

University of St Andrews



Full metadata for this thesis is available in
St Andrews Research Repository
at:

<http://research-repository.st-andrews.ac.uk/>

This thesis is protected by original copyright

ABSTRACT

The object of this work was mainly the adaptation to other partial molar quantities of the method which McKay and Perring developed for the activity coefficients of solute components in mixed solutions. Equations were deduced which permit the calculation of the partial molar enthalpy of each solute component of a ternary mixed electrolyte solution, at constant partial molar enthalpy of water, and at constant total molality. Similar relations for the partial molar heat capacities were also developed.

The system sodium chloride-calcium chloride-water, due to its important role in natural salt deposits, was chosen to investigate the utility of applying these equations. The calorimetric study of this system was carried out and the partial molar enthalpies of both solutes, sodium chloride and calcium chloride, were determined by the new method. The calorimetric data of the systems sodium chloride-magnesium chloride-water and calcium chloride-magnesium chloride-water were also obtained and in this work the possibility of their treatment by either of the two new adaptations of the McKay-Perring methods is discussed.

To appreciate the differences with temperature of the activity coefficients of the components of the systems under investigation, isopiestic measurements were made on the systems sodium chloride-calcium chloride-water, and calcium chloride-magnesium chloride-water, at 45°C. The activity coefficients were computed by the McKay-Perring method.

Comparison between the calorimetric and the isopiestic results shows that, since the observed changes in $\log \gamma_{\pm}$ with temperature are in any case very small and depend upon a difference between two large quantities, it seems most probable that the enthalpies of dilution give a much more reliable estimate of the small variation in $\log \gamma_{\pm}$ to be expected over a moderate temperature range.

THERMODYNAMICS OF CONCENTRATED

AQUEOUS SOLUTIONS OF

HALIDE MIXTURES

THERMODYNAMICS OF CONCENTRATED AQUEOUS
SOLUTIONS OF HALIDE MIXTURES

A Thesis
presented for the degree of
DOCTOR OF PHILOSOPHY
in the Faculty of Science of the
University of St. Andrews
by
Maria Antonietta Gilchrist Belmar



October 1978

United College of
St. Salvator and St. Leonard
St. Andrews

Th q 247

TO

My Mother

My son Ralph

And my daughter Patricia

DECLARATION

I declare that this thesis is my own composition, that the work of which it is a record has been carried out by me, and that it has not been submitted in any previous application for a Higher Degree.

This thesis describes results of research carried out at the Department of Chemistry, United College of St. Salvator and St. Leonard, University of St. Andrews, under the supervision of Professor P.A.H. Wyatt since the 1st of October 1976.

Maria Antonietta Gilchrist B.

CERTIFICATE

I hereby certify that Maria Antonieta Gilchrist Belmar has spent eight terms of research work under my supervision, has fulfilled the conditions of Ordinance General no. 12 and Resolution of the University Court, 1967, no. 1, and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

P.A.H. Wyatt

Professor

ACKNOWLEDGEMENTS

I wish to express all my gratitude to Professor P.A.H. Wyatt, my supervisor, for his generous help and valuable guidance during the course of this work. Professor Wyatt has been an unfailing source of encouragement and inspiration throughout my tenure and, I acknowledge without reservation my debt to him.

I am especially grateful to Dr. Calvert for his valuable advice regarding to computational problems and for his help during the course of this research work. My thanks are also due to Mr. Zochowski who helped me to have an enjoyable time in the laboratory; and to Mr. Rennie of the workshop.

I am indebted to the British Council for their scholarship, and to Dr. B.M. Lowe of the University of Edinburgh for the loan of part of the isopiestic equipment.

Finally, I wish to thank my daughter Patricia for drawing the diagrams for the thesis.

	<u>CONTENTS</u>	<u>PAGE</u>
Declaration		ii
Certificate		iii
<u>Acknowledgments</u>		iv
Contents		v
Summary		ix
INTRODUCTION		1
<u>CHAPTER 1 : WATER AS SOLVENT</u>		
1.1	Introduction	4
1.2	Structure of water	4
1.3	Ion-water interactions	7
<u>CHAPTER 2 : THERMODYNAMICS OF ELECTROLYTE SOLUTIONS</u>		
2.1	Introduction	10
2.2	Fundamental equation and concepts	11
2.2.1	Activity	12
2.2.2	Activity coefficient	14
2.2.3	Osmotic coefficient	16
2.2.4	Variation of activity with temperature	18
2.2.5	Cross-differentiation relations	20
2.3	Theoretical aspects	21
2.3.1	Activity coefficients at low concentrations	22
2.3.2	Activity coefficients at high concentrations	26
2.3.3	Explicit reference to hydration effects at high concentrations.	31
2.3.4	Limiting equations for the partial molar enthalpy and partial molar heat capacity	34
2.3.4.1	Partial molar enthalpy	34

	<u>PAGE</u>	
2.3.4.2	Partial molar heat capacity	41
2.4	Pitzer's treatment	43
2.5	Mixed electrolyte solutions	50
2.5.1	Introduction	50
2.5.2	Non-ideality of solutions	51
2.5.3	Free energy	51
2.5.4	Activity coefficients in mixed electrolyte solutions.	53
2.5.5	Pitzer's equation for mixed electrolytes	65
2.5.6	Enthalpy changes	67
2.5.7	Application of equations of the Gibbs-Duhem type for mixtures	70
 <u>CHAPTER 3 : THE MCKAY-PERRING METHOD FOR ACTIVITY COEFFICIENTS: APPLICATION TO PARTIAL MOLAR ENTHALPY AND PARTIAL MOLAR HEAT CAPACITY.</u>		
3.1	Introduction	72
3.2	McKay-Perring method for activity coefficients	73
3.2.1	Activity coefficients at constant water activity	75
3.2.2	Activity coefficients at constant total molality	80
3.3	Extension of the McKay-Perring method	83
3.3.1	Application to partial molar enthalpies	83
3.3.1.1	Solute partial molar enthalpies at constant partial molar enthalpies of water	84
3.3.1.2	Solute partial molar enthalpies at constant molality	86
3.3.2	Partial molar heat capacity	88
3.4	Application of the methods	90

	<u>PAGE</u>
<u>CHAPTER 4</u>	<u>EXPERIMENTAL</u>
4.1	Isopiestic method 92
4.1.1	Introduction 92
4.1.2	Isopiestic ratio 95
4.1.3	Equipment 96
4.1.4	Materials 101
4.1.5	Procedure 101
4.1.6	Experimental results 104
4.1.6.1	The system $\text{NaCl}-\text{CaCl}_2-\text{H}_2\text{O}$ at 45°C 104
4.1.6.2	The system $\text{CaCl}_2-\text{MgCl}_2-\text{H}_2\text{O}$ at 45°C 113
4.2	Calorimetry 113
4.2.1	Introduction 113
4.2.2	Equipment 122
4.2.3	Materials 124
4.2.4	Procedure 125
4.2.5	Treatment of experimental data 126
4.2.6	Experimental results 130
4.2.6.1	The system $\text{NaCl}-\text{CaCl}_2-\text{H}_2\text{O}$ 130
4.2.6.2	The system $\text{CaCl}_2-\text{MgCl}_2-\text{H}_2\text{O}$ 142
4.2.6.3	The system $\text{NaCl}-\text{MgCl}_2-\text{H}_2\text{O}$ 150
<u>CHAPTER 5</u>	<u>RESULTS AND DISCUSSION</u>
5.1	Introduction 155
5.2	Isopiestic results 156
5.2.1	The system $\text{CaCl}_2-\text{H}_2\text{O}$ 156
5.2.2	The system $\text{NaCl}-\text{CaCl}_2-\text{H}_2\text{O}$ 161
5.2.3	The system $\text{CaCl}_2-\text{MgCl}_2-\text{H}_2\text{O}$ 172
5.3	Calorimetric results 177

	<u>PAGE</u>
5.3.1 The systems $\text{NaCl-H}_2\text{O}$ and $\text{CaCl}_2\text{-H}_2\text{O}$	177
5.3.2 The system $\text{NaCl-CaCl}_2\text{-H}_2\text{O}$	180
5.3.3 The system $\text{NaCl-MgCl}_2\text{-H}_2\text{O}$	209
5.3.4 The system $\text{CaCl}_2\text{-MgCl}_2\text{-H}_2\text{O}$	213
References	216
Appendix 1	A1 - 1

S U M M A R Y

The object of this work was mainly the adaptation to other partial molar quantities of the method which McKay and Perring developed for the activity coefficients of solute components in mixed solutions. Equations were deduced which permit the calculation of the partial molar enthalpy of each solute component of a ternary mixed electrolyte solution, at constant partial molar enthalpy of water, and at constant total molality. Similar relations for the partial molar heat capacities were also developed.

The system sodium chloride-calcium chloride-water, due to its important role in natural salt deposits, was chosen to investigate the utility of applying these equations. The calorimetric study of this system was carried out and the partial molar enthalpies of both solutes, sodium chloride and calcium chloride, were determined by the new method. The calorimetric data of the systems sodium chloride-magnesium chloride-water and calcium chloride-magnesium chloride-water were also obtained and in this work the possibility of their treatment by either of the two new adaptations of the McKay-Perring methods is discussed.

To appreciate the differences with temperature of the activity coefficients of the components of the systems under investigation, isopiestic measurements were made on the systems sodium chloride-calcium chloride-water, and calcium chloride-magnesium chloride-water, at 45°C. The activity coefficients were computed by the McKay-Perring method.

Comparison between the calorimetric and the isopiestic results shows that, since the observed changes in $\log \gamma_{\pm}$ with temperature are in any case very small and depend upon a difference between two large quantities, it seems most probable that the enthalpies of dilution give a much more reliable estimate of the small variation in $\log \gamma_{\pm}$ to be expected over a moderate temperature range.

INTRODUCTION

There is considerable interest in the thermodynamic properties of aqueous electrolyte solutions not only because of their own theoretical importance but also because of the important role that mixed electrolytes play in such fields of desalination, oceanography, geochemistry, the chemical industry and in the physiological processes of body fluids and cell equilibria.

Mixed electrolytes occur in most salt brines, in sea water and in numerous salt deposits - an example being the natural salts and saltpetre deposits existing in the North of Chile where it is possible to find, with others, cations such as K^+ , Na^+ , Li^+ , Mg^{2+} , Ca^{2+} and anions such as Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-} , etc.

As a result of this theoretical and practical importance of mixed electrolyte solutions, a large effort has been directed toward obtaining the best and most accurate representation of their properties. This is why a great deal of work has been done on single and mixed electrolyte solutions, in the case of the former over a wide range of temperature while for most of the latter results have been recorded only at $25^\circ C$.

The behaviour of solutions containing more than one electrolyte is more complicated and its interpretation more difficult than is the case for single electrolyte solutions; however some progress towards understanding the properties of these mixed solutions has recently been made.

Some years ago, Young and Smith(1) discussed a mixture rule for volumes and enthalpies to facilitate the estimation of the properties of solutions containing two or more electrolytes. Young and co-

workers(2,3) showed that for many systems the heat of mixing two cations in the presence of a common anion was approximately independent of the common anion; this approximation is also useful for divalent common ions, as has been shown by Wood and Anderson(4) who proposed an equation for predicting the properties of symmetric charge mixtures.

Young and co-workers(2) established the cross-square rule for the heat of mixing of reciprocal salt pair. Covington, Lilley and Robinson(5) showed that the cross-square rule holds for the free energy of mixing. McKay(6) and Wu, Smith, and Young(3) made a correlation between heats of mixing and free energies of mixing. Scatchard(7,8,9) and very recently Pitzer(10,11,12) have papers concerning the prediction of thermodynamic properties in mixed electrolyte solutions. Scatchard and Breckenridge(13) used a power series in the ionic concentrations for representing short-range ionic interaction; they applied the principle to their isopiestic measurements of pure and mixed solutions.

In the handling of experimental data McKay and Perring(14,15,16) formulated equations for the calculation of the activity coefficients of each of two solutes from the vapor pressure of the solvent. Argersinger(17) derived explicit relations to calculate the activity and osmotic coefficient of the solvent in mixed aqueous solutions from E.M.F. measurements. Millero and co-workers(18,19,20) have also been concerned with partial molar quantities in their investigations of the properties of sea water as a multicomponent electrolyte solution, but they have dealt mainly with partial molar volumes.

The treatment of experimental data following the methods suggested by McKay and Perring(14,15,16) allows one to obtain partial molar quantities for each of the components in a multicomponent system from data obtained by the variation of only one component in the system; but the method has been used to obtain only activities in three component systems whereas in fact it appears that the method should be quite general, as was suggested by McKay and Perring themselves.

It was the possibility of applying the McKay-Perring treatment to partial molar enthalpies and partial molar heat capacities obtained for systems likely to be of general interest that prompted the work to be described in this thesis.

CHAPTER 1

WATER AS SOLVENT

1. 1 Introduction

Classical theories of solutions considered the solvent only as a provider of the volume in which the solute particles moved, but in the modern theory of liquids the solvent is usually considered as a disordered solid in which short-range order persists, though the long-range order characteristic of the solid state has been lost in thermal agitation.

In spite of the fact that many of the properties of electrolyte solutions are still attributed only to the nature of the solute, one should not forget that it is the solvent which enables the electrolyte to display its peculiarities. That is why the structure of water and the effects of ions on this structure are relevant in the study of electrolyte solutions. Because considerations of such structural effects will ultimately be necessary for the detailed interpretation of the results for the system studied here, a brief summary of the present state in this complex field is here appended. The later discussion in the present thesis will however be restricted to the practical thermodynamic aspects.

1. 2 Structure of water

The theory of the structure and properties of liquids is in a much less well developed state than is that for solids and it is difficult to give a concise view of the subject. Those liquids which behave to a first approximation like an assembly of hard spherical atoms can be treated

reasonably satisfactorily by current methods but the non-spherical nature of water molecules leads to molecular association in the liquid state which complicates the problem for this solvent.

The solid has served as the point of departure for many modern models of the structure of the liquid. In the case of a crystalline solid it is possible to determine, by diffraction, the equilibrium positions and vibrational amplitudes of all the atoms involved, and this information specifies the structure of the crystal, but a liquid, by its very nature, cannot have a structure in this sense.

In water the structural relation between the liquid and the solids has been the subject of speculation since the time of Tamman(21), who suggested that there should be as many different "kinds" of water as there are different phases of ice. However, although the water molecules can be considered to be polymerized by hydrogen bonding(22) the early idea that the different forms of ice correspond to different water polymers is not really valid, in the sense that different discrete, tightly bonded groups of molecules cannot be singled out in the structure.

Scientists, at least since the time of Roentgen(23) who suggested that the liquid contained "ice molecules", have put forward hypotheses about the structure of liquid water, but even at present there exists no universal agreement about it; indeed a large number and variety of models have been and still are being proposed.

The various models can be divided into two main classes:

continuum models and mixture models. The first is exemplified by the treatment of Pople(24) and its characteristic feature is that disorder is introduced into the structure by bending and stretching bonds rather than by breaking them. The other class, the mixture models, describe liquid water as an equilibrium mixture of two or more different structures that are distinguishable in an instantaneous picture, each of them having a well-defined bonding pattern and existing in clusters of similarly bonded molecules. In such mixture theories, each water molecule might participate in from zero to four hydrogen bonds; so species with different numbers of hydrogen bonds are sometimes distinguished.

The fundamental difference between these two approaches arises from a different assessment of the importance of the cooperative aspect of the hydrogen bonding. In the continuum models it is suggested that the individual hydrogen bonds may be distorted independently and quite arbitrarily and thus there is to be observed only a general uniform structure. In the mixture models, however, there is considered to be a large amount of co-operation involved in bonding, and thus there will be a tendency to form fully-bonded clusters of water molecules.

The modern mixture theory of water began with the important paper by Bernal and Fowler(25) who proposed three molecular arrangements: water I, tridymite-like, or ice-like, this structure being rather rare but present to some extent below 4°C ; water II, a more dense quartz-like structure predominating at ordinary temperatures; and water III, a close-packed, ammonia-like liquid, of most importance at high temperatures approaching the critical point.

Their theory incorporated two important features: that the nearest-neighbour coordination number is 4 and that the density maximum is produced by variations in the distance to second neighbours.

From the diverse models of the structure of liquid water it is possible to conclude that many of the theories and findings are consistent with a model of water (at any instant) composed of a perturbed "ice-like" lattice, plus interstitial molecules with fewer constraints and hence greater freedom of movement. Marchi and Eyring(26) expressed a partition function for water in terms of two assumed components: (i) ice-like molecules and (ii) freely rotating monomers.

It may also be concluded that hydrogen bonding and near tetrahedral co-ordination are certainly dominant features of the water structure and, whether the arrangement of molecules is thought of in terms of sharply defined clusters or in terms of continuously distorted hydrogen bonds, the average coherence length is several molecular diameters and thus several dozens of molecules may become involved in this short-range order.

1. 3 Ion-water interactions

The significance of the structure of water for the properties of aqueous solutions became particularly clear after the appearance of the work of Bernal and Fowler(25). According to Bernal and Fowler, the action of ions on water may be compared with the effects of raising or lowering its temperature. Thus, some ions produce an effect on water similar to a lowering of temperature and other ions act in the same way as an increase of temperature.

The ions alter the water structure because of the difference between the interaction of ions and water molecules and the

interaction of water molecules with each other. The change in the water structure by ions in the formation of the solution is due then to the following factors: the entry of particles with a different radius from that of the water molecule, the difference in co-ordination numbers of the ions and the water molecules, and the re-orientation of the water molecules nearest to the ions.

The hydration of ions plays an important part in the problems associated with interactions in solution. According to Bockris(96) the hydration of ions may be divided into two regions: close hydration associated with the interaction of water, and distant hydration which involves interaction between an ion and a molecule of water beyond the immediate vicinity of the former. The change of the structure of water is the consequence of the polarization of the successive shells of water molecules in response to the field of the ions.

According to Samoilov(27) the hydration can be negative or positive. If the exchange of molecules of water nearest the ions occurs more frequently than the exchange of the nearest molecules in water, the hydration is negative, e.g. K^+ , Cs^+ , Cl^- . If, however, the exchange of molecules nearest the ions occurs less frequently than the exchange of nearest molecules in water, the hydration will be positive, e.g. Mg^{2+} , Li^+ , Na^+ . The concept of positive and negative hydration is in agreement with Frank's(28) division of the ions into the two groups: structure makers and structure breakers.

Fabricand et al(29) measured proton spin-lattice relaxation times versus concentration of aqueous alkali halides and came to the conclusion that the configurations of water molecules around ions

like Li^+ and Na^+ are more stable than that of pure water, while the configurations around ions showing negative hydration are less stable than those of pure water. This effect correlates with the structure-breaking properties, as opposed to structure-making properties of Li^+ and Na^+ .

Millero(30) used the multilayer hydration models of Frank and Wen(31) and Eigen and Wicke(32) for ion-water interactions to interpret the value of the partial molar volume of an ion at infinite dilution. According to him the latter quantity is composed of four components, namely the crystal, the electrostriction, the disordered or void-space, and the caged or structured contributions to the partial molar volume. Depending upon which region is predominant, he divides ions into three classes viz electrostrictive structure-making, disordered structure-breaking, and hydrophobic structure-making ions.

It is important to emphasize that even at present a great deal of work is still being done in this field, and several new publications appear every year. Some fairly recent books dealing with these themes are those by Kavanau(33), Eisenberg and Kauzmann(34) and Horne(35).

CHAPTER 2

2. 1 Introduction

The discussion of the thermodynamic properties of electrolyte solutions requires a study of all the partial molar quantities of the components of the solution. These partial quantities may be divided into two types:-

- a) the partial molar free energy of the solute and the solvent;
- b) the partial molar quantities which may be derived from the determination of the pressure and temperature coefficient of the relative partial molar free energy or activity, such as the relative partial molar enthalpy, heat capacity and volume.

In this chapter the basic thermodynamic background will be presented.

2. 2 Fundamental equations and concepts

The total Gibbs free energy, G , of a fixed quantity of electrolyte solution of given composition is dependent only on the temperature and pressure. When the composition is changed at fixed temperature and pressure, the partial molar Gibbs free energies, or chemical potentials, μ , of the solvent and solutes can be defined as:

$$\mu_A = G_A = \left(\frac{\partial G}{\partial n_A} \right)_{P, T, n_j} \quad (2.1)$$

$$\mu_i = G_i = \left(\frac{\partial G}{\partial n_i} \right)_{P, T, n_A, n_j \neq i} \quad (2.2)$$

where the subscript A refers to the solvent and j to the solutes present in the solution; n_A is the number of moles of solvent and n_j the number of moles of solute.

As there is more interest in changes occurring in these quantities they are usually expressed as differences between absolute values and specified standard state values. For electrolyte solutions, the standard state for the solvent is always the pure solvent under the same conditions of temperature and pressure as the solution. For the solute, it is convenient to choose certain "hypothetical solutions" at the same temperature and pressure, since the pure solute which is commonly a solid very often has properties different from those it has in solutions.

The hypothetical solutions are effectively solutions of unit concentration (under certain specified conditions) on one of the following concentration scales:

- a) the molal scale (m = moles of solute per kilogram of solvent);

b) the molar scale ($c = \text{moles of solute per litre of solution}$):

c) the mole fraction scale ($x_j = \text{moles of solute divided by the total number of moles in the system}$).

2. 2. 1 Activity

By the use of chemical potentials it is possible to develop an adequate thermodynamics of solutions if suitable restrictions are imposed, but it is usually desirable to introduce additional, more restricted functions. An additional function which has been used extensively in solution thermodynamics is the activity.

The activity, a_i , of a pure chemical species or a constituent of a solution may be defined by the equations

$$\mu_i = \mu_i^{\circ} + R T \ln a_i \quad (2.3)$$

or

$$G_i = G_i^{\circ} + R T \ln a_i \quad (2.4)$$

where μ_i or G_i° are the chemical potential or the partial molar free energy, respectively, of the constituent, i , in some arbitrary standard state. The activity function is more restricted than the chemical potential or partial molar free energy, because its definition usually involves the introduction of a separate standard state for each phase.

In this way, the activity of the solvent, a_A , is defined by

$$G_A = G_A^{\circ} + R T \ln a_A \quad (2.5)$$

where G_A° is the partial molar Gibbs free energy in the standard state (pure solvent at the same temperature and pressure).

Similarly, an activity can be defined for the solute on each of the standard scales previously mentioned.

These definitions are:

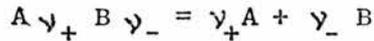
$$G_i = G_i^{\circ} (m) + R T \ln a_i (m) \quad (2.6)$$

$$G_i = G_i^{\circ} (c) + R T \ln a_i (c) \quad (2.7)$$

$$G_i = G_i^{\circ} (x) + R T \ln a_i (x) \quad (2.8)$$

If the number of moles of solute is always calculated on the basis of the anhydrous substance, the quantity G_i is unique for a given solution, pressure and temperature.

Alternative expressions for the activity of an electrolyte are obtained by considering its dissociation in solution. Thus, if an electrolyte, $A \nu_+ B \nu_-$, dissociates into ν_+ cations and ν_- anions according to:



its activity may be written

$$a = a_+^{\nu_+} \cdot a_-^{\nu_-} = a_{\pm}^{\nu} \quad (2.9)$$

where $\nu = \nu_+ + \nu_-$ is the total number of ions, a_+ and a_- are the conventional individual activities of the ionic constituents, and a_{\pm} is the mean activity of the ions. Accordingly, the partial molar free energy of an electrolytic component of a solution may be written

$$\begin{aligned} G_{AB} &= G_{AB}^{\circ} + R T \ln (a_+^{\nu_+} a_-^{\nu_-}) \\ &= G_{AB}^{\circ} + \nu R T \ln a_{\pm} \end{aligned} \quad (2.10)$$

Generally the definition of activity involves the introduction of a separate standard state for each phase and this must therefore be defined before the activity can be given a definite numerical value.

2. 2. 2 Activity coefficient

For each ionic species, + or -, of the electrolyte $A_{\nu_+}B_{\nu_-}$ in solution, it is possible to define an activity coefficient on the appropriate scale. Thus:

$$\text{molal scale} \quad a_+ (m) = \gamma_+ \cdot m_+ \quad (2.11)$$

$$\text{molar scale} \quad a_+ (c) = \gamma_+ \cdot c_+ \quad (2.12)$$

$$\text{mole fraction scale} \quad a_+ (x) = \gamma_+ \cdot x_+ \quad (2.13)$$

where γ , y , and f are called the molal, molar, and rational activity coefficients. The ionic concentrations are simply related to those of the electrolyte as a whole by the equations:

$$m_+ = \gamma_+ \cdot m \quad (2.14)$$

$$c_+ = \gamma_+ \cdot c \quad (2.15)$$

$$x_+ = \gamma_+ \cdot x \quad (2.16)$$

Similar relations can be written for the anion.

