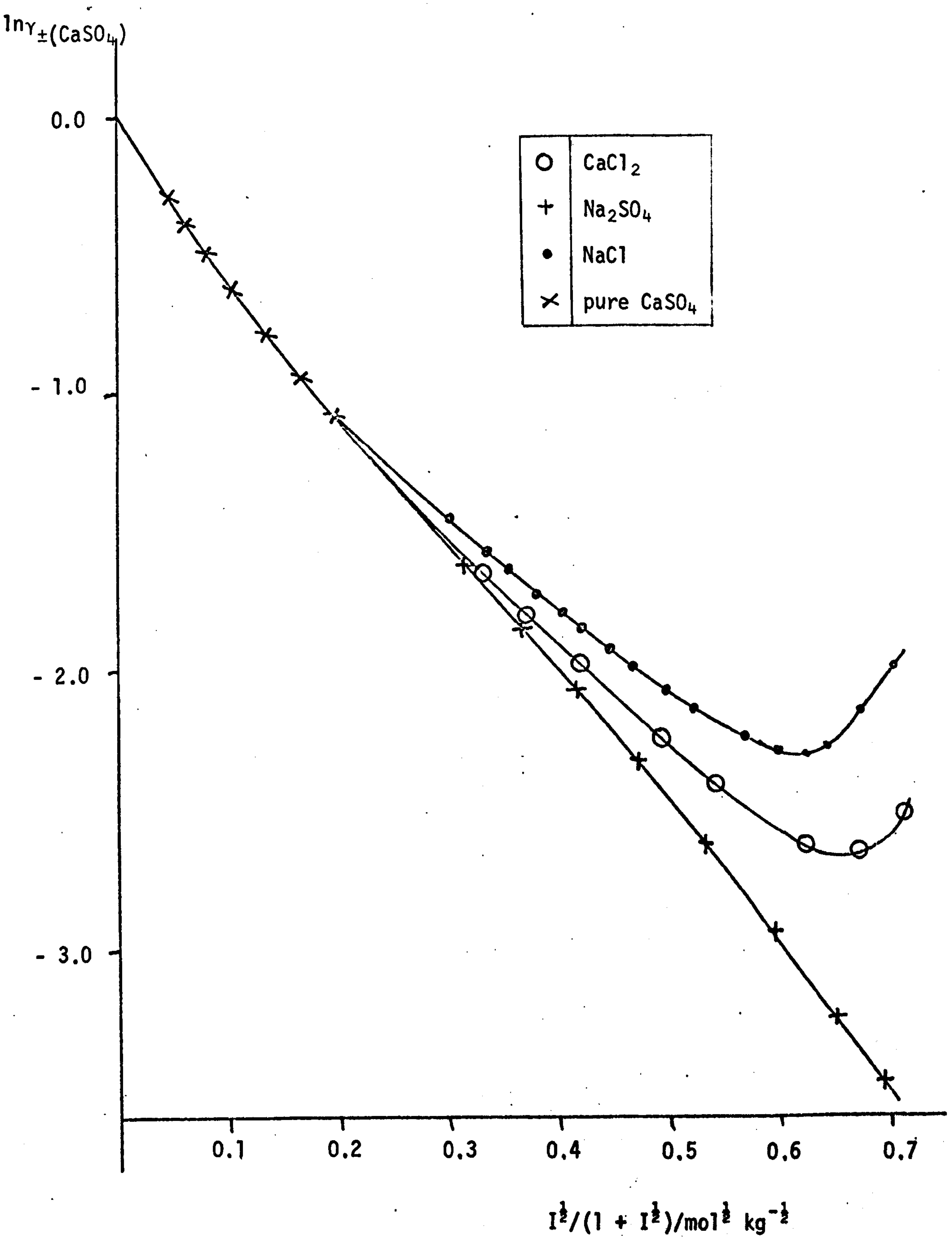
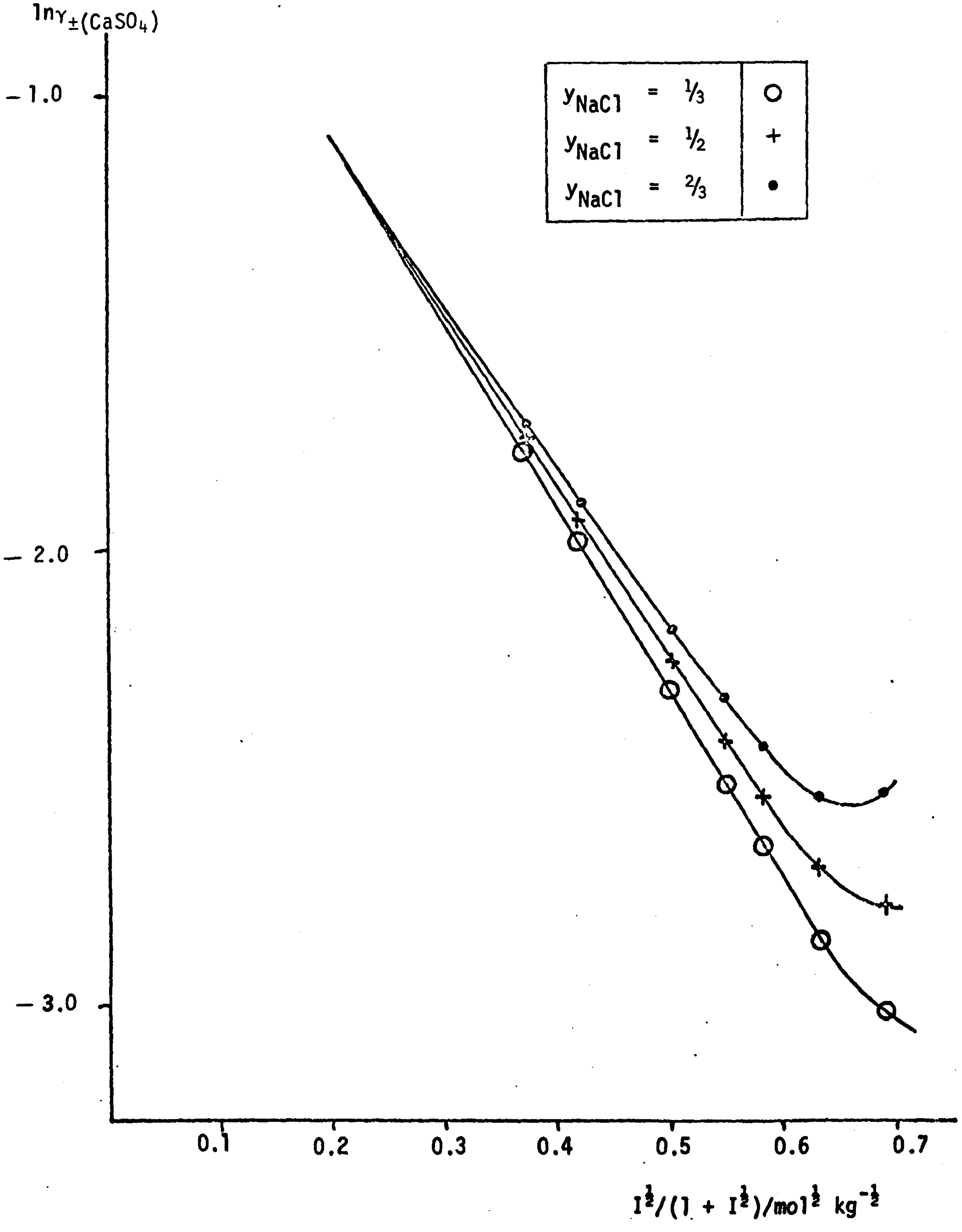


FIGURE 7.8.2 ACTIVITY COEFFICIENTS OF $CaSO_4$ AT SATURATION IN THE PRESENCE OF MIXED $NaCl - Na_2SO_4$ SOLUTIONS



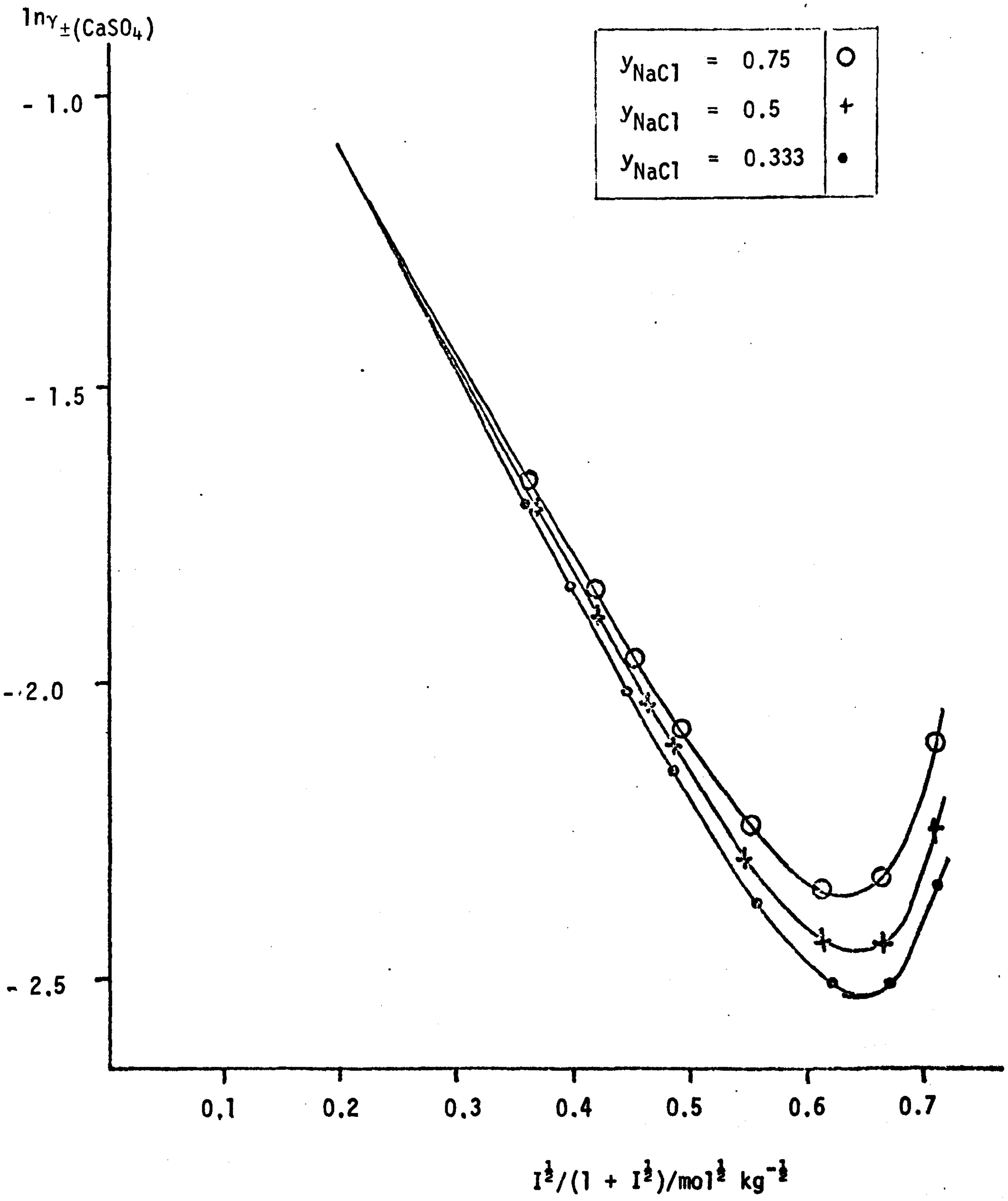


FIGURE 7.8.3 ACTIVITY COEFFICIENTS OF $CaSO_4$ AT SATURATION IN THE PRESENCE OF MIXED NaCl - $CaCl_2$ SOLUTIONS

(iii) ±0.5% in $m_{Ca^{2+}}$ and $m_{SO_4^{2-}}$. This is an estimate of possible systematic errors.

(iv) ±0.2% in a_{H_2O}.

The resulting uncertainty in $\gamma_\pm$ is ±2.9% of which ±2.2% arises from possible systematic errors. At the highest concentrations of added electrolytes, wider error limits would be appropriate and at the lowest concentrations the uncertainty in $\gamma_\pm$ would be smaller. The high precision of the results is clearly demonstrated by the smooth nature of the curves presented in Figures 7.8.1, 7.8.2 and 7.8.3.

At the highest concentrations of added salts, calcium sulphate activity coefficients in the NaCl and Na_2SO_4 solutions differed by factors in excess of 4. This demonstrates the importance of specific ion-ion interactions and the inadequacy of Lewis and Randall's "Principle of Ionic Strength" (95). It is interesting to note that qualitative differences between the calcium sulphate activity coefficients in the three single salt solutions may be explained by invoking the known (96) associative interactions between calcium and sulphate ions and between sodium and sulphate ions. Such associative interactions reduce the stoichiometric activity coefficients of the ions concerned. As a result, the activity coefficients are highest for NaCl-$CaSO_4$ solutions and lowest for Na_2SO_4-$CaSO_4$ solutions.

7.9 COMPARISON OF EXPERIMENTAL ACTIVITY COEFFICIENTS WITH VALUES PREDICTED USING SCATCHARD'S "IONS AS COMPONENTS" TREATMENT

In Scatchard's (97,98) "ions as components" treatment, the excess free energy of electrolyte mixtures (G^e) is divided into a Debye-Hückel contribution $(G^e)^{DH}$, and a non-Debye-Hückel contribution $(G^e)^n$. The second term then represents all the non-electrostatic contributions to G^e, and the residual electrostatic contributions not accounted for by $(G^e)^{DH}$. The non-Debye-Hückel term is expressed as a series of interaction terms involving products of the ion equivalent concentrations (m_i'):

$$\left(\frac{G^e}{RTW}\right)^n = \sum_i \sum_j b_{ij} m_i' m_j' + \sum_i \sum_j \sum_k d_{ijk} m_i' m_j' m_k' + \text{higher terms} \tag{E.7.9.1}$$

W is the number of kilograms of solvent and $m_i' = m_i z_i$, where m_i is the molality of species i and z_i is the absolute value of the valence of species i. The individual b_{ij} and d_{ijk} coefficients cannot be independently determined, but the coefficients can be arranged in groups each of which is measurable. Scatchard divides $(G^e)^n$ into two terms, $(G^e)^{nI}$ and $(G^e)^{nII}$. Best fit values of the grouped coefficients in $(G^e)^{nI}$, together with the best fit values for the distance of closest approach parameter in the Debye-Hückel term, may be evaluated from measurements on single salts. Values for the grouped coefficients in $(G^e)^{nII}$ may be derived from measurements on binary electrolyte solutions having a common ion. Expressions for the osmotic coefficient and mean ionic activity coefficients are derived from appropriate differentiations of the excess free energy. These expressions, together with a knowledge of the grouped coefficients and distances of closest approach for a particular system, enable the properties of any solution in the system to be calculated. Osmotic coefficients and mean ionic activity coefficients of the component electrolytes may be calculated at two levels of approximation. The full equations should give the most accurate values, but if contributions from $(G^e)^{nII}$ are neglected, reasonable estimates for dilute mixed electrolyte solutions may be calculated using experimental data on single electrolyte solutions alone.

Scatchard, Rush and Johnson (98) have used the above treatment for the system Mg^{2+}-Na^+-SO_4^{2-}-Cl^--H_2O (System I). Parameters derived from single salt osmotic coefficient data were obtained from the best fit parameters compiled by Lietzke and Stoughton (41). Osmotic coefficient data (91), on the four binary electrolyte systems with a common ion, were used to evaluate best fit parameters to the equation for $(\phi - 1)^{nII}$ (equation f, Table III, ref. 98). These parameters were used to calculate sodium chloride activity coefficients in mixed electrolyte solutions, and to calculate osmotic coefficients for the two binary electrolyte mixtures in system I which do not contain a common ion. The agreement between calculated and experimental results was very good up to the maximum concentrations studied (I = 8 molal).

In view of the success of this approach, it was thought that the treatment might prove capable of reasonable predictions of calcium sulphate activity coefficients in the system Na^+-Ca^{2+}-Cl-SO_4^{2-}-H_2O (System II). This was initially checked by using a straightforward comparison of experimental $CaSO_4$ activity coefficients in system II, with computed $MgSO_4$ activity coefficients in system I. In a second treatment, an attempt was made to derive parameters to fit osmotic coefficients in system II, and to subsequently use these parameters to compute $CaSO_4$ activity coefficients in the same system. Such a treatment is theoretically impossible for system II at the ionic strengths used in this study. Two of the properties required to derive best fit parameters are unmeasurable. This is a consequence of the limited solubility of gypsum. The properties concerned are:

(i) activity or osmotic coefficient data for pure $CaSO_4$ solutions up to the maximum ionic strength (~6 molal) of the system concerned;

(ii) osmotic coefficient data for the systems $CaSO_4$-Na_2SO_4-H_2O and $CaSO_4$-$CaCl_2$-H_2O up to the same ionic strength.

It is true that osmotic coefficients can be measured for these two systems at high ionic strengths, but the ionic strength fraction of $CaSO_4$ must necessarily be very small. It follows that the experimental data obtained, could not be sensibly used to give coefficients related to interactions in such ion groups as $Ca^{2+}SO_4^{2-}Na^+$ or $Ca^{2+}SO_4^{2-}Cl^-$. These problems were obviated by using hypothetical values for the unknown properties.

Tables I to VI of reference 98 are reproduced in Appendix II.3. These give expressions for free energy, osmotic coefficients and activity coefficients; definitions of the grouped coefficients, and parameters derived by Scatchard *et al* for best fit values of parameters for system I.

7.9.1 Calculation of $MgSO_4$ activity coefficients in the system Mg^{2+} - Na^+ - SO_4^{2-} - Cl^- - H_2O

Mean ionic activity coefficients were calculated using the equations given in Table V of reference 98. This part of the computer programme was checked by calculating trace activity coefficients of NaCl in Na_2SO_4, $MgCl_2$ and $MgSO_4$ solutions. The 34 parameters in Table VI of reference 98 were used to give trace activity coefficients at the concentrations given in Table VIII of the same paper. The resulting values of $\ln\gamma_\pm$ were in exact agreement with those presented by Scatchard *et al.*

Activity coefficients of $MgSO_4$ were then calculated for solution compositions which corresponded to equivalent experimental compositions in the system with Mg^{2+} replaced by Ca^{2+}. The calculated activity coefficients of $MgSO_4$ in system I were then compared with experimental activity coefficients of $CaSO_4$ (saturated) in system II.

The parameters listed in Table VI of reference 98 were deduced from osmotic coefficient data with ions a, b, f and g defined as Na^+, Mg^{2+}, Cl^- and SO_4^{2-} respectively. The activity coefficient expressions given in Table V of the same paper, refer to the electrolyte af. It follows that in order to calculate $MgSO_4$ activity coefficients, the parameters given in Scatchard's Table VI must be rearranged to be consistent with the definition of a, b, f and g as Mg^{2+}, Na^+, SO_4^{2-} and Cl^- respectively. The four parameters for each single salt were easily rearranged so that the NaCl parameter for terms in af were replaced by $MgSO_4$ parameters and similar changes were made for the single salt terms in ag, bf and bg. Rearrangement of the 18 parameters derived from data on binary common ion electrolyte solutions was not so straightforward. The required changes are given in the Table 7.9.1. The numbering of parameters in column 2 was chosen so that the 7 parameters set to zero by Scatchard (98) were designated z (12) to z (18). This was for convenience in the computational methods discussed in the next section. The rationale behind these relationships is obvious for such parameters as $B_{ab}^{(0,1)}$ and $b_{abf}^{(0,2)}$. For a parameter such as $B_{aab}^{(1,2)}$, it must be recalled that it is a composite parameter made up of coefficients which are symmetrical with respect to a-b interactions. This is clear from the definition of $B_{aab}^{(1,2)}$ given in Table II of reference 98, in terms of individual d_{ijk} coefficients. The sign changes which are necessary for 6 of the parameters, arise from the unsymmetrical nature of the equations for $(\phi - 1)^{nII}$. Terms involving odd powers of $(x_a - x_b)$ and $(x_f - x_g)$ require a change of sign if the definitions of a and b, and f and g are reversed. x_j is the fraction of the total molal equivalent concentration contributed by ions of type j:

$$x_j = \frac{m_j'}{\frac{1}{2}\sum_i m_i'}$$

TABLE 7.9.1 INTERRELATIONSHIPS BETWEEN PARAMETERS

Parameter	Value of Parameter with a, b, f and g defined respectively as	
	Na^+, Mg^{2+}, Cl^-, SO_4^{2-}	Mg^{2+}, Na^+, SO_4^{2-}, Cl^-
$B_{ab}^{(0,1)}$	z (1)	z (1)
$B_{abf}^{(0,2)}$	z (2)	z (5)
$B_{abf}^{(0,3)}$	z (3)	z (6)
$B_{aab}^{(1,2)}$	z (12)	- z (12)
$B_{aabf}^{(1,3)}$	z (4)	- z (14)
$B_{aaab}^{(2,3)}$	z (13)	z (13)
$B_{abg}^{(0,2)}$	z (5)	z (2)
$B_{abg}^{(0,3)}$	z (6)	z (3)
$B_{aabg}^{(1,3)}$	z (14)	- z (4)
$B_{fg}^{(0,1)}$	z (7)	z (7)
$B_{afg}^{(0,2)}$	z (8)	z (17)
$B_{afg}^{(0,3)}$	z (9)	z (11)
$B_{ffg}^{(1,2)}$	z (10)	- z (10)
$B_{affg}^{(1,3)}$	z (15)	- z (18)
$B_{fffg}^{(2,3)}$	z (16)	z (16)
$B_{bfg}^{(0,2)}$	z (17)	z (8)
$B_{bfg}^{(0,3)}$	z (11)	z (9)
$B_{bffg}^{(1,3)}$	z (18)	- z (15)

7.9.2 Hypothetical properties of pure calcium sulphate solutions at concentrations above the solubility limit

Properties of aqueous calcium sulphate solutions could be measured at concentrations above the gypsum solubility limit by using supersaturated solutions. While this suggestion may not be unreasonable for concentrations slightly higher than saturation, it is not possible for solutions of ionic strengths up to 6 molal. The best which can sensibly be achieved is to combine information extrapolated from the properties of $CaSO_4$ solutions up to saturation, with the real properties of comparable 2:2 sulphates at higher concentrations. Hypothetical activity and osmotic coefficients obtained in this manner should be most reliable at concentrations just above the solubility limit, but the reliability must deteriorate at higher concentrations. This is not a problem of vital importance when calculating solvent properties for mixed solutions in system II, but could be important when calculating $CaSO_4$ activity coefficients. This distinction arises from the different weighting factors used for the properties of pure $CaSO_4$ solutions in the equations for $(\phi - 1)^{DH}$ and $(\phi - 1)^{nI}$ (Table III, ref. 98), and for $\ln\gamma_\pm^{DH}$ and $\ln\gamma_\pm^{nI}$ (Table V, ref. 98). In the equations for ϕ, the factor $x_{Ca^{2+}}\, x_{SO_4^{2-}}$ is always present and this must always be small. In the equations for $\ln\gamma_\pm$ other factors are used which can be relatively large, particularly for $CaSO_4$ in concentrated solutions of $CaCl_2$ and Na_2SO_4.

As a first step in the assignment of activity and osmotic coefficients to supersaturated $CaSO_4$ solutions, the properties of unsaturated solutions measured in Part I of this thesis were extrapolated to higher concentrations. This was carried out using an analytical procedure similar to that used in section 3.2.13. The following equations were used:

$$K_D = \frac{\alpha^2 m \gamma_f^2}{(1 - \alpha)\, \gamma_{CaSO_4^o}} \qquad (E.7.9.2)$$

$$\gamma_{CaSO_4^o} = \exp (0.23\, I') \qquad (E.7.9.3)$$

$$\gamma_f = \frac{-|Z_+Z_-|\, S\, (I')^{\frac{1}{2}}}{1 + q/a_o\, (I')^{\frac{1}{2}}} + kI' \qquad (E.7.9.4)$$

$$I' = \alpha\, I \qquad (E.7.9.5)$$

$$\gamma_\pm = \gamma_f\, \alpha \qquad (E.7.9.6)$$

All the symbols in these equations have been defined previously. Equation (7.9.3) is equivalent to that used in section 7.7.5 to fit gypsum solubility data over the whole concentration range. The value of q in (E.7.9.4) was fixed at 0.714 nm. The value of k in this equation was linked to the value chosen for K_D in (E.7.9.2). Values used for K_D were 0.0045 and 0.0043 mol kg^{-1}. These two values gave essentially linear relationships between $E^{o'}_{PbSO_4/Pb(Hg)}$ and I' when $E^{o'}$ was calculated using (E.3.2.6.2) with $E^{o}_{PbSO_4/Pb(Hg)}$ set at -352.6 m.v. The corresponding values of k were 0.250 and 0.533 kg mol^{-1}. The two paired values of K_D and k were used to solve equations (7.9.2) to (7.9.6) in an iterative fashion for $\gamma_\pm$. Calcium sulphate molalities (m) were used from 0.001 molal to 4.5 molal. Osmotic coefficients were calculated for each pair of K_D and k values using equations (3.2.13.1) and (3.2.13.5). The first of these equations is inconsistent with (E.7.9.3), since it involves the assumption that ion pairs behave ideally. This was not considered important since only the activity coefficients were used in subsequent analysis.

Values of α, ϕ and $\gamma_\pm$, calculated using K_D = 0.0045 mol kg^{-1} and k = 0.25 kg mol^{-1}, are shown in columns 2, 3 and 4 of Table 7.9.2. Activity coefficients calculated using the other pair of K_D

TABLE 7.9.2 HYPOTHETICAL PROPERTIES OF $CaSO_4$ SOLUTIONS COMPARED WITH REAL PROPERTIES OF $MgSO_4$ SOLUTIONS

$CaSO_4$ molality /mol kg^{-1}	α	ϕ	$\gamma_\pm$	$\gamma_\pm$	$\gamma_\pm$	$\gamma_\pm$	ϕ	ϕ
0.001	0.892	0.878	0.698	0.696	0.708		0.884	
0.005	0.746	0.777	0.479	0.476	0.493	0.543	0.785	0.805
0.01	0.670	0.732	0.386	0.384	0.399	0.435	0.739	0.740
0.02	0.594	0.693	0.304	0.302	0.313	0.326	0.694	0.660
0.05	0.495	0.650	0.216	0.215	0.218		0.637	
0.10	0.424	0.626	0.164	0.164	0.161	0.134	0.598	0.477
0.2	0.356	0.607	0.124	0.124	0.116	0.0917	0.561	0.466
0.3	0.318	0.599	0.106	0.105	0.0945	0.0773	0.541	0.505
0.4	0.291	0.594	0.0942	0.0938	0.0817	0.0710		0.555
0.6	0.255	0.587	0.0802	0.0796	0.0666	0.0663		0.649
0.8	0.231	0.583	0.0716	0.0708	0.0579	0.0644		0.711
1.0	0.212	0.579	0.0656	0.0646	0.0524	0.0621		0.737
2.0	0.160	0.570	0.0504	0.0486	0.0451	0.0422		0.572
3.0	0.133	0.563	0.0433	0.0411	0.0532	0.0525		0.936

Columns 2, 3 and 4: values derived from equations (7.9.2) to (7.9.6) using $K_D = 0.0045$ mol kg^{-1} and $k = 0.25$ kg mol^{-1}

Column 5: as for columns 2, 3 and 4 but with $K_D = 0.0043$ mol kg^{-1} and $k = 0.533$ kg mol^{-1}

Columns 6 and 8: properties of pure $MgSO_4$ solutions (Pitzer, ref. 49)

Columns 7 and 9: hypothetical properties of pure $CaSO_4$ solutions calculated using best fit values

and k values are shown in column 5. The two sets of activity coefficients are remarkably similar considering the wide concentration range used.

Properties of aqueous 2:2 sulphates at 25°C are given by Pitzer in Tables 3 and 5 of reference 49. Pitzer obtained activity coefficients at low concentrations from the freezing point measurements of Brown and Prue (5). He used a similar analysis to that of Gardner and Glueckauf (2,3) (discussed in Part I of this thesis) and obtained similar results. Ion association into pairs and triplets was assumed. Activity coefficients of free ions were calculated using a Debye-Hückel equation with the distance of closest approach parameter set at the Bjerrum distance. The osmotic coefficients were corrected for the temperature difference ($0^{o}C$ to $25^{o}C$) by using heat of dilution data. Activity coefficients at high concentrations were placed on an absolute basis by multiplying the relative values given by Robinson and Stokes (43) by appropriate factors. The values tabulated by Pitzer (49) are therefore self consistent over the whole concentration range used for each salt.

Intercomparison of the osmotic and activity coefficients of the nine 2:2 sulphates studied by Pitzer shows that the solutions have similar properties over the whole concentration range. It is therefore reasonable to assume that supersaturated calcium sulphate solutions would have comparable properties. Within the experimental range, the activity coefficients of $CaSO_4$ solutions calculated from the e.m.f. measurements described in Part I, are about half way between the values for $CaSO_4$ and $MgSO_4$ solutions tabulated in reference 49. Pitzer's values for the osmotic and activity coefficients of $MgSO_4$ solutions are given in columns 6 and 8 of Table 7.9.2. These values are in surprisingly good agreement with the hypothetical osmotic and activity coefficients in columns 3 and 4. Better agreement could have been forced on the data by empirically introducing a larger value of K_D (or expressions for triplet formation) together with a larger value of k. The $CaSO_4$ activity coefficients in column 4 are smaller than the $MgSO_4$ coefficients at low concentrations, but become higher at a point between 0.05 molal and 0.1 molal. There is a second cross-over point between 2 and 3 molal. It was assumed that the best estimate of hypothetical $CaSO_4$ activity coefficients was the values in column 4 up to the concentration of the first cross-over, and values in column 6 above this concentration.

Having deduced reasonable values for activity and osmotic coefficients of $CaSO_4$ solutions above the solubility limit, the next problem was to use this data to obtain best fit parameters to the equations of Scatchard (98). The equations for activity and osmotic coefficients simplify for single electrolyte solutions to the form of (E.3.1.5) and (E.7.7.8), respectively. The only discrepancy is that the coefficients of the extension terms to the D-H term differ by factors dependent upon the charge type.

It is well known (20) that the properties of 2:2 sulphates cannot be adequately represented by simple Debye-Hückel type equations. This fact results in a number of unfortunate consequences:

(i) non-linear least squares fitting of experimental (or hypothetical) activity or osmotic coefficients to give best fit values of A, B, C and D in (E.3.1.5) or (E.7.7.8) is difficult, especially at low concentrations;

(ii) assuming problem (i) can be overcome, the standard error of the resulting fit cannot be expected to be small if data covering a wide range is used;

(iii) best fit parameters derived to fit the osmotic coefficient equation, cannot be expected to give a good fit to activity coefficient data (or vice versa).

The overall objective of this section was to predict $CaSO_4$ activity coefficients. It follows from (iii) above, that best fit parameters for pure $CaSO_4$ are better derived from the hypothetical activity coefficients rather than from the osmotic coefficients. This choice was made, and divergent solutions were avoided by initially using a restricted concentration range, and gradually extending the range to lower concentrations. At high concentrations the parameters given by Lietzke and Stoughton (41) for $MgSO_4$ could safely be used as starting parameters in the iterative process; but as more of the low concentration data in column 4 of Table 7.9.2 was included, different starting parameters were required. An optimum solution was sought which gave a good fit over the experimental ionic strength range (0.06 to 6.0 molal) without giving physically ridiculous values to the parameters. Inclusion of too much low concentration data resulted in very small or even negative values for the distance of closest approach parameter. A zero value for this parameter is clearly unsatisfactory since equation (7.7.8) then predicts an infinitely large osmotic coefficient. The set of best fit parameters chosen were:

$$a'_{af} = 0.34482 \quad \mathrm{kg^{\frac{1}{2}}\ mol^{-\frac{1}{2}}} = A$$

$$B^{(1)}_{af} = 1.1187 \quad \mathrm{kg\ mol^{-1}} = 2B$$

$$B^{(2)}_{af} = -0.34287 \quad \mathrm{kg^{2}\ mol^{-2}} = 4C$$

$$B^{(3)}_{af} = 0.033135 \quad \mathrm{kg^{3}\ mol^{-3}} = 8D$$

These parameters, when substituted into equations (3.1.5) and (7.7.8), or the equivalent expressions of Scatchard (98), gave the activity and osmotic coefficients shown in columns 7 and 9 of Table 7.9.2. The parameters were obtained by fitting data for the concentration range 0.004 to 3.0 molal. The goodness of fit below 0.015 molal was not of consequence, but the number of data points used in this region was important since it influenced the quality of fit in the experimental range.

7.9.3 Derivation of best fit parameters for the system Ca^{2+}-Na^{+}-SO_4^{2-}-Cl^{-}-H_2O

Parameters derived from data on single salts were easily obtained. The values given in Table VI of reference 98 for Na_2SO_4 and NaCl solutions required no further modification. Parameters for $CaSO_4$ solutions were derived in the previous section and the compilation of Lietzke and Stoughton (41) was used to give values for $CaCl_2$ solutions. The relationships between the single salt parameters for $CaCl_2$ in Scatchard's (98) equations and those given in reference 41 (cf. E.3.1.5) are

$$a'_{ag} = A = 1.6129 \quad \mathrm{kg^{\frac{1}{2}}\ mol^{-\frac{1}{2}}}$$

$$B^{(1)}_{ag} = 9/4\ B = 0.10273 \quad \mathrm{kg\ mol^{-1}}$$

$$B^{(2)}_{ag} = 27/8\ C = 0.028934 \quad \mathrm{kg^{2}\ mol^{-2}}$$

$$B^{(3)}_{ag} = 81/16\ D = -0.0013861 \quad \mathrm{kg^{3}\ mol^{-3}}$$

The remaining task was to obtain best fit parameters for osmotic coefficient data on the four binary electrolyte mixtures having a common ion. It has already been mentioned that suitable data is not available for $CaSO_4$-Na_2SO_4-H_2O or $CaSO_4$-$CaCl_2$-H_2O. It was therefore necessary to make the assumption that osmotic coefficients in these systems were approximated reasonably well by ϕ values in the equivalent systems with Ca^{2+} replaced by Mg^{2+}. Osmotic coefficient data for the $CaCl_2$-$NaCl$-H_2O system were taken from the paper by Robinson and Bower (93). Data for the three remaining systems were taken from Wu, Rush and Scatchard (91).

Values of $(\phi - 1)^{DH}$ and $(\phi - 1)^{nI}$ were calculated for each composition studied in the four binary electrolyte systems, by using equations (b), (c) and (d) of Table III in reference 98. The experimental osmotic coefficients were then substituted into equation (a) of Table III, and values of $(\phi - 1)^{nII}$ were calculated for each composition.

A linear least squares procedure was used to obtain best fit values of the 18 parameters in equation (f) of Table III. The program was checked in two ways.

(i) Parameters z (12) to z (18) inclusive were set to zero and best fit values of z (1) to z (11) were computed for system (I). The binary electrolyte osmotic coefficient data and single salt parameters used in this analysis were the same as those used in reference 98. The resulting 11 parameters were identical to those listed in Table VI of reference 98.

(ii) All the 18 parameters were allowed to vary and the least squares procedure was carried out using a, b, f and g defined as both Na^+, Ca^{2+}, Cl^-, SO_4^{2-} (Definition I) and Ca^{2+}, Na^+, SO_4^{2-}, Cl^- (Definition II). The resulting sets of best fit parameters were related in the manner indicated by Table 7.9.1. Differences in the magnitudes of equivalent parameters were confined to the seventh significant figure.

The values of the parameters computed using definition I were as follows:

PARAMETER SET I

$z(1) = -3.684 \times 10^{-2}$
$z(2) = 4.236 \times 10^{-2}$
$z(3) = -6.355 \times 10^{-3}$
$z(4) = -1.037 \times 10^{-2}$
$z(5) = -2.041 \times 10^{-1}$
$z(6) = 5.409 \times 10^{-2}$
$z(7) = 6.933 \times 10^{-2}$
$z(8) = -3.588 \times 10^{-2}$
$z(9) = 4.049 \times 10^{-3}$
$z(10) = 2.516 \times 10^{-2}$
$z(11) = 1.229 \times 10^{-1}$
$z(12) = 5.087 \times 10^{-2}$
$z(13) = 8.393 \times 10^{-5}$
$z(14) = -1.178 \times 10^{-2}$
$z(15) = -3.893 \times 10^{-3}$
$z(16) = 3.978 \times 10^{-4}$
$z(17) = -3.937 \times 10^{-1}$
$z(18) = 3.612 \times 10^{-2}$

The variance of fit defined by $\left[(\phi - 1)^{nII}_{obs} - (\phi - 1)^{nII}_{calc}\right]^2/(N - M) = V$, where N is the number of data points and M the number of variable parameters, was found to be 4.29×10^{-4}.

The calculations were repeated for definition I with parameters z (12) to z (18) set at zero. These are the same parameters given zero values for system I by scatchard (98), presumably on the basis that their exclusion did not significantly increase the standard deviation of the fit between observed and calculated osmotic coefficients. The best fit parameters obtained were:

PARAMETER SET II

$z(1) = -3.807 \times 10^{-2}$
$z(2) = 3.759 \times 10^{-2}$
$z(3) = -5.360 \times 10^{-3}$
$z(4) = -4.453 \times 10^{-4}$
$z(5) = -2.133 \times 10^{-1}$
$z(6) = 5.643 \times 10^{-2}$

$z(7) = -2.103 \times 10^{-1}$
$z(8) = 9.631 \times 10^{-2}$
$z(9) = -9.293 \times 10^{-3}$
$z(10) = 1.185 \times 10^{-3}$
$z(11) = 2.132 \times 10^{-2}$

$$V = 5.85 \times 10^{-4}$$

An additional set of parameters was computed in the same manner as above, but using definition II. A consequence of the structure of the computer program, was that a different set of interaction parameters were set to zero. The best fit values of the 11 non zero coefficients were:

PARAMETER SET III

$z(1) = -3.571 \times 10^{-2}$
$z(2) = -2.156 \times 10^{-1}$
$z(3) = 5.698 \times 10^{-2}$
$z(4) = -5.420 \times 10^{-4}$
$z(5) = 3.622 \times 10^{-2}$
$z(6) = -5.166 \times 10^{-3}$

$z(7) = -2.663 \times 10^{-2}$
$z(8) = -2.093 \times 10^{-1}$
$z(9) = 6.733 \times 10^{-2}$
$z(10) = -1.213 \times 10^{-2}$
$z(11) = 1.443 \times 10^{-3}$

$$V = 5.39 \times 10^{-4}$$

7.9.4 Calculation of $CaSO_4$ activity coefficients in the system Ca^{2+}-Na^+-SO_4^{2-}-Cl^--H_2O

Mean ionic activity coefficients for $CaSO_4$ were calculated for solutions having the compositions used in the gypsum solubility measurements. The equations given in Table V of reference 98 were used for this purpose. The activity coefficients were calculated using the single salt data only, and also by using the full equations with parameter sets I, II and III. The parameters listed in set III could be used directly in the activity coefficient expression without any changes of sign or arrangement. More precisely, the relationship between the z parameters and the coefficients in equation (c) of Table V (98) are as indicated in columns 1 and 2 of Table 7.9.1. The required relationship when using sets I and II, is as indicated in columns 1 and 3 of the same table.

7.9.5 Comparison with experimental $CaSO_4$ activity coefficients

Calculated activity coefficients of $MgSO_4$ in system I and calculated activity coefficients of $CaSO_4$ in system II, were compared with experimental activity coefficients of $CaSO_4$ in system II.

TABLE 7.9.3 MEAN SQUARE DEVIATIONS OF CALCULATED AND EXPERIMENTAL $\ln\gamma_\pm$ VALUES

Foreign Solutes	Number of Data Points (n)	$\frac{1}{n}\sum(\ln\gamma_\pm^{calc} - \ln\gamma_{\pm CaSO_4}^{expt})^2$ where $\gamma_\pm^{calc}$ is					
		$\gamma_{\pm MgSO_4}^{nI}$	$\gamma_{\pm MgSO_4}^{nII}$	$\gamma_{\pm CaSO_4}^{nI}$	$\gamma_{\pm CaSO_4}^{nII}$ (I)	$\gamma_{\pm CaSO_4}^{nII}$ (II)	$\gamma_{\pm CaSO_4}^{nII}$ (III)
$CaCl_2$	18	0.1393	0.1197	0.774	0.1829	0.0177	0.0324
Na_2SO_4	32	0.0742	0.0981	0.0421	0.00755	0.00598	0.00595
NaCl	48	0.0334	0.0407	0.00987	0.0422	0.0140	0.00779
$NaCl/CaCl_2$	41	0.0868	0.0864	0.0547	0.1939	0.00903	0.0345
$NaCl/Na_2SO_4$	48	0.0561	0.0848	0.0511	0.0303	0.00330	0.00595
All data	187	0.0681	0.0795	0.0423	0.0800	0.0091	0.0152

The results are summarised in Table 7.9.3. This table gives the mean square deviation between the logarithms of calculated and experimental activity coefficients for each of the experimental systems studied. The overall mean square deviation for all the data is also shown.

Values given in column 3 were derived using only parameters for the single salts in system I. Column 5 gives the equivalent results calculated using parameters for single salts in system II. As expected, the second set of parameters gave better agreement between calculated and experimental activity coefficients. Inclusion of the parameters for binary common ion mixtures in system I, (column 4) gave worse overall agreement between calculated $\ln\gamma_{\pm(MgSO_4)}$ values and experimental $\ln\gamma_{\pm(CaSO_4)}$ values than when these parameters were excluded. Inclusion of the equivalent set of parameters (set II) for system II gave a substantially improved agreement (column 7). Parameter set III did not give quite as good fit as set II. Parameter set I gave a poorer fit to the experimental activity coefficients than the values computed using only single salt parameters. At first sight, this last result is unexpected, but it is not unreasonable. The number of significant figures shown for the best fit parameters are not in any sense meant to give an indication of individual parameter accuracy. The standard deviations of the individual parameters were generally of the same magnitude, and often significantly larger, than the best fit values of the parameters. The interparameter correlation coefficients were also often close to unity. Consequently, while any set of parameters taken as a whole provide a good fit to the osmotic coefficient data from which they were derived, a quite different set of values for the same parameters could fit the data almost as well. This situation leads to problems when the best fit parameters are used to predict the properties of solutions of different compositions to those from which the parameters were derived. The use of non zero values for all 18 nII parameters exacerbates these problems, because it is unrealistic to expect certain of the terms to make significant contributions to the excess free energy. Interactions between four cations or four anions are clearly included in this category, and probably interactions involving three ions of like sign should also be included. Inclusion of coefficients for these interaction terms as variable parameters will give best fit values which are probably of no real physical significance. It follows that use of these coefficients in a predictive sense is likely to give incorrect estimates, especially at high concentrations where the concentration product of the ionic species concerned is high. As a corollary to this discussion, it should be pointed out that parameter set II was not the best set of values found. Calcium sulphate activity coefficients were inadvertently calculated without making the necessary sign changes to the parameters concerned. This "error" led to a slightly better fit for parameter set II, and a substantially improved fit for set I compared to the results obtained with all the signs correct. No significance is attached to this result, other than to illustrate that improved fits could be obtained by making arbitrary changes to the computed parameters.

While Table 7.9.3 gives an adequate comparative summary of the different sets of calculated activity coefficients, it does not provide any detail, nor does it give a very clear idea of the magnitude of the differences between calculated and experimental results. Tables 7.3.1, 7.3.2, 7.4.1, 7.5.1 and 7.6.1 list values of the ratio R. This is defined as the ratio of activity coefficients calculated using parameter set II to the experimental activity coefficients. Inspection of these ratios shows that the calculated coefficients were generally within 10% of the experimental values. Larger deviations were present at high concentrations of $CaCl_2$ and NaCl. The relatively few deviations in excess of 10% made major contributions to the values in Table 7.9.3. Deviations at low ionic strength also made important contributions. This latter effect was a direct result of the inability of the Debye-Hückel expression to fit activity coefficients for pure $CaSO_4$ solutions.

In view of the major assumptions used, and the wide range of ionic strengths and solution compositions studied, the calculated activity coefficients are considered to be in remarkably good agreement with the experimental results. Quite a good approximation was achieved simply by using the single salt parameters for system I. A much better approximation would have resulted if the equation and parameters for pure $MgSO_4$ solutions gave activity coefficients which were in agreement with literature values. At the solubility limit for gypsum in pure water, the computed $MgSO_4$ activity coefficient was nearly 20% larger than the value interpolated for $MgSO_4$ from Pitzer's (49) Table 3. This is, in part, a consequence of the limited concentration range of osmotic coefficient data fitted by Lietzke and Stoughton (41), to give the $MgSO_4$ single salt parameters, but is primarily a result of the inadequacy of the electrostatic term to represent the concentration dependence of 2:2 sulphates. The agreement between experimental activity coefficients and values calculated using parameter set II is as good as can reasonably be expected. Further attempts to compute a better set of parameters by using a different choice of non-zero coefficients were consequently not thought to be worthwhile.

7.9.6 Prediction of $CaSO_4$ activity coefficients in the Ca^{2+}-Na^+-SO_4^{2-}-Cl^--H_2O system by utilising the experimental gypsum solubilities

The previous sections have discussed the use of Scatchard's "ions as components" treatment in the prediction of $CaSO_4$ activity coefficients using only osmotic coefficient data. A less demanding task is to use experimental gypsum solubility measurements to predict calcium sulphate activity coefficients for solutions of different composition. Insufficient time was available to carry out this work but the principles involved are discussed below.

The single salt parameters for system II are unaffected. The objective is to obtain a set of "common ion" parameters which best fit the experimental $CaSO_4$ activity coefficients. This can be carried out by calculating values of $(\ln\gamma_\pm)^{nII}_{CaSO_4}$ using equation (a) of Table IV and equations (a) and (b) of Table V (reference 98). The resulting values can be fitted to equation (c) of Table V by a linear least squares procedure to give best fit values for the 18 coefficients.

The most reliable set of coefficients would be obtained by utilising all the solubility data, but data for the three binary electrolyte solutions would be adequate.

7.10 APPLICATION OF REILLY, WOOD AND ROBINSON'S EQUATIONS

The treatment of Reilly, Wood and Robinson (117) was applied to the gypsum solubility measurements in the three single electrolyte solutions. It was assumed that calcium sulphate in the solutions could be considered as being present in trace amounts. This considerably reduced the complexity of the equations, but is clearly a poor approximation at low concentrations of foreign electrolyte. Application of equation (13.2.1) (this is the corrected form of equation A-9 of reference 117 - see Part III) to the three single salt solutions under these circumstances gives:

$$\ln\gamma_{\pm CaSO_4(\text{trace in NaCl})} = 1.5\,(1 - \overset{o}{\phi}_{CaCl_2} + \ln\overset{o}{\gamma}_{\pm CaCl_2}) +$$

$$\cdot\ 1.5\,(1 - \overset{o}{\phi}_{Na_2SO_4} - \ln\overset{o}{\gamma}_{\pm Na_2SO_4}) - 6\,(1 - \overset{o}{\phi}_{NaCl}) -$$

$$2\ln\overset{o}{\gamma}_{\pm\,NaCl} + 1.5\,I\,(g^{Cl}_{Ca,Na} + g^{Na}_{SO_4,Cl}) \qquad \text{(E.7.10.1)}$$

$$\ln\gamma_{\pm CaSO_4(\text{trace in }CaCl_2)} = (1 - \overset{o}{\phi}_{CaSO_4} + \ln\overset{o}{\gamma}_{\pm\,CaSO_4}) - 2\,(1 - \overset{o}{\phi}_{CaCl_2}) +$$

$$2\,I\,g^{Ca}_{SO_4,\,Cl} \qquad \text{(E.7.10.2)}$$

and

$$\ln\gamma_{\pm CaSO_4(\text{trace in }Na_2SO_4)} = (1 - \overset{o}{\phi}_{CaSO_4} + \ln\overset{o}{\gamma}_{\pm CaSO_4}) - 2\,(1 - \overset{o}{\phi}_{Na_2SO_4}) +$$

$$2\,I\,g^{SO_4}_{Ca,\,Na} \qquad \text{(E.7.10.3)}$$

In these equations the activity and osmotic coefficients given a superscript "o" refer to solutions of single salts at the same ionic strength as the solution in which the $CaSO_4$ is present as a trace. The $g^{X}_{Y,Z}$ parameters are defined in Part III, and may be evaluated from measurements on the binary electrolyte solution containing XY and XZ and the component single electrolyte solutions all at the same ionic strength. It is evident that $g^{Ca}_{SO_4,\,Cl}$ and $g^{SO_4}_{Ca,\,Na}$ cannot be calculated directly because of the limited solubility of gypsum. Evaluation of $g^{Cl}_{Ca,\,Na}$ and $g^{Na}_{SO_4,\,Cl}$ is feasible. Osmotic coefficient data is available on the relevant systems and this enables values of $\omega^{Na}_{SO_4,\,Cl}$ and $\omega^{Cl}_{Ca,\,Na}$ to be calculated (this has been done for the second of these quantities in Part III, where $\omega^{X}_{Y,\,Z}$ is referred to as ω_0). Integration of $\omega^{X}_{Y,\,Z}$ according to equation (9.1.5) from I = 0 up to the ionic strength concerned is necessary in order to calculate $g^{X}_{Y,\,Z}$. The integration cannot be carried out accurately due to the limited range of $\omega^{X}_{Y,\,Z}$ values. This problem may be obviated by using the assumption that $\omega^{X}_{Y,\,Z} \approx g^{X}_{Y,\,Z}$ at any given ionic strength. A variety of more complicated assumptions are suggested by Friedman (Figure 18.3, reference 94) but their accuracy is indeterminate. In view of these problems, $g^{X}_{Y,Z}$ contributions were neglected. After making this additional simplifying assumption, all the quantities on the R.H.S. of (E.7.10.1) are easily calculable. Subtraction of (E.7.10.3) from (E.7.10.2) gives, for solutions of the same ionic strength:

$$\ln \frac{\gamma_{\pm CaSO_4(\text{trace in } CaCl_2)}}{\gamma_{\pm CaSO_4(\text{trace in } Na_2SO_4)}} = 2\,(\phi^{o}_{CaCl_2} - \phi^{o}_{Na_2SO_4}) + 2\,I\,(g^{Ca}_{SO_4,\,Cl} - g^{SO_4}_{Ca,\,Na}) \qquad (E.7.10.4)$$

in which the unknown properties of pure $CaSO_4$ solutions at high concentrations have been eliminated.

Properties of solutions containing trace amounts of $CaSO_4$ were calculated using (E.7.10.1) and (E.7.10.4). Activity and osmotic coefficients of pure solutions of NaCl, $CaCl_2$ and Na_2SO_4 were calculated using (E.3.1.5) and (E.7.7.8) with appropriate parameters obtained from reference 41. The results were compared with the equivalent experimental properties for solutions in which $CaSO_4$ was present at saturation concentrations. Activity coefficients of $CaSO_4$ in Na_2SO_4 solutions, at the same ionic strength as the $CaSO_4$-$CaCl_2$ solutions, were obtained by graphical interpolation. Activity coefficients of $CaSO_4$ in NaCl solutions were calculated using two assumptions:

(i) quantities on the R.H.S. of (E.7.10.1) were given values corresponding to the ionic strength of the sodium chloride only;

(ii) the same quantities were given values appropriate to the ionic strength of NaCl plus $CaSO_4$.

It can be seen from Table 7.10.1 that these two assumptions give quite different results, particularly at low sodium chloride concentrations. This implies that the saturated concentrations of $CaSO_4$ are too high to expect the trace activity coefficient expression to serve as more than a guide. Apparent values of $g^{Cl}_{Ca,\,Na} + g^{Na}_{SO_4,\,Cl}$ are also tabulated in Table 7.10.1.