According to eqn(2.9) the activity of the electrolyte as a whole is

$$a = a_+^{\nu_+} \cdot a_-^{\nu_-}$$

and hence, upon introducing the eqns(2.11) - (2.16), one gets on each scale

$$a (m) = (\gamma_+^{\nu_+} \cdot \gamma_-^{\nu_-}) \cdot m^{\nu_+} \cdot \gamma_+^{\nu_+} \cdot \gamma_-^{\nu_-} \quad (2.17)$$

$$a (c) = (\gamma_+^{\nu_+} \cdot \gamma_-^{\nu_-}) \cdot c^{\nu_+} \cdot \gamma_+^{\nu_+} \cdot \gamma_-^{\nu_-} \quad (2.18)$$

$$a (x) = (\gamma_+^{\nu_+} \cdot \gamma_-^{\nu_-}) \cdot x^{\nu_+} \cdot \gamma_+^{\nu_+} \cdot \gamma_-^{\nu_-} \quad (2.19)$$

The equations (2.17) - (2.19) can be simplified by introducing a "mean ionic activity coefficient" defined by:

$$\gamma_{\pm}^{\nu} = \gamma_{+}^{\nu_{+}} \cdot \gamma_{-}^{\nu_{-}} \quad (2.20)$$

and similar expressions for y_{\pm} and f_{\pm} .

A mean ionic molality

$$m_{\pm}^{\nu} = (\nu_{+}^{\nu_{+}} \cdot \nu_{-}^{\nu_{-}})^{1/\nu} m^{\nu} \quad (2.21)$$

mean ionic molarity, c_{\pm} , and mean ionic mole fraction, x_{\pm} , can also be defined.

In this way, the fundamental relationships between the partial molar free energy and the activity coefficients on the x -, m -, and c - scales may be stated as follows:

$$G = G^{\circ}(x) + \nu R T \ln(f_{\pm} \cdot x_{\pm}) \quad (2.22)$$

$$G = G^{\circ}(m) + \nu R T \ln(\gamma_{\pm} \cdot m_{\pm}) \quad (2.23)$$

$$G = G^{\circ}(c) + \nu R T \ln(y_{\pm} \cdot c_{\pm}) \quad (2.24)$$

If the reference state is chosen so that $f_{\pm} = \gamma_{\pm} = y_{\pm} = 1$

at infinite dilution of solute at all temperatures and pressures, on introducing the limiting values of x_{\pm}/m_{\pm} and c_{\pm}/m_{\pm} at infinite dilution, the following relations may be obtained:

$$\begin{aligned} G^{\circ}(x) &= G^{\circ}(m) + \nu R T \ln(1000/M_1) \\ &= G^{\circ}(c) + \nu R T \ln(1000 d_0/M_1) \end{aligned} \quad (2.25)$$

and

$$\left. \begin{aligned} \ln f_{\pm} &= \ln \gamma_{\pm} + \ln(1 + \nu m M_1/1000) \\ \ln f_{\pm} &= \ln y_{\pm} + \ln[d/d_0 + c(\nu M_1 - M_2)/1000 d_0] \\ \ln \gamma_{\pm} &= \ln y_{\pm} + \ln(d/d_0 - c M_2/1000 d_0) \end{aligned} \right\} \quad (2.26)$$

In these equations M_1 and M_2 are the molecular weights of solvent and solute respectively, and d_0 and d are the densities of solvent and solution.

For a solution containing more than one electrolyte it is possible to write for each solute relations similar to those in (2.26) but including the summations, $\sum \nu_m, \sum \nu_c$, etc over all the solute species. For example one gets for the first relation

$$\ln f_{\pm} = \ln \gamma_{\pm} + \ln (1 + \sum \nu_m M_1 / 1000) \quad (2.27)$$

2. 2. 3 Osmotic coefficient

In dilute solution work the molal scale is used for solutes and the rational scale for the solvent. Because the solvent mole fraction and activity depart so little from unity, the rational activity coefficient of the solvent also remains very close to unity, and is therefore not such a good indicator of deviations from ideal behaviour as the solute activity coefficient. To obtain a more sensitive measure of the non-ideality of solutions in terms of the solvent, Bjerrum(39) introduced the concept of osmotic coefficient. The rational osmotic coefficient, g , is defined by

$$G_A = G_A^{\circ} + g R T \ln x_A \quad (2.28)$$

and the practical osmotic coefficient or molal osmotic coefficient, ϕ , by

$$G_A = G_A^{\circ} - \phi R T \sum m_i M_A / 1000 \quad (2.29)$$

where M_A is molecular weight of solvent and the factor $\sum m_i$ represents the summation over all solute species present.

The relation between the two coefficients is

$$\phi = \frac{-g \ln x_A}{\sum m_i M_A / 1000} \quad (2.30)$$

For a single electrolyte dissociating into ν ions, $\sum m_i$ equals νm and eqn (2.29) reduces to

$$\ln a_A = - \phi \nu m \cdot \frac{M_A}{1000} \quad (2.31)$$

or, for aqueous solutions

$$\ln a_w = - \frac{\nu m}{55.508} \phi \quad (2.32)$$

where a_w is water activity.

The partial molar Gibbs free energies of the components of a solution are related by the Gibbs-Duhem equation:

$$S d T - V d P + \sum_i n_i d G_i = 0 \quad (2.33)$$

where the summation covers both solute and solvent species, and n_i represents the number of moles of the i th species. Under constant pressure and temperature one gets

$$\sum_i n_i d G_i = 0 \quad (2.34)$$

or

$$\sum_i x_i d G_i = 0 \quad (2.35)$$

Differentiating eqn (2.32) and substituting into eqn (2.35) in the form

$$\left. \begin{aligned} x_w d \ln a_w + x_B d \ln a_B &= 0 \\ 55.508 d \ln a_w + \nu m d \ln \gamma_{\pm} m &= 0 \end{aligned} \right\} \quad (2.36)$$

leads to the important equation, first derived by Bjerrum for the relation between the practical osmotic coefficient and the activity coefficient,

$$d [m (1 - \phi)] + m d \ln \gamma_{\pm} = 0 \quad (2.37)$$

or, for the more general case,

$$d \left\{ \sum_i m_i (1 - \phi) \right\} + \sum_i m_i d \ln \gamma_i = 0 \quad (2.38)$$

Integration of these equations gives

$$\phi = 1 + \frac{1}{m} \int_0^m m \, d \ln \gamma_{\pm} \quad (2.39)$$

and

$$\phi = 1 + \frac{1}{\sum_i m_i} \int_0^m \sum_i m_i \, d \ln \gamma_i \quad (2.40)$$

Equation (2.39) allows values of ϕ to be calculated from values of mean activity coefficient, γ_{\pm}

2. 2. 4 Variation of the activity with temperature

From the definition of the activity of an electrolyte on the molality scale and the eqn (2.17)

$$\begin{aligned} G_B &= G_B^{\circ} + R T \ln a_B \\ &= G_B^{\circ} + \nu R T \ln (\gamma_+^{\nu+} \gamma_-^{\nu-}) + \nu R T \ln m + \nu R T \ln \gamma_{\pm} \end{aligned} \quad (2.41)$$

Differentiation of this equation divided by T with respect to temperature at constant pressure and composition gives

$$\left(\frac{\partial [G_B/T]}{\partial T} \right)_{m,p} = \left(\frac{\partial [G_B^{\circ}/T]}{\partial T} \right)_p + \nu R \left(\frac{\partial \ln \gamma_{\pm}}{\partial T} \right)_{m,p} \quad (2.42)$$

The partial molar enthalpy of a solute in solution is given by the well-known thermodynamic equation

$$H_B = - T^2 \frac{\partial (G_B/T)}{\partial T}$$

so that eqn (2.42) becomes

$$H_B = H_B^{\circ} - \nu R T^2 \left(\frac{\partial \ln \gamma_{\pm}}{\partial T} \right)_{m,p} \quad (2.43)$$

where H_B° is the partial molar enthalpy in the standard state.

At infinite dilution, $\gamma_{\pm} = 1$ at all temperatures, so that

$$H_B^{\infty} = H_B^{\circ}$$

that is, the partial molar enthalpies have the same value in the standard state and at infinite dilution.

Usually, the partial molar enthalpies are expressed relative to infinite dilution and then they are called relative partial molar enthalpies, L_B :

$$L_B = H_B - H_B^{\circ} \quad (2.44)$$

or

$$L_B = -\nu R T^2 \left(\frac{\partial \ln \gamma_{\pm}}{\partial T} \right)_{m,p} \quad (2.45)$$

It must be noted that in these equations, the activity coefficient may be expressed in the molal scale, or in the mole fraction scale, but not in the molar scale since in this scale the composition of a solution of fixed molarity varies with the temperature.

Differentiation of eqn (2.44) with respect to temperature at constant pressure serves to define the important quantities, the partial molar heat capacity, $C_{p(B)}$, and relative partial molar heat capacity, $C_{p(B)} - C_{p(B)}^{\circ}$, at constant pressures. Thus,

$$\left(\frac{\partial H_B}{\partial T} \right)_{m,p} - \left(\frac{\partial H_B^{\circ}}{\partial T} \right)_{p} = C_{p(B)} - C_{p(B)}^{\circ} = \left(\frac{\partial L_B}{\partial T} \right)_{m,p} \equiv J_B \quad (2.46)$$

or considering eqn (2.43)

$$C_{p(B)} = C_{p(B)}^{\circ} - \nu R \left(T^2 \frac{\partial^2 \ln \gamma_{\pm}}{\partial T^2} + 2 T \frac{\partial \ln \gamma_{\pm}}{\partial T} \right)_{m,p} \quad (2.47)$$

Again

$$C_{p(B)}^{\infty} = C_{p(B)}^{\circ}$$

that is, the partial molar capacities have also the same value in the standard state and at infinite dilution. The symbol J_B represents the partial molar heat capacity relative to infinite dilution.

The corresponding relations for the solvent are usually

expressed in terms of its activity, a_A , thus

$$H_A = H_A^o - R T^2 \left(\frac{\partial \ln a_A}{\partial T} \right)_{m,p} \quad (2.48)$$

and

$$C_{p(A)} = C_{p(A)}^o - R \left(T^2 \frac{\partial^2 \ln a_A}{\partial T^2} + 2 T \frac{\partial \ln a_A}{\partial T} \right)_{m,p} \quad (2.49)$$

2.2. 5 Cross-differentiation relations

The differential of the total Gibbs free energy can be written

$$dG = -S \cdot dT + V \cdot dP + \mu_1 \cdot dn_1 + \dots + \mu_c \cdot dn_c \quad (2.50)$$

Under constant pressure and temperature this equation reduces to

$$dG = \mu_1 \cdot dn_1 + \mu_2 \cdot dn_2 + \dots + \mu_c \cdot dn_c = \sum_i^c \mu_i \cdot dn_i \quad (2.51)$$

Since this equation is homogeneous and of the first degree in the extensive variable, n_1, n_2, \dots, n_c , it may be integrated at constant $\mu_1, \mu_2, \dots, \mu_c$ to yield

$$G = \mu_1 \cdot n_1 + \mu_2 \cdot n_2 + \dots + \mu_c \cdot n_c = \sum_i^c \mu_i \cdot n_i \quad (2.52)$$

Complete differentiation of this equation gives

$$dG = \sum_i^c \mu_i \cdot dn_i + \sum_i^c n_i \cdot d\mu_i \quad (2.53)$$

which, by combination with eqn (2.51) yields

$$\sum_i^c n_i \cdot d\mu_i = 0 \quad (2.54)$$

This equation relates the changes in the chemical potentials of the components of a phase, at constant temperature and pressure.

The condition of integrability of eqn (2.50) and the definitions of chemical potential

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{P,T, n_2, \dots, n_c} = \left(\frac{\partial H}{\partial n_i} \right)_{P,T, n_2, \dots, n_c} \quad (2.55)$$

imply that at constant temperature and pressure the chemical potentials are related by equations of the type

$$\left(\frac{\partial \mu_1}{\partial n_2} \right)_{n_1, n_3, \dots, n_c} = \left(\frac{\partial \mu_2}{\partial n_1} \right)_{n_2, \dots, n_c} \quad (2.56)$$

These relations are of great value in the thermodynamic treatment of systems containing two or more electrolytes and the solvent. For example they have been used by McKay and Perring (15) to calculate activity coefficients of the components of mixed electrolyte solutions from isopiestic measurements. Also Argersinger (17) used them to calculate activity coefficients of the solvent from E.M.F. measurements.

In this work the cross-differentiation relations will be applied to partial molar enthalpies and partial molar heat capacities.

2.3 Theoretical Aspects

Besides the fundamental thermodynamic relations it is necessary to consider some theoretical aspects with respect to the evaluation of certain thermodynamic properties. The activity coefficient of the solute is usually more convenient to handle than the chemical potential; that is why the problem has been to find a theoretical expression for the activity coefficient. Such expressions, after appropriate differentiation, for example with respect to the temperature, allow equations for other quantities such as partial molar enthalpies, partial molar heat capacities, etc., to be derived.

2.3.1 Activity coefficients at low concentration

The theory of interionic attraction effects presented by Debye and Hückel (40) has been of great value in the practical treatment of electrolyte solutions. It provides not only a limiting law for activities but also for enthalpies, heat capacities, etc., which may be expressed in the most general form by

$$\ln f_{\pm} = -\phi_{(f)} \Gamma^{\frac{1}{2}} \quad (2.57)$$

$$L_2 = H_2 - E_2^{\circ} = \phi_H \Gamma^{\frac{1}{2}} \quad (2.58)$$

$$J_2 = C_{p_2} - C_{p_2}^{\circ} = \phi_{C_p} \Gamma^{\frac{1}{2}} \quad (2.59)$$

$\phi_{(f)}$, ϕ_H , and ϕ_{C_p} are the theoretical limiting slopes, and $\Gamma \equiv \sum c_i z_i^2$ is the ional concentration of the electrolyte. The limiting slope $\phi_{(f)}$ is defined in terms of the absolute temperature, the dielectric constant of the solvent, and the valence type of the electrolyte. (In this thesis the total electrolyte concentration will mostly be expressed in terms of the ionic strength defined in molal terms as $I = \frac{1}{2} \sum m_i z_i^2$. This is clearly related to the ional concentration by a factor of 2 and by the density).

In the derivation of eqn.(2.57) Debye and Hückel assumed that the deviation in the behaviour of electrolytic solutions from ideality may be attributed entirely to Coulombic forces (long-range forces) between the ions which are regarded as point charges, that the energy of the electrical interactions between ions is small compared to its thermal energy, and that strong

electrolytes are completely dissociated. The electrostatic potential in solution at a point, fixed with relation to a particular ion is calculated from a linear form of the Poisson-Boltzmann equation.

In solutions containing a single electrolyte, the ional concentration is proportional to the concentration, c , and the theoretical equation may be rewritten in terms of $c^{\frac{1}{2}}$; this requires a redefinition of the limiting slope. The limiting law, converted to decadic logarithms, may be written

$$\log f_{\pm} = - A' |Z_i Z_j| c^{\frac{1}{2}} \quad (2.60)$$

where Z_i and Z_j are the valence of the ions i and j , respectively and A' is given by

$$A' = (2 N/1000)^{\frac{1}{2}} (e^3/2.303k^{\frac{3}{2}}) (1/DT)^{\frac{3}{2}} \quad (2.61)$$

where

- N is the Avogadro's constant
- k the Boltzmann's constant
- e the electronic charge
- D the dielectric constant of the solvent
- T the absolute temperature

The Debye-Hückel limiting law is strictly valid only at high dilutions, in the limit of zero concentration.

An extension of the Debye-Hückel limiting law usually considered as part of the basic theory is the use of a distance of closest approach parameter, \bar{a} . Debye and Hückel

themselves introduced this parameter because they realized the importance of a limit to the attraction between ions because of their finite size (short-range interactions between ions). The theoretical equation including this short-range interaction is

$$\log f_{\pm} = - \frac{A c^{\frac{1}{2}}}{1 + Bc^{\frac{1}{2}}} \quad (2.62)$$

where $B = \kappa \bar{a}$ is defined by

$$\kappa^2 \equiv (4\pi e^2 / DkT) \sum n_i Z_i^2 \quad (2.63)$$

and possesses the dimensions of a reciprocal distance. 'A' now includes the product $|Z_i Z_j|$ of the charge types. The eqn.(2.62) is valid up to concentrations of about 0.1 molar.

There have been a number of attempts to extend the Debye-Hückel theory at higher concentrations. Hückel (41) modified the equation for the changing of the dielectric constant by the solute. He considered a linear variation of the dielectric constant with the concentration of the ions, obtaining the equation

$$\log f_{\pm} = - \frac{A c^{\frac{1}{2}}}{1 + B c^{\frac{1}{2}}} + C c \quad (2.64)$$

but, even when the dielectric constant is altered by addition of ions, it is not the only important factor in more concentrated solutions and, in fact, eqn.(2.64) represents the experimental results only up to approximately 1 molar. In order to obtain a better fit in more concentrated solutions,

it is necessary to introduce into the equation terms containing higher powers of c , as will be shown in the next section.

Guggenheim (42) obtained a similar equation but valid only up to 0.1 molar. He started with eqn.(2.62) which, for 1:1 electrolytes in aqueous solution at 25°C and with $\bar{a} = 3.04 \text{ \AA}$, becomes

$$\log f_{\pm} = - \frac{0.506 c^{\frac{1}{2}}}{1 + c^{\frac{1}{2}}} \quad (2.65)$$

and obtained

$$\log f_{\pm} = - \frac{0.506 c^{\frac{1}{2}}}{1 + c^{\frac{1}{2}}} + \lambda c \quad (2.66)$$

The term λ includes contributions such as changes in the dielectric constant, ion pair formation, and effects due to ion size. The objection to this equation is that it implies that all ions have the same \bar{a} value.

Another important contribution to the theory of electrolyte solutions which, in fact, antedate those of the Debye-Hückel theory, is that of Bjerrum (39) who proposed a $c^{\frac{1}{3}}$ behaviour for the variation of the activity coefficient, considering that above a certain concentration the ions form a quasi-lattice in solution. It has been thought that even at very low concentration this theory could replace that of Debye and Hückel if the fluctuation term of the elect-

rostatic theory becomes large enough. Also at relatively high concentration it is possible to obtain satisfactory results by adding additional terms to the cube-root term (43,44).

2.3.2 Activity coefficients at high concentrations

Some of the assumptions have been made in deriving the limiting law are no longer valid at appreciable concentrations. A theory of more concentrated solutions must consider, for example, Coulombic effects at close approach, and also non-Coulombic effects. Classically, these effects have been treated by considering expansions in series of the individual ion concentration.

One attempt, after Debye and Hückel added the term \bar{a} to account for short-range interactions, was that of Hückel who added the linear term to allow for the change of the dielectric constant (eqn.(2.64)). It has been said that, with the addition of terms in higher powers of the concentration it is possible to obtain better results for more concentrated solutions and, in fact,

the activity coefficients of many 1:1 electrolytes from 0 to 4 molar may be calculated very accurately by the equation

$$\log f_{\pm} = - \frac{Ac^{\frac{1}{2}}}{1 + Bc^{\frac{1}{2}}} + Cc + Dc^2 \quad (2.67)$$

The terms Cc and Dc^2 are positive, and opposite in sign to the first term.

Lietzke and Stoughton(49) have developed a useful analytical method for osmotic and activity coefficients. The expressions consist of a Debye-Hückel term with the addition of a polynomial in the ionic strength, the coefficients of which are determined from experimental osmotic or activity coefficients by a fitting procedure. According to eqn (2.62), the variation of the mean molal activity coefficient of the salt J with the ionic strength, I , is given by

$$\ln \gamma_{\pm} = \frac{-S I^{\frac{1}{2}}}{1 + A_J I^{\frac{1}{2}}} \quad (2.68)$$

where $I (= \frac{1}{2} \sum m_j z_j^2)$ is the ionic strength, S is the Debye-Hückel limiting slope, and A_J contains the distance of closest approach parameter.

When the expression (2.68) is differentiated and substituted in eqn (2.39), and the integration performed analytically the following equation is obtained for the osmotic coefficient, ϕ_J , of the salt J,

$$\phi_J = 1 - \frac{S}{A_J I} \left[(1 + A_J I^{\frac{1}{2}}) - 2 \ln (1 + A_J I^{\frac{1}{2}}) - (1 + A_J I^{\frac{1}{2}})^{-1} \right] \quad (2.69)$$

Lietzke and Stoughton, then, suggested adding the polynomial in the ionic strength to eqn (2.69) and not directly to eqn (2.68). In this way, the expression

$$\phi_J = 1 - \frac{S}{A_J^2 I} \left[\beta - 2 \ln \beta - \beta^{-1} \right] + \mathcal{L}_1 I + \mathcal{L}_2 I^2 + \mathcal{L}_3 I^3 + \dots \quad (2.7)$$

is obtained, where $\beta = 1 + A_J I^{\frac{1}{2}}$. Then, the equation for the activity coefficient becomes

$$\ln \gamma_{\pm} = -\frac{S}{\beta} + (2\mathcal{L}_1) I + \left(\frac{3}{2}\mathcal{L}_2\right) I^2 + \left(\frac{4}{3}\mathcal{L}_3\right) I^3 + \dots \quad (2.7)$$

The best fit is obtained when all the parameters, i.e. $A_J, \mathcal{L}_1, \mathcal{L}_2, \dots$, are considered as adjustable. They can be determined by a least square method, from eqn (2.70) and may be used in eqn (2.71) to determine the corresponding activity coefficients. Lietzke and Stoughton found that eqn (2.70) fits the osmotic coefficient data for about 20 salts over concentration ranges of 0.1 - 6 molal.

An important contribution to the theory of concentrated solutions is that of Scatchard(45,46)) particularly for the alkali halides. This contribution is also an extension of the Debye-Hückel theory and in it the ion-ion, ion-molecule, and molecule-molecule interactions are considered separately. Scatchard's equation for the activity coefficient is

$$\ln \gamma_{\pm} = -\ln (1 + \nu_s N_s / N_0) + \frac{e^2 N}{2RTD_0} \left[\frac{Z_1 Z_2 \kappa}{1 + \kappa a} + \left(\frac{\kappa}{1 + \kappa a} + X \right) Z_1 Z_2 V_s \text{md}_0 \right. \\ \left. + \frac{4\nu_1 \nu_2}{\nu_s} \left(\frac{V_2 Z_1^2}{b_1} + \frac{V_1 Z_2^2}{b_2} \right) \text{md}_0 \right] + \frac{A \text{md}_0 (2 + \nu_s \text{md}_0)}{RT (1 + V_s \text{md}_0)^2} \quad (2.72)$$

where

N_s is the number of moles of electrolyte
 N_o the number of moles of solvent
 V_1, V_2 the molar volumes of the ions
 V_o the molar volume of solvent
 b_1, b_2 are parameters representing the radii of the ions, effective for salting out
 a is the sum of the radii effective in ionic collision

The other terms are defined by

$$m d_o = N_s / V_o N_o \quad V_s = \nu_1 V_1 + \nu_2 V_2$$

$$\nu_s = \nu_1 + \nu_2$$

$$D = D_o V_o N_o / V$$

$$\kappa^2 = \frac{8\pi N^2 e^2 Z_1 Z_2 \nu_s N_s}{1000 RTDV}$$

$$X = \frac{\kappa}{1 + \kappa a} - Y$$

$$Y = \left[(1 + \kappa a) - 2 \ln (1 + \kappa a) - (1 + \kappa a)^{-1} \right] / \kappa^2 a^3$$

$$A = 2 \nu_1 \nu_2 V_1 V_2 (2 a_{12} - a_{10} - a_{20}) / \nu_s$$

where a_{12} , a_{10} , and a_{20} are the mutual cohesive energy densities.

In eqn.(2.72) the first term on the right represents the conversion from rational activity coefficient to molal activity coefficient, the second represents both the Debye-

Hückel term for ion-ion interaction and the salting out effect, or the ion-molecule term, and the final term expresses a non-electrolyte molecule-molecule interaction, i.e., an interaction between ions and solvent molecules independent of the presence of charge on the solute species.

In contrast with the other equations, where the \bar{a} parameter has to be derived from experimental data, in this theory the ionic radii are determined from crystallographic measurements.