At high NaCl concentrations, the sum of these g values is not too dependent on the choice of

TABLE 7.10.1 COMPARISON OF EXPERIMENTAL AND CALCULATED $CaSO_4$ ACTIVITY COEFFICIENTS IN NaCl SOLUTIONS

Molality of NaCl /mol kg^{-1}	$\ln\gamma_{\pm}$(CALC) - $\ln\gamma_{\pm}$(EXPTL)	Apparent Value of $g^{Cl}_{Ca,Na} + g^{Na}_{SO_4,Cl}$ /kg mol^{-1}	$\ln\gamma_{\pm}$(CALC) - $\ln\gamma_{\pm}$(EXPTL)	Apparent Value of $g^{Cl}_{Ca,Na} + g^{Na}_{SO_4,Cl}$ /kg mol^{-1}
0.281	0.328	- 0.78	0.185	- 0.31
0.335	0.312	- 0.62	0.184	- 0.26
0.396	0.300	- 0.51	0.183	- 0.23
0.504	0.282	- 0.37	0.182	- 0.19
0.611	0.271	- 0.30	0.183	- 0.16
0.807	0.257	- 0.21	0.188	- 0.13
1.03	0.247	- 0.16	0.192	- 0.11
1.52	0.240	- 0.11	0.210	- 0.081
2.02	0.245	- 0.081	0.232	- 0.069
2.54	0.256	- 0.067	0.256	- 0.062
3.02	0.265	- 0.059	0.276	- 0.057
4.01	0.255	- 0.042	0.278	- 0.044
5.49	0.372	- 0.045	0.401	- 0.047

Columns 2 and 3 are calcualted on the basis: $I = m_{NaCl}$

Columns 4 and 5 are calculated on the basis: $I = m_{NaCl} + 4M_{CaSO_4}$

ionic strength definition, and the magnitude of the sum is not unreasonable.

Table 7.10.2 compares the experimental ratio of $CaSO_4$ activity coefficients in $CaCl_2$ and Na_2SO_4 solutions with the ratio of trace activity coefficients calculated using (E.7.10.4). The solubility of gypsum in $CaCl_2$ and Na_2SO_4 solutions is considerably less than in NaCl solutions, so (E.7.10.4) should give better agreement with the experimental results than (E.7.10.1). The assumption that g terms are negligible is also better justified for the former equation, since a difference rather than a sum of g terms is involved. If both assumptions were fully justified, columns 2 and 3 of Table 7.10.2 would give identical results. The observed differences are quite large at high salt concentrations, but are relatively small at low concentrations. The magnitude of the difference in g values is larger than expected, but is not implausible.

The overall conclusion of this section was that the treatment of reference 117, applied with the present assumptions was not capable of accurate predictions of calcium sulphate activity

TABLE 7.10.2 EXPERIMENTAL AND CALCULATED VALUES FOR RATIO OF $CaSO_4$ ACTIVITY COEFFICIENTS IN $CaCl_2$ AND IN Na_2SO_4 SOLUTIONS

Molality of $CaCl_2$ or Na_2SO_4 /mol kg^{-1}	Experimental value of $\ln \frac{\gamma_{\pm CaSO_4 \text{ in } CaCl_2}}{\gamma_{\pm CaSO_4 \text{ in } Na_2SO_4}}$	$2(\phi^{o}_{CaCl_2} - \phi^{o}_{Na_2SO_4})$	Apparent Value of $g^{SO_4}_{Na,Ca} - g^{Ca}_{SO_4,Cl}$ /kg mol^{-1}
0.155	0.094	0.192	0.097
0.251	0.150	0.272	0.077
0.420	0.245	0.404	0.061
0.703	0.38	0.606	0.052
1.14	0.58	0.92	0.049
1.69	0.87	1.33	0.045

coefficients in the three single salt solutions. It would have been interesting to apply equation (13.2.1) in its full form to all the solubility data. This would have required knowledge of the properties of pure $CaSO_4$ solutions above the solubility limit (*cf.* Scatchard's "ions as components" treatment). While this is feasible, inclusion of all the g terms would be quite impractical, so that the calculations would be limited to the use of single salt properties.

8. SUMMARY OF CONCLUSIONS

The conclusions derived from the work described in Part II are summarised below.

(i) The solubility of gypsum in water at 25°C was found to be 0.01518 ±0.00004 mol kg^{-1}. This result was obtained from measurements made using two quite different experimental techniques. The two experimental methods gave mean values within 0.04% of the above solubility.

(ii) Gypsum solubility measurements in solutions of NaCl, Na_2SO_4 and $CaCl_2$ were used to derive a value of (2.65 ±0.3) × 10^{-5} mol^2 kg^{-2} for the thermodynamic solubility product of gypsum. Equations were obtained which gave a good fit to the experimental solubilities of gypsum up to a molal ionic strength of approximately six.

(iii) It was shown that a recent treatment of mixed electrolyte solutions proposed by Scatchard, could be used to provide good estimates of calcium sulphate activity coefficients in the systems studied. Reasonable estimates could be obtained by using literature osmotic coefficient data for the system Mg^{2+} - Na^{+} - SO_4^{2-} - Cl^{-} - H_2O. More accurate predictions could be made by substituting osmotic coefficient data involving calcium chloride for some of the equivalent data involving magnesium chloride, and also by substituting hypothetical data on calcium sulphate solutions for equivalent data on magnesium sulphate solutions.

(iv) It was found that the treatment of mixed electrolyte solutions used by Wood and coworkers is of limited applicability in the systems studied.

PART III

SOME ASPECTS OF THE THERMODYNAMIC PROPERTIES OF DILUTE BINARY ELECTROLYTE SOLUTIONS

9. INTRODUCTION

In recent years there has been much interest (100) in charge asymmetric electrolyte mixtures. This interest has been divided mainly between two areas. Firstly, the prediction of thermodynamic properties of multicomponent mixtures from an experimental knowledge of the properties of single electrolyte solutions and of binary mixtures in which a common ion is involved. Secondly, experimental evidence has been sought to confirm the limiting laws predicted by Friedman (94). It is the second area of interest with which Part III of this thesis is concerned.

9.1 BRIEF SYNOPSIS OF FRIEDMAN'S (94) PREDICTIONS

The theoretical treatment of Friedman (94) is based largely on the cluster expansion approach of J. E. Mayer (101). This treatment leads to the conclusion that as the concentration of mixed electrolyte solutions containing a common ion approaches zero, certain parameters which remain finite for charge symmetric mixtures, become non-finite in the limit for asymmetric mixtures. The theory predicts the limiting gradients as the ionic strength approaches zero, and the introduction of assumed ion sizes enables "primitive model" calculations to be made which extend the concentration range over which the theory gives realistic estimates for excess thermodynamic properties.

Excess thermodynamic properties of binary electrolyte mixtures were expressed as

$$\Delta m\, X^{ex}(y, I) = X^{ex}(y, I) - y\, X^{ex}(1, I) - \left[1 - y\right] X^{ex}(0, I) \qquad (E.9.1.1)$$

where y is the fraction of the total ionic strength of the mixture contributed by electrolyte A; $X^{ex}(y, I)$ is the excess thermodynamic property (e.g. excess free energy of solution) per kg of solvent at total ionic strength I and ionic strength fraction y; $\Delta m\, X^{ex}(y, I)$ is the change in the excess property per kg of solvent for the mixing process carried out at constant ionic strength from appropriate quantities of single electrolyte solutions.

The y dependence of $\Delta m\, X^{ex}$ is assumed to be of the form:

$$\Delta m\, X^{ex}(y, I) = I^2 RT\, y\left[1 - y\right] \sum_p x_p \left[1 - 2y\right]^p \qquad p = 0, 1, 2, \ldots\ldots\ldots \qquad (E.9.1.2)$$

where the expansion parameters x_p are dependent on I but independent of y. The magnitude of $\Delta m\, X^{ex}$ is dependent primarily on x_0. If the terms involving asymmetry ($p > 0$) are neglected (E.9.1.2) reduces to

$$\Delta m\, X^{ex}(y, I) = I^2 RT\, y\left[1 - y\right] x_0 \qquad (E.9.1.3)$$

Friedman's treatment allows the limiting ionic strength dependence of the various x_0 parameters to be predicted as the concentration approaches zero. If a solution containing a mixture of 2:1, 1:1 charge type electrolytes is considered, and the Gibbs function of the solution (G) is substituted for

X, then the relevant limiting law is

$$g_0 = 0.457 \ln I \qquad \text{(E.9.1.4)}$$

The derivation of this limiting law is given in Appendix III 1. Other limiting laws may be derived from (E.9.1.4) by carrying out appropriate differentiations. When X represents the solvent free energy (G_ω), the limiting law for the expansion parameter (ω_0) is obtained from

$$\omega_0 = \frac{\partial(g_0 I)}{\partial I} \qquad \text{(E.9.1.5)}$$

This gives

$$\omega_0 = 0.457 + 0.457 \ln I \qquad \text{(E.9.1.6)}$$

The nomenclature used for the equations in this introduction is that of Friedman (94), except that the sign of ω_0 is reversed. This is to compensate for his surprising definition of $\Delta m\, G_\omega^{ex}$ (equation 16.31 in reference 94), in which the sign of this quantity is inconsistent with the equations from which it is derived (16.30 and 16.10). The limiting law for the enthalpy expansion parameter is obtained using

$$h_0 = -T \left(\frac{\partial g_0}{\partial T}\right)_P \qquad \text{(E.9.1.7)}$$

The prelogarithmic factor in (E9.1.4) is temperature dependent via the solvent density and dielectric constant but ionic strength defined on the molality scale is temperature independent. Differentiation of (E.9.1.4) according to (E.9.1.7) gives

$$RTh_0 = -633 \log_{10} I \qquad \text{(E.9.1.8)}$$

It is clear that all three limiting laws predict that the respective expansion parameters will approach + or - infinity as I approaches zero. At higher concentrations, estimates of the magnitudes of these parameters may be obtained by the use of so-called "primitive model calculations". Friedman employs the approximation

$$g_0\ (\text{calc.}) = \frac{\mathcal{G}_{02}\ \kappa^2}{\lambda\ I} \qquad \text{(E.9.1.9)}$$

where κ is the Debye reciprocal length

and λ is the Coulomb length or 8π times the Bjerrum distance q_B.

For unsymmetrical mixtures this is a good approximation since:

(i) $\mathcal{G}_0 \approx \sum_u \mathcal{G}_{ou} \qquad u = 2, 3, 4, \ldots\ldots$

and for unsymmetrical mixtures $\mathcal{G}_{ou}$ is zero for $u > 2$.

(ii) $\mathcal{G}_0 \dfrac{\kappa^2}{\lambda I} = g_0 - b - e_0$

where b and e_0 arise from the difference in mixing processes in which volume is the independent variable ($\mathfrak{g}_0$) and pressure is the independent variable (g_0). At low ionic strengths b and e_0 approach zero.

$\mathfrak{g}_{02}$ may be calculated from

$$\frac{\kappa^2}{\lambda}\,\mathfrak{g}_{02} = \frac{2\,J_{12}}{(z_1 - z_3)(z_2 - z_3)} - \frac{J_{11}}{(z_1 - z_3)^2} - \frac{J_{22}}{(z_2 - z_3)^2}$$

$$+ \frac{z_1 - z_2}{(z_1 - z_3)(z_2 - z_3)}\left[\frac{2J_{23}}{z_2 - z_3} - \frac{2J_{13}}{z_1 - z_3} - \frac{(z_1 - z_2)\;J_{33}}{(z_1 - z_3)(z_2 - z_3)}\right] \qquad \text{(E.9.1.10)}$$

This equation holds for binary mixtures of electrolytes having a common ion of charge z_3. J_{ij} is an ionic solution integral for the ions i and j which is dependent on L_{ij} and K_{ij}. These are defined by

$$L_{ij} = \frac{-\,z_i\,z_j\,\lambda}{4\,\pi\,a_{ij}} \qquad \text{(E.9.1.11)}$$

and

$$K_{ij} = \kappa\,a_{ij} \qquad \text{(E.9.1.12)}$$

where a_{ij} is the shortest internuclear separation of ions i and j. Values of J are tabulated in the appendix of reference 94 as a function of L and K. This enables values of g_0 to be calculated subject to uncertainties in equation (9.1.9) and uncertainties in the various a_{ij} values. Other expansion parameters such as ω_0 and h_0 may be calculated by carrying out the appropriate differentiations of g_0.

9.2 COMPARISON WITH EXPERIMENT

Wood and co-workers have made enthalpy of mixing measurements for a wide range of electrolyte mixtures. The systems which are of particular interest here are alkali metal chlorides with magnesium chloride (102) and also with calcium chloride and with barium chloride (112). The experimental values of h_0 for all these systems show an increase (as predicted by the limiting law) when the ionic strength is reduced. The upturn is especially marked for the mixture of caesium chloride with magnesium chloride, but even for this system the results do not show a quantitative approach to the limiting law. It is unfortunate that the results do not extend below 0.5 I, but presumably Wood considered that the small enthalpy changes at lower concentrations would lead to excessively large uncertainties in the calculated h_0 values.

Activity coefficients for the systems $HCl - AlCl_3 - H_2O$ and $HCl - CeCl_3 - H_2O$ published in reference 43 were used by Friedman (94) to calculate values of g_0 at concentrations down to 1.0 I. Again a qualitative but not a quantitative approach to the relevant limiting law was evident.

9.3 OBJECTS OF PRESENT WORK

The main object of Part III of this thesis was to make additional tests of the limiting laws given in section 9.1.

No reference is made in the literature to any experimental tests of equation (9.1.6) for ω_0. From one viewpoint a test of the limiting law for ω_0 is preferable to a test for g_0. This is because ω_0 is calculated from osmotic coefficients which are directly measurable, while g_0 is calculated from activity coefficients which at some stage must rely on an extrapolation to zero ionic strength. In the calculation of g_0, any error in this extrapolation becomes increasingly important as the ionic strength approaches zero.

Considerable experimental data for osmotic coefficients of 1:1, 2:1 electrolyte mixtures is available in the literature. Osmotic coefficients for all the single electrolyte solutions involved are also available. The data for mixed electrolytes have been analysed (e.g. 91, 105) with the implicit assumption that parameters equivalent to ω_0 remain finite as I approaches zero. This assumption must involve an error of unknown magnitude when the same parameters are used to calculate activity coefficients. The present intention is to re-analyse this osmotic coefficient data without prejudice as to the nature of the concentration dependence of ω_0 and to scrutinise the results to see if any approach to the limiting law is evident.

Two problems with the activity coefficient data analysed by Friedman are that the results do not extend below 0.5 I and that hydrochloric acid was a component of both the systems. Friedman (94) suggests that the presence of H^+ ions was unfortunate since comparison between experiment and primitive model calculations are likely to be unsatisfactory for this particular ion. Both of these problems were avoided by measuring calcium chloride activities in mixtures with calcium sulphate at total ionic strengths between 0.0041 and 0.033 molal. It was thought that at these low concentrations a quantitative approach of experimental g_0 values to the limiting law might be observed.

10. EXPERIMENTAL

10.1 MATERIALS AND APPARATUS

These were all as described in Part I.

10.2 TEST SOLUTIONS

A stock solution of calcium sulphate having a concentration of 0.01 molal, and three stock solutions of calcium chloride were prepared. The latter had concentrations of approximately 0.0147, 0.00171 and 0.00014 molal. Eight test solutions were prepared by adding varying weights of the $CaCl_2$ solutions to approximately constant weights of $CaSO_4$ solution. The weight of extra water required to give a solution exactly 0.001 molal in $CaSO_4$ was then added. The final concentrations of calcium chloride are given in Table 11.1.

10.3 SILVER-SILVER CHLORIDE ELECTRODES

Bias potentials for the Ag/AgCl electrodes were found to have increased to as much as 110 μv. This was considered unacceptable and the electrodes were interconnected and heated for 30 minutes at 70°C in a pure 0.001 molal solution of calcium chloride. After cooling and standing overnight, the largest bias potential was found to be 40 μv which was less than a third of the expected standard deviation of the e.m.f. measurements.

10.4 MEASUREMENTS

Ten cells were used, identical in design to those used as reference cells in Part I. Two of these were used with pure $CaCl_2$ solutions, the first as a primary reference cell, and the second to check that the response of the calcium membrane electrode was Nernstian.

A minimum of nine transfer measurements were made with each test solution over a period of three days. All conditions were as described in Part I, and nitrogen was bubbled through all the solutions. The pH of each solution was measured at the end of the third day.

11. EXPERIMENTAL RESULTS

The concentration of $CaCl_2$ in the primary reference cell was 0.01468 molal. Observed transfer potentials between this cell and the test cells are given in Table 11.1. The transfer potentials between the two reference cells were always found to be within 0.1 m.v. of that predicted using Lietzke and Stoughton's parameters (41) in equation (E.3.1.5) for $CaCl_2$ activity coefficients. The solution pH values are also given in Table 11.1. These are seen to lie in a narrow band around pH 6, and were therefore satisfactory. The pH of the $CaCl_2$ reference solutions were 5.96 and 5.88.

Examination of the transfer potentials did not suggest that any time dependence was present, so the results for each solution were averaged, and 95% confidence limits of the mean values were calculated.

TABLE 11.1 RESULTS FOR MIXED $CaSO_4$ (0.001 m) - $CaCl_2$ SOLUTIONS

Molality of $CaCl_2$	Date of Measurement	Observed Transfer Potential /absolute millivolts	Solution pH	Mean Transfer Potential/m.v.	95% Confidence Limits for Mean /m.v.
0.009790	7/2/72	13.09, 13.15, 13.25, 13.23		13.21	± 0.072
	8/2/72	13.15, 13.14, 13.19, 13.21			
	9/2/72	13.46, 13.26	5.90		
0.004310	7/2/72	40.53, 40.71, 40.62, 40.56		40.60	± 0.072
	8/2/72	40.65, 40.45, 40.79, 40.51			
	9/2/72	40.62, 40.53	5.87		
0.002060	7/2/72	64.85, 65.01, 64.83, 64.76		64.83	± 0.050
	8/2/72	64.82, 64.79, 64.82, 64.82			
	9/2/72	64.86, 64.76	5.91		
0.0010104	7/2/72	87.67, 87.71, 87.60, 87.41		87.44	± 0.110
	8/2/72	87.32, 87.36, 87.32, 87.35			
	9/2/72	87.35, 87.31	5.94		
0.0005469	7/2/72	106.15, 106.19, 106.01, 105.90		105.95	± 0.099
	8/2/72	105.79, 105.84, 105.99, 105.99			
	9/2/72	105.85, 105.80	5.99		
0.0002246	7/2/72	131.10, 130.81, 131.01		131.01	± 0.140
	8/2/72	130.66, 130.92, 131.24, 131.12			
	9/2/72	131.17, 131.10	6.00		
0.00009915	7/2/72	153.29, 153.27, 153.40		153.35	± 0.084
	8/2/72	153.41, 153.33, 153.29, 153.18			
	9/2/72	153.45, 153.55	6.13		
0.00004495	7/2/72	173.17, 173.11, 173.20		173.12	± 0.051
	8/2/72	172.99, 173.16, 173.18, 173.12			
	9/2/72	173.05, 173.12	6.15		

12. ANALYSIS OF LITERATURE OSMOTIC COEFFICIENT DATA

12.1 METHOD OF CALCULATION

The equation used to calculate ω_o for 2:1, 1:1 electrolyte mixtures was (E.7.8.5):

$$y_A\, y_B\, I\, \omega_o \quad = \quad 2y_A\, (\phi_{mix} - \phi_A^o) \; + \; y_B\, (\phi_{mix} - \phi_B^o)$$

The symbols were defined in section 7.8. The derivation of (E.7.8.5) from equation 6 of Reilly and Wood (103) is given in Appendix III.2.

Osmotic coefficients for mixed electrolyte solutions were obtained from the following sources:

System	Source
$NaCl - CaCl_2 - H_2O$	Robinson and Bower (93)
$NaCl - BaCl_2 - H_2O$	Robinson and Bower (104)
$KCl - CaCl_2 - H_2O$	Robinson and Covington (105)
$KCl - BaCl_2 - H_2O$	Robinson and Bower (106)
$NaCl - MgCl_2 - H_2O$	Platford (107)

Equation (7.8.5) requires that for each system, osmotic coefficients for pure aqueous solutions of each single electrolyte are known at every ionic strength for which measurements were made in the mixtures. Equation (7.7.8) was used for interpolation purposes, and best fit parameters for each electrolyte were computed by a non linear least squares procedure. Since ω_o is a measure of what may reasonably be called a second order non-ideality effect, it is clear that accurate values of ϕ^o were required. The osmotic coefficients of NaCl and KCl from various sources have been analysed by Robinson (113,114) to give "best" values, and these have generally been taken as reference standards. Solutions of these salts have then been used to determine osmotic coefficients of other electrolytes by the isopiestic technique. In this present study self consistency was achieved by using the best fit parameters to (E.7.7.8) computed by Lietzke and Stoughton (41) for pure NaCl and pure KCl solutions. Osmotic coefficients for all other solutions, either of single or mixed electrolytes, were recalculated from raw unsmoothed data using the parameters of (41) to interpolate osmotic coefficients for the reference solutions. A number of sets of isopiestic data are available in the literature for each of the pure 2:1 chloride solutions. These were treated separately to give best fit parameters to (E.7.7.8). After inspection of the results to check that none of the sets were inconsistent with the bulk of the results, all the data for each salt were combined, and overall best fit parameters were obtained. Where data were available up to very high concentrations, only results for solutions having an ionic strength below 9 molal were included in the analysis. Calcium chloride was used as the reference salt for one of the sets of magnesium chloride isopiestic measurements. This data set was analysed by using the best fit parameters for $CaCl_2$ obtained in this present study when all available data was utilised.

When calculating ω_0 values for each system, two sets of best fit parameters were used for the osmotic coefficients of the pure 2:1 salts. Calculations of ω_0 were always made using the set of parameters derived from all the available isopiestic data. In addition, ω_0 values were calculated using the particular set of best fit parameters for each 2:1 salt which had been computed from isopiestic measurements made at the same time as those on the mixed electrolyte system concerned. These latter parameters could not be relied upon to give osmotic coefficients as accurate as those calculated using parameters for all the data, but had the advantage that the ϕ^0 and ϕ_{mix} values should be more internally consistent.

12.2 RESULTS AND DISCUSSION

Table 12.2.1 gives the results of the least squares fitting of osmotic coefficients for the pure alkaline earth chlorides. The results of Lietzke and Stoughton (41) are shown for comparison. In general the results for the different sets of data were in reasonable agreement. The only exception was the data of reference 104 for $BaCl_2$. At the lowest ionic strengths this gave slightly higher osmotic coefficients than the other data analysed, and resulted in quite different best fit parameters. This example emphasises the dangers of using best fit parameters to extrapolate outside the range of the data from which they were derived. Within the experimental ionic strength range used in reference 104, the best fit parameters give osmotic coefficients which are in reasonable agreement with osmotic coefficients derived using the other data for $BaCl_2$. Outside this range the two sets of osmotic coefficients diverge markedly.

The calculated ω_0 values for each system are presented in Figures 12.2.1 to 12.2.5. With the exception of seven low concentration data points for the $BaCl_2$ - NaCl - H_2O system, all the points were calculated using ϕ^0 values for 2:1 salts computed from "all data" parameters. In general the differences in ω_0 values calculated by the two methods were so small that showing both sets of values would have been pointless. The six lowest ionic strength results for the system $BaCl_2$ - NaCl - H_2O comprised a group of isopiestic measurements referred to as "Set 1" in reference 104, and presumably were from an individual "run". The two sets of parameters gave rise to quite different ω_0 values for these six points but all the remaining data gave good agreement between the two calculation procedures. Both the calculated ω_0 values are shown in Figure 12.2.5 for these points. The very sharp convergence of the results at higher concentrations is demonstrated by the inclusion in Figure 12.2.5 of both ω_0 values for the seventh point. Inspection of the results for this system suggests that the ω_0 values calculated using the "all data" parameters are anomalous. This implies that some error was present in the data for Set 1 which affected both the mixed $BaCl_2$ - NaCl solutions and the pure $BaCl_2$ solutions in an equivalent manner. One possible cause could have been an error in the concentration of the NaCl reference solutions.

Some asymmetry in the ω_0 values was present for all the data and was particularly apparent for the $CaCl_2$ - NaCl - H_2O system. This y dependence of the data did not, however, obscure the main feature of results which was a negative gradient of the ω_0 values as a function of ionic strength.

TABLE 12.2.1 BEST FIT PARAMETERS TO EQUATION (7.7.8) FOR SOLUTIONS OF $MgCl_2$, $CaCl_2$ AND $BaCl_2$

Salt	Reference Salt	Data Source Reference Number	Number of Data Points	Best Fit Parameters		Variance of Fit: $\sigma^2/(N-4)$	Range of Ionic Strength
$MgCl_2$	$CaCl_2$	111	13	A 1.6813 B 0.05552	C 0.01147 D -0.000421	1.54×10^{-8}	0.92 - 6.2
	NaCl	107	17	A 1.7000 B 0.05320	C 0.01240 D -0.000457	1.05×10^{-4}	0.24 - 8.3
	KCl	108	27	A 1.7454 B 0.05259	C 0.01192 D -0.000424	9.20×10^{-6}	0.34 - 6.0
	Combined Results		57	A 1.7131 B 0.05522	C 0.01103 D -0.000321	1.34×10^{-6}	0.34 - 8.3
	cf. Reference 41			A 1.6007 B 0.06633	C 0.009003 D -0.000255	1.50×10^{-5}	0.30 - 15.0
$CaCl_2$	NaCl	93	16	A 1.5366 B 0.05422	C 0.006518 D -0.000126	5.24×10^{-7}	1.1 - 8.6
	KCl	105	9	A 1.4963 B 0.05832	C 0.005568 D -0.000069	5.17×10^{-7}	1.5 - 6.4
	KCl	110	29	A 1.6513 B 0.03830	C 0.01046 D -0.000465	5.54×10^{-6}	0.27 - 6.6
	NaCl	109	29	A 1.5964 B 0.04990	C 0.007264 D -0.000175	2.20×10^{-7}	0.27 - 8.9
	Combined Results		83	A 1.5859 B 0.04982	C 0.007033 D -0.000143	1.71×10^{-5}	0.27 - 8.9
	cf. Reference 41			A 1.6129 B 0.04566	C 0.008573 D -0.000274	4.03×10^{-6}	0.006 - 18.0
$BaCl_2$	NaCl	104	12	A 1.8332 B -0.01432	C 0.017497 D -0.001586	3.4×10^{-6}	1.1 - 5.3
	KCl	106	12	A 1.5727 B 0.01925	C 0.005811 D -0.000366	1.71×10^{-7}	1.6 - 5.1
	KCl	110	19	A 1.5554 B 0.02233	C 0.004718 D -0.000223	2.88×10^{-6}	0.26 - 5.4
	Combined Results		43	A 1.5791 B 0.01773	C 0.006708 D -0.000481	3.96×10^{-6}	0.26 - 5.4
	cf. Reference 41			A 1.5993 B 0.01232	C 0.008811 D -0.000692	8.4×10^{-7}	0.03 - 5.4

FIGURE 12.2.1 ω_0 VALUES FOR THE $CaCl_2$ - KCl - H_2O SYSTEM

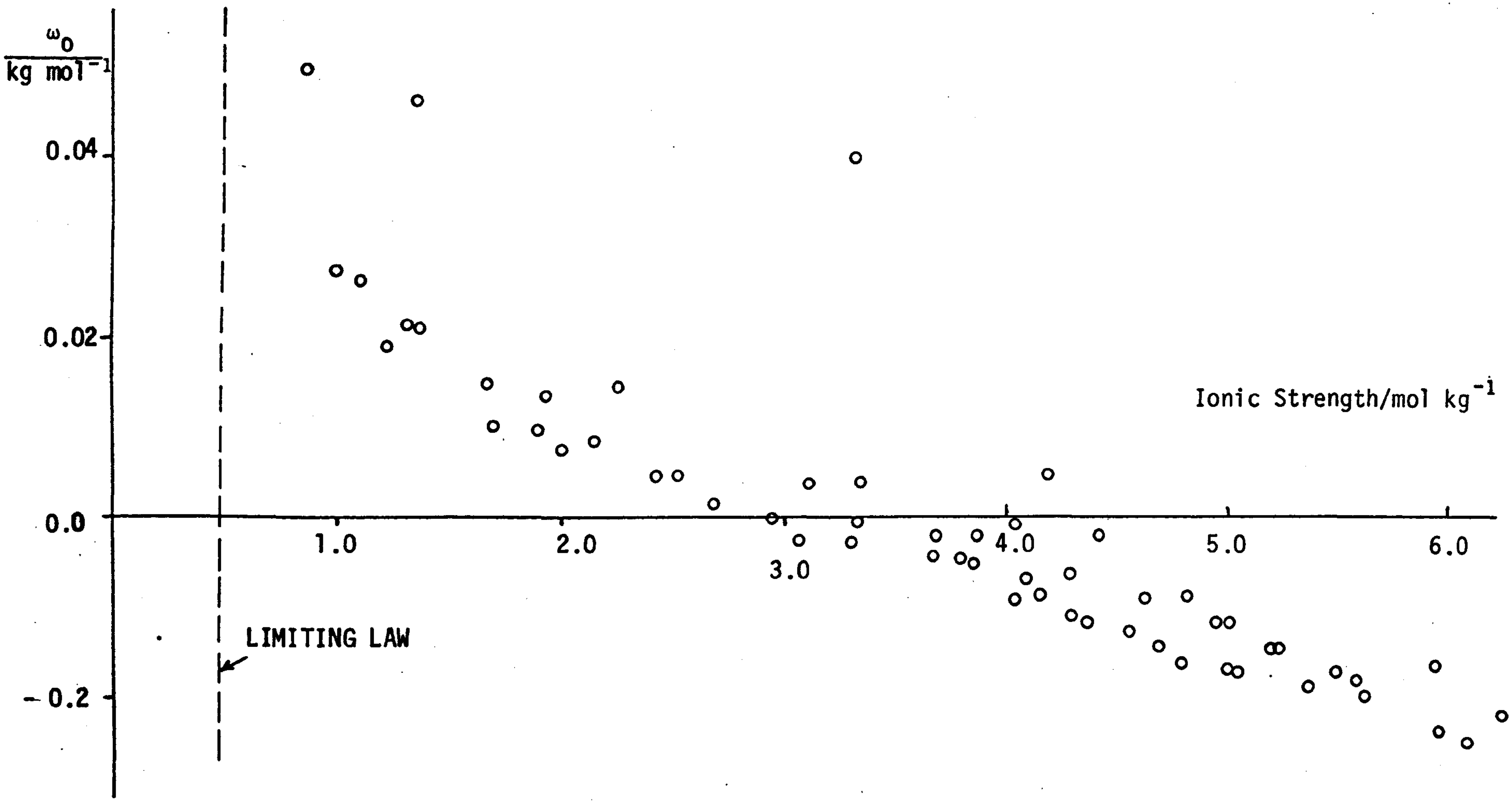


FIGURE 12.2.2 ω_0 VALUES FOR THE $CaCl_2$ - NaCl - H_2O SYSTEM

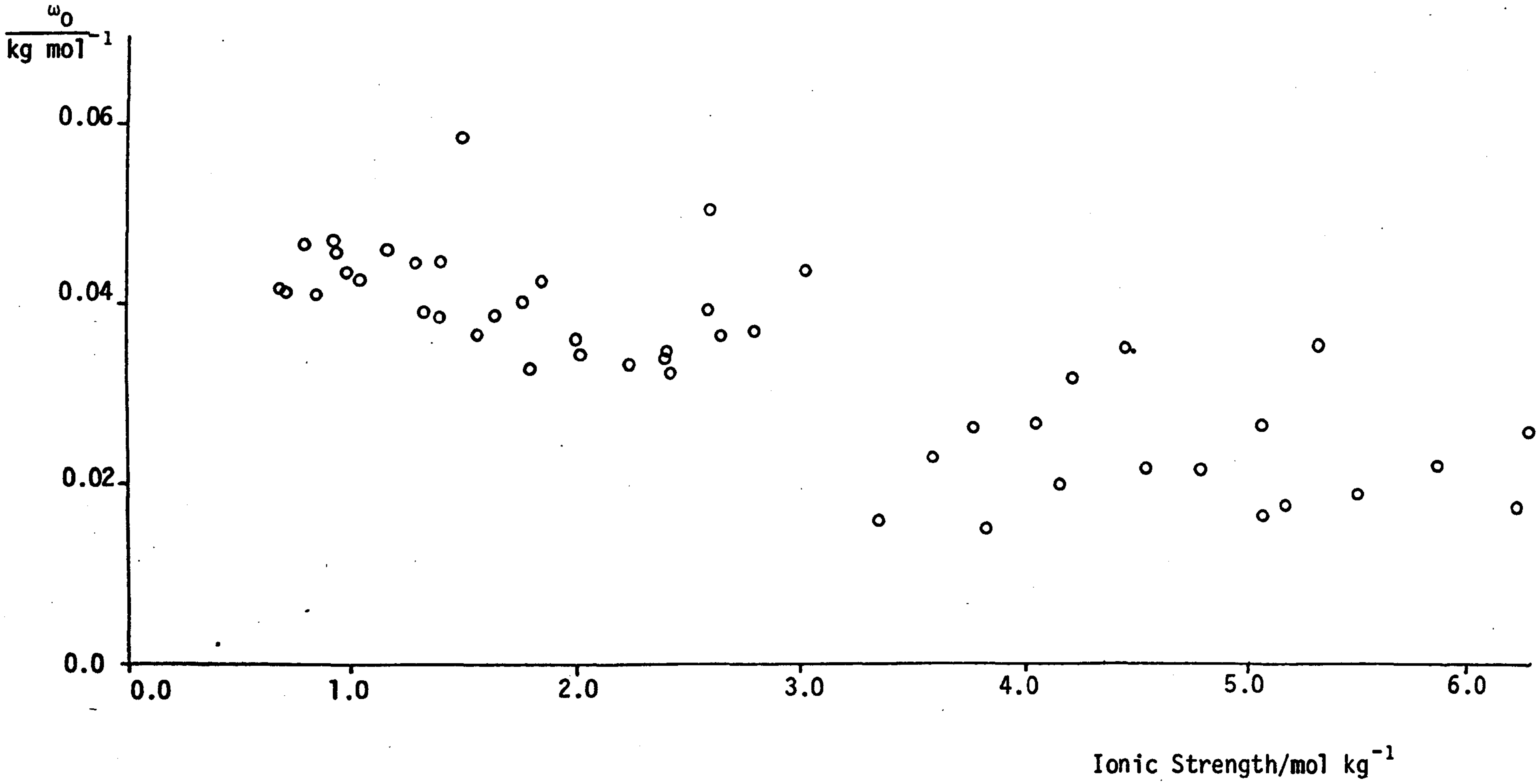


FIGURE 12.2.3 ω_0 VALUES FOR THE $MgCl_2$ - NaCl - H_2O SYSTEM

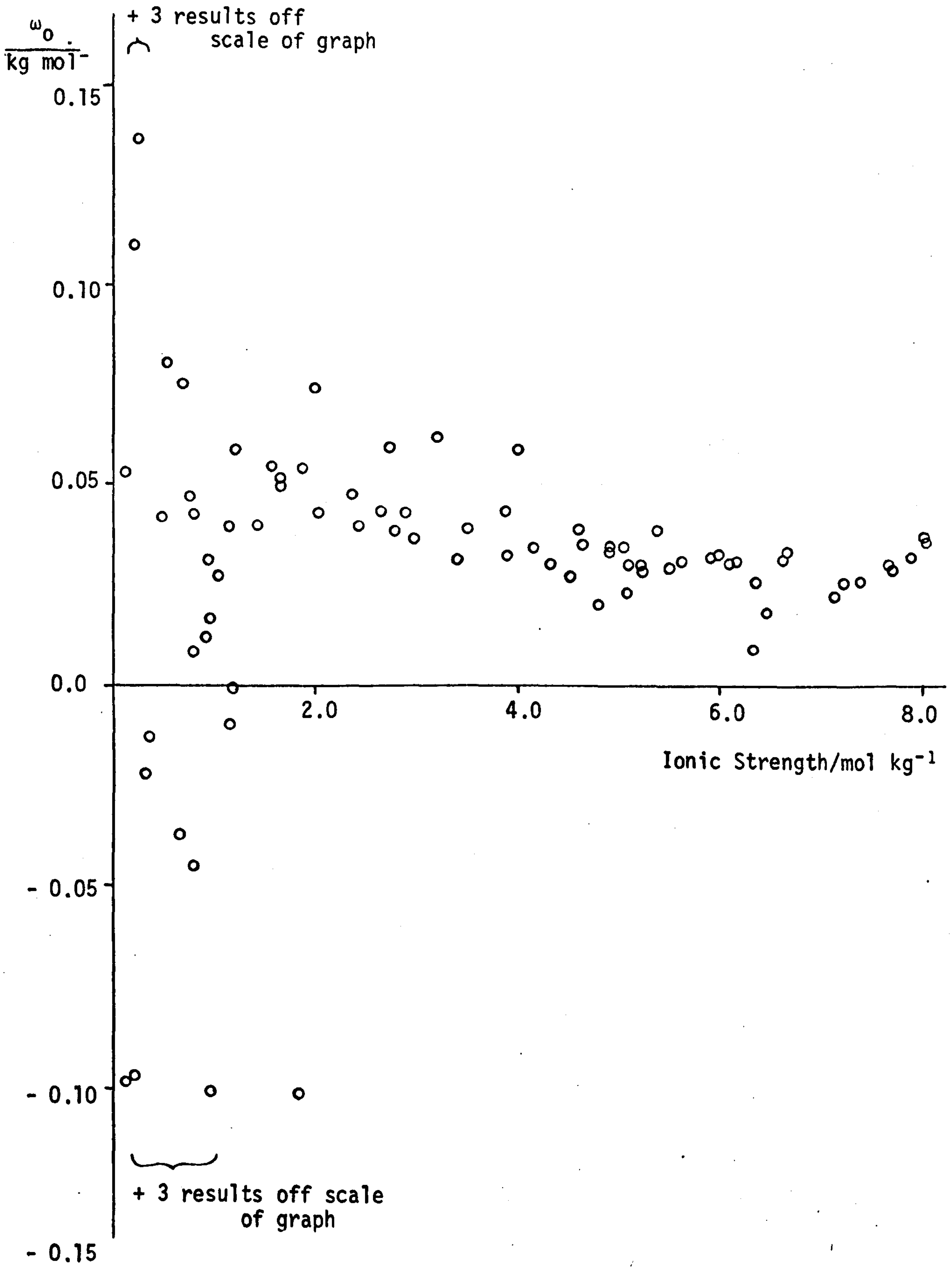


FIGURE 12.2.4 ω_0 VALUES FOR THE $BaCl_2$ - KCl - H_2O SYSTEM

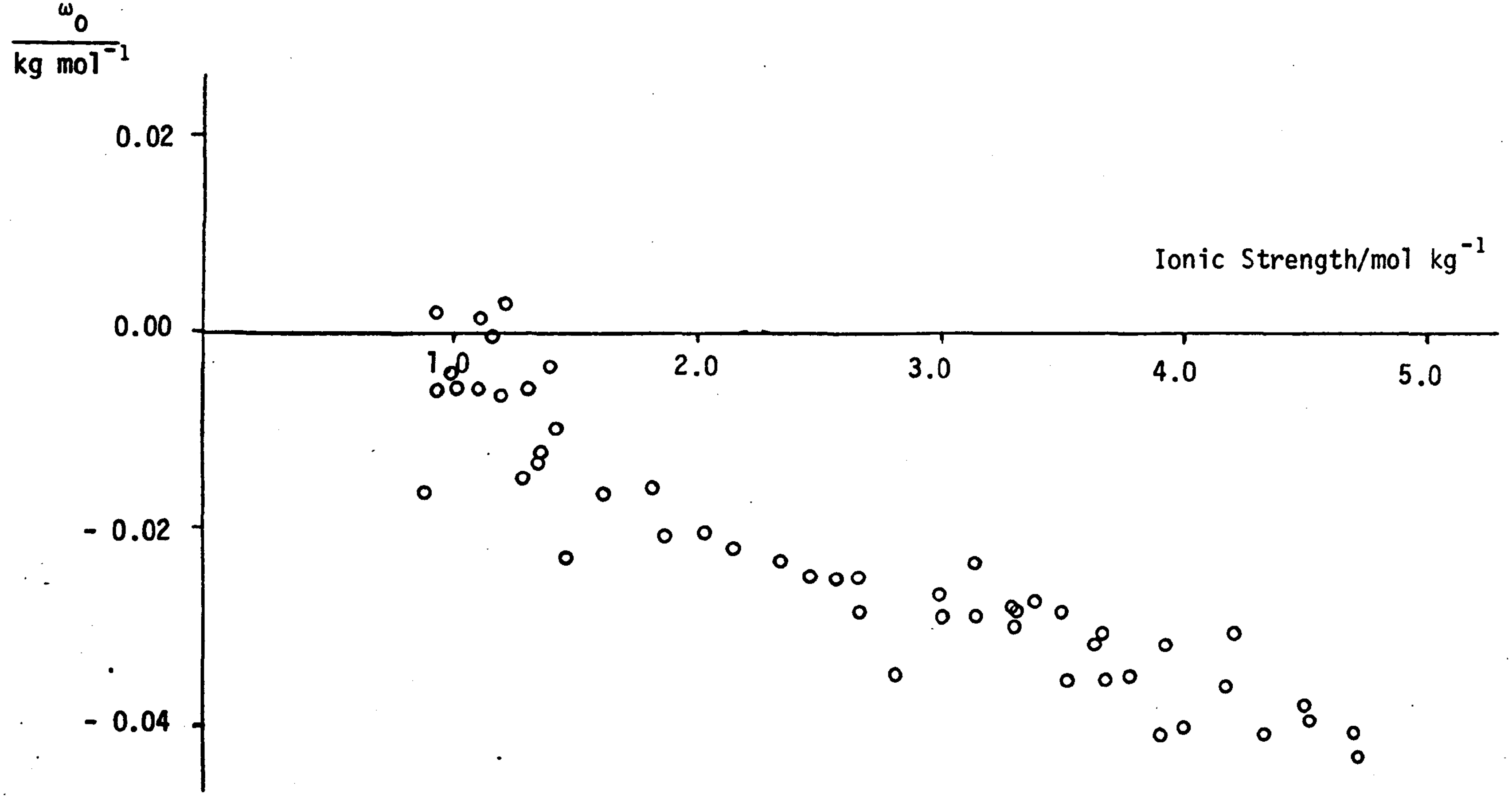
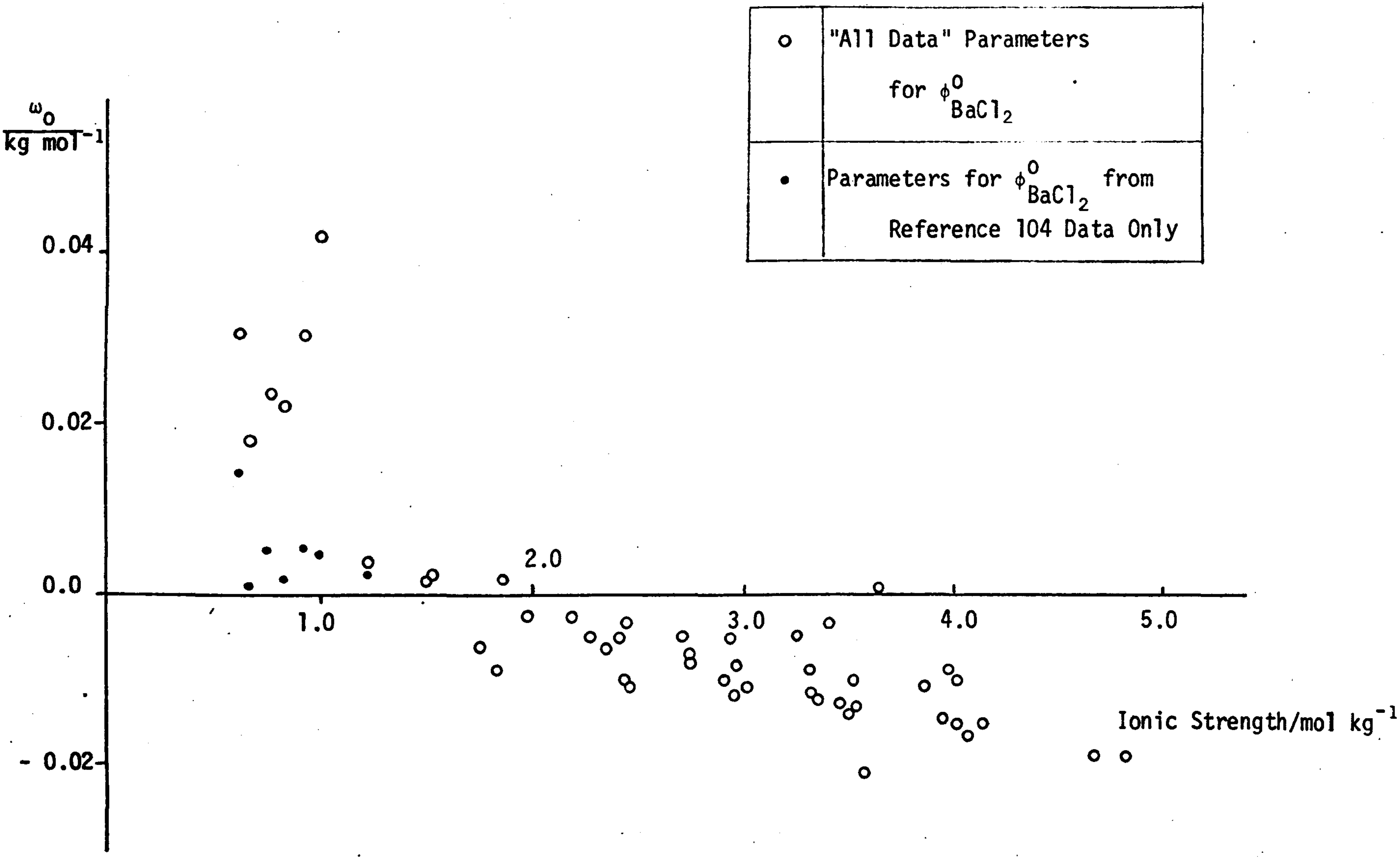


FIGURE 12.2.5 ω_0 VALUES FOR THE $BaCl_2$ - NaCl - H_2O SYSTEM



This trend is in sharp contrast to the theoretical limiting law. To aid comparison, ω_0 values were evaluated using (E.9.1.5) and are shown in Figure 12.2.1. The dashed line representing this limiting law is shown as a straight line. It should really be slightly curved, the gradient decreasing as the ionic strength increases.

It is unfortunate that with the exception of the $MgCl_2$- NaCl data, the results do not extend below an ionic strength of 0.6 molal. The isopiestic data for solutions of ionic strength below one molal is of such poor precision for this system, that it is almost worthless. If, however, these results are not rejected, they may be optimistically construed as providing indications of a downturn in the ω_0 values at low concentrations.

In section 14.2 these results are compared with primitive model calculations.

13. ANALYSIS OF ACTIVITY COEFFICIENT DATA FOR THE $CaSO_4$ - $CaCl_2$ - H_2O SYSTEM

13.1 METHOD OF CALCULATING g_0 VALUES

Friedman's (94) equation (16.29) is taken as a starting point:

$$\Delta m\, G^{ex}(y, I) = G^{ex}(0, t) - \left[1 - y\right] G^{ex}(0, I) - y\, G^{ex}(1, I)$$

$$+ 2t \int_0^y g_A^{ex}\left(y', t/\left[1 - y'\right]\right)\left[1 - y'\right]^{-2} dy' \qquad \text{(E.13.1.1)}$$

The symbolism is that of Friedman. Quantities enclosed by parentheses indicate values of the variables upon which the preceding quantity depends. y is the fraction of total ionic strength contributed by the electrolyte (A) whose excess free energy is known in the mixed solution. t is the ionic strength contribution of electrolyte B which must be constant. g_A^{ex} is a reduced form of the mean ionic partial molal excess free energy of electrolyte A defined by

$$g_A^{ex} = \frac{RT}{|Z_+ Z_-|_A} \ln \gamma_{\pm A} \qquad \text{(E.13.1.2)}$$

Consequently, for the system under consideration, the information required to calculate $\Delta m G^{ex}$ at a given ionic strength fraction (y_A) of $CaCl_2$ and total ionic strength I is:

(i) the excess free energy of pure $CaSO_4$ solution per kg of solvent at the ionic strength (t) of $CaSO_4$ in the mixed solution;

(ii) the same quantity at the total ionic strength of the mixed solution;

(iii) the excess free energy of pure $CaCl_2$ solution per kg of solvent at the total ionic strength of the mixed solution;

(iv) the y_A dependence of $CaCl_2$ activity coefficients in the mixed solution from the given y_A value down to y_A = zero.

For a solution of a single electrolyte the excess free energy per kg of solvent is given by

$$G^{ex} = \nu RT m (1 - \phi + \ln\gamma_{\pm}) \qquad \text{(E.13.1.3)}$$

where ν is the number of moles of ions per mole of solute,
m is the stoichiometric molality of solute,
and ϕ and $\gamma_{\pm}$ are stoichiometric quantities.

The procedure used to calculate the four terms on the R.H.S. of equation (13.1.1) is outlined below.

(i) Osmotic coefficients of pure calcium sulphate solutions were calculated as described in section 3.2.13 of Part I. Activity coefficients were calculated on the same basis as the osmotic coefficients in order to be self consistent. The same pair of K_D and q values were used to calculate values of γ_f by the iterative procedure, described in sections 3.2.5 and 3.2.6, and these values were corrected for the linear term in the ionic strength of free ions using

$$\ln\gamma_f' = \ln\gamma_f + 0.533\ I' \qquad (E.13.1.4)$$

Stoichiometric activity coefficients were then calculated using

$$\gamma_\pm = \frac{m_f\ \gamma_f'}{m} \qquad (E.13.1.5)$$

The first term in Equation (13.1.1) could then be computed from

$$2\ RT\ m_B\ (1 - \phi + \ln\gamma_\pm)_B \qquad (E.13.1.5a)$$

with m_B equal to 0.25 t and the terms in the brackets taking values corresponding to I = t. This first term is therefore a constant.

(ii) The second term was calculated in a similar manner except that equation (13.1.5a) was multiplied by the necessary ionic strength fraction and all the quantities in the equation were set to values corresponding to the total ionic strength of each solution.

(iii) For the third term, the parameters of Lietzke and Stoughton (41) for calcium chloride were used in equations (7.7.8) and (3.1.5) to calculate osmotic and activity coefficients at the total ionic strength of each solution. The magnitude of this term was then given by

$$3y_A\ RT\ m_A\ (1 - \phi + \ln\gamma_\pm)_A$$

with m_A equal to one third of the total ionic strength of each solution.

(iv) This term was re-expressed as

$$RT\ t \int_0^{y_A} \frac{\ln\gamma_{\pm A}^{mix}}{(1 - y_A')^2}\ d\,y_A' \qquad (E.13.1.6)$$

Experimental values of $\ln\gamma_{\pm A}^{mix}$ were evaluated from the mean transfer potentials given in Table 11.1 by the methods used in Part I.

The test cells were represented as

$$\underset{}{Ag / AgCl /} \underset{(m_A)}{CaCl_2}\ ,\ \underset{(m_B)}{CaSO_4}\ ,\ \underset{(m_C)}{AgCl}\ \text{/ calcium electrode} \qquad \text{Cell IV C}$$

and the cell potential written as

$$E_{IVC} = "E^0_{Ca}" - E^0_{AgCl/Ag} + \frac{RT}{2F}\ln\left(a_{Ca^{2+}}\, a^2_{Cl^-}\right)_{IVC}$$

After subtracting the potential of the reference cell III, the transfer potential was given by

$$E_T\ (C) \quad = \quad \frac{RT}{2F}\left[\ln\ (m_A + m_B)(2m_A + m_C)^2(\gamma_{\pm A}^{mix})^3 \quad - \quad \ln\ 4(m\gamma_{\pm})^3_{REF}\right] \qquad (E.13.1.7)$$

It is seen from the form of this equation that the effect of dissolved silver chloride on the potential of the Ag/AgCl electrode was taken into consideration, but the response of the calcium electrode to dissolved silver ions was neglected. This was because the concentration of dissolved AgCl was always insignificant compared to the concentration of calcium ions, but at the lowest y_A values it was an important fraction of the chloride ion concentration. A method of estimating the solubility of silver chloride in the mixed $CaSO_4$-$CaCl_2$ solutions was therefore required. It was assumed that at the low ionic strengths used,

$$\ln\gamma_{\pm AgCl} \quad = \quad \frac{-\ 1.172\ \ I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} \qquad (E.13.1.8)$$

was an adequate expression for the activity coefficient. By substituting the literature value (119) for the ideal solubility (m_s) of AgCl in pure water at 25^{o}C into

$$K_{sp}\ (AgCl) \quad = \quad m_s^2\ \gamma_{\pm}^2 \qquad (E.13.1.9)$$

a value for the thermodynamic solubility product was obtained. This was used in the equation

$$K_{sp}\ (AgCl) \quad = \quad m_C\ (m_C + 2m_A)\ \gamma_{\pm}^2 \qquad (E.13.1.10)$$

to estimate m_C at each m_A value. The ionic strength used in (E.13.1.8) was taken to be $4m_B + 3m_A$.