The osmotic and activity coefficients calculated by this theory agree satisfactorily with the literature data but the application of the equation is in general quite complicated and, in addition to the crystallographic measurements, two constants have to be derived from two experimental activity or osmotic coefficients, namely the relation of the ionic volume to the crystallographic radius and the numerical value of the coefficient of the last term in eqn.(2.72).

2.3.3 Explicit reference to hydration effects
at high concentrations.

Recognition of the non-Coulombic effects, such as specific interaction of the ions and hydration, is a necessary component of a rigorous theory of electrolytes. The ions interact strongly with water and this interaction perturbs the excess free energy at higher concentrations since for example, ions with very strong electric fields would remove water molecules from solution, excluding their use as solvent by other ions.

There have been several treatments of hydration, which have been more or less successful in fitting the experimental data, but again the problem is that there is no independent way of calculating the parameters; they can only be obtained by fitting the curves, and hence the hydration parameters may have a vague meaning.

Bjerrum (50) produced the first quantitative treatment of hydration in terms of the average number of water molecules bound to the ions of the salt. The Bjerrum equation for the mean activity coefficient is,

$$\ln \bar{\gamma}_{\pm} = \ln \gamma_{\pm}^{\prime} - \frac{h}{\bar{\nu}} \ln a_w + \ln \left[1 - \frac{(h - \nu)}{55.508} \right] \quad (2.73)$$

where

γ_{\pm} is the observed activity coefficient,
 γ'_{\pm} a hypothetical activity coefficient calculated
from the assumed electrostatic form (a $c^{\frac{1}{3}}$ law),
 h is the hydration number,
 ν the total number of moles, and
 a_w is the water activity.

The water activity is not fixed by the equation but can be related to the salt activity using the Gibbs-Duhem equation. The last term of eqn.(2.73) represents the change in activity coefficient due to hydration-induced change in concentration.

Robinson and Stokes (51) obtained a similar equation for $\ln \gamma_{\pm}$ but in their equation the term in $\ln a_w$ signifies a loss in free energy attributed to the water component that has been removed from the solvent. They also showed that, using the concept of limited penetration of the anion into the hydration shell of the cation, it is possible to obtain a two-parameter (h and a) equation and further, through a relationship between these two parameters, a one-parameter equation for the activity coefficient up to moderate concentrations (viz. up to $hm \ 12$).

They (51) combined Bjerrum's treatment of ion-solvent interactions with the Debye-Hückel treatment of ion-ion interactions. The equation they obtained, for aqueous solutions at 25°C, is

$$\log \gamma_{\pm} = \log \gamma_{\pm}'' - \frac{n}{\nu} \log a_w - \log (1 - 0.018(n-\nu)m) \quad (2.74)$$

where

- $\log \gamma_{\pm}''$ is the Debye-Hückel term
- n the number of molecules of water in the hydration shells
- ν the number of ions in one molecule of solute
- m the stoichiometric molality of the solution and related to the molality, m^1 , of the hydrated ions by the expression

$$m^1 = \frac{55.51 m}{55.51 - nm} = \frac{m}{1 - 0.018 nm}$$

Eqn (2.74) contains two parameters, n and \bar{a} , and is capable of representing the activity coefficient over a wide range of concentration.

Glueckauf(52) modified this treatment. He considered only the concentration change term and not the water activity component and also used volume-fraction statistics in place of the mole-fraction statistics which are used in the other two treatments. He calculates the total excess free energy assuming that a fixed number of water molecules is firmly bound and that the activities of solvent and hydrated solute each depend on their volume fraction in solution.

The Gibbs excess free energy, G_s , for the hydration component, in volume fraction statistics is given by

$$G_s = kT \sum_i \{n_i \ln (N_i V_i / V)\} \quad (2.75)$$

where N_i is the number of hydrated ions or solvent molecules, V_i the partial molar volume, and V the total volume.

Differentiation of (2.75) with respect to solvent or solute component leads to the partial molar excess free energies and for the molal activity coefficient the following expression is obtained

$$\begin{aligned} \log \gamma_{\pm} &= \log \gamma_{\pm}^{elec} + \frac{h - \nu}{\nu} \log (1 + 0.018 \text{ m r}) \\ &- \frac{h}{\nu} \log (1 - 0.018 \text{ m h}) + \frac{0.018 \text{ m r} (r + h - \nu)}{2.3 (1 + 0.018 \text{ m r})} \end{aligned} \quad (2.76)$$

where r is the ratio of the apparent molar volume of the salt to the molar volume of pure water.

This equation is able to represent the data up to high concentrations and the new hydration numbers obtained become nearly additive for the separate ions. Its advantages over the other equations are that the individual ionic hydration numbers vary less with concentration and do not vary with the salt type. The disadvantages are that the electrical component is indefinite and the hydration component is obtained as a difference.

2. 3. 4 Partial molar enthalpy and partial molar heat capacity

2.3.4. 1 Partial molar enthalpy

The total enthalpy of a solution composed by n_1 moles of solvent and n_2 moles of solute is given by

$$H = n_1 H_1 + n_2 H_2 \quad (2.77)$$

where H_1 and H_2 are the partial molar enthalpies of the solvent and solute, respectively.

Since the absolute values of enthalpies are experimentally undefined, it is necessary to employ a reference state which normally is an infinitely dilute solution. If H° is the total enthalpy in this condition, it is possible to write

$$H^{\circ} = n_1 H_1^{\circ} + n_2 H_2^{\circ} \quad (2.78)$$

By definition of the apparent molar enthalpy of the solute, ϕ_H , an equation similar to eqn (2.77) may be written, i.e.,

$$H = n_1 H_1^{\circ} + n_2 \phi_H \quad (2.78)$$

which gives the total enthalpy in terms of the partial molar enthalpy of the solvent at infinite dilution and of ϕ_H . It is to be noted that at infinite dilution ϕ_H is equal to H_2° .

Combination of these equations leads to the relation

$$H - H^{\circ} = n_1 (H_1 - H_1^{\circ}) + n_2 (H_2 - H_2^{\circ}) = n_2 (\phi_H - \phi_H^{\circ}) \quad (2.79)$$

or

$$L = n_1 L_1 + n_2 L_2 = n_2 \phi_L \quad (2.80)$$

where

$\phi_H - \phi_H^{\circ} = \phi_L$ is the relative apparent molar enthalpy of the solute,

$H_2 - H_2^{\circ} = L_2$ the relative partial molar enthalpy of the solute,

$H_1 - H_1^{\circ} = L_1$ the relative partial molar enthalpy of the solvent.

In terms of the enthalpy of dilution, ΔH_D , for the isothermal isobaric addition of an infinite quantity of pure solvent to a solution containing one mol of solute in n_1/n_2 mols of solvent, the following equation may be written

$$n_2 \Delta H_D = - n_1 L_1 - n_2 L_2 = - n_2 \phi_L \quad (2.81)$$

This relation shows that the apparent molar enthalpy is equal to the heat of dilution but with opposite sign.

Values for the partial molar enthalpy of the solute and the solvent are needed in many thermodynamic calculations. In order to evaluate these quantities there must be available data extending to very small concentrations from which extra-polation to infinite dilution will introduce no appreciable uncertainty.

For extrapolating the data for electrolytes to infinite dilution the extension of the Debye-Hückel theory is very useful. The Gibbs free energy of a solute in two systems, one being an infinitely dilute solution and the other a dilute solution of molality m , may be separated into two parts:

- the "classical" or that due to the free energy change with concentration where the molecules of solute are considered as particles of an ideal solution, and

- the "electrical" or that due to the free energy change resulting from the electrical forces of the ions.

At very low concentrations, according to the Debye-Hückel theory,

$$G_2 - G_2^{\circ} = RT \ln m + \left[- \frac{N^{3/2} e^3}{D^{3/2} T^{1/2}} \left(\frac{\pi}{1000 k} \right)^{1/2} (\sum \nu_i Z_i^2)^{3/2} m^{1/2} \right] \quad (2.82)$$

and according to the thermodynamic relation

$$\frac{\partial}{\partial T} \left(\frac{G_2 - G_2^0}{T} \right) = - \frac{H_2 - H_2^0}{T} \quad (2.83)$$

the expression

$$H_2 - H_2^0 = -\frac{3}{2} \frac{N^{3/2} e^3}{D^{3/2} T^{1/2}} \left(\frac{\pi}{1000k} \right)^{1/2} \left(1 + \frac{T}{D} \cdot \frac{dD}{dT} \right) \left(\sum v_i z_i^2 \right)^{3/2} m^{1/2} \quad (2.84)$$

is obtained. The original Debye-Hückel theory is useful only at very low concentrations, as has been previously mentioned.

Bjerrum(53) treated the theoretical derivation of Debye and Hückel and derived the integral heat of dilution, $V_c = -n_1 L_1 - L_2$, of a strong electrolyte as a limiting expression similar to eqn (2.84)

A more exact treatment of the fundamental theory of Debye and Hückel was that by Gronwall, La Mer and Sandved(54) which was applied by Lange and Meixner(55) to a new calculation of theoretical integral heats of dilution. The expression

$$V_c = -\frac{N}{n} \sum_{j=1}^s n_j \frac{z_j e}{D a_j} \left[\psi_j - \frac{z_j e}{D a_j} \right] \left[1 + \frac{T}{D} \frac{dD}{dT} \right] / \text{ergs mol}^{-1} \quad (2.85)$$

represents the integral heat of dilution which is accordingly equal to the ionic electrical potential energy at the concentration c (expressed in mols of salt per liter of solution) less that at infinite dilution, multiplied by the factor $\left[1 + (T/D) (dD/dT) \right]$.

In the derivation of this equation it is assumed that strong electrolytes are completely dissociated at all concentrations and the distribution of the ions (considered as rigid charged spheres with average minimum distance of approach "a") in solution is determined by their thermal motion and the Coulombic forces acting among them. The influence of the solvent was represented by its dielectric constant alone, the value of D being independent of the number and nature of the ions present, then $dD/dc = 0$; also da/dT was considered zero.

According to eqn (2.35), for aqueous solutions at room temperature V_c (or $-\Delta H$ in the present notation) should always be positive, i.e., heat should be evolved by the dilution. For extreme dilutions the limiting law retains its validity and V_c becomes proportional to $c^{\frac{1}{2}}$.

Differentiation with respect to the temperature of the Debye-Hückel equation for the rational activity coefficient, in a form similar to eqn (2.64), and its substitution into the relation

$$H_2 - H_2^0 = - \nu RT^2 \left(\frac{\partial \ln f_{\pm}}{\partial T} \right)_P \quad (2.86)$$

leads to the following equation

$$H_2 - H_2^0 = \frac{\phi_H \Gamma^{\frac{1}{2}}}{1 + A \Gamma^{\frac{1}{2}}} + \frac{W_H \Gamma}{(1 + A \Gamma^{\frac{1}{2}})^2} + K_H \Gamma \quad (2.87)$$

where

$$\phi_H = - 2.303 \nu RT^2 \phi_f \cdot \frac{3}{2} \left[\frac{1}{T} + \frac{\partial \ln D}{\partial T} + \frac{\alpha}{3} \right] \quad (2.88)$$

$$W_H = 2.303 \nu RT^2 \phi_f A \cdot \frac{1}{2} \cdot \left[\frac{1}{T} + \frac{\partial \ln D}{\partial T} + \alpha - \frac{2 \partial \ln a}{\partial T} \right] \quad (2.89)$$

and

$$K_H = - 2.303 \nu RT^2 B \left[\frac{\partial \ln B}{\partial T} - \alpha \right] \quad (2.90)$$

In these equations ϕ_H, ϕ_f are the limiting slopes in their most general form, Γ the ionic concentration, $B \Gamma$ the empirical linear term added to the Debye-Hückel expression of $\log f_{\pm}$ and A is $\frac{1}{a} \kappa$. The term α is the coefficient of thermal expansion of the solution.

The sign of δ_H is governed by the term $\delta \ln D / \delta T$, which is negative, and usually greater than $1/T$ by an amount exceeding $d/3$. Therefore, for water and most other solvents, the Debye-Hückel theory requires that L_2 increases with the square root of the ionic concentration at extreme dilution. The value of the slope is very sensitive to experimental uncertainties in measuring the temperature coefficients of D , so the value derived depends upon the source of the dielectric constant data.

Similar equations were derived by Harned and Hecker(56) and by Harned and Ehlers(57). The first (56) used for L_2 an expression equivalent to Hückel's equation for $\ln f_{\pm}$ and demonstrated the importance of the contribution of the term containing B in moderately dilute solutions. They compared the values of dB/dT with those of dc/dT , which in all cases is negative above 5°C , and concluded that if dB/dT is positive and greater than dc/dT , the term containing these derivatives in their equation had to be subtracted from the other but if dB/dT were negative the term in dB/dT and dc/dT had to be added. The equation was said to be valid up to approximately 1 molar and they proposed the addition of a term such as Dc^n to the Debye-Hückel equation, for higher concentrations.

Harned and Ehlers(57) employed a term Dc^2 with success. They added the term to the extended equation represented by the Gronwall, La Mer, and Sandved(54) extension of the theory. The equation was used up to 4 molar.

One extension of the Debye-Hückel equation, which has been extensively used, is

$$\ln \gamma_{\pm} = \frac{S I^{\frac{1}{2}}}{1 + A I^{\frac{1}{2}}} + B I + C I^2 + D I^3 + \dots \quad (2.91)$$

The parameters B, C, D are the same as the parameters $\alpha_1, \alpha_2, \alpha_3$ in eqn (2.70) (This different notation of the authors has been preserved here to avoid comparison with α , the coefficient of thermal expansion.) The temperature dependence (58) of these coefficients can be assumed to have the general form

$$B = B_1/T + B_2 \ln T + B_3 + B_4 T \quad (2.92)$$

Using eqn (2.91) the relative partial molar enthalpy of the solute, L_2 , is given by

$$\begin{aligned} L_2 = \nu R T^2 \left[Q_1 \cdot \left(-\frac{2 d \ln a^0}{dT} + \alpha + \frac{1}{T} + \frac{d \ln D}{dT} \right) \right. \\ + Q_2 \cdot \left(\frac{\alpha}{3} + \frac{1}{T} + \frac{d \ln D}{dT} \right) \\ \left. + \left(\frac{dB}{dT} - B\alpha \right) I + \left(\frac{dC}{dT} - 2 C\alpha \right) I^2 + \dots \right] \quad (2.93) \end{aligned}$$

where Q_1 and Q_2 are given by

$$Q_1 = \frac{z_+ z_- e^2 K^2 a^0 I}{4 D k T (1 + K a^0 I^{\frac{1}{2}})^2} \quad (2.94)$$

$$Q_2 = \frac{-3 K e^2 I^{\frac{1}{2}}}{4 D k T (1 + K a^0 I^{\frac{1}{2}})} \quad (2.95)$$

The coefficient of thermal expansion, α , results from the differentiation of the density with respect to the temperature. The density used in these equations is that of the solvent; slightly different expressions would result if the density of the solution (which is a function of concentration) were used. However, it has been shown that the difference is small and is compensated for by

the empirical adjustment of the higher-order terms in the data-fitting process. The parameter \bar{a}^0 is usually assumed to be temperature independent; it can also be taken as an adjustable parameter but generally there is no improvement in the fit. It is to be noted that the equation which results by setting the parameters B, C, and D to zero contains only the terms which are derived from the theoretical treatment of Debye and Hückel.

2. 3. 4. 2 Partial molar heat capacity

The relations between the total heat capacity, C_p , of a binary solution and the partial molar heat capacities of the solvent and solute are similar to those enthalpies in section (2.3.4.1). Partial differentiation of eqns (2.77) and (2.78) with respect to the temperature at constant pressure yields:-

$$C_p = n_1 C_{p1} + n_2 C_{p2} \quad (2.96)$$

and

$$C_p = n_1 C_{p1}^0 + n_2 \phi_{C_p} \quad (2.97)$$

also $\phi_{C_p}^0 = C_{p2}^0$ at infinite dilution.

From these relations the following equation may be obtained

$$C_p - C_p^0 = n_1 (C_{p1} - C_{p1}^0) + n_2 (C_{p2} - C_{p2}^0) = n_2 (\phi_{C_p} - \phi_{C_p}^0) \quad (2.98)$$

In these equations:

C_{p1} and C_{p2} are the partial molar heat capacity of the solvent and solute respectively,

C_{p1}^0 the partial molar heat capacity of the pure solvent,

ϕ_{C_p} is the apparent molar heat capacity of the solute,

$C_{p_1} - C_{p_1}^{\circ} \equiv J_1$ the relative partial molar heat capacity
of the solvent,

$C_{p_2} - C_{p_2}^{\circ} \equiv J_2$ the relative partial molar heat capacity
of the solute,

and

$\phi_{C_p} - \phi_{C_p}^{\circ} \equiv \phi_J$ the relative apparent molar heat capacity.

According to this equation or by partial differentiation
of (2.79) or (2.80) with respect to the temperature

$$\left(\frac{\partial L}{\partial T}\right)_p = n_1 \left(\frac{\partial L_1}{\partial T}\right)_p + n_2 \left(\frac{\partial L_2}{\partial T}\right)_p$$

or

$$J = n_1 J_1 + n_2 J_2 = n_2 \phi_J \quad (2.99)$$

Only the relative values of the heat capacity can
be obtained from the temperature variation of activities.

In general,

$$J_2 \left(\frac{\partial L_2}{\partial T}\right)_{p,x} = -\nu_R \frac{\partial}{\partial T} \left[T^2 \left(\frac{\partial \ln f}{\partial T}\right) \right] \quad (2.100)$$

This relation shows that the limiting equation for J_2
can be obtained either through the limiting equations for
the relative partial molar enthalpy or those for the activity
coefficient. The simplest case is when

$$L_2 = \phi_H T^{\frac{1}{2}}$$

or

$$\log f_{\pm} = \phi_f T^{\frac{1}{2}}$$

Differentiation of either of these equations gives

$$J_2 = \mathcal{J}_{C_p} T^{\frac{1}{2}}$$

where

$$\mathcal{J} = \frac{3}{4} \left[1 + 2 \frac{T}{D} \frac{\partial D}{\partial T} + 5 \left(\frac{T}{D} \frac{\partial D}{\partial T} \right)^2 + \frac{2T^2}{DV} \frac{\partial D}{\partial T} \frac{\partial V}{\partial T} + \frac{2}{3} \frac{T}{V} \frac{\partial V}{\partial T} + \left(\frac{T}{V} \frac{\partial V}{\partial T} \right)^2 - \frac{2T^2}{D} \frac{\partial^2 D}{\partial T^2} - \frac{2}{3} \frac{T^2}{V} \frac{\partial^2 V}{\partial T^2} \right] \quad (2.101)$$

In this expression, the coefficient of thermal expansion, α , has been replaced by equivalent functions of the volume V , which may be either the specific volume or the total volume of the solution.

The value of \mathcal{J}_{C_p} , like that of \mathcal{J}_H , is very sensitive to experimental uncertainties in measuring the temperature coefficient of D ; this emphasizes the experimental nature of the values quoted for these theoretical slopes. This is important when considering either the validity or the utility of the limiting laws for partial molar quantities.

2.4 Pitzer's Treatment

This thesis is mainly directed towards new methods of obtaining data from mixture solutions, and the detailed theoretical interpretation of the data obtained will therefore be left for a later investigation: it will then be very

important to have some relations to compare the values obtained by these methods with those predicted by the theory. There are various methods available, as will be shown in the next section, but it seems that a very good approach will be that developed by Pitzer (11).

Pitzer with the guidance of the recent theories of electrolytes, developed semi-empirical equations which represent accurately thermodynamic properties of aqueous solutions, including mixtures with any number of components. The equations are compact and convenient in that only few parameters need to be tabulated for each substance, that the mathematical calculations are not too complicated and the parameters have physical meaning as far as possible.

Pitzer divides his theory into three parts:

- 1) the selection of the molecular model, i.e., the interionic potentials of mean force,
- 2) the calculation of the interionic radial distribution functions from this model,
- 3) the calculation of thermodynamic functions from the potentials and the radial distribution functions.

He characterizes his model by the interionic potential equation

$$u_{ij}(r) = u_{ij}^*(r) + Z_i Z_j e^2 / Dr \quad (2.102)$$

where

$Z_i e$ is the charge on the i^{th} ion,
 r the distance between the i and j ions,
 D the dielectric constant of the solvent,
 u_{ij}^* is a short range function giving the difference between the true interionic potential of mean force and the electrostatic term.

Pitzer considers the distance of closest approach in terms of a distance given by the sum of ionic radii which may differ for the positive and negative ions in a salt. According to Pitzer, whereas Debye and Hückel ignore the kinetic effect of the hard-core on properties such as osmotic pressure, the effect can be allowed for by introducing the potential

$$\begin{aligned} u_{ij} &= \infty & r < a \\ u_{ij} &= Z_i Z_j e^2 / Dr & r \geq a \end{aligned} \quad (2.103)$$

into the pressure equation, and then obtaining

$$\begin{aligned} \pi - c k T &= (e^2 / 6D) \sum_i \sum_j c_i c_j Z_i Z_j \int_0^\infty g_{ij}(r) 4\pi r^2 dr \\ &+ \frac{2}{3} (\pi a^3 k T) \sum_i \sum_j c_i c_j g_{ij}(a) \end{aligned} \quad (2.104)$$

where

Π is the osmotic pressure

C_i, C_j the concentrations of species i and j

C the total solute concentration C_i

$g_{ij}(r)$ the radial distribution

In this equation the second term involving $g(a)$, the radial distribution function at the outer surface of contact, constitutes the kinetic effect of the hard core.

From these relations he obtained the osmotic coefficient and suggested that the properties of electrolyte solutions can be expressed by an electrostatic term plus a virial coefficient series in which the virial coefficients may be functions of the ionic strength of the solution. The virial coefficient undergoes an initially rapid decrease from the value at zero concentration to a smaller and relatively constant value at high concentrations. The different long-range electrostatic term was found superior to that derived by Debye and Hückel from a charging process.

The Pitzer equation for the total excess Gibbs free energy for a solution containing n_w kilograms of solvent and n_i, n_j, \dots moles of solute species i, j, \dots , is

$$\frac{G^{ex}}{RT} = n_w f(I) + \frac{1}{n_w} \sum_{ij} \lambda_{ij}(I) n_i n_j + \frac{1}{n_w^2} \sum_{ijk} \mu_{ijk} n_i n_j n_k \quad (2.105)$$

where

$f(I)$ is a function of ionic strength, temperature and solvent properties. It expresses the effect of the long-range electrostatic forces,

$\lambda_{ij}(I)$ is also a function of ionic strength and expresses the

effect of short-range forces between i and j,

μ_{ijk} does not depend on ionic strength and it accounts for the triple ion interaction.

Differentiation of eqn (2.105) with respect to n_w and n_i , respectively leads to the Pitzer expressions for the osmotic and activity coefficients. For a single electrolyte, MX, the total excess Gibbs free energy, the osmotic coefficient, and the activity coefficient are given by

$$G^{\text{ex}}/n_w RT = f^{\text{GX}} + m^2 (2\nu_M \nu_X) B_{\text{MX}}^{\text{GX}} + m^3 \left[2(\nu_M \nu_X)^{3/2} \right] C_{\text{MX}}^{\text{GX}} \quad (2.106)$$

$$\phi - 1 = \left| \frac{Z_M Z_X}{m} \right| f^{\phi} + m (2\nu_M \nu_X / \nu) B_{\text{MX}}^{\phi} + m^2 \left[2(\nu_M \nu_X)^{3/2} / \nu \right] C_{\text{MX}}^{\phi} \quad (2.107)$$

$$\ln \gamma = \left| \frac{Z_M Z_X}{m} \right| f^{\gamma} + m (2\nu_M \nu_X / \nu) B_{\text{MX}}^{\gamma} + m^2 \left[2(\nu_M \nu_X)^{3/2} / \nu \right] C_{\text{MX}}^{\gamma} \quad (2.108)$$

where

ν_M and ν_X are the numbers of M and X ions

$\nu = \nu_M + \nu_X$ the total number of ions

Z_M and Z_X the charges of the ions M and X, in electronic units,

m the stoichiometric molality

and

$$f^{\phi} = - A_{\phi} \left[I^{1/2} / (1 + bI^{1/2}) \right] \quad (2.109)$$

$$f^{\gamma} = - A_{\gamma} \left[I^{1/2} / (1 + bI^{1/2}) + (2/b) \ln (1 + bI^{1/2}) \right] \quad (2.110)$$

$$f^{\text{GX}} = - A_{\phi} (4I/b) \ln (1 + bI^{1/2}) \quad (2.111)$$

$$B_{\text{MX}}^{\phi} = \beta_{\text{MX}}^{(0)} + \beta_{\text{MX}}^{(1)} e^{-\alpha I^{1/2}} \quad (2.112)$$

$$B_{\text{MX}}^{\gamma} = 2\beta_{\text{MX}}^{(0)} + (2\beta_{\text{MX}}^{(1)} / \mathcal{L}^2 I) \left[1 - \exp(-\mathcal{L} I^{1/2}) (1 + \mathcal{L} I^{1/2} - \frac{1}{2} \mathcal{L}^2 I) \right] \quad (2.113)$$

$$B_{\text{MX}}^{\text{GX}} = \beta_{\text{MX}}^{(0)} + (2\beta_{\text{MX}}^{(1)} / \mathcal{L}^2 I) \left[1 - \exp(-\mathcal{L} I^{1/2}) (1 + \mathcal{L} I^{1/2}) \right] \quad (2.114)$$

$$C_{MX}^{\phi} = (3/2 \nu_M \nu_X) (\nu_M \mu_{MMX} + \nu_X \mu_{MXX}) \quad (2.115)$$

$$C_{MX}^{\nu} = (3/2) C_{MX}^{\phi} \quad (2.116)$$

$$C_{MX}^{GX} = (1/2) C_{MX}^{\phi} \quad (2.117)$$

In these relations

$I = \frac{1}{2} \sum m_i Z_i^2$ is the ionic strength

$A_{\phi} = \frac{1}{3} \left[(2 \pi N a_{\pm} / 1000)^{1/2} (e^2 / DkT)^{3/2} \right]$ is the Debye-Hückel coefficient for the osmotic function.