The major problem of this analysis was evaluation of the integral in (E.13.1.6) using the experimental activity coefficients obtained from (E.13.1.7). The latter were not sufficiently numerous or precise, especially at low y_A values, to enable a simple "trapezoidal area" technique to be used with any accuracy.

At very low y_A values, the system is essentially at constant ionic strength, and the trace activity coefficient of $CaCl_2$ in the $CaSO_4$ solution should be represented reasonably accurately by Harned's Rule (47):

$$\ln\ \gamma_{\pm A}^{mix} \quad = \quad \ln\ \gamma_{\pm A}\ (\text{trace in B}) \ + \alpha\ m_A$$

where α is a constant. It was assumed that deviations from this equation at higher y_A values could be represented by the addition of empirical terms in powers of y_A giving

$$\ln\ \gamma_{\pm A}^{mix} \quad = \quad A\ +\ By_A\ +\ Cy_A^2\ +\ Dy_A^3\ +\ Ey_A^4 \qquad (E.13.1.11)$$

The experimental activity coefficients were fitted to (E.13.1.11) by the method of least squares to obtain best fit values of the parameters A to E. The integration of expression (13.1.6) could then be carried out analytically after substitution of (E.13.1.11) for $\ln\gamma_{\pm A}^{mix}$. The first three terms were standard forms and the last two terms could be integrated by parts provided the substition

$y_A = 1 - y_B$ was made at an appropriate stage. The resulting analytical form of the integral was:

$$A\left[\frac{1}{y_B} - 1\right] + B\left[\ln y_B + \frac{1}{y_B} - 1\right] + C\left[2\ln y_B + \frac{1}{y_B} - y_B\right]$$

$$+ D\left[\frac{y_A^3}{y_B} + 3y_A^2\ln y_B + 6y_B\ln y_B - 6y_B - 3y_B^2\ln y_B + \frac{3}{2}y_B^2 + \frac{9}{2}\right]$$

$$+ E\left[\frac{y_A^4}{y_B} + 4y_A^3\ln y_A - 12y_B + 12y_B\ln y_B - 12y_B^2\ln y_B + 6y_B^2 + 4y_B^3\ln y_B\right.$$

$$\left. - \frac{4}{3}y_B^3 + \frac{22}{3}\right]$$

Having evaluated ΔmG^{ex} values as outlined above, g_o was calculated for each solution using the appropriate form of (E.9.1.3):

$$\Delta mG^{ex}(y, I) = I^2 RT\, y(1 - y)\, g_o \qquad \text{(E.13.1.12)}$$

This equation assumes that ΔmG^{ex} is a symmetric function of y. Since y and the ionic strength are directly linked in this study, analysis of the results with higher terms included to account for asymmetry in ΔmG^{ex} would probably not be meaningful.

13.2 METHODS OF PREDICTING CALCIUM CHLORIDE ACTIVITY COEFFICIENTS IN THE MIXED SOLUTIONS

Method A: comparison with the activity coefficients of pure $CaCl_2$ solutions at the same ionic strength as the mixed solutions.

At the low ionic strengths used in this study, Lewis and Randall's "Principle of ionic strength" should be a good first approximation. A more refined treatment is to assume that the free energy of either single or mixed electrolyte solutions is given by a standard electrostatic free energy term modified by terms involving all possible pairwise interactions. This may be considered as a hybrid of two treatments by Guggenheim (115,116). The required expression for the present system is

$$\frac{G}{RT} = \frac{G^{elec}_{standard}}{RT} + A_1 m_{Ca}^2 + A_2 m_{Cl}^2 + A_3 m_{SO_4}^2 + A_4 m_{Ca} m_{Cl}$$

$$+ A_5 m_{Ca} m_{SO_4} + A_6 m_{Cl} m_{SO_4} \qquad \text{(E.13.2.1)}$$

Partial differentiations with respect to calcium ion molality and chloride ion molality give expressions for single ion activity coefficients. These may be combined in an appropriate manner to give expressions for the mean ionic activity coefficient of $CaCl_2$. In the mixed electrolyte solution the resulting expression is

$$3\ln\gamma^{mix}_{\pm CaCl_2} = 3\ln\gamma^{elec}_{\pm stand} + 2(A_1 + A_4)m_{Ca} + (4A_2 + A_4)m_{Cl} + (2A_6 + A_5)m_{SO_4}$$

and in the pure $CaCl_2$ solution is

$$3 \ln \gamma_{\pm CaCl_2} = 3 \ln \gamma^{elec}_{\pm stand} + 2\,(A_1 + A_4)m'_{Ca} + (4A_2 + A_4)m'_{Cl} \qquad (E.13.2.3)$$

The ratio of the two activity coefficients is therefore given by

$$3 \ln \left(\frac{\gamma^{mix}_{\pm}}{\gamma_{\pm}}\right)_{CaCl_2} = 2\,(A_1 + A_4)\,(m_{Ca} - m'_{Ca}) + (4A_2 + A_4)\,(m_{Cl} - m'_{Cl})$$

$$+ \; (2A_6 + A_5)\; m_{SO_4} \qquad (E.13.2.4)$$

By utilising the condition of constant ionic strength for the two solutions, expressed by

$$4\, m_{CaSO_4} + 3\, m_{CaCl_2} = 3\, m'_{CaCl_2} \qquad (E.13.2.5)$$

where the superscript refers to concentrations in the single electrolyte solution, and by expressing the ionic molalities in (E.13.2.4) in terms of m_{CaSO_4} and m_{CaCl_2}, the equation may be simplified to give

$$3 \ln\left(\frac{\gamma^{mix}_{\pm}}{\gamma_{\pm}}\right)_{CaCl_2} = m_{CaSO_4}\,(2A_6 + A_5 - \frac{2}{3} A_1 - \frac{10}{3} A_4 - \frac{32}{3} A_2) \qquad (E.13.2.6)$$

In the present experimental study, the molality of calcium sulphate is held constant, consequently this treatment predicts that any difference in the logarithms of the two activity coefficients should be a constant independent of the concentration of calcium chloride. It is not possible to predict the magnitude of this difference since the values of the parameters involved are not known. Evaluation of suitable parameters should be possible from an analysis of free energy data on appropriate single electrolyte and common ion binary electrolyte solutions. The accuracy and consistency of such an analysis would however be severely handicapped by the difficulty of devising an expression for the standard electrostatic free energy term which was adequate for both $CaCl_2$ and $CaSO_4$ solutions.

Method B: using the treatment of Reilly, Wood and Robinson (117), but neglecting terms involving g.

Reilly, Wood and Robinson (117) have recently published a paper in which equations are derived for the osmotic and activity coefficients of multicomponent electrolyte solutions of unrestricted charge type. Their treatment is based directly on the general equation for the free energy of such solutions given by two of the above authors in reference 103, and is itself dependent on Friedman's (94) approach to mixed electrolyte theory. The equations correctly account for pairwise specific interactions but triplet interactions are only accounted for under special circumstances.

In the present context, the important equation is (A-9) of reference 117. This expresses the mean ionic molal activity coefficient of an electrolyte in a multicomponent mixture in terms of the properties of single electrolyte solutions, and the properties of binary electrolyte mixtures having a common ion. The equation can be used at two levels of approximation depending upon whether the latter properties are included or not. Unfortunately equation (A-9) of reference 117 has two errors in the last line. This line should read

$$\frac{EZ_{pq}}{2} \frac{\partial}{\partial I} (g_{x_\ell x_m}^{M_k}) \Bigg] - Z_{p\ell} Z_{pm} g_{x_\ell x_m}^{M_k} \Bigg\}$$

The nomenclature is that of reference 117, $g_{x_\ell x_m}^{M_k}$ is simply g_0 for the binary electrolyte system $k\ell$ with km. The complete equation is not presented here, but the corrected form will be referred to as (E.13.2.1). Calcium chloride mean ionic activity coefficients in mixed $CaCl_2$ (A) - $CaSO_4$ (B) solutions may, on the basis of (E.13.2.1), be expressed as

$$\ln \gamma_{\pm_A}^{mix} = \ln\gamma_{\pm_A} + y_B (\tfrac{1}{2} - \phi_A + \tfrac{1}{2} \phi_B) + I y_B (g_{Cl,SO_4}^{Ca} + y_A I \frac{\partial}{\partial I} g_{Cl,SO_4}^{Ca}) \quad (E.13.2.2)$$

in which activity and osmotic coefficients on the R.H.S. of the equation refer to properties of single electrolyte solutions at the same ionic strength as the mixed solution.

In the method of calculation used in this section the terms involving g were set equal to zero. The values of $\ln\gamma_\pm$ and ϕ for pure $CaCl_2$ solutions were computed using the parameters of Lietzke and Stoughton and equation (3.1.5). The osmotic coefficients of pure calcium sulphate solutions were calculated as described in section 3.2.13 of Part I.

Method C: using the full treatment of Reilly, Wood and Robinson (117).

The only source of experimental values of g_{Cl,SO_4}^{Ca} was the results of this present analysis. It was clear that using these values of g in equation (13.2.2) involved a circular argument, but such an approach was considered worthwhile since it provided a means of checking: (i) the self consistency of equations (13.2.2), (13.1.1) and (13.1.12) and (ii) whether ion triplets made a significant contribution to the free energy.

Equation (13.1.1) is a general thermodynamic relationship, but both (E.13.1.12) and (E.13.2.2) fail to properly account for interactions between more than two ions. If such interactions make a significant contribution, the calculated values of g_0 will be in error. It is thought very unlikely that substitution of incorrect values of g_0 and $\frac{\partial}{\partial I} g_0$ into the inadequate equation (13.2.2) would produce compensating errors and give solutions equal to the original experimental activity coefficients.

At the lowest concentrations of $CaCl_2$ used in the mixed solutions, the contribution to the solution free energy made by triplet or higher interactions was expected to be negligible. It follows from this that only three situations could arise when experimental $CaCl_2$ activity coefficients were compared with values computed by method C:

(a) excellent agreement for all $CaCl_2$ concentrations, indicating self consistency of the three equations and the absence of significant triplet interactions;

(b) good agreement at low y_A values but deteriorating agreement as y_A increases, indicating self consistent equations, but significant contributions from triplet interactions;

(c) lack of agreement at all y_A values, indicating that some inconsistency is present in the equations.

The experimental g_o values deduced by the method of section 13.1, were differentiated with respect to ionic strength by a graphical method. Two graphs of g_o were plotted with I as abscissa and tangents were drawn to the best smooth curves through the experimental points. One graph was designed to be accurate at low y_A values, while the second emphasised accuracy at high y_A values.

13.3 RESULTS AND DISCUSSION OF THE CALCULATIONS OUTLINED IN SECTIONS 13.1 and 13.2

Figure 13.3.1 shows the experimental activity coefficients of $CaCl_2$ in the mixed solutions plotted against the ionic strength fraction of $CaCl_2$. Values of $\ln\gamma_{\pm A}^{mix}$ calculated using best fit parameters in equation (13.1.8) are shown at the same y_A values and a best smooth curve is drawn through the latter points. Also illustrated in this figure are experimental values of $\ln\gamma_{\pm A}^{mix}$ divided by y_B^2. The smooth curve through these points shows more clearly the nature of the integration involved in (E.13.1.1).

The 95% confidence limits of the experiment activity coefficients shown in Figure 13.3.1 were calculated from the variance of the transfer potentials. An estimate of systematic errors was not included. The large scatter of the results at low y_A values indicates that at least one of the points is in error by an amount greater than can be reasonably accounted for by random statistical variations. A source of additional error at low calcium chloride concentrations is uncertainty in the solubility of silver chloride. Comparison of columns 4 and 5 in Table 13.3.1 shows that at the lowest y_A value, this solubility had a large effect on the calculated value of $\ln\gamma_{\pm A}^{mix}$. The estimated possible error in the corrections to $\ln\gamma_{\pm A}^{mix}$ made to account for AgCl solubility is ±20% of the correction. Even after adding this uncertainty to that arising from the variance of the transfer potentials, it is still difficult to explain the observed scatter of the low ionic strength results without invoking the possibility of further sources of error such as additional chloride impurities. The susceptibility of the results to small chloride impurities at low y_A values has already been illustrated by the problem of silver chloride solubility, but a further example serves to emphasise this point. At the lowest chloride ion concentration (8.9×10^{-5} molal), an assumed impurity of 0.1 weight per cent $CaCl_2$ in the gypsum used to prepare the solutions would change the calculated value

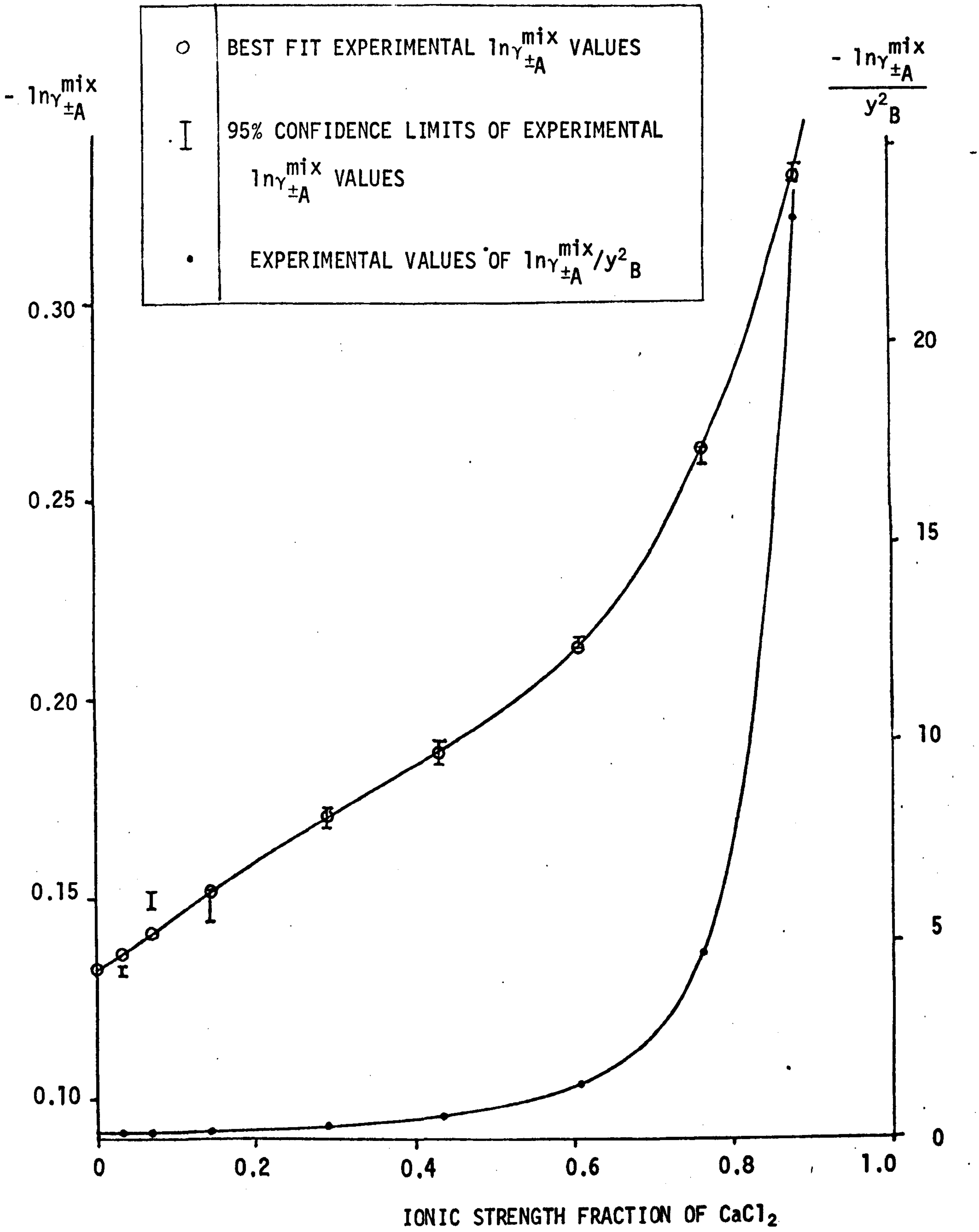


FIGURE 13.3.1 ACTIVITY COEFFICIENTS OF CALCIUM CHLORIDE AS A FUNCTION OF y_A

TABLE 13.3.1 g_0 AND OTHER QUANTITIES INVOLVED IN ITS EVALUATION

Ionic Strength /mol kg^{-1}	y_{CaCl_2}	10^6(Estimated Solubility of AgCl) /mol kg^{-1}	Experimental values of $-\ln\gamma^{mix}_{\pm A}$			$10^5 \times \frac{\Delta_m G^{ex}}{RT}$ /mol kg^{-1}	g_0 /kg mol^{-1}
			(1)	(2)	(3)		
0.03337	0.8801	NEGLIGIBLE	0.3331	0.3331	0.3326	- 7.606	- 0.6475
0.01693	0.7637	NEGLIGIBLE	0.2610	0.2610	0.2623	0.4093	0.0792
0.01018	0.6071	NEGLIGIBLE	0.2141	0.2141	0.2128	1.728	0.6991
0.00703	0.4311	NEGLIGIBLE	0.1863	0.1863	0.1863	1.591	1.312
0.00564	0.2909	0.22	0.1700	0.1701	0.1704	1.514	2.307
0.00467	0.1441	0.50	0.1475	0.1482	0.1517	1.009	3.746
0.00430	0.0692	1.04	0.1459	0.1494	0.1415	0.5362	4.506
0.00413	0.0326	2.22	0.1160	0.1322	0.1368	0.2612	4.844

(1) Calculated directly assuming solubility of silver chloride is zero.

(2) Calculated directly with a correction for estimated solubility of silver chloride.

(3) Calculated using best fit parameters in equation (13.1.11).

of $\ln\gamma^{mix}_{\pm A}$ from - 0.132 to a corrected value of - 0.155.

The most important feature of the results presented in Table 13.3.1 is the monotonic trend of g_0 to more positive values as the ionic strength is reduced. The relatively smooth nature of this trend is illustrated in Figure 13.3.2. These results contrast sharply with the limiting law (E.9.1.4). The magnitude of the experimental g_0 values are not unreasonable, but the signs of the individual values and the sign of the gradient are the opposite of those expected on the basis of Friedman's (94) theoretical predictions. This result is discussed below in an effort to deduce whether the anomally is (i) real; (ii) a result of experimental error, or (iii) due to an inconsistency in the equations, resulting in a reversal of sign.

These possibilities are analysed by comparison of experimental and calculated activity coefficients, and by consideration of the effect of errors from various sources.

FIGURE 13.3.2 COMPARISON OF EXPERIMENTAL g_o VALUES WITH THE LIMITING LAW

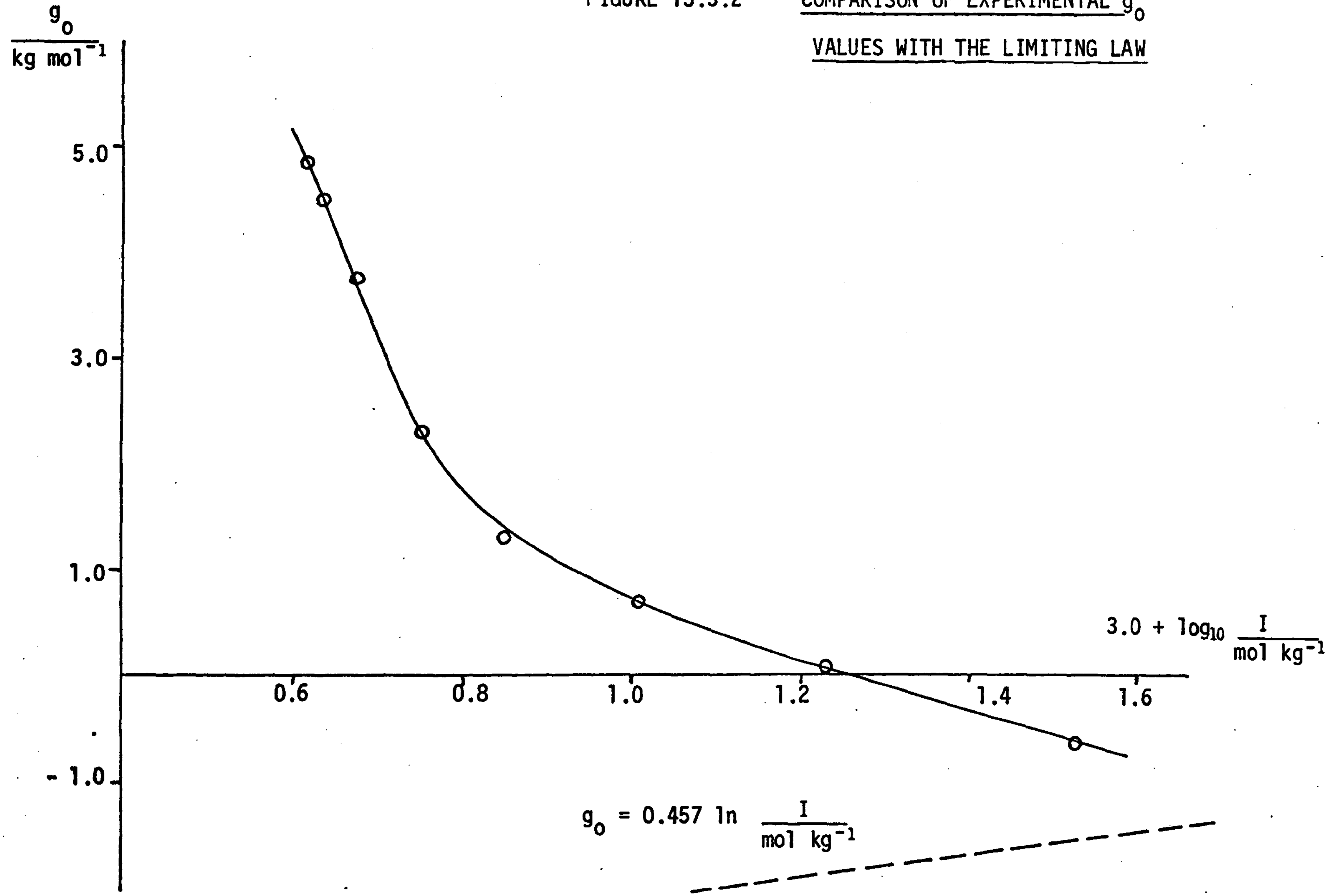


TABLE 13.3.2 COMPARISON OF VARIOUS VALUES OF ln$\gamma_{\pm A}$

y_A	Values of $-\ln\gamma_{\pm A}$				10^3 × Differences in Experimental and Calculated values of $\ln\gamma_{\pm A}$		
	(3)	(A)	(B)	(C)	(3) - (A)	(3) - (B)	(3) - (C)
0.8801	0.3326	0.3277	0.3316	0.3374	- 4.9	- 1.0	4.8
0.7637	0.2623	0.2505	0.2578	0.2608	- 11.8	- 4.5	- 1.5
0.6071	0.2128	0.2025	0.2133	0.2139	- 10.3	0.4	1.1
0.4311	0.1863	0.1725	0.1863	0.1857	- 13.8	0.0	- 0.6
0.2909	0.1704	0.1565	0.1723	0.1698	- 13.9	1.9	- 0.6
0.1441	0.1517	0.1439	0.1614	0.1511	- 7.8	9.8	- 0.5
0.0692	0.1415	0.1386	0.1569	0.1413	- 2.9	15.4	- 0.3
0.0326	0.1368	0.1362	0.1549	0.1367	- 0.6	18.1	- 0.1

(3) Calculated using best fit parameters to equation (13.1.11).

(A) Calculated for pure $CaCl_2$ solutions at same ionic strength as mixture.

(B) Calculated as described under method (B) in section 13.2.

(C) Calculated as described under method (C) in section 13.2.

Table 13.3.2 compares calcium chloride activity coefficients, calculated as described in section 13.2, with experimental values computed using the best fit parameters in equation (13.1.11). The difference between these experimental values and ln$\gamma_{\pm}$ for pure $CaCl_2$ solutions at the same ionic strength as the mixture is shown in column 6 of the table. Method A in section 13.2 predicts that this difference should be constant, but gives no indication of the expected magnitude. The observed differences are seen to be large at intermediate ionic strengths, but the trace activity coefficient of $CaCl_2$ in pure $CaSO_4$ solution is seen to be surprisingly close to the activity coefficient of pure calcium chloride solution at the same ionic strength. Activity coefficients calculated using the treatment of reference 117 but with the omission of terms involving g_0 (method B) are seen to be in reasonable agreement with the experimental value of ln$\gamma_{\pm A}^{mix}$ at intermediate ionic strengths but to deviate markedly at low ionic strengths. Inclusion of the g_0 and $\frac{\partial}{\partial I}(g_0)$ terms (method C) gave very good agreement at low ionic strengths but this concordance deteriorated as y_A increased. These latter results correspond to situation (b) discussed under method C in section 13.2 and indicate that equations (13.2.2), (13.1.1) and (13.1.12) are self consistent. The deterioration of the agreement at high ionic strengths suggests that triplet interactions cannot be disregarded. The poor agreement of experimental values of $\ln\gamma_{\pm A}^{mix}$ with the results of method B at low ionic strengths indicates that either the experimental results are in error or that the large positive g_0 values are correct.

A discussion of errors is appropriate at this point. The most obvious source of error in the observed g_0 values is from the experimental activity coefficients of $CaCl_2$ in the mixed solution. The scatter of $\ln\gamma_{\pm}$ values about the best fit curve (Fig. 13.3.1) suggests that an overall uncertainty of ±0.02 in $\ln\gamma_{\pm}$ is not unreasonably large. Subtracting 0.01 from $\ln\gamma_{\pm}$ (best fit) and recomputing g_0, gave values which were more negative by exactly 2.5 kg mol^{-1} over the whole concentration range. This means that if the experimental g_0 values are required to be in reasonable agreement with the theoretical limiting law, it is necessary to assume that $\ln\gamma_{\pm}$ was correct at the highest ionic strength but was in error by about 0.03 units at the lowest ionic strength. It is also necessary to assume that the magnitude of the error increased smoothly as the ionic strength was lowered. The only method of accounting for an error of this type and magnitude is to assume an approximately constant chloride impurity in the test solutions. The direction of the resulting errors would be of the correct sign, but the quantity of chloride impurity required to account for the magnitude of the effect is considered to be unreasonably large.

The effect of a constant addition of 0.0233 to G^{ex}/RT (pure $CaCl_2$ solutions) was calculated for each solution. At the highest ionic strength this corresponds to 1% change in G^{ex} and at the lowest ionic strength to a 2.5% change. The resulting g_0 values were more negative by a constant factor of 0.583 kg mol^{-1}. The necessary errors in this third term of (E.13.1.1) required to give g_0 values in reasonable agreement with the limiting law are therefore much too large to be considered feasible.

Adding a constant factor to G^{ex}/RT (pure $CaSO_4$ solutions) has no effect since the changes in the first and second terms of (E.13.1.1) exactly cancel. Multiplication of both these terms by a factor of 0.99 gave only small changes in g_0. At the lowest and highest y_A values, g_0 was more negative by 0.15 and 0.07 kg mol^{-1}, respectively. It is clear from this analysis that extremely large percentage errors in G^{ex} for the pure $CaSO_4$ solutions must be assumed if agreement between experimental and limiting law g_0 values is required. The uncertainty in G^{ex} for $CaSO_4$ is higher than for $CaCl_2$ solutions, but the magnitude of the errors required are unreasonably high.

The total uncertainty in g_0 from all these sources was estimated as about ±6 kg mol^{-1}. These large error limits may appear inconsistent with the smooth nature of the experimental g_0 values as a function of ionic strength. This is not contradictory however, since all the component contributions to g_0 were calculated as smooth functions of I. The accuracy of the above error limits is extremely vague, since they are derived in part from pure speculation as to the magnitude of possible chloride impurities. It was assumed that the latter could be at a level equivalent to an impurity in the gypsum of 50 times the manufacturer's specified maximum level (0.003% chloride).

The conclusions of this section are rather unsatisfactory. The self consistency of equations (13.2.2), (13.1.1) and (13.1.2) implies that the unexpected signs of experimental g_0 values are real.

A consideration of errors involved in calculating g_o values was unable to clearly decide whether the results were irreconcilable with the theoretical limiting law, or whether the experimental error could have been sufficiently large to account for the differences.

14. PRIMITIVE MODEL CALCULATIONS

Both the experimental ω_0 and g_0 values discussed in sections 12 and 13 are apparently inconsistent with the higher order limiting laws of Friedman (94). It was thought that these inconsistencies might possibly be resolved by calculations of g_0 and ω_0 on the basis of the primitive model. Such calculations should be more realistic than the limiting law at concentrations above which the latter is inadequate.

14.1 EVALUATION OF g_0 FOR THE SYSTEM $CaSO_4 - CaCl_2 - H_2O$

The primitive model may be represented as a system of hard spheres with charges at their centres in an ideal dielectric fluid. In such a system all forces other than long range electrostatic forces are excluded. In general the sizes of different types of ions may differ, but it is sometimes convenient to assume that all ions are the same size. This latter situation is referred to as a restricted primitive model (R.P.M.)

An outline of the method used to calculate g_0 has been given in section 9.1. The main uncertainty is in the values to be assigned to the various distances of closest approach a_{ij} in equations (9.1.11) and (9.1.12). a_{ij} is the shortest internuclear separation of ions i and j. Experimental data on solutions of single electrolytes can be used to give best fit values to the distance of closest approach parameter "a" in equations of the D-H type. It is not unreasonable to expect these values to provide a guide to a_{+-} distances. It would however be unreasonable to expect these results to give sensible predictions of a_{++} and a_{--} distances, even if the "a" values could be split into a self consistent set of radii for ions in aqueous solution. In a real system there are two opposing effects. Electrostatic effects will tend to make a_{++} and a_{--} distances greater than those predicted from a_{+-} distances. Ion solvation will tend to cause the a_{++} and a_{--} distances to be less than the values predicted from a_{+-} distances. This is because polar solvent molecules such as water will be stabilised in the region between oppositely charged ions, but destabilised in the region between ions of the same sign. As a consequence of these problems, it is extremely difficult to assign realistic values to the various a_{ij} distances. The approach adopted was to make a variety of assumptions in the assignment of values to a_{ij} and then to compare the resulting g_0 values to see how critical the assumptions were.

The tabulated J_{ij} (L, K) values in reference 94 are given at rounded values of L_{ij} and K_{ij}. It was therefore necessary to restrict the choice of a_{ij} values to those which gave round numbers for L_{ij} according to equation (9.1.11). If this was not done, interpolation errors had a large effect on the g_0 values obtained. The value used for $\lambda/4\pi$ (this is twice the Bjerrum distance), required that the a_{ij} values used should be simple ratios of this distance. Calculations of g_0 were consequently made

(i) on the basis of restricted primitive models with a_{ij} set at 0.715 nm, 0.47667 nm

($2\lambda/3$) and 0.3575 nm ($\lambda/2$);

(ii) on the basis of "semi-restricted" primitive models with

(a) all a_{+-} set at $\lambda/2$ and all a_{++} and a_{--} set at λ

(b) all a_{+-} set at λ and all a_{++} and a_{--} set at $\lambda/2$;

(iii) on the basis of a primitive model with a set of a_{ij} values which were a compromise between convenience of computation and an attempt to realistically represent the real system. The distances used are tabulated below:

i.j.	a_{ij}
Ca Ca	λ
Cl Cl	$\lambda/2$
SO_4 SO_4	$2\lambda/3$
Ca Cl	$2\lambda/3$
Ca SO_4	$2\lambda/3$
Cl SO_4	$\lambda/2$

Even with these convenient a_{ij} values, it was possible to carry out the calculations for only two concentrations without the necessity of using imprecise interpolations.

Calculations of g_0 were carried out for each of these models in the following manner. Values of L_{ij} were calculated from (E.9.1.11) for each pair of ions. A value of K_{ij} was chosen for a particular pair of ions such that all the related K_{ij} values for other pairs of ions had values exactly corresponding to those given in the appendix of reference 94. This was not difficult for the restricted primitive model, since all the K_{ij} values were identical. Sets of J_{ij} values were obtained from reference 94 and g_0I calculated from equations (9.1.10) and (9.1.9). The ionic strength was calculated from equation (9.1.12) using the relationship

$$\kappa = b\, I^{\frac{1}{2}} \qquad \text{(E.14.1.1)}$$

where $b = 3.291\ \mathrm{nm}^{-1}\ \mathrm{kg}^{\frac{1}{2}}\ \mathrm{mol}^{-\frac{1}{2}}$ for water at 25°C.

g_0 was evaluated in the above fashion for sets of K_{ij} values equivalent to ionic strengths of up to 0.065 molal. The results are illustrated in Figures 14.1.1 and 14.1.2. To aid comparison, the limiting law is also shown in both of the figures. A few calculations of g_0 were made for the R.P.M. at higher ionic strengths. These showed that whereas the limiting law gave positive g_0 values above an ionic strength of unity, the model calculations gave results which remained negative.

The main conclusion to be drawn from the results, is that in the range of ionic strength investigated for the $CaSO_4$ - $CaCl_2$ - H_2O system, primitive model g_0 values are generally less negative than g_0 values calculated using the limiting law. This conclusion makes reconciliation of the experimental and primitive model g_0 values slightly easier, than for the experimental and limiting

FIGURE 14.1.1 g_0 VALUES CALCULATED USING THE RESTRICTED PRIMITIVE MODEL FOR 2:2, 1:1 ELECTROLYTES IN WATER AT 25°C

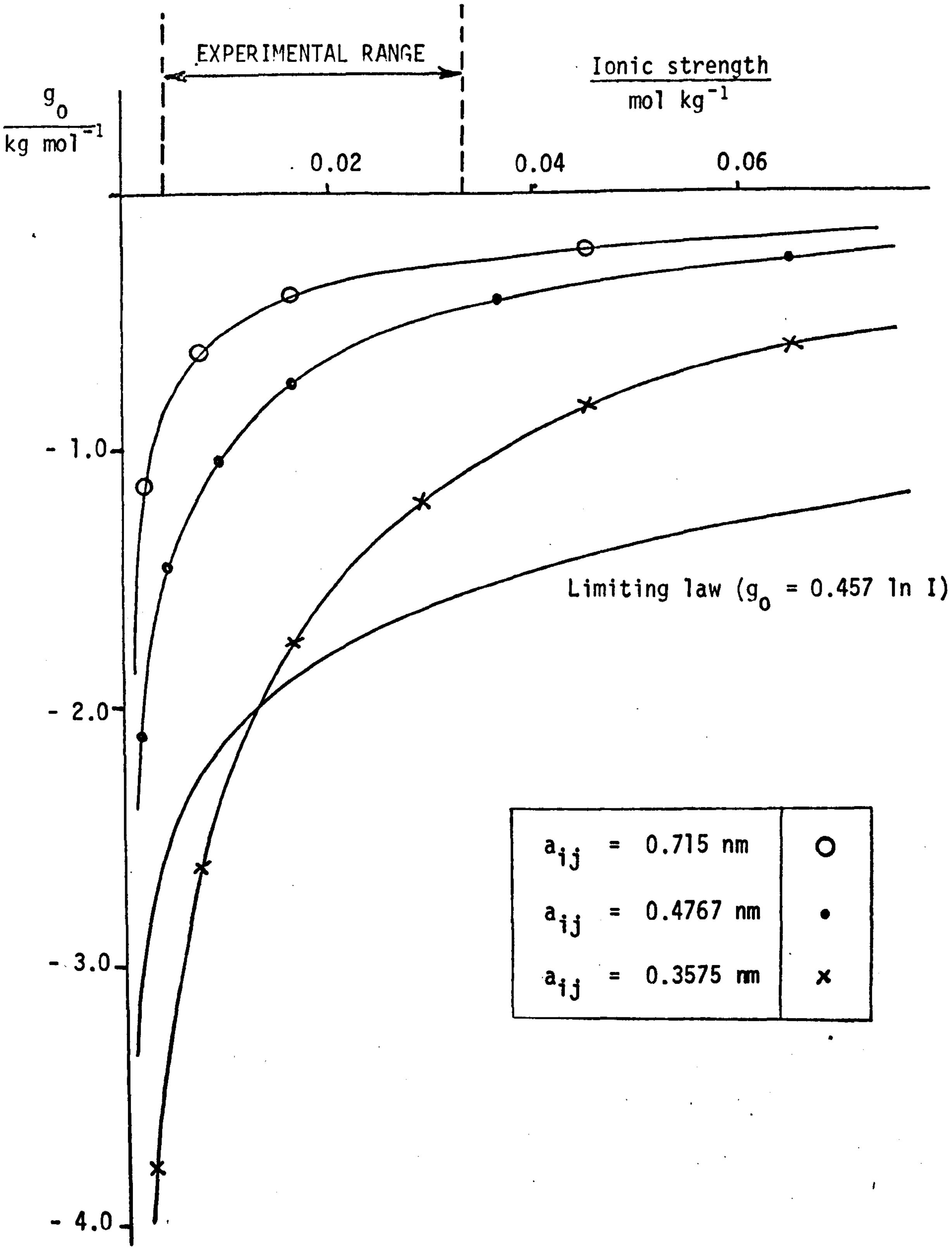
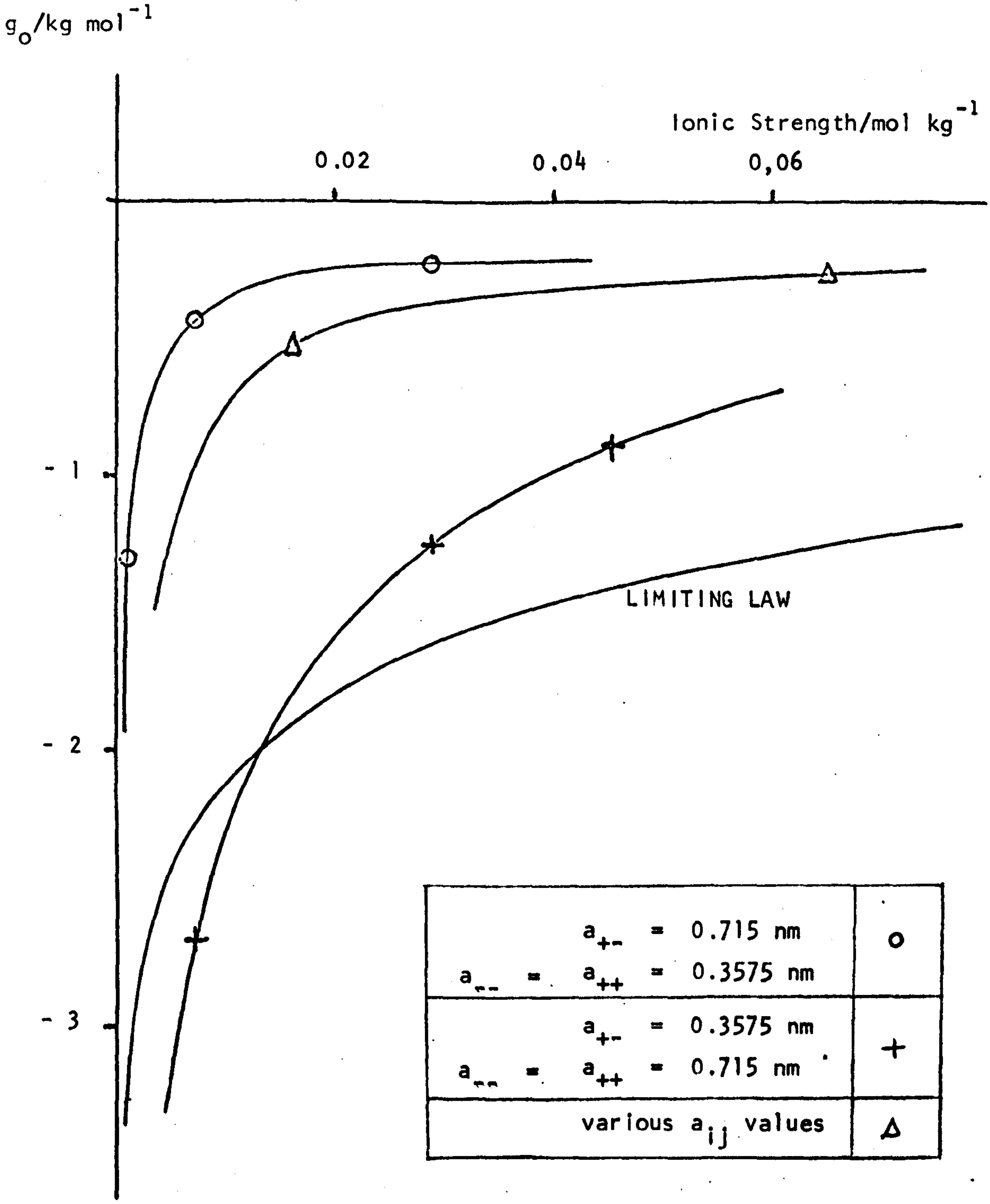


FIGURE 14.1.2 g_o VALUES CALCULATED USING THE PRIMITIVE MODEL FOR 2:2, 1:1 ELECTROLYTES IN WATER AT 25°C



law values, but does not change the basic incompatibility of the results. The calculations presented in section 14.2 suggest that the radii of "bare" rather than hydrated ions are important in determining a_{ij} distances. This suggests that the a_{ij} distances used in this section were too large, and implies that more appropriate primitive model calculations would have given g_0 values which were closer to those predicted by the limiting law.

14.2 EVALUATION OF ω_0 FOR 2:1, 1:1 AQUEOUS ELECTROLYTE MIXTURES

Similar calculations to those described in the previous section were carried out to give values of g_0 for 2:1, 1:1 aqueous electrolyte mixtures. The restricted primitive model was chosen for simplicity and g_0 was evaluated for ionic strengths up to 4 molal. Graphs of g_0I were plotted with I as abscissa, and ω_0 was obtained at any given ionic strength from the gradient of the curve. This method of evaluation follows from the relationship between ω_0 and g_0 given in equation (9.1.5).

The results of this analysis are shown in Figure 14.2.1 for distances of closest approach a_{ij} of 0.3039 nm and 0.1785 nm. These particular a_{ij} distances give ω_0 values which approximately cover the range of experimental ω_0 results. The limiting law for ω_0 is also illustrated in Figure 14.2.1. This was calculated using equation (9.1.6).

These primitive model calculations of ω_0 put the experimental ω_0 values in a new perspective. With the exception of the $MgCl_2$ - NaCl - H_2O system, the experimental ionic strength range is approximately 0.5 to 6.0 molal. Within this range, experimental and model ω_0 values follow the same trend with concentration. At some point below the experimental concentration range, the gradients of the R.P.M. curves change sharply to give qualitative agreement with the limiting law.

Within the experimental concentration range, the use of smaller a_{ij} distances in R.P.M. calculations gave more positive ω_0 values. In all of the electrolyte solutions studied, the only anion present was the chloride ion. Consequently a correlation should exist linking the sum of the effective cation radii and the experimental ω_0 values for each system at a given ionic strength. Mean ω_0 values at $I = 1.5$ and 3.0 molal were estimated for each system from Figures 12.2.1 to 12.2.5. The sum of each pair of cation radii was calculated using ion sizes given by Pauling (118) and also using hydrated ionic diameters deduced in Part IV of this thesis. Table 14.2.1 compares the predicted a_{++} distances using these two assumptions, with the mean ω_0 values. It is evident from this table that the relationship between a_{ij} distances and R.P.M. ω_0 values, was qualitatively the same as that between a_{++} distances calculated from Pauling ionic radii and experimental ω_0 values. The inverse relationship resulted when the sum of cation radii was calculated using estimated radii of hydrated ions. This result suggests that a_{ij} distances are more closely related to the radii of "bare" rather than solvated ions. Quantitative comparison of the experimental and primitive model results also supports this hypothesis, though the reliance which can be placed on the absolute magnitude of R.P.M. calculations is questionable. If this hypothesis proved to be correct, it would raise the question of why radii of hydrated ions correlate with single electrolyte excess free energies, but radii of "bare" ions correlate with excess free energies of mixing.

FIGURE 14.2.1 ω_0 VALUES CALCULATED USING THE RESTRICTED PRIMITIVE MODEL FOR 2:1, 1:1 ELECTROLYTE MIXTURES

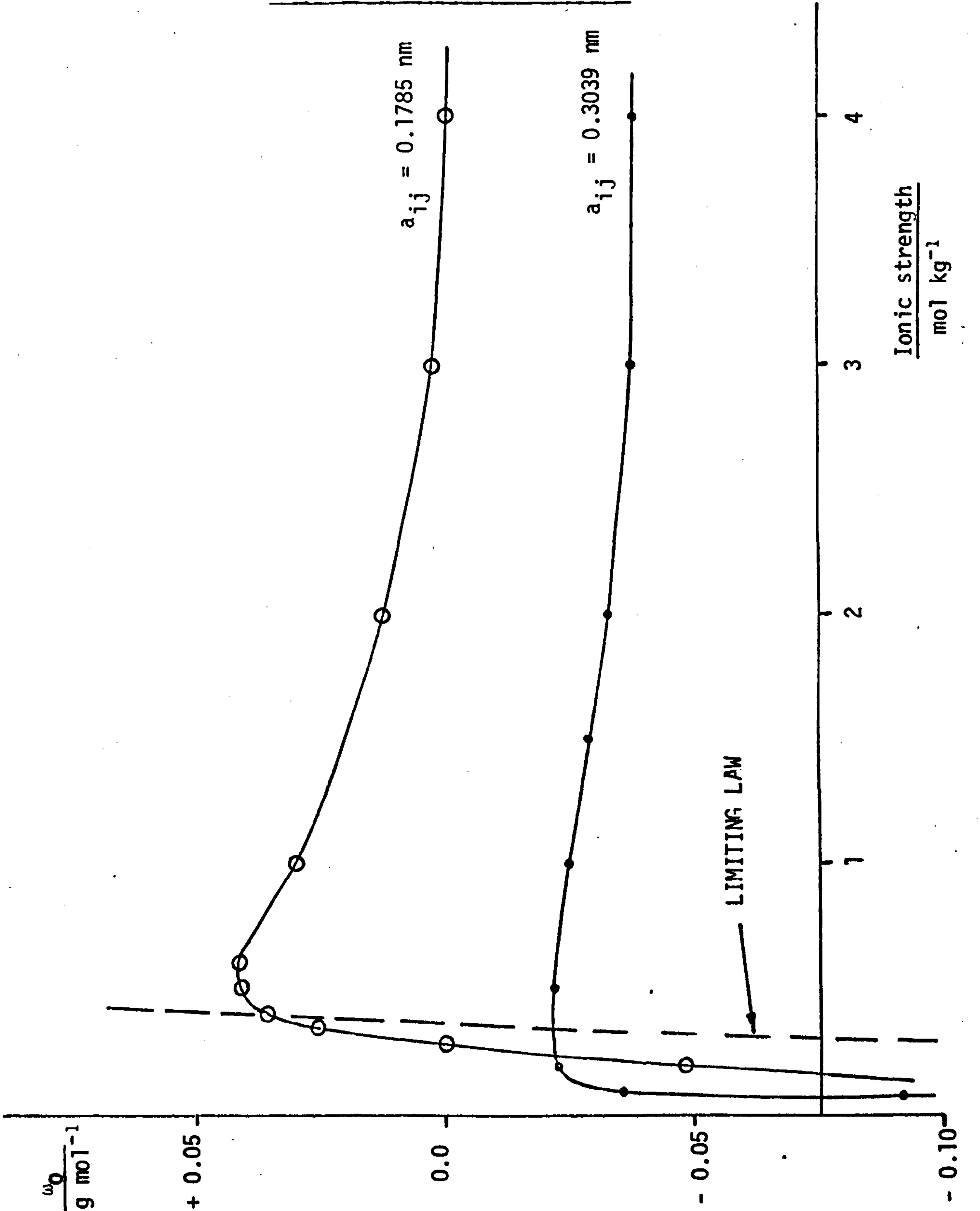


TABLE 14.2.1 COMPARISON OF EXPERIMENTAL ω_0 VALUES WITH SUMS OF CATION RADII

Cation Pair	Sum of Pauling (118) Radii/nm	Sum of Hydrated Ion Radii/nm	Estimated Mean Value of ω_0 /kg mol^{-1}	
			I = 3 molal	I = 1.5 molal
Mg^{2+}, Na^+	0.160	0.574	0.045	0.047
Ca^{2+}, Na^+	0.194	0.559	0.034	0.042
Ca^{2+}, K^+	0.232	0.515	0.002	0.018
Ba^{2+}, Na^+	0.230	0.538	-0.010	0.001
Ba^{2+}, K^+	0.268	0.494	-0.028	-0.014

15. SUMMARY OF CONCLUSIONS

The work described in Part III led to the following conclusions.

(i) Analysis of electromotive force measurements in mixed calcium sulphate-calcium chloride solutions, failed to provide experimental confirmation of a higher order limiting law proposed by Friedman.

(ii) Literature osmotic coefficient data on mixed solutions of alkali and alkaline earth chlorides were found to be consistent with primitive model calculations based on the cluster expansion work of Friedman. The results could be correlated with the Pauling radii of the cations concerned. The model calculations indicated that a higher order limiting law for solvent properties is not applicable at the concentrations studied.

PART IV

EVALUATION OF AN ALTERNATIVE TO THE DEBYE-HÜCKEL EXPRESSION

16. SUMMARY

This work was not especially fruitful, and since it was not closely linked with the remainder of the thesis, is presented here in summary form only.

Glueckauf (6) has proposed empirical equations for the electrostatic contributions to the excess free energy of single electrolyte solutions. He demonstrated in the same paper that use of these equations enabled the residual non electrostatic contributions to the osmotic coefficient to be represented to high concentrations by a single term linear in concentration. This was possible regardless of the charge type of the solute, a result which contrasts sharply with the situation when a D-H electrostatic term is used.

Non electrostatic contributions to the excess free energy arise from many sources, but excess properties of electrolyte solutions have been treated by Stokes and Robinson (122) and Glueckauf (123) by assuming that ionic hydration makes the only significant contribution. In both these papers, electrostatic contributions were taken to be of D-H form. It was thought that a similar analysis using Glueckauf's (6) equations might remove some of the inconsistencies present in the earlier work. In particular it was hoped that the distance of closest approach parameter could be sensibly correlated with the linear term coefficient via a set of individual ion hydration numbers. If this treatment proved satisfactory, it was intended to modify the equations in such a manner that mixed electrolyte solutions could be analysed, and finally to apply the equations to the system studied in Part II.

Osmotic coefficients for alkali and alkaline earth halides and sulphates were taken from reference 43. A non-linear least squares procedure was used to fit this data using equations 9a and 9b of reference 6. Calculations were made using non electrostatic contributions represented by a term linear in concentration and also by using both linear and quadratic terms. A knowledge of density—concentration properties was necessary before the above fitting procedure could be carried out. It was assumed that the concentration properties of electrolyte solutions could be represented by the empirical equation:

$$\frac{c}{m} = \frac{d_o^{25}}{d_o^T}\left(d_o^T + Q_1 m + Q_2 m^2 + Q_3 m^3\right)$$

where c is the solution molarity, m is molality and d_o^T is the density of pure water at T°C. A linear least squares procedure was used to obtain best fit values of Q_1, Q_2 and Q_3 for each electrolyte. Density data was taken from references 124 and 125. Osmotic coefficients for four of the electrolyte solutions were fitted using both Glueckauf (6) and D-H electrostatic equations, and by using molarity and molality concentration scales. The variance of fit was compared using all four treatments.

Hydration numbers, defined as the number of firmly bound water molecules associated with one mole of solute in solution, were calculated in two ways.

(i) It was assumed that the hydrated radii of K^+ and F^- ions were identical. Comparison of best fit distances of closest approach with Pauling ionic radii, enabled the number of water molecules associated with each ion to be calculated. An assumed effective molecular volume for H_2O was necessary.

(ii) The best fit linear term constants were equated to hydration numbers using the treatment of Gardner and Glueckauf (2). For a solution of a single fully dissociated electrolyte, equations 9 and 10 of reference (2) simplify to

$$\phi = \phi^{el} + 1 + 0.009 (2h - \nu) m$$

where h, the hydration number of the solute, is related to the best fit linear term constant by a simple equation, the form of which depends upon the charge type.

The results of these calculations are briefly summarised below.

(i) Least squares analysis confirmed Glueckauf's (6) suggestion that his proposed equations were capable of fitting osmotic coefficient data to high concentrations using only a two parameter equation. This could not be achieved in a satisfactory manner using the D-H expression.