The terms b and \mathcal{L} are the same for all solutes and their values are 1.2 and 2.0, respectively. The parameters $\beta^{(0)}$ and $\beta^{(1)}$ define the second virial coefficient; the contribution to $\beta^{(0)}$ comes from the interaction of like and unlike charged ions and that to $\beta^{(1)}$ comes from the short-range interaction unlike charged ions. They also get a contribution due to the correction to f for the effective distance of closest approach (since the electrostatic interaction function was not changed for individual solutes). The parameter C^{ϕ} defines the third virial coefficient, which is usually very small, and sometimes negligible. The quantities $\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ} are adjusted for a given salt at fixed temperature by a least-square fit of osmotic or activity coefficient data.

For 2:2 and higher type electrolytes it is convenient to add a term to eqn (2.112), i.e.

$$B^{\phi} = \beta^{(0)} + \beta^{(1)} \exp(-\alpha_1 I^{1/2}) + \beta^{(2)} \exp(-\mathcal{L}_2 I^{1/2}) \quad (2.118)$$

In this case, $\alpha_1 = 1.4$ and $\mathcal{L}_2 = 12.0$; $\beta^{(2)}$ represents the anomalous behaviour of some electrolytes (for example 2:2 electrolytes) in the range below 0.1 molar.

The equations developed by Pitzer have been fitted to the

experimental coefficients for over 200 pure electrolytes at 25°C within experimental accuracy. And, since the more important parameters are determined from the single solutes, the equations extended to mixtures allow the prediction of the properties of such mixtures. The corresponding equations for mixtures will be presented in the next section.

The equations have also been applied over wide temperature ranges, which allows enthalpies and heat capacities in various types of electrolytes to be obtained.

The total excess Gibbs free energy may be written

$$G^{\text{ex}} = n_w \nu_m RT (1 - \phi + \ln \gamma_{\pm}) \quad (2.119)$$

and

$$L = - T^2 \left[\partial(G^{\text{ex}}/T) / \partial T \right]_{p,m} \quad (2.120)$$

which leads to

$$L = \nu_m RT^2 \left[(\partial\phi / \partial T)_{p,m} (\partial \ln \gamma_{\pm} / \partial T)_{p,m} \right]. \quad (2.121)$$

Differentiation of eqn (2.107) and (2.108) with respect to the temperature gives the equation for the relative molar enthalpy, ϕ_L

$$\phi_L = \nu |z_M z_X| (A_H / 3.6) \ln (1 + uT^{1/2}) - 2 \nu_M \nu_X RT^2 (m B_{MX}^1 + m^2 C_{MX}^1) \quad (2.122)$$

where

$$B_{MX}^1 = (\partial B_{MX} / \partial T)_{I,P} \quad (2.123)$$

$$C_{MX}^1 = \frac{1}{2} (\nu_M \nu_X)^{1/2} (\partial C_{MX} / \partial T)_{I,P} \quad (2.124)$$

$A_H = - 9A_{\phi} RT^2 \left[T^{-1} + (\partial \ln D / \partial T)_p + \alpha / 3 \right]$ is the Debye-Hückel coefficient for enthalpy.

From the temperature derivative of eqn (2.122) an expression for the relative heat capacity, ϕ_C , is obtained, namely

$$\phi_{c_p} = c_{p2}^{\circ} + \gamma \left| \frac{z_M z_X}{\nu} \right| \frac{A c_p}{3.6} \ln (1 + bI^{\frac{1}{2}}) - 2 \gamma_M \gamma_X RT^2 (mB_{MX}^{11} + m^2 C_{MX}^{11}) \quad (2.125)$$

Silvester and Pitzer(59) applied these equations to NaCl from 0 to 300°C and up to 6 molar, finding good agreement within the experimental data used for the fit.

2. 5 Mixed electrolyte solutions

2. 5. 1 Introduction

In the study of the properties of single electrolytes in solution it is essential to understand the interionic forces which distinguish an aqueous solution of a non-electrolyte. As a result of these interionic forces, the single electrolyte solutions are themselves non-ideal.

Properties such as free energy, enthalpy, and volume are of interest in the study of mixed electrolyte solutions and are often discussed in terms of "excess" functions, that is, those which the mixture possesses over and above that expected from the single electrolyte solutions from which the mixed solution is formed. The study of mixed electrolyte solutions implies then a study of further departures from ideality resulting from specific interactions between the constituents, and therefore it may present more difficult problems to solve than for single electrolyte solutions.

Recently there has been a revival of interest in the study of mixed electrolyte solutions. A considerable amount of experimental evidence has concerned the excess free energy, expressed in terms of the chemical potentials or activity coefficients, of mixed electrolyte solutions. However, more recently, valuable studies of the enthalpies of mixed electrolyte solutions have become available.

2. 5. 2 Non-ideality of solutions

With the instinctive belief that the mole fraction is the proper measure of ideality, an ideal solution can be defined as one for which the solvent activity is equal to the mole fraction of the solvent, and then the activity coefficient of the solute, on the mole fraction scale, is unity at all concentrations. The following relations may be written

$$a_s = x_s \quad (2.126)$$

and

$$G_B = G_B^0 + \nu RT \ln x_B \quad (2.127)$$

and similar equations hold if the solution contains more than one solute.

For solutions of electrolytes the following approximation can be made

$$\ln a_s = \ln x_B = - \ln \left[1 + (\nu M_s m_B / 1000) \right] \approx - \frac{\nu M_s m_B}{1000} \quad (2.128)$$

where M_s is the molecular weight of the solvent. Then, it is possible to adopt as definition of ideality

$$\ln a_s = - \frac{\nu M_s m_B}{1000} \quad (2.129)$$

With this definition, the activity coefficient of solute, on the molality scale, and the osmotic coefficient, are unity at all concentrations.

If two ideal solutions were mixed supposing that there is no interaction, the activity coefficient of each solute would still be unity. But since a solution containing only one electrolyte is not ideal, in mixing two of these solutions, one salt does influence the activity coefficient of the other.

2. 5. 3 Free Energy

The total free energy of a solution can be written

$$G = G^{\text{id}} + G^{\text{el}} + G^{\text{solv}} + G^{\text{E}} \quad (2.130)$$

where

G^{id} is the free energy of the ideal solution,

G^{el} the free energy resulting from interionic forces of the Debye-Hückel type,

G^{solv} the free energy due to ion-solvent interaction,

G^{E} the free energy due to ion-ion interactions apart from those of the Debye-Hückel type.

The contributions due to ion-solvent and ion-ion interactions both take similar forms, in a power series in m_B , and it was found that in both expressions the term in the first power of m_B is always dominant. It is, therefore, difficult to separate ion-solvent from ion-ion interactions and usually the terms G^{solv} and G^{E} are combined so eqn (3.5) becomes

$$G = G^{\text{id}} + G^{\text{el}} + G^{\text{E}} \quad (2.131)$$

It follows from the definition of an activity coefficient that

$$\nu_B \ln \gamma_B = \nu_B z_1 z_2 \ln \gamma^{\text{DH}} + \frac{1}{RT} \left(\frac{\partial G^{\text{E}}}{\partial n_B} \right)_{n_s, n_c} \quad (2.132)$$

where

$$\ln \gamma^{\text{DH}} = - \frac{2.303 A I^{1/2}}{1 + \beta I^{1/2}} \quad (2.133)$$

and

$$\frac{\nu_B m_B + \nu_c m_c}{I} (\phi - 1) = \phi^{\text{DH}} - \frac{1000}{M_s I R T} \left(\frac{\partial G^{\text{E}}}{\partial n_s} \right)_{n_B, n_c} \quad (2.134)$$

where

$$\phi^{\text{DH}} = - \frac{4.606 A}{\beta^3 I} \left[(1 + \beta I^{1/2}) - (1 + \beta I^{1/2})^{-1} - 2 \ln (1 + \beta I^{1/2}) \right] \quad (2.135)$$

The total free energy of a solution cannot be obtained by direct measurement. Then, it is convenient to represent G^{E} as any appropriate

function and, by differentiation with respect to n_s at constant n_B, n_C , to obtain an expression for the osmotic coefficient or, by differentiation with respect to n_B at constant n_s, n_C , to derive an equation for the activity coefficient.

2. 5. 4 Activity coefficients in mixed electrolyte solutions.

An alternative approach to the Bjerrum ion pairing method to study short-range interactions is the specific interaction model of Brønsted(60). He assumed that like-charged ions do not have or have only weak specific interactions and that the interactions between unlike-charged ions have to be regarded as more important because configurations involving such interactions occur much more frequently. Guggenheim(42,61) and others (62,63) have extended the Brønsted theory and their approach leads ultimately to the following equation

$$\frac{G^E}{RT} = \frac{n_1 n_2 B_{12} + n_1 n_4 B_{14} + n_2 n_3 B_{23} + n_3 n_4 B_{34}}{W_s n_s} \quad (2.136)$$

for a system containing n_B moles of electrolyte B (n_1 moles of cations and n_2 moles of anions), n_C moles of electrolyte C (n_3 moles of cations and n_4 moles of anions), and n_s moles of solvent,

where $W_s = \frac{M_s}{1000}$

In accordance with Brønsted's approach, to obtain this equation, the summation in eqn (2.136) has been made only over pairs of oppositely charged ions (Brønsted's Principle of specific interaction), and it was assumed that the solution is dilute so that $n_s \gg n_j$.

By differentiation of eqn (2.136) with respect to n_s at constant n_1, n_2, n_3, n_4 , an expression for the osmotic coefficient is obtained

$$\begin{aligned}
 (\nu_B m_B + \nu_C m_C) (\phi - 1) &= I \phi^{\text{DH}} + m_1 m_2 B_{12} + m_1 m_4 B_{14} \\
 &+ m_2 m_3 B_{23} + m_3 m_4 B_{34} \quad (2.137)
 \end{aligned}$$

By differentiation with respect to n_1 (or n_2) at constant n_3, n_4 (or n_1), n_3, n_4

$$\ln \gamma_1 = Z_1^2 \ln \gamma^{\text{DH}} + m_2 B_{12} + m_4 B_{14} \quad (2.138)$$

and

$$\ln \gamma_2 = Z_2^2 \ln \gamma^{\text{DH}} + m_1 B_{12} + m_3 B_{23} \quad (2.139)$$

so that

$$\begin{aligned}
 \nu_B \ln \gamma_B &= \nu_B Z_1 Z_2 \ln \gamma^{\text{DH}} + \nu_1 m_2 B_{12} + \nu_1 m_4 B_{14} + \nu_2 m_1 B_{12} \\
 &+ \nu_2 m_3 B_{23} \quad (2.140)
 \end{aligned}$$

and also

$$\begin{aligned}
 \nu_C \ln \gamma_C &= \nu_C Z_3 Z_4 \ln \gamma^{\text{DH}} + \nu_3 m_2 B_{23} + \nu_3 m_4 B_{34} \\
 &+ \nu_4 m_1 B_{14} + \nu_4 m_3 B_{34} \quad (2.141)
 \end{aligned}$$

may be obtained.

For a system consisting of two 1:1 electrolytes

$$\nu_B = \nu_C = 2, \quad m_B = m_1 = m_2, \quad m_C = m_3 = m_4$$

and at constant total molality $m = m_B + m_C$ the equations become

$$2(\phi - 1) = \phi^{\text{DH}} + \left[y_B^2 B_{12} + y_B y_C (B_{14} + B_{23}) + y_C^2 B_{34} \right] m \quad (2.142)$$

$$2 \ln \gamma_B = 2 \ln \gamma^{\text{DH}} + \left[2y_B B_{12} + y_C (B_{14} + B_{23}) \right] m \quad (2.143)$$

$$= 2 \ln \gamma_B^{\circ} + \left[B_{14} + B_{23} - 2 B_{12} \right] y_C m \quad (2.144)$$

$$2 \ln \gamma_C = 2 \ln \gamma^{\text{DH}} + \left[2 y_C B_{34} + y_B (B_{14} + B_{23}) \right] m \quad (2.145)$$

where

$$Y_B = m_B / (m_B + m_C)$$

$$Y_C = m_C / (m_B + m_C)$$

$$Y_B + Y_C = 1$$

If the two electrolytes have an ion in common, eqn (2.142)

becomes

$$2(\phi - 1) = \phi^{\text{DH}} + \left[B_{12} + y_c (B_{23} - B_{12}) \right] m \quad (2.146)$$

or

$$\phi = \phi_B^{\circ} + (\phi_C^{\circ} - \phi_B^{\circ}) y_c \quad (2.147)$$

where the ϕ_i° represent the osmotic coefficient of the electrolytes in their own solutions. In this case, the osmotic coefficient of the mixture and the logarithm of the activity coefficient of each electrolyte are linear functions of the composition of the electrolyte mixture. A plot of $\ln \gamma_B$, $\ln \gamma_c$, and ϕ against y_c shows that all three lines are parallel.

In a system without common ions $\ln \gamma_B$ depends on B_{12} , B_{14} and B_{23} and $\ln \gamma_c$ depends on B_{34} , B_{14} and B_{23} . The plots of the activity coefficients are straight lines but they are not parallel; and the plot of the osmotic coefficient is no longer a straight line.

For a system of a 1:1 electrolyte and 2:2 electrolyte, where

$$\nu_1 = \nu_2 = 1, \nu_B = 2; \nu_3 = 1, \nu_4 = 2, \nu_c = 3$$

$$m_B = m_1 = m_2, m_c = m_3, 2m_c = m_4$$

$$Z_1 = Z_2 = Z_4 = 1, Z_3 = 2$$

eqn (2.140) becomes

$$2 \ln \gamma_B = 2 \ln \gamma^{\text{DH}} + 2 (m_B + m_c) B_{12} + m_c B_{23} \quad (2.148)$$

eqn (2.141) becomes

$$3 \ln \gamma_c = 6 \ln \gamma^{\text{DH}} + (m_B + 4 m_c) B_{23} + 2 m_B B_{12} \quad (2.149)$$

and eqn (2.137) gives

$$\begin{aligned} (2m_B + 3m_c) (\phi - 1) = I \phi^{\text{DH}} + m_B^2 B_{21} + m_B m_c (2 B_{12} + B_{23}) \\ + 2 m_c^2 B_{23} \end{aligned} \quad (2.150)$$

or introducing the total ionic strength

$$I = m_B + 3 m_C, \gamma_B = m_B/I, \gamma_C = 3 m_C/I$$

$$(\gamma_B + 1) (\phi - 1) = \phi^{DH} + B_{12} I + \frac{1}{3} \left[(B_{23} - 4B_{12}^2) - \frac{1}{3} (B_{23} - 3 B_{12}^2) \gamma_C \right] \gamma_C I \quad (2.151)$$

Also

$$2 \ln \gamma_B = 2 \ln \gamma^{DH} + 2 B_{12} I + \frac{1}{3} (B_{23} - 4B_{12}^2) \gamma_C I \quad (2.152)$$

and

$$3 \ln \gamma_C = 6 \ln \gamma^{DH} + \frac{4}{3} B_{23} I + (2 B_{12} - \frac{1}{3} B_{23}) \gamma_B I \quad (2.153)$$

Here, the osmotic coefficient curve is a quadratic, but the plots of the activity coefficients are straight lines.

One of the basic findings of the specific interaction model is the empirical relationship called Harned's Rule: "the logarithm of the activity coefficient of one electrolyte in a mixture at constant total molality is directly proportional to the molality of the other component". Or

$$\log \gamma_B = \log \gamma_{B(0)} - \mathcal{L}_B m_C \quad (2.154)$$

where

γ_B is the mean activity coefficient of electrolyte B in the presence of electrolyte C (of molality m_C)

$\gamma_{B(0)}$ is the mean activity coefficient of electrolyte B in the binary solution at the molality, m , of the mixture; and when $m_C = m =$ total molality

$$\log \gamma_{(0)B} = \log \gamma_{B(0)} - \mathcal{L}_B^m \quad (2.155)$$

so that

$$\log \gamma_B = \log \gamma_{(0)B} + \mathcal{L}_B^m \quad (2.156)$$

and for the other component

$$\log \gamma_C = \log \gamma_{C(0)} - \mathcal{L}_C m_B = \log \gamma_{(0)C} + \mathcal{L}_C^m \quad (2.157)$$

Here

$\gamma_{(0)B}$ is the limiting value of the activity coefficient of B, i.e., the value of γ_B when the solution contains only C
 $\gamma_{(0)C}$ is the limiting value of γ_C

The parameters α_B and α_C are functions of the total molality, m , but not of the individual molalities, m_B , m_C . This rule has been shown to hold for many two-salt systems up to high concentrations.

Sometimes it is necessary to add terms to eqn (2.155) and (2.157) so that

$$\log \gamma_B = \log \gamma_{B(0)} - \alpha_B m_C - \beta_B m_C^2 \quad (2.158)$$

$$\log \gamma_C = \log \gamma_{C(0)} - \alpha_C m_B - \beta_C m_B^2 \quad (2.159)$$

where the parameter β is independent of m , m_B and m_C . It has been shown that if Harned's rule holds for one electrolyte it does not necessarily hold for the other electrolyte in the mixture.

Sometimes it is of interest to consider variations at constant total ionic strength or variations at "constant total ionic concentration" instead of constant molality and it has been shown that for many systems the following equations hold

$$\log \gamma_B = \log \gamma_B^0 - \alpha_B^I I_C - \beta_B I_C^2 \quad (2.160)$$

$$\log \gamma_C = \log \gamma_C^0 - \alpha_C^I I_B - \beta_C I_B^2 \quad (2.161)$$

where

$$I_C = k_C m_C \quad ; \quad I_B = k_B m_B \quad ; \quad I = I_B + I_C$$

and α_B , β_B , are functions of the total ionic strength but not of the individual concentrations. It is to be noted that Harned's rule is equivalent to the statement that $\beta_B = 0$ and $\beta_C = 0$. Here γ_B^0 and γ_C^0 are the activity coefficients of the electrolytes B and C, respectively, in solutions containing only B or only C at the same

total ionic strength, I , as the mixed solution.

In systems such as water-sodium chloride-barium chloride it has also been shown (64) that similar equations hold, namely

$$\log \gamma_B = \log \gamma_B^{\circ} - \alpha_B m_C \quad (2.162)$$

$$\log \gamma_C = \log \gamma_C^{\circ} - \alpha_C m_B \quad (2.163)$$

Here, now, γ_B° and γ_C° are the activity coefficients of the electrolytes B and C, respectively, in the simple binary solution at a molality equal to the ionic concentration of the mixed solution as measured (for example, as $m = m_B + 1.5 m_C$).

The property of a chemical potential of being a partial differential coefficient of the total free energy with respect to concentration imposes certain restrictions on the coefficients of equations (2.158) and (2.159). For 1:1 electrolytes, for example, it has been shown that

$$\alpha_B + \alpha_C = \text{constant} - 2 m (\beta_B + \beta_C) \quad (2.164)$$

and in the simpler case where $\beta_B = \beta_C = 0$ then

$$\alpha_B + \alpha_C = \text{constant, independent of } m.$$

This result was deduced by Glueckauf, McKay, and Mathieson (65)

Similar equations (with appropriate modifications) hold for the more general case of a mixture of electrolytes of different valence types, for which the β terms are not zero. For example for a solution of electrolyte B (giving ν_B ions) at molality m_B , and electrolyte C (giving ν_C ions) at molality m_C , if

$$\log \gamma_B = \log \gamma_B^{\circ} - A_B m_C - B_B m_C^2 \quad (2.165)$$

$$\log \gamma_C = \log \gamma_C^o - A_C m_B - B_C m_B^2 \quad (2.166)$$

then

$$k_B k_C (\nu_B A_B + \nu_C A_C) = \text{constant} - 2 (\nu_B k_B B_B + \nu_C k_C B_C) \mathcal{J} \quad (2.167)$$

where

\mathcal{J} is a linear combination of the form $\mathcal{J} = k_B m_B + k_C m_C$

A_B and A_C are functions of \mathcal{J} but not of m_B and m_C individually

B_B and B_C are parameters independent of \mathcal{J} , m_B , and m_C .

It is often useful to consider what values \mathcal{L}_B and \mathcal{L}_C might be expected to have when the total ionic strength becomes very small. For a mixture of a 1:1 and a 1:2 electrolytes with a common ion, eqns (2.140) and (2.141) can be rewritten in the form

$$\log \gamma_1 = \log \gamma^{st} + B_{21} m_2 + B_{31} m_3 \quad (2.168)$$

$$\log \gamma_2 = \log \gamma^{st} + B_{21} m_2 \quad (2.169)$$

$$\log \gamma_3 = 4 \log \gamma^{st} + B_{31} m_1 \quad (2.170)$$

where γ^{st} is the activity coefficient calculated on the assumption that the only interionic interaction is of the Debye-Hückel type.

And, remembering that

$$2 \log \gamma_B = \log \gamma_1 + \log \gamma_2 \quad (2.171)$$

and

$$3 \log \gamma_C = \log \gamma_3 + 2 \log \gamma_1 \quad (2.172)$$

the following expressions are obtained

$$\log \gamma_B = \log \gamma^{st} + (m_B + m_C) B_B + \frac{1}{2} m_C B_C \quad (2.173)$$

and

$$\log \gamma_C = 2 \log \gamma^{st} + \frac{2}{3} m_B B_B + \frac{1}{3} (m_B + 4 m_C) B_C \quad (2.174)$$

where $B_B = B_{21}$ and $B_C = B_{31}$

The activity coefficient of either salt in its own solution in the absence of the other salt, at a total ionic strength, I , is now given as:

$$\log \gamma_B^o = \log \gamma^{st} + I B_B \quad (2.175)'$$

$$\log \gamma_C^o = 2 \log \gamma^{st} + \frac{4}{9} I B_C \quad (2.176)'$$

where $I = I_B + I_C = m_B + 3 m_C$

B_B and B_C can be calculated from data on dilute single salt solutions.

Let be γ^{tr} the "trace" activity coefficient of a salt, that is the activity coefficient of a salt when it is present in vanishingly small amount in a solution which contains virtually only the other salt.

Eqs (2.173) and (2.174) give:

$$\log \gamma_B^{tr} = \log \gamma^{st} + \frac{1}{3} I (B_B + \frac{1}{2} B_C) \quad (2.175)$$

and

$$\log \gamma_C^{tr} = 2 \log \gamma^{st} + \frac{1}{3} I (2 B_B + B_C) \quad (2.176)$$

Hence,

$$\alpha_B = I^{-1} \log (\gamma_B^o / \gamma_B^{tr}) = \frac{2}{3} B_B - \frac{1}{6} B_C \quad (2.177)$$

and
$$\alpha_C = I^{-1} \log (\gamma_C^o / \gamma_C^{tr}) = \frac{1}{9} B_C + \frac{2}{3} B_B \quad (2.178)$$

From eqns (2.175) and (2.176) it can be seen that, in this case

$$\log \gamma_B^{tr} = \frac{1}{2} \log \gamma_C^{tr}$$

For two electrolytes of any charge type, it can be shown that

$$Z_3 Z_4 \ln \gamma_B^{tr} = Z_1 Z_2 \ln \gamma_C^{tr} \quad (2.179)$$

It is not always true that the activity coefficient of a solute is directly proportional to the composition of the mixture and this may be a problem, especially for more concentrated solutions.

Scatchard(66) gives another treatment of ion-ion interaction. In the treatment of Scatchard the excess free energy, G^E , is expressed as a sum of contributions calculated from the limiting two-component solutions (A terms, solute indicated by single subscript) and contributions involving concentration of two solute components (a series of B terms, the solute indicated by a double subscript). The equation for binary solutes is as follows

$$G^E/RT = (n_A^* + n_B^*) \left[A + (A_B - A_A) y_B + B_{AB}^{(0)} y_B (1 - y_B) + B_{AB}^{(1)} y_B (1 - y_B) (1 - 2y_B) \right] \quad (2.180)$$

where

R is the gas constant

T the absolute temperature

$$n_J^* = n_J \frac{1}{2} \sum_i \nu_{iJ} \cdot Z_i^2$$

here

n_J is the number of moles of solute J

ν_{iJ} the number of moles of ion i in 1 mol of component J

Z_i the valence of ion i

The parameters A_J and B_{JK} are functions of the ionic strength, the temperature, pressure, and solvent, and are characteristic of the solutes specified in the subscript but not of the solute composition. Differentiation of eqn (2.180) with respect to the amount of solvent gives the following expression for the osmotic coefficient

$$\phi = 1 + \frac{I}{\nu_A m_A + \nu_B m_B} \left[\alpha_A + (\alpha_B - \alpha_A) y_B + \beta_{AB}^{(0)} y_B (1 - y_B) + \beta_{AB}^{(1)} y_B (1 - y_B) (1 - 2y_B) \right] \quad (2.181)$$

where

$$\alpha_J = \frac{\partial A_J}{\partial \ln I} \quad \text{and} \quad \beta_{JK}^{(t)} = \frac{\partial B_{JK}^{(t)}}{\partial \ln I}$$

If eqn (2.180) is differentiated with respect to the number of moles of a given solute, the following equations for the activity coefficients of components A and B are obtained

$$\begin{aligned} \ln \gamma_A = & \frac{I_A}{\nu_A m_A} \left[A_A + \alpha_A + (\alpha_B - \alpha_A) y_B + \beta_{AB}^{(0)} y_B \right. \\ & + (B_{AB}^{(0)} - \beta_{AB}^{(0)}) y_B^2 + \beta_{AB}^{(1)} y_B + 3 (B_{AB}^{(1)} - \beta_{AB}^{(1)}) y_B^2 \\ & \left. - 2 (2 B_{AB}^{(1)} - \beta_{AB}^{(1)}) y_B^3 \right] \end{aligned} \quad (2.182)$$

$$\begin{aligned} \ln \gamma_B = & \frac{I_B}{\nu_B m_B} \left[A_B + \alpha_B + (\alpha_A - \alpha_B) y_A + \beta_{AB}^{(0)} y_A \right. \\ & + (B_{AB}^{(0)} - \beta_{AB}^{(0)}) y_A^2 - \beta_{AB}^{(1)} y_A - 3 (B_{AB}^{(1)} - \beta_{AB}^{(1)}) y_A^2 \\ & \left. + 2 (2 B_{AB}^{(1)} - \beta_{AB}^{(1)}) y_A^3 \right] \end{aligned} \quad (2.183)$$

In these equations the contributions from the limiting two-component systems are given as a Debye-Hückel term plus a power series in I

$$\begin{aligned} \alpha_J = & \frac{2 S}{a_J^3 I} \left[1 + a_J I^{\frac{1}{2}} - (1 + a_J I^{\frac{1}{2}})^{-1} - 2 \ln (1 + a_J I^{\frac{1}{2}}) \right. \\ & \left. + a_J^{(1)} I + a_J^{(2)} I^2 + a_J^{(3)} I^3 \right] \end{aligned} \quad (2.184)$$

$$A_J + \alpha_J = \frac{2 S I^{\frac{1}{2}}}{1 + a_J I^{\frac{1}{2}}} + 2 a_J^{(1)} I + \frac{3}{2} a_J^{(2)} I^2 + \frac{4}{3} a_J^{(3)} I^3 \quad (2.185)$$

where a_J is the distance of closest approach parameter for component J.

The B and β terms are expanded as

$$\beta_{AB}^{(0)} = b_{AB}^{(0,1)} I + b_{AB}^{(0,2)} I^2 + b_{AB}^{(0,3)} I^3 \quad (2.186)$$

$$\beta_{AB}^{(1)} = b_{AB}^{(1,2)} I^2 + b_{AB}^{(1,3)} I^3 \quad (2.187)$$

$$B_{AB}^{(0)} = b_{AB}^{(0,1)} I + \frac{1}{2} b_{AB}^{(0,2)} I^2 + \frac{1}{3} b_{AB}^{(0,3)} I^3 \quad (2.188)$$

$$B_{AB}^{(1)} = \frac{1}{2} b_{AB}^{(1,2)} I^2 + \frac{1}{3} b_{AB}^{(1,3)} I^3 \quad (2.189)$$

where the $b_{AB}^{(j,i)}$ terms are $\beta_{AB}^{(j,i)} / I^i$

It has been shown that for almost all mixtures the curves for $(\alpha_i - \alpha_j) / I$ against I approach the zero axis with increasing concentration rapidly in dilute solutions and less rapidly as the concentration increases. For mixtures without a common ion the curves for $\beta^{(0)} / I$ have the same form, but for the mixtures with a common ion $\beta^{(0)} / I$ is zero at zero concentration and the limiting slope is finite. For mixtures with a common ion $\beta^{(1)} / I$ is always zero. For the mixtures without a common ion, $\beta^{(1)} / I$ is small and nearly proportional to the ionic strength.

Many workers have used this method successfully; for example, Wu, Rush, and Scatchard(67) reported results for binary mixtures of NaCl - Na₂ SO₄, Na₂ SO₄ - Mg SO₄, Mg SO₄ - MgCl₂, and MgCl₂ - NaCl in water at ionic strengths for the mixtures up to 9.4, 8.8, 6.8, and 5.9 respectively.

Bronsted's approach may be supplemented by introducing into eqn (2.136) terms which allow for the possibility of interactions between ions of like charge, as Guggenheim has shown(61).

For 1:1 electrolytes the following equation may be written

$$(G - G^{st})/RT = B_{12} m_1 m_2 + B_{14} m_1 m_4 + B_{23} m_2 m_3 + B_{34} m_3 m_4 \\ + \delta_{13} m_1 m_3 + \delta_{24} m_2 m_4 \quad (2.190)$$

the terms δ allow for the interactions between ions of like charge. The equations for the osmotic and activity coefficient are given by

$$2(\phi - \phi^{st}) = \left[y_B^2 B_{12} + y_B y_C (B_{14} + B_{23} + \delta_{13} + \delta_{14}) + y_C^2 B_{34} \right] m \quad (2.191)$$

$$2 \ln \gamma_B^A = 2 \ln \gamma_B^{st} + 2B_{12} m + (B_{14} + B_{23} - 2B_{12} + \delta_{13} + \delta_{24}) y_C m \quad (2.192)$$

$$2 \ln \gamma_C^A = 2 \ln \gamma_C^{st} + 2B_{34} m + (B_{14} + B_{23} - 2B_{34} + \delta_{13} + \delta_{24}) y_B m \quad (2.193)$$

and the excess free energy of the mixed solution by

$$G^E/RT = y_B y_C m^2 (B_{14} + B_{23} + \delta_{13} + \delta_{24} - B_{12} - B_{34}) \quad (2.194)$$

For two electrolytes with a common ion, for example the ions labelled 2 and 4,

$$2(\phi - \phi^{st}) = (y_B B_{12} + y_B y_C \delta_{13} + y_C B_{23}) m \quad (2.195)$$

and

$$\phi = \phi_B^0 + y_C (\phi_C^0 - \phi_B^0) + \frac{1}{2} y_B y_C \delta_{13} m \quad (2.196)$$

$$2 \ln \gamma_B^A / \gamma_B^{A0} = (B_{23} - B_{12} + \delta_{13}) y_C m \quad (2.197)$$

$$2 \ln \gamma_C^A / \gamma_C^{A0} = (B_{12} - B_{23} + \delta_{13}) y_B m \quad (2.198)$$

It may be noted that the osmotic coefficient of a mixed electrolyte solution, even with a common ion, is not a linear function of y_B . However, $\ln \gamma^A$ for each electrolyte still varies linearly with composition but the plots against the composition

no longer have equal slopes. Also, the trace activity coefficients are equal.

2. 5. 5 Pitzer's equation for mixed electrolytes

In section 2.4 it was mentioned that, since the parameters in Pitzer's equation are determined from single solutes, the equations extended to mixtures allow the prediction of their properties. The Pitzer equations for the osmotic and activity coefficients for mixed electrolyte solutions are

$$\begin{aligned} \phi - 1 = & \left(\sum_i m_i \right)^{-1} \left\{ 2 I f^\phi + 2 \sum_c \sum_a m_c m_a \left[B_{ca}^\phi + \frac{(\sum_m Z)}{(Z_c Z_a)^{1/2}} C_{ca}^\phi \right] \right. \\ & + \sum_c \sum_{c'} m_c m_{c'} \left[\theta_{cc'} + \sum_a m_a \psi_{cc'a} + I \theta'_{cc'} \right] \\ & \left. + \sum_a \sum_{a'} m_a m_{a'} \left[\theta_{aa'} + \sum_c m_c \psi_{cqa'} + I \theta'_{aa'} \right] \right\} \quad (2.199) \end{aligned}$$

and

$$\begin{aligned} \ln \gamma_{MX} = & |Z_M Z_X| f^\lambda + (2\nu_M/\nu) \sum_a m_a \left[B_{Ma} + (\sum m_z) C_{Ma} \right. \\ & + (\nu_X/\nu_M) \theta_{Xa} \left. \right] + (2\nu_X/\nu) \sum_c m_c \left[B_{cX} + (\sum m_z) C_{cX} \right. \\ & + (\nu_M/\nu_X) \theta_{Mc} \left. \right] + \sum_c \sum_a m_c m_a \left\{ |Z_M Z_X| B'_{ca} \right. \\ & + \nu^{-1} \left[2\nu_M Z_M C_{ca} + \nu_M \psi_{Mca} + \nu_X \psi_{cax} \right] \left. \right\} \\ & + \frac{1}{2} \sum_c \sum_{c'} m_c m_{c'} \left[(\nu_X/\nu) \psi_{cc'X} + |Z_M Z_X| \theta'_{cc'} \right] \\ & + \frac{1}{2} \sum_a \sum_{a'} m_a m_{a'} \left[(\nu_M/\nu) \psi_{Maa'} + |Z_M Z_X| \theta'_{aa'} \right] \quad (2.200) \end{aligned}$$

where f^ϕ , B^ϕ , C^ϕ , f^λ , B_{MX} ($=B^\lambda$) have the same meaning as in

section 2.4, and

$$e_{MN} = \lambda_{MN} - \left(\frac{z_N}{2z_M} \right) \lambda_{MM} - \left(\frac{z_M}{2z_N} \right) \lambda_{NN} \quad (2.201)$$

$$\psi_{MNX} = 6\mu_{MNX} - \left(\frac{3z_N}{z_M} \right) \mu_{MMX} - \left(\frac{3z_M}{z_N} \right) \mu_{NNX} \quad (2.202)$$

$$e'_{MN} = \frac{de_{MN}}{dI} \quad (2.203)$$

$$(\sum m z) = \sum_c m_c z_c = \sum_a m_a |z_a| \quad (2.204)$$

c and c' are indices covering all cations

a and a' are indices covering all anions

The parameters θ , θ' , and ψ are characteristic of the mixture. θ and ψ are differences between the virial coefficient for interactions of unlike ions of the same sign and the average of interactions of like ions. All θ 's and ψ 's are relatively small; θ depends slightly on the ionic strength but this dependence is usually neglected so that θ' is taken to be zero. Thus, it is possible to obtain quite accurate results up to moderate concentrations with only the pure electrolyte terms, but for maximum accuracy, all terms should be included.

The values of θ and ψ can be obtained by calculating the difference between the experimental value of ϕ or $\ln \gamma$ and the value calculated with the values for all pure-electrolyte terms but with zero values for θ and ψ . This difference multiplied by a function of composition is equal to θ plus ψ times another function of composition. For a MX-NX mixture, for example,

$$\Delta\phi \left[\frac{\sum m_i}{2m_M m_N} \right] = \theta_{MN} + m_X \psi_{MNX} \quad (2.205)$$

and

$$\Delta \ln \gamma_{MX} \left[\nu / 2 \nu_M m_N \right] = \theta_{MN} + \frac{1}{2} (m_X + m_M | z_M / z_X |) \Psi_{MNX} \quad (2.206)$$

Thus, a plot of the quantity on the left against the coefficient of Ψ should give a linear plot with intercept θ and slope Ψ .

Pitzer and Kim(68) investigated 69 sets of mixtures with this method, including mixed electrolytes with three or more solutes; Khoo, Chan and Lim(69,70) interpreted their data on the systems $\text{HCl}-\text{BaCl}_2-\text{H}_2\text{O}$ and $\text{HCl}-\text{CaCl}_2-\text{H}_2\text{O}$ in terms of Scatchard's and Pitzer's equation.

2.5. 6 Enthalpy changes

The excess enthalpy may be calculated from the temperature coefficient of the free energy by means of the thermodynamic relation

$$\frac{d}{dT} \left(\frac{G^E}{T} \right) = - \frac{H^E}{T^2} \quad (2.207)$$

If a solution consisting of y_B kg of water and y_B m moles of electrolyte B is mixed with another solution consisting of y_C kg of water and y_C m moles of electrolyte C to produce a solution consisting of 1 kg of water, y_B m moles of B, and y_C m moles of C, the excess free energy, that is, the free energy of the mixed solution over and above that possessed by the single electrolyte solutions, is given by

$$\frac{G^E}{RT} = W_S^{-1} \ln a_s + 2y_B m \ln y_B m \gamma_B + 2y_C m \ln y_C m \gamma_C$$

$$\begin{aligned} & - y_B W_S^{-1} \ln a_{s(B)} - 2y_B m \ln m \gamma_B^0 - y_C W_S^{-1} \ln a_{s(C)} \\ & - 2y_C m \ln m \gamma_C^0 \end{aligned} \quad (2.208)$$

This equation holds rigorously, but if Harned's rule is written in the form

$$\ln \gamma_B = \ln \gamma_B^0 + Q_B y_C m + R_B y_C^2 m^2 \quad (2.209)$$

$$\ln \gamma_c = \ln \gamma_c^0 + Q_c y_B m + R_c Y_B^2 m^2 \quad (2.210)$$

where Q and R may be functions of the total molality m, but not of the individual molalities m_B and m_C , the following (non-rigorous) relation may be written

$$\frac{G^E}{RT} = y_B y_C m^2 \left[(Q_B + Q_C) + (R_B + R_C) m + \frac{1}{2} (R_C - R_B)(y_B - y_C) m \right] \quad (2.211)$$

and if $R_B = R_C = 0$,

$$\frac{G^E}{RT} = Y_B Y_C m^2 (Q_B + Q_C) \quad (2.212)$$

In terms of the coefficient \mathcal{L} 's and β 's, eqn (2.211) for the special case where $m_B = m_C = \frac{1}{2} m$, becomes

$$G^E = -\frac{1}{4} \log RT m^2 (\alpha_B + \alpha_C + \beta_C m) \quad (2.213)$$

and, according to eqn (2.207) the enthalpy change on mixing is

$$H^E = \frac{1}{4} \log RT^2 m^2 \frac{d}{dT} (\alpha_B + \alpha_C + \beta_C m) \quad (2.214)$$

The data for the system HCl-NaCl-H₂O (63) showed that the temperature coefficient is almost independent of the total molality.

If the excess free energy of a mixture is given by eqn (2.212) the excess enthalpy of mixing takes the form

$$H^E = -y_B y_C m^2 RT^2 \frac{\partial}{\partial T} (Q_B + Q_C) \quad (2.215)$$

The excess free energy is not a quantity which can be measured directly, but measurements of excess enthalpies of mixing can be made directly and calorimetry gives the excess enthalpy with greater ease and accuracy.

Young and co-workers (3) obtained enthalpy changes for all combinations of the form M_1Cl-M_2Cl where M_1, M_2 represent hydrogen or an alkali metal ion. They obtained

$$H^E = y_B y_C m^2 RT \left[h_0 + h_1 (y_B - y_C) \right] \quad (2.216)$$

where h_1 is a measure of skew and is usually very small. If $h_1 = 0$ the plot of H^E against y_B is symmetrical with a maximum (or minimum) at $y_B = 0.5$.

Young and Smith (1) showed as a first approximation that the heat (volume, excess free energy, etc) of mixing at constant ionic strength could be neglected for their systems. In general Young's rule is given by

$$\Phi = \sum E_i \phi_i \quad (2.217)$$

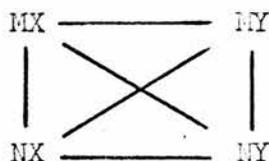
where

Φ is any apparent equivalent property such as volume, heat capacity, etc,

E_i is the equivalent ionic fraction of species i , equal to e_i/e_T , where e_i is the equivalent molality of species i and $e_T = \sum e_i$ is the total equivalent molality of the solution,

ϕ_i is the apparent equivalent property of species i .

The last generalization, the cross-square rule, due to Young and co-workers(2), is that for a reciprocal salt pair the sum of the heats of mixing with common ions equals the sum of the two heats of mixing without common ions. This can be illustrated as



Here the four heats of mixing with common ions are located around the square, and the two heats of mixing without common ions are the two diagonal relations.

Wood and Anderson(4,71) proposed an improved equation for Young's rule. They obtained

$$\begin{aligned} \phi_L^{\text{mixture}} &= \frac{H^E}{m} = \sum_{M,X} y_M y_X \phi_L(MX) \\ &+ (RT I^2/m) \sum_{M \lessgtr N, X} y_M y_N y_X h_{M,N^X} \\ &+ (RT I^2/m) \sum_{X \lessgtr Y, M} x_X y_Y y_M h_{X,Y^M} \end{aligned} \quad (2.218)$$

where

y_M is the ionic strength fraction of M
 $\phi_L(MX)$ the relative apparent molar enthalpy of the pure electrolyte MX at ionic strength I

and the sums take each h_{M,N^X} term once. The term RTh_{M,N^X} is the coefficient for the interaction of the M and N ions (of the same charge) in the presence of the X ion oppositely charged.

Young's first approximation consists of assuming all RTh terms equal to zero, which is equivalent to applying Young and Smith's rule to common ion mixtures only. This is a much better approximation than the original rule since in a common ion mixture there are no changes in cation-anion interactions. The equations have been used to predict heats of mixing accurately, for three cations in the presence of a common anion(71)

2. 5. 7 Application of equations of the Gibbs-Duhem type for mixtures.

The thermodynamic treatment of systems containing two electrolytes and the solvent component has been advanced considerably by Glueckauf(65) McKay(16,72) and their colleagues. Their contributions demonstrated the value of introducing the cross differentiation equations.

By application of the cross differentiation relation in the form

$$\left(\frac{\partial \ln a_1}{\partial n_w} \right)_{n_1, n_2} = \left(\frac{\partial \ln a_w}{\partial n_1} \right)_{n_2, n_w} = \dots \quad (2.219)$$

McKay and Perring have derived relations which are particularly useful for the computation of activity coefficients in mixtures from isopiestic vapour pressure measurements.

Due to the importance of this method in the development of this thesis, the derivation of the McKay and Perring equations will be carried out in a separate chapter, (Chapter 3).

CHAPTER 3

THE MCKAY-PERRING METHOD FOR ACTIVITY COEFFICIENTS:

APPLICATION TO PARTIAL MOLAR ENTHALPY

AND PARTIAL MOLAR HEAT CAPACITY

3. 1 Introduction

McKay and Perring(15), using strict thermodynamic principles, derived equations which permit the calculation of the activity coefficients of involatile solutes in mixed solutions, from solvent vapour pressure measurements. One of these equations was found to be specially appropriate for application to isopiestic experiments and since then it has been widely used for ternary systems.

Previously, it was supposed that the best that could be achieved was to determine the third activity, after having measured the other two, by using the Gibbs-Duhem relation. However, McKay and Perring found it to be possible, from measurements of the activity of one component only (for example the solvent activity), to calculate the activity of all other components in the system. Among the systems to which the methods can be applied are mixed electrolyte solutions, systems involving complexes, systems in which a solute is partitioned between solvents, and ion exchange systems.

The McKay-Perring method is based on the validity of the cross-differentiation relation. It was developed, explicitly, for the computation of activity coefficients and, even though the authors suggested that the equations could be generalized by replacing the $(\ln a)'s$ by any suitable partial molar quantity, up to now only activity coefficients have been treated in this way.

The purpose of this thesis was, precisely, directed towards the application of the method to these other partial molar quantities, which do not seem to appear in the literature at all, and especially to partial molar enthalpies and partial molar heat capacities of mixed electrolyte solutions, providing in this way a simple and elegant method of obtaining data on these systems.

Since the theory for the free energy serves as a convenient model for the other properties, and the related activity coefficient measurements have also been carried out here, the McKay-Perring activity coefficient treatment will now be presented in some detail.

3. 2. McKay-Perring method for activity coefficients

In ternary and more complex systems, the activities of the different components are connected by various cross-differentiation relations of the type

$$\left(\frac{\partial \ln a_1}{\partial n_2} \right)_{n_1, n_3} = \left(\frac{\partial \ln a_2}{\partial n_1} \right)_{n_1, n_3} \quad (3.1)$$

$$\left(\frac{\partial \ln a_1}{\partial n_2} \right)_{a_2, a_3} = \left(\frac{\partial \ln a_2}{\partial n_1} \right)_{a_1, n_3} \quad (3.2)$$

$$\left(\frac{\partial \ln a_1}{\partial \ln a_2} \right)_{n_1, n_3} = - \left(\frac{\partial n_2}{\partial n_1} \right)_{a_2, n_3} \quad (3.3)$$

where

a_i is the activity of the component i ,

n_i is the number of moles of i

To reduce from two to one the number of constancy conditions, in a ternary system, it is convenient to convert the basic relations into more convenient forms; for example, forms involving mole ratio

(molality) or mole fraction. The variables are now intensive, and eqn (3.1), for example, can be rewritten

$$\left(\frac{\partial \ln a_1}{\partial r_{23}} \right)_{r_{13}} = \left(\frac{\partial \ln a_2}{\partial r_{13}} \right)_{r_{23}} \quad (3.4)$$

where $r_{ij} = n_i/n_j$

or if component 3 is taken as the solvent

$$\left(\frac{\partial \ln a_1}{\partial m_2} \right)_{m_1} = \left(\frac{\partial \ln a_2}{\partial m_1} \right)_{m_2} \quad (3.5)$$

here m_i represents the molality of each component and is defined as

$$0.001 M_s m_i = n_i/n_3 \quad (3.6)$$

M_s is the molecular weight of the solvent.

Eqn (3.4) integrated at constant r_{13} gives

$$\left\{ \ln a_1/a_1^* = \int_{r_{23}^*}^{r_{23}} \left(\frac{\partial \ln a_2}{\partial r_{13}} \right)_{r_{23}} dr_{23} \right\}_{r_{13}} \quad (3.7)$$

This equation gives the variation of a_1 with r_{23} at constant r_{13} , but not the variation with r_{13} . This disability can be overcome by choosing some reference state for which a_1 is known. For example:

- i) by reference to an infinitely dilute solution in component 2, so that $a_1 \rightarrow r_{12}$ as $r_{23} \rightarrow \infty$

$$\left\{ \ln (a_1/r_{12}) = \int_{\infty}^{r_{23}} \left(\frac{\partial \ln a_2}{\partial r_{23}} \right)_{r_{23}} dr_{23} \right\}_{r_{13}} \quad (3.8)$$

which gives a_1 absolutely.

ii) by reference to the binary system consisting of component 1 and the solvent only, then, $r_{23} = 0$ may be taken as the lower limit of integration, and

$$\left\{ \ln (a_1/a_1^0) = \int_0^{r_{23}} (\partial \ln a_2 / \partial r_{13})_{r_{23}} d r_{23} \right\}_{r_{13}} \quad (3.9)$$

where a_1^0 is the value of a_1 at $r_{23} = 0$

The difficulties arising at the limits can be overcome by introducing activity and osmotic coefficients.