(ii) The difference between calculations made using the different concentration scales was only marginal if judged by the computed variance of fit.

(iii) The two sets of computed hydration numbers were not self consistent, even allowing for a scale factor difference.

(iv) Neither set of hydration numbers were additive and the values obtained were similar to those deduced in references 122 and 123.

It was concluded that Glueckauf's alternative to the D-H expression is to be preferred on the grounds that fewer parameters are required to give a reasonable fit to experimental data. Use of these alternative expressions together with the assumption that all non electrostatic effects can be treated as due to ion hydration did not appear to be justified.

APPENDIX II.1 INVESTIGATION OF THE COMPOSITION OF TWO CALCIUM SULPHATE SAMPLES

EXPERIMENTAL

Weighed samples of B.D.H. and H. & W. Analar "$CaSO_4 \cdot 2H_2O$" were heated in air for various periods at temperatures up to 470°C. Calcined samples were cooled in a desiccator containing P_2O_5 and quickly reweighed.

Portions of the original materials were analysed for sulphur content. An instrumental method of analysis was employed in which the sample is heated to 1500°C in a stream of oxygen. The resulting SO_3 is titrated against base at constant pH. The base is generated electrolytically, and the electrical energy required to maintain a constant pH is monitored. This is directly proportional to the total sulphur content of the sample.

The original materials, heat treated samples, and a portion of B.D.H. material which had been equilibrated with water, were all examined by powder X-ray diffraction.

RESULTS AND DISCUSSION

The results of heat treatment experiments are given in Tables A.II.1.1, A.II.1.2 and A.II.1.3. Theoretical weight losses are 15.7% from gypsum to hemihydrate at 128°C, and 20.9% from gypsum to soluble anhydrite at 163°C. It is apparent from the results that the B.D.H. sample was not pure gypsum and that the material was not homogeneous. The H. & W. sample had weight losses which were reproducible within expected experimental error and which were close to the theoretical value.

The results of the sulphur analysis were:

B.D.H. Material	-	50.62% and 50.50%	SO_3 by weight
H. & W. Material	-	46.19% and 46.13%	SO_3 by weight.

The theoretical values for $CaSO_4$ and $CaSO_4 \cdot 2H_2O$ are 58.8% and 46.5% respectively. The accuracy of the analysis method is not known at these high sulphur content levels, but the results are in general concord with those of the heat treatment experiments.

Comparison of the powder X-ray diffraction pattern of the untreated H. & W. material with information in the A.S.T.M. Index (58), indicated that the sample was pure gypsum. All the observed peaks were present at the predicted diffraction angles, and had approximately the correct intensity ratios. No additional peaks were observed. The untreated B.D.H. material gave a more complicated diffraction pattern. Analysis of this pattern indicated that the major phase was gypsum, but strong additional peaks corresponding to natural anhydrite were also present. Weaker lines could be assigned to $CaSO_4 \cdot \frac{1}{2}H_2O$ or soluble anhydrite or to both of these phases. Estimation of the relative proportions of the four phases was difficult since a number of intense peaks were

TABLE A.II.1.1

B.D.H. Material: Percentage Weight Loss on Calcination

Heat Treatment	Sample Number		
	1	2	3
4.5 hr at 240°C	15.02	15.16	
22 hr at 240°C	15.15	15.23	
+ 4.5 hr between 240°C and 300°C		15.34	
17 hr between 240°C and 300°C			15.67
+ 17 hr between 450°C and 470°C		15.49	

TABLE A.II.1.2

B.D.H. and H. & W. Materials: Comparison of Percentage Weight Losses

Heat Treatment	B.D.H.	H. & W.
4 hr at 50°C	1.64	0.02
+ 17 hr at 116°C to 118°C	14.01	19.92
+ 5 hr at 140°C to 150°C	14.21	20.23
+ 60 hr at 240°C	14.63	20.37

TABLE A.II.1.3

H. & W. Material: Consistency of Percentage Weight Losses

Heat Treatment	Sample Number			
	4	5	6	7
5 hr at 240°C	20.11	20.17	20.09	20.19
22 hr at 240°C	20.30	20.27	20.23	20.31

nearly coincident.

Examination of the B.D.H. material after equilibration with water showed that the only phase remaining was $CaSO_4 \cdot 2H_2O$. It was also deduced that contact with water had resulted in significant crystal growth in the 200 direction of the gypsum crystallites. No crystal growth in the $14\bar{1}$ direction was discernable. These inferences were made using measurements of "½ peak width" at the relevant angles. Line broadening due to small crystallite size becomes measurable when crystallites are smaller than about 0.1 µm. This implies that for the untreated B.D.H. sample, the mean crystallite thickness in the 200 direction (i.e. perpendicular to 200 planes) was less than 0.1 µm.

All the peaks present in diffraction traces of the calcined materials could be assigned to various mixtures of natural anhydrite, soluble anhydrite and $CaSO_4 \cdot \frac{1}{2}H_2O$. Lines assigned to hemihydrate were always found to be weak and broad. It was inferred that this was a result of surface hydration subsequent to calcination. In a sample calcined at 470°C, natural anhydrite was the only phase which could be detected. Samples calcined at lower temperatures were found to have increasing proportions of soluble anhydrite and hemihydrate present. The positions and relative intensities of the peaks, suggested that the calcined materials were not physical mixtures of well formed phases, but were single inhomogeneous phases having structures intermediate between the end members.

The major conclusions of this investigation are given in section 6.7.2.

APPENDIX II.2 CALCULATION OF THE MOLALITY OF $CaSO_4$ AND $CaCl_2$ IN SOLUTIONS ANALYSED VOLUMETRICALLY

Molecular weight of $CaCl_2$ = M1 g

Molecular weight of $CaSO_4 \cdot 2H_2O$ = M2

Molecular weight of H_2O = M3

Concentration of $CaCl_2$ stock solution = C molal

Weight of $CaCl_2$ stock solution in original sample = W1 g

Weight of additional water in original sample = W2

Weight of water in stock solution $= W1 \dfrac{1000}{1000 + (C \times M1)} = W3$

Total weight of water in solution before any gypsum dissolves $= W2 + W3 = W4$

Total weight of solution before any gypsum dissolves $= W1 + W2 = W5$

Weight of sample taken for analysis = W6

Moles of calcium in analysis sample = m1

Let moles of $CaSO_4$ in analysis sample = m2

Then weight of analysis sample - weight of dissolved gypsum $= W6 - (m2 \times M2) = W7$

Moles of $CaCl_2$ in analysis sample $= W7 \times Y$

where $Y = \dfrac{W1}{W5} \; \dfrac{C}{1000 + (C \times M1)}$

m2 is then given by $m1 = m2 + W6 \times Y - m2 \times M2 \times Y$

or $m2 = \left[m1 - (W6 \times Y)\right]/(1 - M2 \times Y)$

Weight of H_2O in analysis sample $= 2 \times m2 \times \dfrac{M3}{M2} + W7 \times \dfrac{W4}{W5} = W8$

Molality of $CaCl_2 = W7 \times Y \times 1000/W8$

Molality of $CaSO_4 = m2 \times 1000/W8$

APPENDIX II.3

This appendix presents Tables I to VI reproduced from the paper (98) by Scatchard, Rush and Johnson.

Table I: Free Energy Equations

(a) $$\left(\frac{G^e}{RTW}\right) = \left(\frac{G^e}{RTW}\right)^{DH} + \left(\frac{G^e}{RTW}\right)^{nI} + \left(\frac{G^e}{RTW}\right)^{nII}$$

(b) $$\left(\frac{G^e}{RTW}\right)^{DH} = m'S\sum_a^{+}\sum_f^{-} x_a x_f (z_a + z_f)\frac{X_{af}}{a'_{af}}$$

(c) $$X_{af} = \frac{a'^2_{af}I - 2a'_{af}\sqrt{I} + 2\ln(1 + a'_{af}\sqrt{I})}{a'^2_{af}I}$$

(d) $$\left(\frac{G^e}{RTW}\right)^{nI} = \sum_a^{+}\sum_f^{-} x_a x_f\left(B^{(1)}_{af}m'^2 + \frac{1}{2}B^{(2)}_{af}m'^3 + \frac{1}{3}B^{(3)}_{af}m'^4 + \cdots\right)$$

(e) $$\begin{aligned}\left(\frac{G^e}{RTW}\right)^{nII} = &\sum_a^{+}\sum_b^{+}\sum_f^{-} x_a x_b x_f\left(B^{(0,1)}_{ab}m'^2 + \frac{1}{2}B^{(0,2)}_{abf}m'^3 + \frac{1}{3}B^{(0,3)}_{abf}m'^4\right)\\ &+ x_a x_b x_f (x_a - x_b)\left(\frac{1}{2}B^{(1,2)}_{aab}m'^3 + \frac{1}{3}B^{(1,3)}_{aabf}m'^4\right) + x_a x_b x_f (x_a - x_b)^2\frac{1}{3}B^{(2,3)}_{aaab}m'^4\\ &+\sum_a^{+}\sum_f^{-}\sum_g^{-} x_a x_f x_g\left(B^{(0,1)}_{fg}m'^2 + \frac{1}{2}B^{(0,2)}_{afg}m'^3 + \frac{1}{3}B^{(0,3)}_{afg}m'^4\right)\\ &+ x_a x_f x_g (x_f - x_g)\left(\frac{1}{2}B^{(1,2)}_{ffg}m'^3 + \frac{1}{3}B^{(1,3)}_{affg}m'^4\right) + x_a x_f x_g (x_f - x_g)^2\frac{1}{3}B^{(2,3)}_{fffg}m'^4\\ &+\sum_a^{+}\sum_b^{+}\sum_f^{-}\sum_g^{-} x_a x_b x_f x_g\frac{1}{3}B^{(2,3)}_{abfg}m'^4\end{aligned}$$

Table II: Definition of B Coefficients

$$B^{(1)}_{af} = b_{aa} + 2\ b_{af} + b_{ff}$$

$$B^{(2)}_{af} = 2(d_{aaa} + 3\ d_{aaf} + 3\ d_{aff} + d_{fff})$$

$$B^{(3)}_{af} = 3(f_{aaaa} + 4\ f_{aaaf} + 6\ f_{aaff} + 4\ f_{afff} + f_{ffff})$$

9 similar terms involving ag, bf, and bg

$$B^{(0,1)}_{ab} = 2\ b_{ab} - b_{aa} - b_{bb}$$

$$B^{(0,2)}_{abf} = 2\left[\frac{3}{2}(d_{aab} + d_{abb} - d_{aaa} - d_{bbb}) + 3(2\ d_{abf} - d_{aaf} - d_{bbf})\right]$$

$$\begin{aligned} B^{(0,3)}_{abf} = 3\Big[\ & 6(f_{aabf} + f_{abbf} - f_{aaaf} - f_{bbbf}) + 3(2\ f_{abff} - f_{aaff} - f_{bbff}) \\ & + (f_{aaab} + f_{abbb} - f_{aaaa} - f_{bbbb}) + \frac{3}{4}(2\ f_{aabb} - f_{aaaa} - f_{bbbb})\Big] \\ & + 3[3(2\ f_{abff} - f_{aaff} - f_{bbff})]^{*} \end{aligned}$$

$$B^{(1,2)}_{aab} = 2\left[\frac{1}{2}(3\ d_{aab} - 3d_{abb} - d_{aaa} + d_{bbb})\right]$$

$$B^{(1,3)}_{aabf} = 3\ [2\ f_{aaab} - 2\ f_{abbb} - f_{aaaa} + f_{bbbb} + 2(3\ f_{aabf} - 3\ f_{abbf} - f_{aaaf} + f_{bbbf})]$$

$$B^{(2,3)}_{aaab} = 3\left[f_{aaab} + f_{abbb} - f_{aaaa} - f_{bbbb} - \frac{3}{4}(2\ f_{aabb} - f_{aaaa} - f_{bbbb})\right]$$

6 additional terms involving a common anion by substituting f for a, g for b, and a for f

3 additional terms with common cation by substituting g for f

3 additional terms with common anion by substituting b for a

$$B^{(2,3)}_{abfg} = 3[24\ f_{abfg} - 6\ f_{abff} - 6\ f_{abgg} - 6\ f_{aafg} - 6\ f_{bbfg}]$$

Table III: Osmotic Coefficient Equations

(a) $\phi - 1 = (\phi - 1)^{DH} + (\phi - 1)^{nI} + (\phi - 1)^{nII}$

(b) $(\phi - 1)^{DH} = \dfrac{S}{\Sigma_i x_i/z_i} \sum_a^{+} \sum_f^{-} x_a x_f (z_a + z_f) \dfrac{Z_{af}}{a'_{af}}$

(c) $Z_{af} = \dfrac{\partial X_{af}}{\partial \ln I} = \dfrac{1 + a'_{af}\sqrt{I} - [1/(1 + a'_{af}\sqrt{I})] - 2 \ln (1 + a'_{af}\sqrt{I})}{a'^{2}_{af} I}$

(d) $(\phi - 1)^{nI} = \dfrac{1}{\Sigma_i x_i/z_i} \sum_a^{+} \sum_f^{-} x_a x_f (B^{(1)}_{af}\, m' + B^{(2)}_{af}\, m'^{2} + B^{(3)}_{af}\, m'^{3} + \cdots)$

(e) $$(\phi - 1)^{nII} = \frac{1}{\Sigma_i x_i/z_i} \Bigg[\sum_a^{+} \sum_b^{+} \sum_f^{-} x_a x_b x_f (B^{(0,1)}_{ab}\, m' + B^{(0,2)}_{abf}\, m'^{2} + B^{(0,3)}_{abf}\, m'^{3})$$

$$+ x_a x_b x_f (x_a - x_b)\ (B^{(1,2)}_{aab}\, m'^{2} + B^{(1,3)}_{aabf}\, m'^{3}) + x_a x_b x_f (x_a - x_b)^2\, B^{(2,3)}_{aaab}\, m'^{3}$$

$$+ \sum_a^{+} \sum_f^{-} \sum_g^{-} x_a x_f x_g (B^{(0,1)}_{fg}\, m' + B^{(0,2)}_{afg}\, m'^{2} + B^{(0,3)}_{afg}\, m'^{3})$$

$$+ x_a x_f x_g (x_f - x_g) (B^{(1,2)}_{ffg}\, m'^{2} + B^{(1,3)}_{affg}\, m'^{3}) + x_a x_f x_g (x_f - x_g)^2\, B^{(2,3)}_{fffg}\, m'^{3} \Bigg]$$

(f) for a solution containing only ions a, b, f, and g:

$$(\phi - 1)^{nII} = \frac{1}{\Sigma_i x_i/z_i} \Big\{ x_a x_b x_f [B^{(0,1)}_{ab}\, m' + B^{(0,2)}_{abf}\, m'^{2} + B^{(0,3)}_{abf}\, m'^{3}] + x_a x_b x_f (x_a - x_b)$$

$$\times [B^{(1,2)}_{aab}\, m'^{2} + B^{(1,3)}_{aabf}\, m'^{3}] + x_a x_b x_f (x_a - x_b)^2\, B^{(2,3)}_{aaab}\, m'^{3}$$

$$+ x_a x_b x_g [B^{(0,1)}_{ab}\, m' + B^{(0,2)}_{abg}\, m'^{2} + B^{(0,3)}_{abg}\, m'^{3}] + x_a x_b x_g (x_a - x_b) [B^{(1,2)}_{aab}\, m'^{2} + B^{(1,3)}_{aabg}\, m'^{3}]$$

$$+ x_a x_b x_g (x_a - x_b)^2\, B^{(2,3)}_{aaab}\, m'^{3}$$

$$+ x_a x_f x_g [B^{(0,1)}_{fg}\, m' + B^{(0,2)}_{afg}\, m'^{2} + B^{(0,3)}_{afg}\, m'^{3}] + x_a x_f x_g (x_f - x_g) [B^{(1,2)}_{ffg}\, m'^{2} + B^{(1,3)}_{affg}\, m'^{3}]$$

$$+ x_a x_f x_g (x_f - x_g)^2\, B^{(2,3)}_{fffg}\, m'^{3}$$

$$+ x_b x_f x_g [B^{(0,1)}_{fg}\, m' + B^{(0,2)}_{bfg}\, m'^{2} + B^{(0,3)}_{bfg}\, m'^{3}] + x_b x_f x_g (x_f - x_g) [B^{(1,2)}_{ffg}\, m'^{2} + B^{(1,3)}_{bffg}\, m'^{3}]$$

$$+ x_b x_f x_g (x_f - x_g)^2\, B^{(2,3)}_{fffg}\, m'^{3} \Big\}$$

Table IV: Activity Coefficient Equations

(a) $$(\ln \gamma_\pm)_{pq} = (\ln \gamma_\pm)_{pq}^{DH} + (\ln \gamma_\pm)_{pq}^{nI} + (\ln \gamma_\pm)_{pq}^{nII}$$

(b) $$(\ln \gamma_\pm)_{pq}^{DH} = z_p z_q S \left[\sum_a^{+} x_a \cdot \frac{(z_a + z_q)}{(z_p + z_q)} \cdot \frac{X_{aq}}{a'_{aq}} + \sum_f^{-} x_f \cdot \frac{(z_p + z_f)}{(z_p + z_q)} \cdot \frac{X_{pf}}{a'_{pf}} - \sum_a^{+} \sum_f^{-} x_a x_f \cdot \frac{(z_a + z_f)}{(z_p + z_q)} \cdot \frac{X_{af}}{a'_{af}} \right.$$
$$\left. + \frac{1}{\Sigma_i x_i z_i} \sum_a^{+} \sum_f^{-} x_a x_f (z_a + z_f) \frac{Z_{af}}{a'_{af}} \right]$$

(c) $$(\ln \gamma_\pm)_{pq}^{nI} = \frac{1}{(1/z_p) + (1/z_q)} \left[\sum_a^{+} x_a \left(B_{aq}^{(1)} m' + \frac{1}{2} B_{aq}^{(2)} m'^2 + \frac{1}{3} B_{aq}^{(3)} m'^3 \right) + \sum_f^{-} x_f \left(B_{pf}^{(1)} m' + \frac{1}{2} B_{pf}^{(2)} m'^2 + \frac{1}{3} B_{pf}^{(3)} m'^3 \right) \right.$$
$$\left. + \sum_a^{+} \sum_f^{-} x_a x_f \left(\frac{1}{2} B_{af}^{(2)} m'^2 + \frac{2}{3} B_{af}^{(3)} m'^3 \right) \right]$$

(d) $$(\ln \gamma_\pm)_{pq}^{nII} = \frac{1}{(1/z_p) + (1/z_q)} \left[\sum_a^{+} B_{ap}^{(0,1)} m'_a + \frac{1}{2} B_{aap}^{(1,2)} (m_a'^2 - 2 m'_a m'_p) + \frac{1}{3} B_{aaap}^{(2,3)} (m_a'^3 - 4 m_a'^2 m'_p + 3 m'_a m_p'^2) \right.$$
$$+ \sum_f^{-} B_{fq}^{(0,1)} m'_f + \frac{1}{2} B_{ffq}^{(1,2)} (m_f'^2 - 2 m'_f m'_q) + \frac{1}{3} B_{fffq}^{(2,3)} (m_f'^3 - 4 m_f'^2 m'_q + 3 m'_f m_q'^2)$$
$$+ \sum_a^{+} \sum_f^{-} \frac{1}{2} B_{apf}^{(0,2)} m'_a m'_f + \frac{1}{3} B_{apf}^{(0,3)} m'_a m'_f m' + \frac{1}{3} B_{aapf}^{(1,3)} (m_a'^2 m'_f - 2 m'_a m'_p m'_f)$$
$$+ \sum_a^{+} \sum_b^{+} \frac{1}{2} B_{abq}^{(0,2)} m'_a m'_b + \frac{1}{3} B_{abq}^{(0,3)} m'_a m'_b m' + \frac{1}{3} B_{aabq}^{(1,3)} (m_a'^2 m'_b - m'_a m_b'^2) + \sum_a^{+} \sum_b^{+} \sum_f^{-} \frac{1}{3} B_{abf}^{(0,3)} m'_a m'_b m'_f$$
$$+ \sum_a^{+} \sum_f^{-} \frac{1}{2} B_{afq}^{(0,2)} m'_a m'_f + \frac{1}{3} B_{afq}^{(0,3)} m'_a m'_f m' + \frac{1}{3} B_{affq}^{(1,3)} (m'_a m_f'^2 - 2 m'_a m'_f m'_q)$$
$$\left. + \sum_f^{-} \sum_g^{-} \frac{1}{2} B_{pfg}^{(0,2)} m'_f m'_g + \frac{1}{3} B_{pfg}^{(0,3)} m'_f m'_g m' + \frac{1}{3} B_{pffg}^{(1,3)} (m_f'^2 m'_g - m'_f m_g'^2) + \sum_a^{+} \sum_f^{-} \sum_g^{-} \frac{1}{3} B_{afg}^{(0,3)} m'_a m'_f m'_g \right]$$

Table V: Activity Coefficient Equations

For component af in a solution containing ions a,b,f, and g:

$$(a)\quad (\ln \gamma_\pm)^{DH}_{af} = z_a z_f S \left\{ (x_a + x_f - x_a x_f)\frac{X_{af}}{a'_{af}} + x_b x_g\left[\frac{(z_a + z_g)}{(z_a + z_f)}\cdot\frac{X_{ag}}{a'_{ag}} + \frac{(z_b + z_f)}{(z_a + z_f)}\cdot\frac{X_{bf}}{a'_{bf}} - \frac{(z_b + z_g)}{(z_a + z_f)}\cdot\frac{X_{bg}}{a'_{bg}}\right]\right.$$

$$\left. + \frac{1}{x_a z_a + x_b z_b + x_f z_f + x_g z_g}\left[x_a x_f (z_a + z_f)\frac{Z_{af}}{a'_{af}} + x_a x_g (z_a + z_g)\frac{Z_{ag}}{a'_{ag}} + x_b x_f (z_b + z_f)\frac{Z_{bf}}{a'_{bf}} + x_b x_g (z_b + z_g)\frac{Z_{bg}}{a'_{bg}}\right]\right\}$$

$$(b)\quad (\ln \gamma_\pm)^{nI}_{af} = \frac{1}{(1/z_a) + (1/z_f)}\left[B^{(1)}_{af}(m'_a + m'_f) + \frac{1}{2}B^{(2)}_{af}(m'_a m' + m'_f m' + m'_a m'_f) + \frac{1}{3}B^{(3)}_{af}(m'_a m'^2 + m'_f m'^2 + 2\, m'_a m'_f m')\right.$$

$$+ B^{(1)}_{bf} m'_b + \frac{1}{2}B^{(2)}_{bf}(m'_b m' + m'_b m'_f) + \frac{1}{3}B^{(3)}_{bf}(m'_b m'^2 + 2\, m'_b m'_f m')$$

$$+ B^{(1)}_{ag} m'_g + \frac{1}{2}B^{(2)}_{ag}(m'_g m' + m'_a m'_g) + \frac{1}{3}B^{(3)}_{ag}(m'_g m'^2 + 2\, m'_a m'_g m')$$

$$\left. + \frac{1}{2}B^{(2)}_{bg} m'_b m'_g + \frac{2}{3}B^{(3)}_{bg} m'_b m'_g m'\right]$$

$$(c)\quad (\ln \gamma_\pm)^{nII}_{af} = \frac{1}{(1/z_a) + (1/z_f)}\left[B^{(0,1)}_{ab} m'_b + \frac{1}{2}B^{(0,2)}_{abf}(m'_b m'_f + m'_a m'_b) + \frac{1}{3}B^{(0,3)}_{abf}(m'_b m'_f m' + m'_a m'_b m' + m'_a m'_b m'_f) + \frac{1}{2}B^{(0,2)}_{abg} m'_b m'_g\right.$$

$$+ \frac{1}{3}B^{(0,3)}_{abg}(m'_b m'_g m' + m'_a m'_b m'_g) + \frac{1}{2}B^{(1,2)}_{aab}(2\, m'_a m'_b - m'^2_b) + \frac{1}{3}B^{(1,3)}_{aabf}(2\, m'_a m'_b m'_f + m'^2_a m'_b - m'^2_b m'_f - m'_a m'^2_b)$$

$$+ \frac{1}{3}B^{(1,3)}_{aabg}(2\, m'_a m'_b m'_g - m'^2_b m'_g) + \frac{1}{3}B^{(2,3)}_{aaab}(3\, m'^2_a m'_b - 4\, m'_a m'^2_b + m'^3_b)$$

$$+ B^{(0,1)}_{fg} m'_g + \frac{1}{2}B^{(0,2)}_{afg}(m'_f m'_g + m'_a m'_g) + \frac{1}{3}B^{(0,3)}_{afg}(m'_f m'_g m' + m'_a m'_g m' + m'_a m'_f m'_g) + \frac{1}{2}B^{(0,2)}_{bfg} m'_b m'_g$$

$$+ \frac{1}{3}B^{(0,3)}_{bfg}(m'_b m'_g m' + m'_b m'_f m'_g) + \frac{1}{2}B^{(1,2)}_{ffg}(2\, m'_f m'_g - m'^2_g) + \frac{1}{3}B^{(1,3)}_{affg}(m'^2_f m'_g + 2\, m'_a m'_f m'_g - m'_f m'^2_g - m'_a m'^2_g)$$

$$\left. + \frac{1}{3}B^{(1,3)}_{bffg}(2\, m'_b m'_f m'_g - m'_b m'^2_g) + \frac{1}{3}B^{(2,3)}_{fffg}(3\, m'^2_f m'_g - 4\, m'_f m'^2_g + m'^3_g)\right]$$

Table VI: B Parameters for the System Na (a)-Mg (b)-Cl (f)-SO_4 (g)

$a'_{af} = 1.45397$
$B_{af}^{(1)} = 0.04472$
$B_{af}^{(2)} = 0.018616$
$B_{af}^{(3)} = -0.0010724$
$a'_{ag} = 1.24072$
$B_{ag}^{(1)} = -0.14805$
$B_{ag}^{(2)} = 0.024513$
$B_{ag}^{(3)} = -0.0009847$
$a'_{bf} = 1.60067$
$B_{bf}^{(1)} = 0.14924$
$B_{bf}^{(2)} = 0.030385$
$B_{bf}^{(3)} = -0.0012884$
$a'_{bg} = 1.37486$
$B_{bg}^{(1)} = -0.10848$
$B_{bg}^{(2)} = 0.033704$
$B_{bg}^{(3)} = -0.001520$

$B_{ab}^{(0,1)} = 0.0630$
$B_{abf}^{(0,2)} = -0.0228$
$B_{abf}^{(0,3)} = 0.00221$
$B_{aab}^{(1,2)} = 0$
$B_{aabf}^{(1,3)} = -0.00068$
$B_{aaab}^{(2,3)} = 0$
$B_{abg}^{(0,2)} = -0.0066$
$B_{abg}^{(0,3)} = -0.00147$
$B_{aabg}^{(1,3)} = 0$
$B_{fg}^{(0,1)} = -0.0243$
$B_{afg}^{(0,2)} = 0.01105$
$B_{afg}^{(0,3)} = -0.00079$
$B_{ffg}^{(1,2)} = -0.00246$
$B_{affg}^{(1,3)} = 0$
$B_{fffg}^{(2,3)} = 0$
$B_{bfg}^{(0,2)} = 0$
$B_{bfg}^{(0,3)} = 0.00031$
$B_{bffg}^{(1,3)} = 0$

APPENDIX III.1 DERIVATION OF LIMITING LAWS FOR g_0

The starting point for these derivations is equation 17.8 of Friedman (94):

$$\frac{G^{ex} - G^{ex}\,(\text{D.H.L.L.})}{RT} = -\frac{1}{3V}\left[\frac{n_3}{n_2}\right]^2 S^2 I^2 \ln I + O\,(I^2) \qquad \text{(E.III.1.1)}$$

G^{ex} (D.H.L.L.)	is the excess free energy of a solution per kg of solvent calculated on the basis of the Debye-Hückel limiting law;
V	is the specific volume (litres of solution per kg of solvent);
S	is the constant in the D-H limiting law given a value in (94) of $1.1723\ \text{mol}^{-\frac{1}{2}}\ l^{\frac{1}{2}}$;
I	is the molal ionic strength;
n_M	is a reduced M^{th} moment of the concentration of charge types and is defined by $n_M = \mu_M / c$;
μ_M	$= \sum_i c_i z_i^M$
c_i	is the number of i-type ions per litre;
c	is the total number of ions per litre;
$O(I^2)$	is a term which becomes negligible at sufficiently low concentrations.