3. 2. 1 Activity coefficients at constant water activity

For a ternary mixed electrolyte solution composed of n_1 moles of solute 1, n_2 moles of solute 2, and n_w moles of solvent, eqn (3.1) may be rewritten

$$\left(\frac{\partial \ln a_1}{\partial n_w} \right)_{n_1, n_2} = \left(\frac{\partial \ln a_w}{\partial n_1} \right)_{n_2, n_w} \quad (3.10)$$

or, written in the intensive form,

$$\left(\frac{\partial \ln a_1}{\partial (n_w/n_2)} \right)_{n_1/n_2} = \left(\frac{\partial \ln a_w}{\partial (n_1/n_2)} \right)_{n_w/n_2} \quad (3.11)$$

But,

$$n_1 = \frac{n_w M_w}{1000} m_1 \quad (3.12)$$

$$n_2 = \frac{n_w M_w}{1000} m_2 \quad (3.13)$$

therefore

$$\frac{n_1}{n_2} = \frac{m_1}{m_2} \quad (3.14)$$

and

$$\frac{n_w}{n_2} = \left(\frac{1000}{M_w} \right) \frac{1}{m_2} \quad (3.15)$$

hence, eqn (3.11) becomes

$$\frac{M_w}{1000} \left(\frac{\partial \ln a_1}{\partial (1/m_2)} \right)_{m_1/m_2} = \left(\frac{\partial \ln a_w}{\partial (m_1/m_2)} \right)_{1/m_2} \quad (3.16)$$

or, if the solvent is water

$$0.018 \left(\frac{\partial \ln a_1}{\partial (1/m_2)} \right)_{m_1/m_2} = \left(\frac{\partial \ln a_w}{\partial (m_1/m_2)} \right)_{1/m_2} \quad (3.17)$$

By multiplying both sides by $(\partial(1/m_2)/\partial \ln a_w)_{m_1/m_2}$

$$0.018 \left(\frac{\partial \ln a_1}{\partial \ln a_w} \right)_{m_1/m_2} = \frac{(\partial \ln a_w / \partial (m_1/m_2))_{m_2}}{(\partial \ln a_w / \partial (1/m_2))_{m_1/m_2}} \quad (3.18)$$

but

$$d \ln a_w = \left(\frac{\partial \ln a_w}{\partial (m_1/m_2)} \right)_{1/m_2} \cdot d(m_1/m_2) + \left(\frac{\partial \ln a_w}{\partial (1/m_2)} \right)_{m_1/m_2} \cdot d(1/m_2) \quad (3.19)$$

thus, at constant activity of water

$$\frac{\left\{ \frac{\partial \ln a_w}{\partial (m_1/m_2)} \right\}_{1/m_2}}{\left\{ \frac{\partial \ln a_w}{\partial (1/m_2)} \right\}_{m_1/m_2}} = - \left(\frac{\partial (1/m_2)}{\partial (m_1/m_2)} \right)_{a_w} \quad (3.20)$$

By comparing eqns (3.18) and (3.20)

$$0.018 \left(\frac{\partial \ln a_1}{\partial \ln a_w} \right)_{m_1/m_2} = - \left(\frac{\partial (1/m_2)}{\partial (m_1/m_2)} \right)_{a_w} \quad (3.21)$$

If the total molality, m , is any convenient linear combination of the form

$$m = k_1 m_1 + k_2 m_2 \quad (3.22)$$

$$d \ln m = \frac{k_1 d m_1 + k_2 d m_2}{k_1 m_1 + k_2 m_2} \quad (3.23)$$

but, at constant m_1/m_2 , $d m_2 = k' d m_1$; thus

$$d \ln m = d \ln m_1 \quad (3.24)$$

Now, if solute 1 dissociates into ν_1 ions

$$\begin{aligned} d \ln a_1 &= \nu_1 d \ln m_{\pm} \gamma_{\pm} \\ &= \nu_1 d \ln \gamma_{\pm} + \nu_+ d \ln m_+ + \nu_- d \ln m_- \end{aligned} \quad (3.25)$$

but, at m_1/m_2 , $m_+ \propto m_1$ and $m_- \propto m_1$, then

$$d \ln a_1 = \nu_1 d \ln \gamma_{\pm} + (\nu_+ + \nu_-) d \ln m_1 \quad (3.26)$$

where

$$\nu_+ + \nu_- = \nu_1$$

From (3.24) and (3.26)

$$\partial \ln a_1 = \nu_1 \partial \ln m \gamma_1 \quad (3.27)$$

where γ_1 represents the mean activity coefficient of component 1

Eqns (3.21) and (3.27) give

$$0.018 \nu_1 \left(\frac{\partial \ln m \gamma_1}{\partial \ln a_w} \right)_{m_1/m_2} = - \left(\frac{\partial (1/m_2)}{\partial (m_1/m_2)} \right)_{a_w} \quad (3.28)$$

Introducing the fractions

$$x_1 = \frac{k_1 m_1}{m} \quad ; \quad x_2 = \frac{k_2 m_2}{m} \quad (3.29)$$

$$\frac{d (1/m_2)}{d (m_1/m_2)} = \frac{k_1}{m^2} \left[\frac{d m}{d \ln x_2} + \frac{k_1}{m} \right] \quad (3.30)$$

also

$$\dot{x}_1 = \frac{k_1 (m_1/m_2)}{k_2 + k_1 (m_1/m_2)} \quad (3.31)$$

then at constant m_1/m_2 , x_1 is constant hence,

$$0.018 \nu_1 \left(\frac{\partial \ln m \gamma_1}{\partial \ln a_w} \right)_{x_1} = - \frac{k_1}{m^2} \left(\frac{\partial m}{\partial \ln x_2} \right)_{a_w} - \frac{k_1}{m} \quad (3.32)$$

It is not convenient to integrate this equation as it

stands owing to the behaviour of the integrands at infinite dilution, but it can be combined with the Gibbs-Duhem equation for a binary solution of component 1, which leads to

$$0.018\gamma_1 \left(\frac{d \ln M_1 \Gamma_1}{d \ln a_w} \right) = - \left(\frac{k_1}{M_1} \right) \quad (3.33)$$

where

$M_1 = k_1 m_1$ is the molality of the component 1 in the binary solution,

Γ_1 the mean activity coefficient of component 1 in this solution.

If the ternary and the binary solutions are isopiestic, then a_w has the same meaning in both equations, eqns (3.32) and (3.33).

By subtracting (3.33) from (3.32)

$$0.018\gamma_1 (\delta \ln m \gamma_1 - d \ln M_1 \Gamma_1) = k_1 \left[- \frac{1}{m^2} \left(\frac{\partial m}{\partial \ln x_2} \right)_{a_w} - \frac{1}{m} + \frac{1}{M_1} \right] d \ln a_w \quad (3.34)$$

Hence, integration at constant x_1 gives

$$0.018\gamma_1 \ln (m \gamma_1 / M_1 \Gamma_1) = k_1 \int_0^{\ln a_w} \left\{ - \frac{1}{m^2} \left(\frac{\partial m}{\partial \ln x_2} \right)_{a_w} - \frac{1}{m} + \frac{1}{M_1} \right\} d \ln a_w \quad (3.35)$$

If the binary solution (the reference solution) is equilibrated with a series of mixed solutions in different proportions, i.e., with different values of x_2 , but having all the same water activity, it is possible to obtain m , M_1 , and $(\partial m / \partial \ln x_2)_{a_w}$; and if the mean activity coefficient of the reference solution is known, eqn (3.35) allows the activity coefficient of component 1 in the ternary solution to be calculated. But the evaluation of the integral in eqn (3.35) presents some difficulty. This can be avoided by considering that the immediate result of the experiment is M_1/m which is the isopiestic

ratio, R . (see section 4.2, where it is explained that M_1 is the molality in the binary reference system having the same water activity as the ternary mixture of total molality m_1 defined as in eqn (3.22)).

By introducing R into eqn (3.35), the following equation is obtained

$$\ln \gamma_1 = \ln \Gamma_1 + \ln R + \frac{k_1}{0.018 \nu_1} \int_0^{ln a_w} \left\{ -\frac{1}{m^2} \left(\frac{\partial m}{\partial \ln x_2} \right)_{a_w} - \frac{R-1}{M_1} \right\} d \ln a_w \quad (3.36)$$

According to eqn (2.32) it is possible to write

$$d \ln a_w = -\frac{0.018 \nu_1 M_1}{k_1} d \phi_1 = -\frac{0.018 \nu_1}{k_1} d (M_1 \phi_1) \quad (3.37)$$

and by combining it with eqn (3.36)

$$\ln \gamma_1 = \ln \Gamma_1 + \ln R + \int_0^{M_1 \phi_1} \left\{ \frac{1}{m^2} \left(\frac{\partial m}{\partial \ln x_2} \right)_{a_w} + \frac{R-1}{M_1} \right\} d (M_1 \phi_1) \quad (3.38)$$

where ϕ_1 is the osmotic coefficient of the reference solution.

$$\text{As } R = \frac{M_1}{m} \quad (3.39)$$

then

$$\left(\frac{\partial R}{\partial \ln x_2} \right)_{a_w} = \left(\frac{\partial (M_1/m)}{\partial \ln x_2} \right)_{a_w} \quad (3.40)$$

hence

$$\frac{1}{m^2} \left(\frac{\partial m}{\partial \ln x_2} \right)_{a_w} = -\frac{X_2}{M_1} \left(\frac{\partial R}{\partial X_c} \right)_{a_w} \quad (3.41)$$

which transforms eqn (3.36) into

$$\ln \gamma_1 = \ln \Gamma_1 + \ln R + \int_0^{M_1 \phi_1} \left\{ -\frac{X_2}{M_1} \left(\frac{\partial R}{\partial X_c} \right)_{a_w} + \frac{R-1}{M_1} \right\} d (M_1 \phi_1) \quad (3.42)$$

The quantity in the integral is determined by the tangent to

the curve of R against x_2 for the particular water activity; this tangent will, in general, be a function of x_2 . The experiments must then be repeated at this particular value of x_2 to determine $\partial R/\partial x_2$ as a function of $M_1 \phi_1$, to be able to perform the integration.

There is no theoretical way of predicting the variation of $\partial R/\partial x_2$ with $M_1 \phi_1$ but a considerable simplification is obtained if the isopiestic ratio can be expressed, as Robinson proposed, by the relation

$$R = 1 - ax_2 - bx_2^2 \quad (3.43)$$

where a and b are functions of M_1 but not of x_2 . By using this relation, eqn.(3.42) becomes

$$\ln \gamma_1 = \ln \Gamma_1 + \ln R + x_2^2 \int_0^{M_1 \phi_1} \left(\frac{b/M_1}{b/M_1} \right) d(M_1 \phi_1) \quad (3.44)$$

If the isopiestic ratio is linear in x_2 , then $b = 0$ and

$$\ln \gamma_1 = \ln \Gamma_1 + \ln R \quad (3.45)$$

Similar equations may be written for the activity coefficient of the other component.

3.2.2 Activity coefficients at constant total molality

A parallel transformation of eqn.(3.21) can be carried out for working at constant m. By analogy with the derivation of eqn. (3.21), by multiplying by $(\partial(1/m_2)/\partial m)_{m_1/m_2}$

$$0.018 (\partial \ln a_1/\partial m)_{m_1/m_2} = (\partial \ln a_w/\partial (m_1/m_2))_{m_2} \cdot (\partial(1/m_2)/\partial m)_{m_1/m_2} \quad (3.46)$$

Now

$$m = m_2 \left(k_1 \frac{m_1}{m_2} \right) + k_2 m_2 = \left(k_1 \frac{m_1}{m_2} \right) \left(\frac{1}{1/m_2} \right) + k_2 \left(\frac{1}{1/m_2} \right) \quad (3.47)$$

then

$$\begin{aligned} \left(\frac{\partial m}{\partial (1/m_2)} \right)_{m_1/m_2} &= \left(k_1 \frac{m_1}{m_2} \right) \left(- \frac{1}{(1/m_2)^2} \right) - k_2 \left(\frac{1}{(1/m_2)^2} \right) \\ &= \left(k_1 \frac{m_1}{m_2} + k_2 \right) \left(- m_2^2 \right) = - m_2 m \end{aligned} \quad (3.48)$$

also

$$\left(\frac{\partial \ln a_w}{\partial (m_1/m_2)} \right)_{m_2} = m_2 \left(\frac{\partial \ln a_w}{\partial m_1} \right)_{m_2} \quad (3.49)$$

then

$$\left(\frac{\partial \ln a_w}{\partial (m_1/m_2)} \right)_{m_2} \left(\frac{\partial (1/m_2)}{\partial m} \right)_{m_1/m_2} = - \left(\frac{\partial \ln a_w}{\partial m_1} \right)_{m_2} / m \quad (3.50)$$

An equation is required in terms of the variables x_2 and m . By the relation

$$d \ln a_w = \left(\frac{\partial \ln a_w}{\partial \ln x_2} \right)_m \cdot d \ln x_2 + \left(\frac{\partial \ln a_w}{\partial m} \right)_{x_2} \cdot dm \quad (3.51)$$

one obtains

$$\left(\frac{\partial \ln a_w}{\partial m_1} \right)_{m_2} = \left(\frac{\partial \ln a_w}{\partial \ln x_2} \right)_m \cdot \left(\frac{\partial \ln x_2}{\partial m_1} \right)_{m_2} + \left(\frac{\partial \ln a_w}{\partial m} \right)_{x_2} \left(\frac{\partial m}{\partial m_1} \right)_{m_2} \quad (3.52)$$

But

$$\ln x_2 = - \ln (1 + k_1 m_1 / k_2 m_2) \quad (3.53)$$

$$\left(\frac{\partial \ln x_2}{\partial m_1} \right)_{m_2} = - \left(\frac{k_1}{m} \right) \quad (3.54)$$

and from eqn (3.22)

$$\left(\frac{\partial m}{\partial m_1} \right)_{m_2} = k_1 \quad (3.55)$$

Hence, from (3.52), (3.54), and (3.55)

$$\left(\frac{\partial \ln a_w}{\partial m_1} \right)_{m_2} = - \frac{k_1}{m} \left(\frac{\partial \ln a_w}{\partial \ln x_2} \right)_m + k_1 \left(\frac{\partial \ln a_w}{\partial m} \right)_{x_2} \quad (3.56)$$

and combining eqns (3.46), (3.50), and (3.56), the following equation is obtained

$$0.018 \left(\frac{\partial \ln a_1}{\partial m} \right)_{m_1/m_2} = k_1 \left\{ \frac{1}{m^2} \left(\frac{\partial \ln a_w}{\partial \ln x_2} \right)_m - \frac{1}{m} \left(\frac{\partial \ln a_w}{\partial m} \right)_{x_2} \right\} \quad (3.57)$$

After subtracting a similar equation for the binary system at the same molality, and on integration at constant x_1 of the equation so obtained, one gets in terms of the activity coefficient

$$0.018 \nu_1 \ln (Y_1/Y_1^0) = k_1 \int_0^m \left\{ \frac{1}{m^2} \left(\frac{\partial \ln a_w}{\partial \ln x_2} \right)_m - \frac{1}{m} \left(\frac{\partial \ln (a_w/a_w^0(1))}{\partial m} \right)_{x_2} \right\} dm \quad (3.58)$$

where Y_1^0 and a_w^0 refer to the binary solution at the same molality as the mixture. By converting to decadic logarithms

$$0.018 \nu_1 \log (Y_1/Y_1^0) = k_1 \int_0^m \left\{ \frac{1}{m^2} \left(\frac{\partial \ln a_w}{\partial x_2} \right)_m \cdot x_2 - \frac{1}{m} \left(\frac{\partial \ln (a_w/a_w^0(1))}{\partial m} \right)_{x_2} \right\} dm \quad (3.59)$$

By using the function

$$\psi_1 = (1/x_2 m^2) \log (a_w/a_w^0(1)) \quad (3.60)$$

it is possible to obtain

$$\begin{aligned} \frac{1}{m^2} \cdot \left(\frac{\partial \log a_w}{\partial x_2} \right)_m \cdot x_2 - \frac{1}{m} \cdot \left(\frac{\partial \log (a_w/a_w^0(1))}{\partial m} \right)_{x_2} &= x_2^2 \left(\frac{\partial \psi_1}{\partial x_2} \right)_m \\ &\quad - x_2 \psi_1 - \underline{\underline{x_2 m \left(\frac{\partial \psi_1}{\partial m} \right)_{x_2}}} \end{aligned} \quad (3.61)$$

The doubly underlined term in this particular application appears to have been overlooked by McKay and Perring, but it may be significant unless it necessarily disappears on integration with respect to m at constant x_2 , which does not seem likely at first sight.

3. 3 Extension of the McKay-Perring method.

3. 3. 1 Application to partial molar enthalpies

One of the basic cross-differentiation relations for partial molar enthalpies in a ternary system may be written as

$$\left(\frac{\partial H_k}{\partial n_i}\right)_{n_j, n_k} = \left(\frac{\partial H_i}{\partial n_k}\right)_{n_j, n_i} \quad (3.62)$$

By multiplying both sides by $(\partial n_k / \partial H_k)_{n_i, n_j}$

$$\left(\frac{\partial H_i}{\partial H_k}\right)_{n_i, n_j} = \left(\frac{\partial H_k}{\partial n_i}\right)_{n_k, n_j} \cdot \left(\frac{\partial n_k}{\partial H_k}\right)_{n_i, n_j} \quad (3.63)$$

and by using the cyclic rule with the variables H_i , H_k , and n_i

$$\left(\frac{\partial H_i}{\partial H_k}\right)_{n_i, n_j} \cdot \left(\frac{\partial H_k}{\partial n_i}\right)_{H_i, n_j} \cdot \left(\frac{\partial n_i}{\partial H_i}\right)_{H_k, n_j} = -1 \quad (3.64)$$

Then

$$\begin{aligned} \left(\frac{\partial H_i}{\partial H_k}\right)_{n_i, n_j} &= -\left(\frac{\partial H_i}{\partial n_i}\right)_{H_k, n_j} \cdot \left(\frac{\partial n_i}{\partial H_k}\right)_{H_i, n_j} \\ &= -\left(\frac{\partial H_i}{\partial n_k}\right)_{H_k, n_j} \cdot \left(\frac{\partial n_k}{\partial n_i}\right)_{H_k, n_j} \cdot \left(\frac{\partial n_i}{\partial H_k}\right)_{H_i, n_j} \end{aligned} \quad (3.65)$$

From eqns (3.63) and (3.65) one obtains

$$\left(\frac{\partial H_i}{\partial n_k}\right)_{H_k, n_j} = \left(\frac{\partial H_k}{\partial n_i}\right)_{H_i, n_j} \quad (3.66)$$

On the other hand, if the cyclic rule is written using the variables H_k , n_i and n_k , the following equation is obtained

$$\left(\frac{\partial H_i}{\partial n_k}\right)_{n_j, n_i} = - \left(\frac{\partial n_k}{\partial n_i}\right)_{H_k} \quad (3.67)$$

Equations (3.62), (3.66), and (3.67) may be considered as basic cross-differentiation relations for the partial molar enthalpies in a ternary system. In these equations, H represents the partial molar enthalpy, n the number of moles and the subscripts i, j, and k stand for the components of the system.

3. 3. 1. 1. Solute partial molar enthalpies at constant partial molar enthalpy of water.

Consider the system composed of the solutes 1 and 2 in the solvent 3. Equation (3.62) becomes now

$$\left(\frac{\partial H_1}{\partial n_3}\right)_{n_1, n_2} = \left(\frac{\partial H_3}{\partial n_1}\right)_{n_3, n_2} \quad (3.68)$$

which, in the intensive form and by considering eqn (3.6), transforms into

$$0.018 \quad \left(\frac{\partial H_1}{\partial (1/m_2)}\right)_{m_1/m_2} = \left(\frac{\partial H_3}{\partial (m_1/m_2)}\right)_{1/m_2} \quad (3.69)$$

Multiplying both sides by $[\partial(1/m_2)/\partial H_3]_{m_1/m_2}$, one gets

$$0.018 \quad \left(\frac{\partial H_1}{\partial H_3}\right)_{m_1/m_2} = \left(\frac{\partial H_3}{\partial (m_1/m_2)}\right)_{1/m_2} \cdot \left(\frac{\partial (1/m_2)}{\partial H_3}\right)_{m_1/m_2} \quad (3.70)$$

Now

$$d H_3 = \left(\frac{\partial H_3}{\partial (m_1/m_2)}\right)_{1/m_2} \cdot d (m_1/m_2) + \left(\frac{\partial H_3}{\partial (1/m_2)}\right)_{m_1/m_2} \cdot d (1/m_2) \quad (3.71)$$

at constant H_3

$$\left(\frac{\partial H_3}{\partial (m_1/m_2)}\right)_{1/m_2} \cdot \left(\frac{\partial (1/m_2)}{\partial H_3}\right)_{m_1/m_2} = - \left(\frac{\partial (1/m_2)}{\partial (m_1/m_2)}\right)_{H_3} \quad (3.72)$$

Hence

$$0.018 \left(\frac{\partial H_1}{\partial H_3} \right)_{m_1/m_2} = - \left(\frac{\partial (1/m_2)}{\partial (m_1/m_2)} \right)_{H_3} \quad (3.73)$$

By introducing the total molality, m , as any convenient linear combination of the form of eqn. (3.22), the fractions x_1 and x_2 as given by eqns (3.29), and eqn (3.30), the following equation is obtained

$$0.018 \left(\frac{\partial H_1}{\partial H_3} \right)_{x_1} = - \frac{k_1}{m^2} \cdot \left(\frac{\partial m}{\partial \ln x_2} \right)_{H_3} - \frac{k_1}{m} \quad (3.74)$$

The constancy of x_1 when m_1/m_2 is constant is implicit in eqn (3.31)

Eqn (3.74) may be combined with the Gibbs-Duhem equation, for the binary system of the solute and the solvent, written in the form

$$0.018 \frac{\partial \mathcal{H}_1}{\partial H_3} = - \frac{k_1}{M_1} \quad (3.75)$$

where M_1 and \mathcal{H}_1 are the values of m and H_1 , respectively, in the binary solution at the same partial molar enthalpy of water as the mixed solution. In this condition H_3 has the same meaning in both equations, (3.74) and (3.75), and subtraction of the latter from the former gives

$$0.018 \left[\frac{\partial H_1}{\partial H_3} - \frac{\partial \mathcal{H}_1}{\partial H_3} \right]_{x_1} = - k_1 \left[\frac{1}{m^2} \cdot \left(\frac{\partial m}{\partial \ln x_2} \right)_{H_3} - \frac{1}{m} + \frac{1}{M_1} \right] \quad (3.76)$$

Hence, on integration at constant x_1

$$H_1 - \mathcal{H}_1 = \frac{k_1}{0.018} \int_0^{H_3} \left\{ \frac{1}{m^2} \left(\frac{\partial m}{\partial \ln x_2} \right)_{H_3} - \frac{1}{m} + \frac{1}{M_1} \right\} d H_3 \quad (3.77)$$

A similar equation can be obtained for the other solute component of the mixture.

The application of these equations requires only the experimental determination of the partial molar enthalpy of water in the binary and ternary systems, and a knowledge of the partial molar enthalpy of each component in binary solution. The latter may be obtained from the experimental data on the binary system, by using the Gibbs-Duhem equation.

From calorimetric experiments one can derive the molalities m and M_1 of a set of solutions which have the same partial molar enthalpy of water, and hence the value of $(\partial m / \partial \ln x_2)_{H_3}$.

For the application of eqn (3.77) it is, then, necessary for the binary systems to have a range of molalities with the same partial molar enthalpy of water.