The definition of $\Delta m G^{ex}$ for a binary electrolyte mixture (equation 9.1.1) is

$$\Delta m G^{ex}\,(y,\,I) = G^{ex}\,(y,\,I) - y\,G^{ex}\,(1,\,I) - (1-y)\,G^{ex}\,(0,\,I) \qquad \text{(E.III.1.2)}$$

If (E.III.1.1) is re-written as an expression for G^{ex}, and the result is substituted into (E.III.1.2), the terms in G^{ex} (D.H.L.L.) cancel, and if the divergence term in I^2 is neglected, $\Delta m G^{ex}$ may be expressed as

$$\frac{\Delta m G^{ex}}{RT} = -\frac{S^2}{3V}\,I^2 \ln I\left(\left[\frac{n_3}{n_2}\right]^2_{mix} - y\left[\frac{n_3}{n_2}\right]^2_{A} - (1-y)\left[\frac{n_3}{n_2}\right]^2_{B}\right) \qquad \text{(E.III.1.3)}$$

where y is the ionic strength fraction of electrolyte A.

Consider the particular electrolyte mixture discussed in section III, this is of a 2:1, 2:2 charge type. If the 2:2 salt ($CaSO_4$) is represented by A, the three ratio's of n_M may be evaluated as follows:

The mixture

$$\mu_2 = 2\,L\,I_c$$

(L is the Avogadro constant and I_c is the ionic strength defined on the molar concentration scale)

$$\mu_3 = 8\,c_{Ca^{2+}} - 8\,c_{SO_4^{2-}} - c_{Cl^-}$$

$$= L\,(8\,M_B + 8\,M_A - 8\,M_A - 2\,M_B)$$

$$= 6\,L\,M_B$$

(M_x is the molarity of electrolyte x)

$$= 2 L I_c (1 - y)$$

hence $$\left[\frac{\mu_3}{\mu_2}\right]^2 = \left[\frac{n_3}{n_2}\right]^2 = (1 - y)^2 \qquad \text{(E.III.1.4)}$$

Pure $CaSO_4$ at the same ionic strength

$$\mu_2 = 2 L I_c$$

$$\mu_3 = 8\, c_{Ca^{2+}} - 8\, c_{SO_4^{2-}} = \text{zero}$$

hence $$\left[\frac{n_3}{n_2}\right]^2 = \text{zero} \qquad \text{(E.III.1.5)}$$

Pure $CaCl_2$ at the same ionic strength

$$\mu_2 = 2 L I_c$$

$$\mu_3 = 8\, c_{Ca^{2+}} - c_{Cl^-}$$

$$= L I_c (8/3 - 2/3) = 2 L I_c$$

hence $$\left[\frac{\mu_3}{\mu_2}\right]^2 = \left[\frac{n_3}{n_2}\right]^2 = 1 \qquad \text{(E.III.1.6)}$$

From equations (III.1.3), (III.1.4), (III.1.5) and (III.1.6), ΔmG^{ex} is given by

$$\Delta mG^{ex} = \frac{S^2}{3V} RT\, I^2\, y(1 - y) \ln I \qquad \text{(E.III.1.7)}$$

It consequently follows from the definition of g_0 (E.13.1.12) that the limiting law for g_0 as I approaches zero is given by

$$g_0 = \frac{S^2}{3V} \ln I \qquad \text{(E.III.1.8)}$$

As I approaches zero, V approaches the specific volume of pure water (1.00293 $\ell\ kg^{-1}$) so that numerically the limiting law at 25°C is

$$g_0 = 1.052 \log_{10} I$$

For a 2:1, 1:1 electrolyte mixture, exactly the same limiting law is obtained, but for a 3:1, 1:1 mixture the limiting law is given by

$$g_0 = \frac{4S^2}{3V} \ln I \qquad \text{(E.III.1.9)}$$

APPENDIX III.2 DERIVATION OF EQUATION (7.8.5) FOR ω_o

Reilly and Wood (103) have derived an equation for the free energy of any electrolyte solution (G), in terms of (i) the free energies of single electrolyte solutions ($G^o_{M_\ell x_m}$) at the same ionic strength as the mixture, and (ii) parameters derived from the excess free energy of mixing of binary electrolytes with a common anion (giving $g^{x_m}_{M_k M_\ell}$) and common cation (giving $g^{M_k}_{x_\ell x_m}$). The equation correctly predicts the excess free energy of mixing due to pairwise ionic interactions for all mixtures, and for certain mixtures of restricted charge types accounts for the majority of triplet interactions. Using the symbolism of reference (103), the equation is written as

$$G = \sum_{\ell=1}^{\ell=i} \sum_{m=1}^{m=i} \frac{E^M_\ell E^x_m Z_{\ell m}}{2 E I} G^o_{M_\ell x_m} +$$

$$\frac{RT}{4E} \sum_{k=2}^{k=i} \sum_{\ell=1}^{\ell=(k-1)} \sum_{m=1}^{m=j} E^M_k E^M_\ell E^x_m Z_{km} Z_{\ell m} g^{x_m}_{M_k M_\ell} +$$

$$\frac{RT}{4E} \sum_{k=1}^{k=i} \sum_{\ell=2}^{\ell=j} \sum_{m=1}^{m=(\ell-1)} E^M_k E^x_\ell E^x_m Z_{k\ell} Z_{km} g^{M_k}_{x_\ell x_m} \qquad \text{(E.III.2.1)}$$

E^M_ℓ is the number of molal equivalents of cation M_ℓ of molality m^M_ℓ and charge Z^M_ℓ; $Z_{\ell m}$ is the sum of the modulus of charges on cation M_ℓ and anion x_m; E is the total number of equivalents of anions or of cations, and I is the molal ionic strength. All extensive properties in (E.III.2.1) are on the basis of one kg of solvent.

The second two terms on the R.H.S. of equation (III.2.1) correspond to the excess free energy of mixing (ΔmG^{ex}) for the constant ionic strength process in which quantities of single electrolyte ($M_\ell x_m$) solutions containing $E^M_\ell E^x_m Z_{\ell m}/(2EI)$ kg of solvent are mixed. The weight of solvent taken for each electrolyte is therefore numerically equal to the ionic strength fraction ($y_{M_\ell x_m}$) of $M_\ell x_m$ in the final mixed solution. (E.III.2.1) may consequently be simplified to:

$$G = \sum_{\ell=1}^{\ell=i} \sum_{m=1}^{m=j} y_{M_\ell x_m} G^o_{M_\ell x_m} + \Delta mG^{ex}$$

or alternatively in terms of the excess partial specific (per kg) free energy of the solvent

$$G^{ex}_\omega = \sum_{\ell=1}^{\ell=i} \sum_{m=1}^{m=j} y_{M_\ell x_m} G^{o\ ex}_{\omega(M_\ell x_m)} + \Delta mG^{ex}_\omega \qquad \text{(E.III.2.2)}$$

ΔmG^{ex}_ω is given by (94; see equation 16.18)

$$\Delta mG^{ex}_\omega = \frac{\partial}{\partial\left(\frac{1}{m}\right)} \left(\frac{\Delta mG^{ex}}{m}\right)_{T,\,P,\,X} \qquad \text{(E.III.2.3)}$$

where x is the set of ion molality (x_i) fractions and m is the total ionic molality. The equivalent expression for G_ω^{ex} may be derived in the following manner:

$$\frac{\partial}{\partial\left(\frac{1}{m}\right)}\left(\frac{G^{ex}}{m}\right)_x = G^{ex} - m\left(\frac{\partial G^{ex}}{\partial m}\right)_x \tag{E.III.2.4}$$

The total specific Gibbs function may be expressed as

$$G^{ex} = G_\omega^{ex} + m\sum_i x_i\,\mu_i^{ex} \tag{E.III.2.5}$$

Differentiation with respect to the total ionic molality at constant x gives:

$$\left(\frac{\partial G^{ex}}{\partial m}\right)_x = \left(\frac{\partial G_\omega^{ex}}{\partial m}\right)_x + m\sum_i x_i\left(\frac{\partial \mu_i^{ex}}{\partial m}\right)_x + \sum_i x_i\,\mu_i^{ex} \tag{E.III.2.6}$$

But from the Gibbs-Duhem relationship:

$$dG_\omega^{ex} + m\sum_i x_i\,d\mu_i^{ex} = 0$$

after differentiation

$$\left(\frac{\partial G_\omega^{ex}}{\partial m}\right)_x + m\sum_i x_i\left(\frac{\partial \mu_i^{ex}}{\partial m}\right)_x = 0$$

it is clear that (E.III.2.6) may be simplified to

$$\left(\frac{\partial G^{ex}}{\partial m}\right)_x = \sum_i x_i\,\mu_i^{ex}$$

Substituting this expression and (E.III.2.5) into (E.III.2.4) gives the required relationship:

$$\frac{\partial}{\partial\left(\frac{1}{m}\right)}\left(\frac{G^{ex}}{m}\right)_x = G_\omega^{ex} \quad .$$

Consider a mixture of 1:1 and 2:1 electrolytes MX and NX_2. Equation (E.III.2.2) then simplifies to

$$G_\omega^{ex} = y_{MX}\,G_{\omega_{MX}}^{o\ ex} + y_{NX}\,G_{\omega_{NX}}^{o\ ex} + \Delta_m G_\omega^{ex} \tag{E.III.2.7}$$

and $\Delta_m G^{ex}$ simplifies to

$$\Delta_m G^{ex} = \frac{RT}{4E}\,E_N\,E_M\,E_X\,(2\times 3)\,g_{M,N}^{X}$$

Differentiation of this equation according to (E.III.2.3) gives

$$\Delta mG^{ex}_{\omega} = -\frac{3}{2} RT\, m^2 \frac{\partial}{\partial m} \left(\frac{E_M E_N}{m} g^{x}_{M,N} \right)_x$$

which may be simplified to

$$\Delta mG^{ex}_{\omega} = -\frac{3}{2} RT\, E_M E_N \left[g^{x}_{M,N} + \left(\frac{\partial g^{x}_{M,N}}{\partial \ln I} \right)_x \right]$$

or

$$\Delta mG^{ex}_{\omega} = -\frac{3}{2} RT\, E_M E_N\, \omega^{x}_{M,N} \qquad \text{(E.III.2.8)}$$

Substitution of this relationship, together with the definitions of partial specific Gibbs function of solvent in terms of osmotic coefficients, into (E.III.2.7) gives

$$m_{mix} (1 - \phi_{mix}) = y_{MX}\, m^{o}_{MX} (1 - \phi^{o}_{MX}) + y_{NX}\, m^{o}_{NX} (1 - \phi^{o}_{NX}) - \frac{3}{2} E_M E_N\, \omega^{x}_{MN}$$

where m^{o}_{MX} and m^{o}_{NX} are total *ionic* molalities of MX and NX_2 solutions at the same ionic strength as that of the mixture. Rewriting this equation in terms of this ionic strength gives

$$y_{NX}\, y_{MX}\, I\, \omega_o = 2\, y_{MX} (\phi_{mix} - \phi^{o}_{MX}) + y_{NX} (\phi_{mix} - \phi^{o}_{NX}) \qquad \text{(E.7.8.5)}$$

REFERENCES

1. W. M. Latimer, Oxidation Potentials, Prentice Hall, New York, 1952.

2. A. W. Gardner and E. Glueckauf, Proc. Roy. Soc. Lond., A.313, 131 (1969).

3. A. W. Gardner and E. Glueckauf, Trans. Faraday Soc., 66, 1081 (1970).

4. A. W. Gardner and E. Glueckauf, Proc. Roy. Soc. Lond., A.321, 515 (1971).

5. P. G. M. Brown and J. E. Prue, ibid, A.232, 320 (1955).

6. E. Glueckauf, Proc. Roy. Soc. Lond., A.310, 449 (1969).

7. W. L. Marshall and R. Slusher, J. Phys. Chem., 70, 4015(1966).

8. W. M. Latimer, J. F. G. Hicks, Jr. and P. W. Schultz, J. Phys. Chem., 1, 620 (1933).

9. N. Bjerrum, K. Danske Vidensk. Selsk. Math-fys. Medd., 7, 9 (1926).

10. H. Müller, Phys. Z., 28, 324 (1927).

11. T. H. Gronwall, V. K. La Mer and K. Sandved, Phys. Z., 29, 358 (1928).

12. J. G. Kirkwood, Chem. Rev., 19, 275 (1936).

13. A. G. Ostroff and A. V. Metler, J. Chem. Eng. Data, 11, 346 (1966).

14. W. L. Denman, Ind. Eng. Chem., 53, 817 (1961).

15. E. C. Moreno and G. Osborn, Soil Sci. Soc. Am. Proc., 27, 614 (1963).

16. P. B. Bell and J. H. B. George, Trans. Faraday Soc., 49, 619 (1953).

17. M. H. Lietzke, R. W. Stoughton and T. P. Young, J. Phys. Chem., 65, 2247 (1961).

18. F. S. Nakayama and B. A. Rasnick, Anal. Chem., 39, 1022 (1967).

19. K. K. Tanji, Environmental Sc. and Tech., 3, 657 (1969).

20. E. A. Guggenheim and R. H. Stokes, Equilibrium Properties of Aqueous Solutions of Single Strong Electrolytes, Pergamon Press, London, 1969.

21. D. J. G. Ives and G. J. Janz, Reference Electrodes, Academic Press Inc., London, 1961.

22. Constitution of Binary Alloys (Sec. Ed.) McGraw-Hill Book Co., Inc., New York, 1958.

23. H. Fay and E. North, Am. Chem. J., 25, 216 (1901).

24. N. A. Pushin, Z. Anorg. Chem., 36, 207 (1903).

25. W. E. Henderson and G. Stegeman, J. Am. Chem. Soc., 40, 84 (1918).

26. U. B. Bray, J. Am. Chem. Soc., 49, 2372 (1927).

27. I. A. Cowperthwaite and V. K. La Mer, J. Am. Chem. Soc., 53, 4333 (1931).

28. V. K. La Mer and W. G. Parks, J. Am. Chem. Soc., 53, 2040 (1931).

29. J. Shrawder and I. A. Cowperthwaite, J. Am. Chem. Soc., 56, 2340 (1934).

30. M. G. Mellon and W. E. Henderson, J. Am. Chem. Soc., 42, 676 (1920).

31. F. Ishikawa and H. Hagisawa, Bull. Inst. Phys. Chem. Research (Tokyo), 13, 1019 (1934).

32. H. S. Harned and W. J. Hamer, J. Am. Chem. Soc., 57, 33 (1935).

33. V. K. La Mer and E. L. Carpenter, J. Phys. Chem., 40, 287 (1936).

34. G. Baumstark, Dissertation, Catholic University of America, Washington, D.C., 1932.

35. J. N. Butler, J. Electroanalytical, Chem., 17, 309 (1968).

36. G. A. Rechnitz and T. M. Hseu, Anal. Chem., 41, 111 (1969).

37. J. W. Ross, Science, 156, 1378 (1967).

38. R. A. Durst, Ion Selective Electrodes, Nat. Bur. Stds. Special Publication No. 314, 1969.

39. G. A. Rechnitz and Z. F. Lin, Anal. Chem., 40, 696 (1968).

40. J. A. Christiansen and M. Pourbaix, Compt. Rend. Conf. Union Intern. Chim. Pure et Appl., 17th Conf. Stockholm, 88 (1953).

41. M. H. Lietzke and R. W. Stoughton, J. Phys. Chem., 66, 508 (1962).

42. D. A. MacInnes, Principles of Electrochemistry, Reinhold Publishing Corp., New York, 1939.

43. R. A. Robinson and R. H. Stokes, Electrolyte Solutions, Butterworths, London, 1959.

44. A. Seidell, Solubilities of Inorganic and Metal Organic Compounds, Vol. I., 4th Ed., D. van Nostrand Co. Inc., New York, 1958.

45. J. O' M. Bockris and A. K. N. Ready, Modern Electrochemistry, Macdonald and Co., London, 1970.

46. P. J. McCarthy, Introduction to Statistical Reasoning, McGraw-Hill, New York, 1957.

47. H. S. Harned and B. B. Owen, The Physical Chemistry of Electrolyte Solutions, Reinhold Pub. Corp. New York, 1950.

48. E. A. Guggenheim, Disc. Faraday Soc., 24, 53 (1957).

49. K. S. Pitzer , J. C. S. Faraday II, 68, 101 (1972).

51. R. W. Money and C. W. Davis, Trans. Faraday Soc., 28, 609 (1932).

52. J. W. Hamer, J. Am. Chem. Soc., 56, 860 (1934).

53. A. K. Covington, J. V. Dobson and Lord Wynne-Jones, Trans. Faraday Soc., 61, 2057 (1965).

54. H. D. Crockford and J. A. Addlestone, J. Phys. Chem., 40, 203 (1936).

55. D. N. Craig and G. W. Vinal, J. Res. Natl. Bur. Stand., 22, 55 (1939).

56. I. M. Kolthoff, R. W. Perlich and D. Weilblen, J. Phys. Chem., 46, 561 (1942).

57. R. Huston and J. N. Butler, Anal. Chem., 41, 200 (1969).

58. Inorganic Index to the Powder Diffraction File, American Standards for Testing Materials, Philadelphia, Pens., 1969.

59. W. Hertz and M. Hellebrandt, Z. anorg. Chem., 130, 180 (1923).

60. D. M. Tschischikoff and A. S. Schachoff, Zh. Prikl. Khim., 9, 1387 (1936).

61. K. Beck and P. Stegmuller, Arb. Kaisel. Gesundh., 34, 447 (1910).

62. H. S. Harned and W. J. Hamer, J. Am. Chem. Soc., 57, 27 (1935).

63. W. J. Hamer, J. Am. Chem. Soc., 57, 9 (1935).

64. A. K. Covington, J. V. Dobson and Lord Wynne-Jones, Trans. Faraday Soc., 61, 2050 (1965).

65. H. S. Frank and P. T. Thompson, The Structure of Electrolyte Solutions (Ed. W. J. Hamer) Wiley and Sons Inc., New York, 1959,

66. E. A. Guggenheim, Disc. Faraday Soc., 24, 53 (1957).

67. C. W. Outhwaite, J. Chem. Phys., 50, 2277 (1969).

68. D. M. Burley, V. C. L. Hutson and C. W. Outhwaite, Chem. Phys. Letters, 9, 109 (1971).

69. D. M. Burley, V. C. L. Hutson and C. W. Outhwaite, Mol. Phys., 23, 867 (1972).

70. D. N. Card and J. P. Valleau, J. Chem. Phys., 52, 6232 (1970).

71. J. G. Kirkwood, J. Chem. Phys., 2, 767 (1934).

72. A. K. Covington, J. G. Freeman and T. H. Lilley, J. Phys. Chem., 74, 3773 (1970).

73. F. H. Stillinger and R. Lovett, J. Chem. Phys., 48, 3858 (1968).

74. C. W. Davies, Ion Association, Butterworth Inc., Washington, D.C., 1962.

75. C. L. Wilson and D. W. Wilson, Comprehensive Analytical Chemistry, Vol. IB, Elsevier Pub. Co., Amsterdam, 1960, p. 337.

76. F. J. Welcher, The Analytical Uses of Ethylenediaminetetraacetic Acid, D. van Nostrand Co. Inc., Princetown, 1958.

77. G. Schwarzenbach, Compleximetric Titrations, H. Irving, translator, Methuen and Co. Ltd., London, 1957.

78. H. Flaschka , E.D.T.A. Titrations - An Introduction to Theory and Practice, Pergamon Press, London, 1959.

79. C. L. Wilson and D. W. Wilson, Comprehensive Analytical Chemistry, Vol. IC, Elsevier Pub. Co., Amsterdam, 1962.

80. J. S. Fritz and M. Q. Freeland, Anal. Chem., 26, 1593 (1954).

81. J. S. Fritz and S. S. Yamamura, Anal. Chem., 27, 1461 (1955).

82. V. N. Sveshnikova, Izvest. Akad. Nauk, S.S.S.R., 17, 345 (1949).

83. J. D'Ans (1933); see reference 44.

84. F. K. Cameron and A. Seidell, J. Phys. Chem., 5, 643 (1901).

85. H. van Veldhuizen, Thesis, Utrecht, 1929.

86. W. M. Power, B. M. Fabuss and C. N. Satterfield, J. Chem. Eng. Data, 9, 437 (1964).

87. A. E. Hill and J. H. Wills, J. Am. Chem. Soc., 60, 1647 (1938).

88. F. K. Cameron and J. F. Breazeale, J. Phys. Chem., 5, 335 (1904).

89. W. M. Madgin and D. A. Swales, J. Appl. Chem., 6, 482 (1956).

90. K. S. Pitzer and L. Brewer, Thermodynamics (Lewis and Randall), 2nd ed., McGraw-Hill Book Co., New York, 1965, p. 586.

91. Y. C. Wu, R. M. Rush, G. Scatchard, J. Phys. Chem., 72, 4048 (1968).

92. G. Scatchard, J. Am. Chem. Soc., 83, 2636 (1961).

93. R. A. Robinson and V. E. Bower, J. Res. Nat. Bur. Stand., 70A, 313 (1966).

94. H. L. Friedman, Ionic Solution Theory, Interscience Publishers, New York, 1962.

95. G. N. Lewis and M. Randall, J. Am. Chem. Soc., 43, 1112 (1921).

96. T. O. Denney and C. B. Monk, Trans. Faraday Soc., 47, 992 (1951).

97. G. Scatchard, J. Amer. Chem. Soc., 90, 3124 (1968).

98. G. Scatchard, R. M. Rush and J. S. Johnson, J. Phys. Chem., 74, 3876 (1970).

99. J. Rasaiah, Chem. Phys. Letters, 7, 260 (1970).

100. R. H. Wood and P. J. Reilly, Ann. Rev. Phys. Chem., 21, 387 (1970).

101. J. E. Mayer, J. Chem. Phys., 18, 1426 (1950).

102. R. H. Wood, J. D. Patton and M. Ghamkhar, J. Phys. Chem., 73, 346 (1969).

103. P. J. Reilly and R. H. Wood, J. Phys. Chem., 73, 4292 (1969).

104. R. A. Robinson and V. E. Bower, J. Res. Nat. Bur. Stand., 69A, 19 (1965).

105. R. A. Robinson and A. K. Covington, ibid, 72A, 239 (1968).

106. R. A. Robinson and V. E. Bower, ibid, 69A, 439 (1965).

107. R. F. Platford, J. Phys. Chem., 72, 4053 (1968).

108. R. A. Robinson and R. H. Stokes, Trans. Faraday Soc., 35, 733 (1940).

109. R. H. Stokes, Trans. Faraday Soc., 41, 639 (1945).

110. R. A. Robinson, Trans. Faraday Soc., 35, 735 (1940).

111. R. A. Robinson and V. E. Bower, J. Res. Nat. Bur. Stand., 70A, 305 (1966).

112. R. H. Wood and M. Ghamkhar, J. Phys. Chem., 73, 3959 (1969).

113. R. A. Robinson, Proc. Roy. Soc., N.Z., 75, 203 (1945).

114. R. A. Robinson, J. Phys. Chem., 60, 501 (1956).

115. E. A. Guggenheim and J. C. Turgeon, Trans. Faraday Soc., 51, 747 (1955).

116. E. A. Guggenheim, Trans. Faraday Soc., 62, 3446 (1966).

117. P. J. Reilly, R. H. Wood and R. A. Robinson, J. Phys. Chem., 75, 1305 (1971).

118. L. Pauling, The Nature of the Chemical Bond, Cornell University Press, New York, 1940.

119. J. A. Gledhill and G. McP. Malan, Trans. Faraday Soc., 48, 258 (1952).

120. H. W. Thorp and W. C. Gilpin, Soc. Chem. Ind., Chem. Eng. Group (meeting), Oct. 25, 1949.

121. F. C. Gilbert and W. C. Gilpin, J. Soc. Chem. Ind., 65, 111 (1946).

122. R. H. Stokes and R. A. Robinson, J. Am. Chem. Soc., 70, 1870 (1948).

123. E. Glueckauf, Trans. Faraday Soc., 51, 1235 (1955).

124. R. C. Weast (editor), Handbook of Chemistry and Physics, The Chemical Rubber Co., Cleveland, Ohio, 1969.

125. J. Timmermans, The Physico-Chemical Constants of Binary Systems in Concentrated Solutions, Volume 3, Interscience Publ. Inc., New York, 1960.