3. 3. 1. 2. Solute partial molar enthalpies at constant molality

Starting again with eqn (3.69) and by multiplying both sides by $(\partial (1/m_2) / \partial m)_{m_1/m_2}$

$$0.018 \left(\frac{\partial H_1}{\partial m} \right)_{m_1/m_2} = \left(\frac{\partial H_3}{\partial (m_1/m_2)} \right)_{m_2} \cdot \left(\frac{\partial (1/m_2)}{\partial m} \right)_{m_1/m_2} \quad (3.78)$$

Now

$$\left(\frac{\partial H_3}{\partial (m_1/m_2)} \right)_{m_2} = m_2 \left(\frac{\partial H_3}{\partial m_1} \right)_{m_2} \quad (3.79)$$

Also by eqn (3.48)

$$\left(\frac{\partial m}{\partial (1/m_2)} \right)_{m_1/m_2} = -m_2 m \quad (3.48)$$

Then the RHS of Eqn (3.78) becomes

$$- \frac{1}{m} \left(\frac{\partial H_3}{\partial m_1} \right)_{m_2} \quad (3.80)$$

With H_3 in terms of the variables x_2 and m

$$d H_3 = \left(\frac{\partial H_3}{\partial \ln x_2} \right)_m \cdot d \ln x_2 + \left(\frac{\partial H_3}{\partial m} \right)_{x_2} \cdot dm \quad (3.81)$$

$$\begin{aligned} \left(\frac{\partial H_3}{\partial m_1} \right)_{m_2} &= \left(\frac{\partial H_3}{\partial \ln x_2} \right)_m \cdot \left(\frac{\partial \ln x_2}{\partial m_1} \right)_{m_2} + \\ &+ \left(\frac{\partial H_3}{\partial m} \right)_{x_2} \cdot \left(\frac{\partial m}{\partial m_1} \right)_{m_2} \end{aligned} \quad (3.82)$$

But

$$\left(\frac{\partial \ln x_2}{\partial m_1} \right)_{m_2} = - \frac{k_1}{m} \quad (3.54)$$

and

$$\left(\frac{\partial m}{\partial m_1} \right)_{m_2} = - k_1 \quad (3.55)$$

so that

$$\left(\frac{\partial H_3}{\partial m_1} \right)_{m_2} = - \frac{k_1}{m} \cdot \left(\frac{\partial H_3}{\partial \ln x_2} \right)_m + k_1 \cdot \left(\frac{\partial H_3}{\partial m} \right)_{x_2} \quad (3.83)$$

Hence

$$0.018 \left(\frac{\partial H_1}{\partial m} \right)_{m_1/m_2} = k_1 \left\{ \frac{1}{m^2} \left(\frac{\partial H_3}{\partial \ln x_2} \right)_m - \frac{1}{m} \left(\frac{\partial H_3}{\partial m} \right)_{x_2} \right\} \quad (3.84)$$

If \mathcal{H}_1 and \mathcal{H}_3 are the partial molar enthalpies of the component 1 and the solvent, respectively, in the binary system, from the Gibbs-Dunhem equation it follows that

$$0.018 \frac{d\mathcal{H}_1}{dm} = -\frac{k_1}{m} \frac{d\mathcal{H}_3}{dm} \quad (3.85)$$

After subtracting this equation from eqn (3.84) and on integration at constant x_1 , the following equation is obtained

$$H_1 - \mathcal{H}_1 = \frac{k_1}{0.018} \int_0^m \left\{ \frac{1}{m^2} \cdot \left(\frac{\partial H_3}{\partial \ln x_2} \right)_m - \frac{1}{m} \cdot \left(\frac{\partial [H_3 - \mathcal{H}_{3(1)}]}{\partial m} \right)_{x_2} \right\} dm \quad (3.86)$$

There is a similar equation for the partial molar enthalpy of the other component.

From calorimetric experiments one can obtain the partial molar enthalpy of water of a set of solutions which have the same molalities, two of these solutions containing either electrolyte 1 only or electrolyte 2 only, the remainder containing both solutes but in different proportions. From the results it is possible to obtain $(\partial H_3 / \partial \ln x_2)_m$, and, if the experiments have been performed in the required range of concentration, also to obtain $(\partial [H_3 - \mathcal{H}_{3(1)}] / \partial m)_{x_2}$.

To evaluate the integral term in eqn (3.86) it is desirable to find an analytical expression for H_3 and $(H_3 - \mathcal{H}_{3(1)})$ which avoids the difficulties arising at the limit. The analytical expression of H_3 as a function of x_2 and m is also linked with the choice of the constants k_1 and k_2 .

3. 3. 2. Partial molar heat capacity

The partial molar heat capacity seems to be also a suitable quantity for using the cross-differentiation relations. For ternary system it may be written

$$\left(\frac{\partial C_{p_3}}{\partial n_1}\right)_{n_2, n_3} = \left(\frac{\partial C_{p_1}}{\partial n_3}\right)_{n_2, n_1} \quad (3.87)$$

$$\left(\frac{\partial C_{p_1}}{\partial n_3}\right)_{C_{p_3}, n_2} = \left(\frac{\partial C_{p_3}}{\partial n_1}\right)_{C_{p_1}, n_2} \quad (3.88)$$

$$\left(\frac{\partial C_{p_1}}{\partial C_{p_3}}\right)_{n_2, n_1} = -\left(\frac{\partial n_3}{\partial n_1}\right)_{C_{p_3}} \quad (3.89)$$

where

C_p is partial molar heat capacity, n is number of moles, and the suffixes denote the components.

The intensive form of eqn (3.87) may be transformed to obtain relations for C_{p_1} or C_{p_2} at constant partial molar heat capacity

of water, C_{p_3} . Then

$$0.018 \left(\frac{\partial C_{p_1}}{\partial C_{p_3}}\right)_{x_1} = -\frac{k_1}{m^2} \cdot \left(\frac{\partial m}{\partial \ln x_2}\right)_{C_{p_3}} - \frac{k_1}{m} \quad (3.90)$$

This equation is combined with the similar equation for the binary system to yield

$$0.018 \left(\frac{\partial C_{p_1}}{\partial C_{p_3}} - \frac{\partial \ell_{p_1}}{\partial C_{p_3}}\right)_{x_1} = -k_1 \left[\frac{1}{m^2} \cdot \left(\frac{\partial m}{\partial \ln x_2}\right)_{C_{p_3}} - \frac{1}{m} + \frac{1}{M_1} \right] \quad (3.91)$$

Hence, on integration at constant x_1

$$C_{p_1} - \ell_{p_1} = \frac{k_1}{0.018} \cdot \int_0^{C_{p_3}} \left\{ -\frac{1}{m^2} \cdot \left(\frac{\partial m}{\partial \ln x_2}\right)_{C_{p_3}} - \frac{1}{m} + \frac{1}{M_1} \right\} d C_{p_3} \quad (3.92)$$

ℓ_{p_1} refers to the binary solution.

From experiments it is possible to get the molalities m , at different x_2 's, and M_1 of the binary solution, all having the same partial molar heat capacity. Thus, if ℓ_{p_1} is known, C_{p_1} can be obtained from eqn (3.92)

Eqn (3.87) can also be transformed to provide an equation for the determination of C_{p_1} at constant molality:

$$0.018 \left[C_{p_1} - \ell_{p_1} \right] = k_1 \int_0^m \left\{ \frac{1}{m^2} \cdot \left(\frac{\partial C_{p_3}}{\partial \ln x_2} \right)_m - \frac{1}{m} \cdot \left(\frac{\partial (C_{p_3} - \ell_{p_3(1)})}{\partial m} \right)_{x_2} \right\} \quad (3.93)$$

There are similar equations for the other solute component of the mixture.

3.4 Application of the methods

Previously in this thesis it was mentioned that the McKay-Perring method for activity coefficients may be applied at constant activity of the solvent or at constant "molality" of the solutions, this latter being any convenient linear combination of the molalities of the solutes. But, in practice, apparently only the first method has been used; the reason is that it is much easier to obtain the experimental data at constant activity of water, by isopiestic measurement than obtaining the data at constant molality.

The use of only the first method has been possible because of the restriction necessarily existing in the water activity of the solutions; namely it always decreases with increasing concentration of any solute, which makes it possible to find solutions of the same water activity, for both binary and ternary systems, in the whole range of concentrations. The choice of this constant activity method, rather

than the equally justified constant molality method has largely been due to the experimental convenience in the application of the former to the isopiestic technique.

However, for the application of the method to partial molar enthalpies, the situation is different since they are not restricted in the same sense and the partial molar enthalpy of water can vary in either direction during the dilutions. In consequence, there is the possibility that the partial molar enthalpy of water, for the binary solution of one of the components, increases all the time with dilution while in the other it could, for example increase up to a maximum and then decrease. Thus, they will never have, or only in a small range of concentrations, the same partial molar enthalpy of water. If this is the case, it is impossible to apply the first method.

In conclusion, it may be said that for the application of the method for calculating partial molar enthalpies of the solutes in a mixed solution, at constant partial molar enthalpy of water, the binary solutions of each component require to have a whole range of molalities with the same partial molar enthalpy of water. Otherwise, the second method, i.e. that at constant total molality, has to be used. In this latter situation there are no restrictions at all.

The principal object of this thesis will be describe the application for the first time, of this second method to the system $\text{NaCl}-\text{CaCl}_2 - \text{H}_2\text{O}$, in which the water partial molar enthalpy changes in different directions along the binary limits. For comparison, other related systems will be mentioned in less detail to show that calorimetric measurements in some cases may also be capable of treatment by the first method.

CHAPTER 4

EXPERIMENTAL

4. 1 Isoniestic method

4. 1. 1 Introduction

Solutions having equal vapour pressure are called "isopiestic". The isopiestic method is a comparative one and depends on the principle that when two solutions containing different non-volatile solutes in the same volatile solvent (one of them being taken as reference), are placed in good thermal contact in a closed space, they will reach equilibrium due to the distillation of solvent from the solution of higher vapour pressure (i.e. the more dilute) to the solution of lower vapour pressure. The concentrations of the solutions are adjusted, as a result of this distillation, until the vapour pressures of the solutions are the same, and hence, if the solvent activity of the reference solution is known as a function of concentration, the solvent activity of the other solution may be calculated.

De Vries(74), who first used the isopiestic technique, introduced the term "isotonic" to define solutions in equilibrium with respect to solvent transfer, but Bousfield(75) when he introduced the technique used the term "isopiestic" to emphasize, the equality of pressure. The method was further developed by Sinclair(76), Robinson and Sinclair(51,77) Robinson(78) and many others. Scatchard, Hamer and Wood(79) modified the method developed by Sinclair and Robinson(77) to give a greater precision and some of these modifications were also reported by Mason(80) at about the same time.

In the isopiestic technique a weighed amount of solution of known composition is placed in a tared dish; a set of such dishes is placed in a desiccator (used only as container) and they are allowed to

equilibrate through the vapour phase. At the end the dishes are weighed again: any change in weight must be due to gain or loss of solvent.

The essential features of the apparatus and procedure are:

- 1) Good heat conduction through the solutions, and a good thermal buffer to prevent fluctuations of temperature.
- 2) Efficient stirring to assure mixing and heat conduction without heating.
- 3) Adequate evacuation to remove the air; (and prevention of "sputtering" of the solution during this evacuation).
- 4) Small samples to reduce the amount of distillation.

Many workers, over the years, collaborated in improving these factors. A good heat conduction is necessary in the equilibration of the solution since fluctuations of temperature may lead to small differences in the temperature of some of the solutions and the distillation could tend to go in the wrong direction. An efficient heat conduction can be obtained by using metallic dishes sunk into holes machined out of the thermal buffer, which is generally a copper, gold-plated copper, or stainless steel block.

The dishes may be of silver, gold-plated, stainless steel or platinum (ready-made crucibles may be sometimes suitable). Robinson (81) reported that no significant difference could be detected when different materials were used, and so it is possible to use stainless steel dishes successfully when no corrosive solutions are employed. Luk'yanov (82) and Bonner (83,84) used glass dishes mounted in a brass block, but it seems that employing glass is not ideal, since, because of

the much lower thermal conductivity of glass, thermal contact would be poor and equilibrium may take up to ten times as long to attain.

The agitation of the solutions has been achieved by either rocking the desiccator on a pivot or placing it on a inclined rotating table (10° - 45° to the horizontal) in the thermostat bath. Different types of device for this purpose have been reported (77,85) but the rotating inclined plate has been found to be a very good technique.

The evacuation of the apparatus is usually done by means of a water pump, the pressures being reduced to 15 - 20 m m Hg (76). The evacuation must be done slowly to prevent sputtering of the solutions which leads to errors in the final concentrations. Owen and Cooke (73) found it necessary to reduce the pressure in several stages during the equilibration, or to employ freshly boiled solutions. This seems an efficient technique and Mallinson (86) used it successfully. But at the same time is it convenient to connect the vessel not directly to the vacuum line but to a bulb of about the same volume as the vessel itself, as proposed by Scatchard and coworkers (79).

It is desirable to use small quantities of solution in the experiments to minimize the amounts of distillation and so to reach the equilibrium in a shorter time. The time for reaching equilibrium depends on the concentration of the solutions. For concentrated solutions this time may be between 2 or 3 days, but for dilute solutions it is much longer, normally a week or more.

To avoid evaporation or atmospheric contamination, the dishes must be provided with well-fitted lids and they should always be weighed as rapidly as possible. It is also necessary to provide a

good mechanism for raising or lowering the lids, since the seal must be made before opening the desiccator, especially when one has to deal with concentrated solutions.

Actually, the technique has been so improved that for comparisons it is more precise than any of the direct methods of measuring the chemical potential, or activity, of the solvent in binary or more complex solutions, although the absolute value obtained do of course depend on at least one such direct measurement.

4. 1. 2 Isoiestic ratio

Consider two solutions, A and B, initially at the same temperature, the vapour pressure of A being initially greater than that of B. If perfect thermal contact is maintained between both solutions the distillation of solvent will continue until the vapour pressures of the solutions are the same, as has been previously mentioned. The concentrations of solutions in isopiestic equilibrium are related by an isopiestic ratio, R, which may be defined as

$$R = \frac{\nu_A m_A}{\nu_B m_B} \quad (4.1)$$

where

m_A is the molality of electrolyte A in the solution of A,

m_B is the molality of electrolyte B in the other solution, which contains B,

ν_A, ν_B are the numbers of moles of ions formed from one mole of A or B, respectively.

For example, if the electrolyte A (the reference electrolyte) is of 1:1 type and the electrolyte B is of 2:1 type, then

$$R = (2/3) (m_A/m_B) \quad (4.2)$$

The condition of equal vapour pressures gives

$$v_A m_A \phi_A = v_B m_B \phi_B \quad (4.3)$$

and thus, introducing the isopiestic ratio,

$$\phi_B = R \phi_A \quad (4.4)$$

This enables the osmotic coefficient of B to be calculated.

Thus, the isopiestic ratio, R, is the immediate result of an isopiestic measurement and such information is readily transformed into the osmotic coefficient.

For a ternary system formed by the solutes A and B, eqn (4.2) and (4.3) transform into

$$R = \frac{v_R m_R}{(v_A m_A + v_B m_B)} \quad (4.5)$$

and

$$\phi = v_R m_R \phi_R (v_A m_A + v_B m_B) \quad (4.6)$$

where the subscript R stands for the reference solution.

4. 1. 3 Equipment

The apparatus employed in this work was, with some small modifications, that described by Mallinson(86). The equipment is composed of the following parts:

- 1) Thermostat bath
- 2) Desiccator (as container only)
- 3) Thermal buffer
- 4) Dishes and lids

The thermostat bath, shown in fig 4.1, was a 18" x 14" x 14" plastic container, surrounded by 4" of polystyrene foam and enclosed in a wooden case. In this latter was also located the relay, R, and the stirrer system which consisted of a motor, M, linked to three pulleys, P, two of them inclined at 10° to the horizontal.

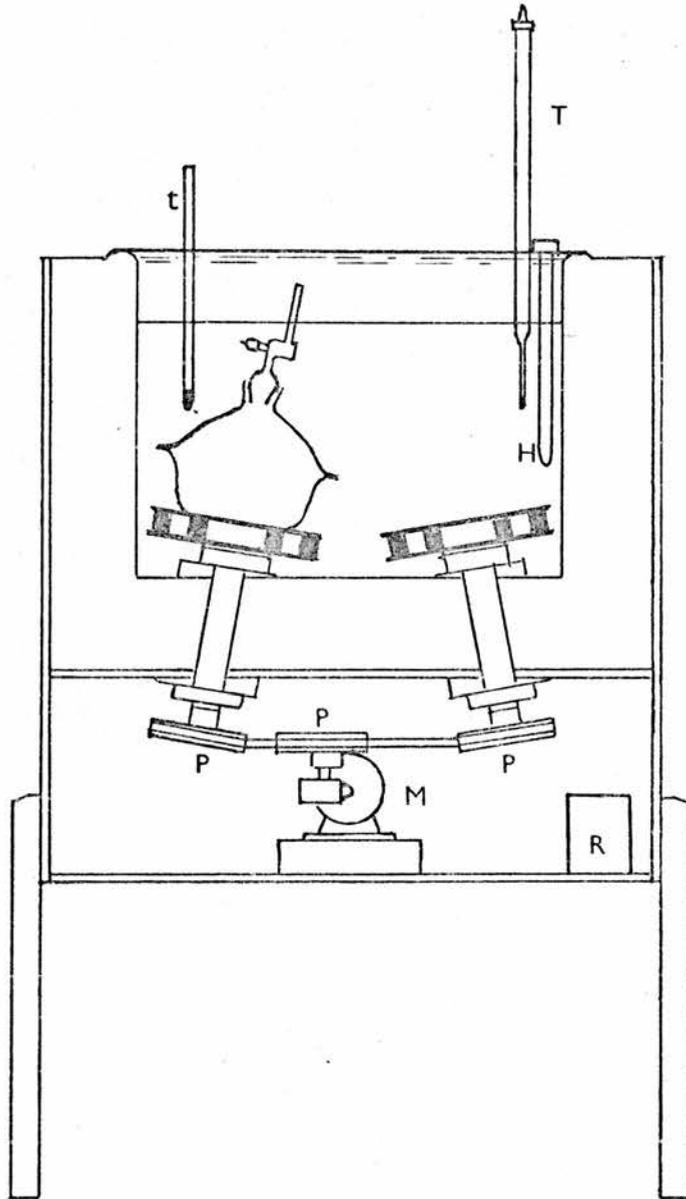


Fig. 4.1 The thermostat bath

The drive shaft of each of these two pulleys passed within a tube (carrying a ball-race and a water seal) through the base of the thermostat bath, and was fixed to a plate supporting a desiccator within the thermostat. Each plate was 7" in diameter, and contained a central recess of 5" diameter, shaped to fit the desiccator base. The drive shaft and water seal are shown in fig 4.2. Each plate was fitted with cavities round the edges to agitate the water in the bath. The bath contained an ordinary thermometer, *t*, which measured the temperature to 0.01°C, and a heating element ("Vitreosil" Electric immersion heater, 500 Watts) linked via the relay device (Ether control relay) to a contact thermometer, *T*.

The desiccator (fig. 4.3) was a 6" Dry Seal type (Jencon's Ltd), fitted with a rubber O-ring seal. The upper fitting *H* carried a right-angle "Rotaflo" tap, *B*, type TF6/13 (Quickfit), with an outlet through which the desiccator was evacuated. A Quickfit-Quartz screw-thread seal, *Q*, at the top of desiccator was used as seal to prevent water from entering the desiccator during the experiments.

The thermal buffer, (fig 4.3, *C*), was a massive stainless steel block, 5" in diameter and 1" deep, containing eight recesses, *D*, 1" in diameter and $\frac{3}{8}$ " deep, symmetrically machined around the block and a central hole, *E*. Through the centre of each recess was a $\frac{3}{32}$ " diameter hole. The thermal buffer was made to rest on the constriction at the base of the desiccator, forming a line contact with the glass.

The stainless steel dishes, 1" in diameter and $\frac{3}{4}$ " deep, have an average weight of approximately 10g and were made to fit tightly into the recesses of the thermal buffer. The stainless steel lids

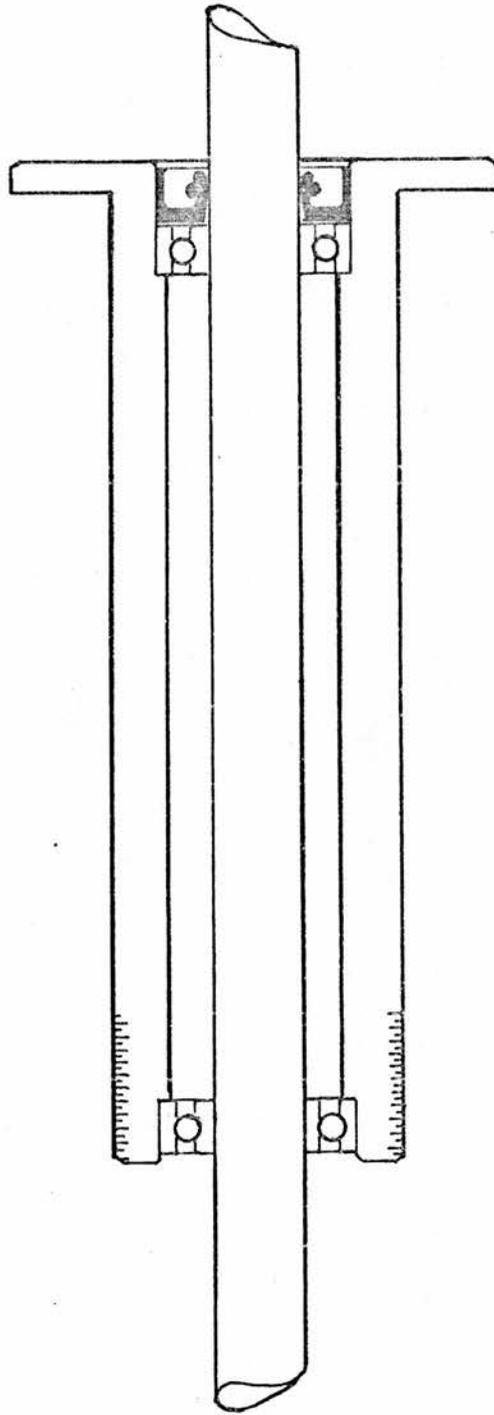


Fig. 4.2 The drive shaft and water seal

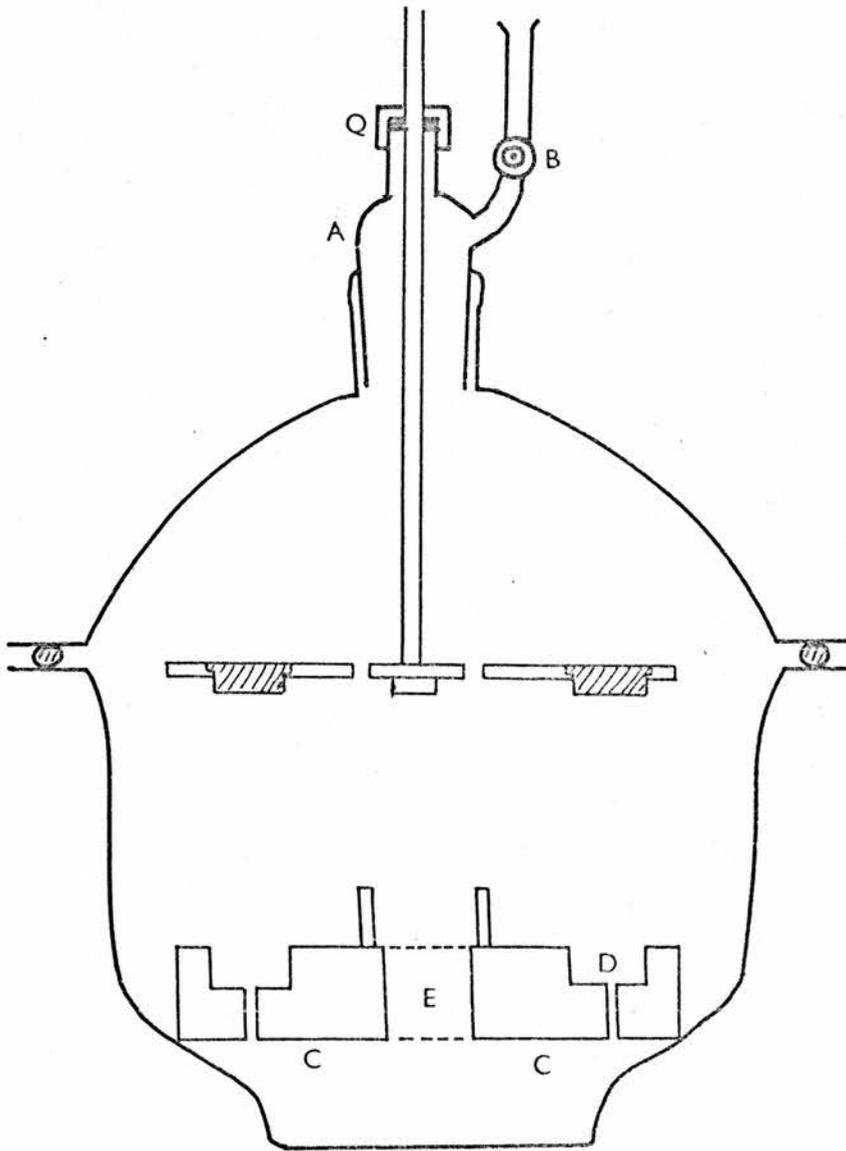


Fig. 4.3 The desiccator

of the dishes rest in holes in a perspex disc which fits over the dishes. The perspex disc has a stainless steel rod in its centre, which passes through the screwthread seal, Q, of the desiccator and allows the lids to be raised away from the dishes during vapour equilibration.

4. 1. 4 Materials

The following reagent-grade chemical salts were used:

NaCl A.R. Fisons

CaCl₂.6H₂O A.R. Hopkin and Williams

MgCl₂.6H₂O A.R. Hopkin and Williams

All the salts were kept in desiccators over their own dry salts, which were previously partially dehydrated for 48 hours at 150 °C in the case of the calcium and magnesium salts.

Stock solutions were prepared by weighing the salts and the distilled water added to make a known volume of solution. The concentrations of the stock solutions were checked by the volumetric Mohr's method for Cl⁻ and also by isopiestic measurement of the solutions at 25 °C, taking sodium chloride as standard. The ternary system NaCl-CaCl₂-H₂O at 25 °C was also checked by the isopiestic method and in all cases satisfactory agreement was obtained with the values reported for isopiestic measurements of these systems. The salts were therefore used without further purification.

The stock solutions were mixed in suitable proportions by weight to give a series of mixed solutions of known concentrations.

4. 1. 5 Procedure

The experimental procedure used for the isopiestic measurements was as follows:

Eight stainless steel dishes were weighed dry and empty and, after adding the solutions under investigation, reweighed. They were handled using a specially designed pair of tweezers to enable accurate weighings.

Two of these dishes contained the reference solution (one of the components of the mixture) and the remaining six contained: two duplicate mixtures in different proportions but with approximately the same molality of the reference solution, and two dishes with the binary solution of the other component. The amount of each sample was approximately 2 grams. If a solution needed to be diluted, the water was added after the samples had been weighed and as quickly as possible. Usually it was necessary to add freshly-boiled water to avoid the "sputtering" of the solution on commencing the evacuation.

The mixed solutions used were prepared, as was previously mentioned, by weighing the amounts of stock solutions necessary to obtain mixtures of a known molality, approximately the same as the reference solution; from them, the necessary amount for weighing in the dishes, was taken. This was done to secure the same initial molality in the duplicates.

The thermal buffer with the dishes was then placed in the desiccator by means of the steel support rod. The lid of the desiccator was firmly fitted and the perspex disc (containing the lids of the dishes) lifted from the dishes. The desiccator was then gradually evacuated for approximately one hour; a buffer flask was also connected between the desiccator and the water pump, to help in avoiding loss of solution due to "sputtering." After

this, the desiccator was submerged in the thermostat bath and secured in the rotating plate. Then, the stirrer motor was switched on.

After approximately 10 days, the desiccator was removed from the bath and the perspex disc was lowered to seal the dishes. Having removed the thermal block with the dishes out of the desiccator, they were weighed and the concentrations of the solutions, from the loss or gain of water in each solution, calculated. When the agreement between the molalities of the duplicate dishes was within $0.001 \text{ mol kg}^{-1}$ it was considered that the equilibrium had been reached. The time of equilibration at 45°C apart from a few exceptions, was between 10 and 12 days, even for more concentrated solutions, which was surprisingly longer than the time reported for the same systems at 25°C .

The next run was done with the same solutions by adding water to dilute them, or by evacuating the desiccator for about 4 hours to concentrate them. As Mallinson (36) reported, the process could be repeated as many times as possible without altering the agreement between duplicate dishes.

The dishes did not suffer corrosion except with concentrated solutions containing mixtures of calcium- and magnesium-chloride. Also the period necessary to reach equilibrium, in these mixtures, was longer than in the system sodium chloride - calcium chloride.

All weighings were made on a "Sartorius" (2602) balance and were corrected for buoyancy effects.

4.1.6 Experimental results

The systems $\text{NaCl}-\text{CaCl}_2-\text{H}_2\text{O}$ and $\text{CaCl}_2-\text{MgCl}_2-\text{H}_2\text{O}$ have been studied by the isopiestic technique at 45°C .

4.1.6.1 The System $\text{NaCl}-\text{CaCl}_2-\text{H}_2\text{O}$ at 45°C

The experimental data for this system are given in table 4.1. The second column gives the molality, M_A , (moles per kilogram of solvent) of a solution containing only sodium chloride, i.e., the molality of the reference solution from which the isopiestic data are calculated. The next two columns give the molalities of sodium chloride, m_A and of calcium chloride, m_B , respectively, in a solution containing both these salts and in isopiestic equilibrium with the sodium chloride solution of molality M_A .

Table 4.2 gives the results calculated immediately from these data. The second column gives again the molality of the reference solution. The third column gives the total molality, m , of the mixed solutions in isopiestic equilibrium with the reference solution of molality M_A . The total molality, m , is defined, according to eqn (3.22), as $m = k_A m_A + k_B m_B$. Here $k_A = 1$ and $k_B = 1.5$ and these were chosen in this form to allow the values of the isopiestic ratio to be approximately one. The fourth column gives values of the ionic fraction, y_B , of calcium chloride in the mixed solution, defined as $y_B = 1.5 m_B / m$. The fifth and sixth columns give the observed isopiestic ratio, $R = M_A / m$, and the calculated isopiestic ratio, respectively. The calculated R was obtained by fitting the data

to eqn.(3.43), i.e.

$$R = 1 - ax_B - bx_B^2$$

by the method of least squares.

In the seventh column are reported the values of ϕ_m , the osmotic coefficient of the mixtures, calculated directly from eqn.(4.6).

Plots of some of these isopiestic ratios against the ionic fraction of calcium chloride are shown in Fig.4.4.

TABLE 4.1

Isopiestic data for the system

NaCl-CaCl₂-H₂O at 45°C

Set	$N_A/\text{mol kg}^{-1}$	$n_A/\text{mol kg}^{-1}$	$n_B/\text{mol kg}^{-1}$
1	0.5213	0.4109	0.07825
		0.2149	0.2112
		0.	0.3600
2	0.5417	0.4267	0.0813
		0.2229	0.2191
		0.	0.3735
3	0.5758	0.4523	0.08614
		0.2360	0.2319
		0.	0.3958
4	0.7369	0.5705	0.1102
		0.2984	0.2933
		0.	0.4972
5	1.2491	0.9436	0.1989
		0.4353	0.5205
		0.	0.7916
6	1.6673	1.2403	0.2616
		0.5653	0.6761
		0.	1.0232
7	2.0381	1.5043	0.3172
		0.6771	0.8098
		0.	1.2131
8	2.5054	1.8979	0.3981
		0.8357	0.9994
		0.	1.4784

Table 4.1 continued

Set	$n_A/\text{mol kg}^{-1}$	$n_A/\text{mol kg}^{-1}$	$m_B/\text{mol kg}^{-1}$
9	2.6154	1.9097	0.4027
		0.8447	1.0102
		0.	1.4933
10	2.8671	1.9246	0.5237
		0.9147	1.0923
		0.	1.6089
11	2.8839	1.9358	0.5317
		0.9195	1.0330
		0.	1.6168
12	3.3990	2.4467	0.5159
		1.0610	1.2688
		0.	1.8492
13	3.5804	2.5705	0.5420
		1.1102	1.3277
		0.	1.9300
14	4.2170	2.7624	0.7588
		1.2877	1.5373
		0.	2.2112
15	5.3194	3.7310	0.7867
		1.5600	1.8057
		0.	2.6499
16	5.6648	3.9574	0.8345
		1.6474	1.9701
		0.	2.7865

Table 4.1 continued

Set	$M_A/\text{mol kg}^{-1}$	$n_A/\text{mol kg}^{-1}$	$n_B/\text{mol kg}^{-1}$
17	5.6860	3.9707	0.8373
		1.6506	1.9739
		0.	2.7928
18	5.7594	4.0208	0.8478
		1.6693	1.9963
		0.	2.8209
19	5.8509	4.0804	0.8604
		1.6917	2.0231
		0.	2.8563
20	5.9597	4.1531	0.8757
		1.7183	2.0549
		0.	2.8990
21	6.0483	4.2087	0.8875
		1.7411	2.0821
		0.	2.9340
22	6.1127	4.2509	0.8964
		1.7568	2.1010
		0.	2.9579
23	6.1753	4.2920	0.9050
		1.7707	2.1173
		0.	2.9822
24	6.24	4.3366	0.9144
		1.7875	2.1374
		0.	3.0057

TABLE 4.2

Results calculated directly from isopiestic measurements

for the system $\text{NaCl}-\text{CaCl}_2 - \text{H}_2\text{O}$ at 45°C

Set	$M_A/\text{mol kg}^{-1}$	$m/\text{mol kg}^{-1}$	y_B	$R_{(\text{obs})}$	$R_{(\text{Calc})}$	ϕ_m
1	0.5213	0.5283	0.2222	0.9868	0.9908	0.910
		0.5317	0.5958	0.9804	0.9775	0.904
2	0.5417	0.5400	1.0000	0.9654	0.9662	0.890
		0.5487	0.2223	0.9873	0.9916	0.911
		0.5516	0.5959	0.9821	0.9790	0.907
3	0.5758	0.5603	1.0000	0.9669	0.9678	0.892
		0.5815	0.2222	0.9902	0.9941	0.915
		0.5859	0.5958	0.9862	0.9834	0.911
4	0.7369	0.5937	1.0000	0.9699	0.9707	0.896
		0.7438	0.2222	0.9907	0.9973	0.920
		0.7384	0.5959	0.9980	0.9932	0.927
		0.7458	1.0000	0.9881	0.9895	0.918
5	1.2491	1.2420	0.2402	1.0058	1.0068	0.956
		1.2161	0.6420	1.0272	1.0264	0.977
		1.1874	1.0000	1.0520	1.0523	1.000
		1.6327	0.2403	1.0212	1.0210	0.994
6	1.6673	1.5795	0.6421	1.0556	1.0557	1.027
		1.5549	1.0000	1.0863	1.0863	1.057
		1.9801	0.2403	1.0293	1.0291	1.024
7	2.0381	1.8918	0.6421	1.0773	1.0774	1.072
		1.8197	1.0000	1.1201	1.1200	1.114
		2.4851	0.2403	1.0404	1.0404	1.071
8	2.5854	2.3348	0.6421	1.1073	1.1073	1.139
		2.2176	1.0000	1.1659	1.1659	1.200

Table 4.2 Continued

Set	$M_A/\text{mol kg}^{-1}$	$m/\text{mol kg}^{-1}$	y_B	$R(\text{obs})$	$R(\text{Calc})$	ϕ_m
9	2.6154	2.5133	0.2403	1.0404	1.0406	1.073
		2.3600	0.6421	1.1082	1.1080	1.143
10	2.8671	2.2400	1.0000	1.1676	1.1677	1.204
		2.7177	0.2918	1.0550	1.0560	1.106
		2.5532	0.6417	1.1230	1.1221	1.177
11	2.8939	2.4134	1.0000	1.1380	1.1383	1.245
		2.7334	0.2918	1.0551	1.0613	1.107
		2.5440	0.6336	1.1336	1.1281	1.189
12	3.3990	2.4252	1.0000	1.1391	1.1908	1.247
		3.2206	0.2403	1.0554	1.0556	1.144
		2.9642	0.6421	1.1467	1.1465	1.243
13	3.5804	2.7733	1.0000	1.2254	1.2255	1.328
		3.3035	0.2403	1.0582	1.0585	1.161
		3.1018	0.6421	1.1543	1.1541	1.266
14	4.2170	2.8950	1.0000	1.2368	1.2369	1.357
		3.9006	0.2918	1.0311	1.0796	1.235
		3.5944	0.6417	1.1732	1.1745	1.340
15	5.3194	3.3168	1.0000	1.2714	1.2710	1.452
		4.9111	0.2403	1.0331	1.0336	1.320
		4.3586	0.6421	1.2205	1.2201	1.488
16	5.6648	3.9749	1.0000	1.3383	1.3384	1.631
		5.2032	0.2403	1.0875	1.0875	1.351
		4.6026	0.6421	1.2308	1.2303	1.529
		4.1798	1.0000	1.3553	1.3553	1.683

Table 4.2 Continued

Set	$M_A / \text{mol kg}^{-1}$	$m / \text{mol kg}^{-1}$	γ_B	$R_{(\text{obs})}$	$R_{(\text{calc})}$	ϕ_m
17	5.6860	5.2267	0.2403	1.0879	1.0384	1.353
		4.6115	0.6421	1.2330	1.2326	1.534
18	5.7594	4.1892	1.0000	1.3573	1.3574	1.688
		5.2925	0.2403	1.0382	1.0388	1.358
		4.6638	0.6421	1.2349	1.2344	1.541
19	5.8509	4.2314	1.0000	1.3611	1.3613	1.699
		5.3710	0.2403	1.0894	1.0900	1.366
		4.7264	0.6421	1.2379	1.2375	1.552
20	5.9597	4.2845	1.0000	1.3656	1.3657	1.712
		5.4667	0.2403	1.0902	1.0911	1.375
		4.6007	0.6421	1.2414	1.2406	1.565
		4.3485	1.0000	1.3705	1.3708	1.728
21	6.0483	5.5400	0.2403	1.0910	1.0921	1.383
		4.8643	0.6421	1.2434	1.2431	1.575
		4.4010	1.0000	1.3743	1.3744	1.741
22	6.1127	5.5955	0.2403	1.0924	1.0928	1.388
		4.9033	0.6421	1.2454	1.2451	1.583
		4.4369	1.0000	1.3777	1.3778	1.751
23	6.1753	5.6495	0.2403	1.0931	1.0940	1.394
		4.9467	0.6420	1.2484	1.2477	1.592
		4.4733	1.0000	1.3805	1.3808	1.760
24	6.24	5.7082	0.2403	1.0932	1.0941	1.398
		4.9956	0.6420	1.2496	1.2499	1.598
		4.5006	1.0000	1.3840	1.3842	1.770

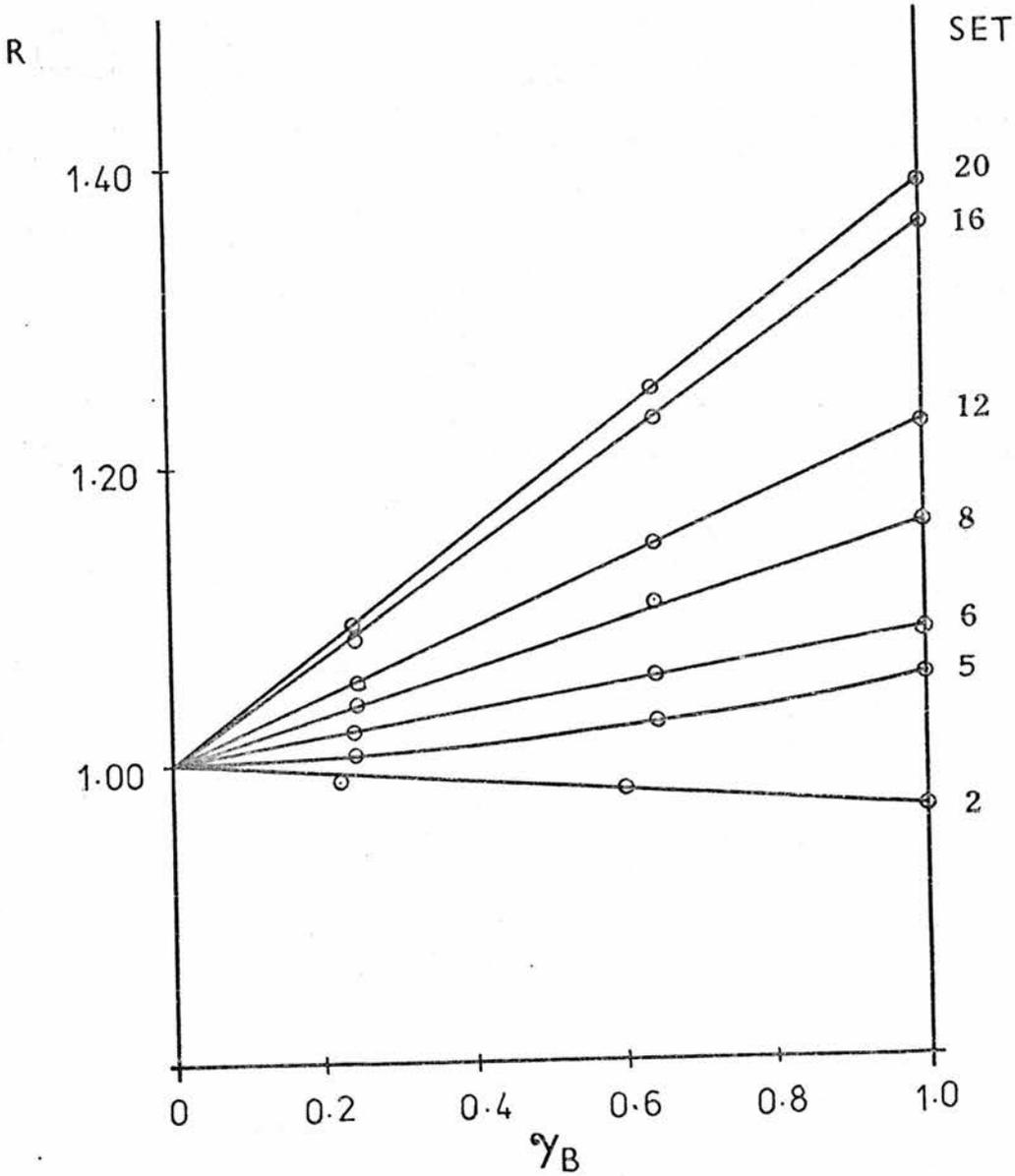


Fig. 4.4 Isopiestic ratio, $R = m_A / (m_A + 1.5 m_B)$, of sodium chloride-calcium chloride solutions against ionic fraction, $y_B = 1.5 m_B / (m_A + 1.5 m_B)$, of calcium chloride at 45°C

4.1.6.2 The System $\text{CaCl}_2\text{-MgCl}_2\text{-H}_2\text{O}$ at 45°C

The experimental isopiestic data for the ternary system $\text{CaCl}_2\text{-MgCl}_2\text{-H}_2\text{O}$ and some direct results are similarly given in tables 4.3 and 4.4. The definitions of the terms are now:

M_C the molality (moles per kilogram of solvent) of a solution containing only calcium chloride; is the molality of the reference solution,

m_C m_D are the molalities of calcium chloride and magnesium chloride, respectively, in a solution containing both these salts and in isopiestic equilibrium with the calcium chloride solution of molality M_C ,

$m = m_C + m_D$, is the total molality of the mixed solutions,

$Y_D = m_D/m$, is the ionic fraction of magnesium chloride in the mixture of calcium chloride and magnesium chloride,

$R = M_C/m$ is the isopiestic ratio.

Plots of some isopiestic ratios against the ionic fraction of magnesium chloride are shown in Fig. 4.5.

4.2 Calorimetry

4.2.1 Introduction

Thermochemical methods determine as directly as possible the quantity of heat associated with an amount of a given reaction or process. The investigation consists essentially of a calorimetric part and a chemical part. The former involves determination of the quantity of energy evolved or absorbed by the reaction or process and the latter involves measurement of the amount of material involved in the change. The desired result is the ratio,

TABLE 4.3

Isoiestic data for the system

CaCl₂-HgCl₂-H₂O at 45°C

Set	$n_c/\text{mol kg}^{-1}$	$m_c/\text{mol kg}^{-1}$	$m_D/\text{mol kg}^{-1}$
1	0.5496	0.5763	0.1603
		0.1788	0.3490
		0.	0.5208
2	0.5537	0.3805	0.1620
		0.1810	0.3531
		0.	0.5241
3	0.5721	0.3944	0.1680
		0.1877	0.3664
		0.	0.5446
4	0.6092	0.4203	0.1790
		0.2001	0.3905
		0.	0.5801
5	0.6920	0.4768	0.2030
		0.2262	0.4415
		0.	0.6581
6	0.9416	0.6478	0.2759
		0.3051	0.5956
		0.	0.8839
7	1.3315	0.9197	0.3918
		0.4341	0.8474
		0.	1.2571
8	1.3485	0.9290	0.3958
		0.4370	0.8531
		0.	1.2707

Table 4.3 continued

Set	$n_c/\text{mol kg}^{-1}$	$m_c/\text{mol kg}^{-1}$	$m_D/\text{mol kg}^{-1}$
9	1.4306	0.9819	0.4177
		0.4609	0.8987
10	1.4592	0.	1.3270
		1.0029	0.4270
		0.4722	0.9216
11	1.4737	0.	1.3535
		1.0127	0.4312
		0.4768	0.9506
12	1.7787	0.	1.3871
		1.2296	0.5236
		0.5817	1.1553
13	1.7800	0.	1.6650
		1.2216	0.5201
		0.5730	1.1182
14	2.3965	0.	1.6634
		1.6391	0.6978
		0.7672	1.4972
15	3.2450	0.	2.2216
		2.2136	0.9424
		1.0307	2.0119
		0.	2.9807

TABLE 4.4

Results calculated directly from isopiestic measurements

for the system $\text{CaCl}_2\text{-MgCl}_2\text{-H}_2\text{O}$ at 45°C

Set	$H_c/\text{mol kg}^{-1}$	$m/\text{mol kg}^{-1}$	y_D	$R(\text{obs})$	$R(\text{Calc})$	ϕ_{in}
1	0.5496	0.5366	0.2937	1.0242	1.0226	0.959
2	0.5537	0.5273	0.6512	1.0413	1.0428	0.975
3	0.5721	0.5203	1.0000	1.0553	1.0548	0.983
4	0.6092	0.5425	0.2936	1.0206	1.0184	0.952
5	0.6920	0.5341	0.6611	1.0367	1.0367	0.967
6	0.9416	0.5241	1.0000	1.0565	1.0558	0.986
7	1.3315	0.5624	0.2937	1.0263	1.0230	0.963
8	1.3495	0.5541	0.6613	1.0417	1.0448	0.977
		0.5446	1.0000	1.0599	1.0589	0.994
		0.5935	0.2937	1.0165	1.0149	0.964
		0.5906	0.6612	1.0315	1.0330	0.978
		0.5801	1.0000	1.0502	1.0497	0.996
		0.6793	0.2936	1.0179	1.0177	0.986
		0.6677	0.6612	1.0364	1.0366	1.004
		0.6581	1.0000	1.0515	1.0514	1.019
		0.9257	0.2937	1.0194	1.0205	1.056
		0.9007	0.6613	1.0454	1.0444	1.083
		0.8839	1.0000	1.0553	1.0657	1.104
		1.3115	0.2987	1.0152	1.0164	1.171
		1.2815	0.6613	1.0390	1.0379	1.193
		1.2571	1.0000	1.0592	1.0596	1.221
		1.3248	0.2983	1.0186	1.0209	1.181
		1.2901	0.6613	1.0460	1.0458	1.212
		1.2707	1.0000	1.0520	1.0627	1.231

Table Continued

Set	$M_c / \text{mol kg}^{-1}$	$m / \text{mol kg}^{-1}$	γ_D	$R(\text{obs})$	$R(\text{Calc})$	ϕ_m
9	1.4306	1.3996	0.2984	1.0221	1.0230	1.211
		1.3596	0.6610	1.0522	1.0514	1.247
		1.3270	1.0000	1.0781	1.0784	1.277
10	1.4592	1.4299	0.2986	1.0205	1.0197	1.218
		1.3938	0.6612	1.0469	1.0477	1.250
		1.3555	1.0000	1.0781	1.0778	1.287
11	1.4737	1.4439	0.2986	1.0206	1.0224	1.224
		1.4074	0.6612	1.0471	1.0454	1.255
		1.3871	1.0000	1.0524	1.0630	1.274
12	1.7787	1.7532	0.2987	1.0145	1.0131	1.321
		1.7170	0.6612	1.0359	1.0372	1.349
		1.6650	1.0000	1.0683	1.0679	1.391
13	1.7800	1.7417	0.2986	1.0220	1.0244	1.331
		1.6912	0.6612	1.0525	1.0503	1.370
		1.6634	1.0000	1.0701	1.0709	1.393
14	2.3965	2.3969	0.2986	1.0255	1.0274	1.569
		2.2644	0.6612	1.0583	1.0565	1.619
		2.2216	1.0000	1.0787	1.0793	1.650
15	3.2450	3.1560	0.2986	1.0282	1.0310	1.925
		3.0426	0.6612	1.0665	1.0638	1.996
		2.9807	1.0000	1.0837	1.0896	2.038

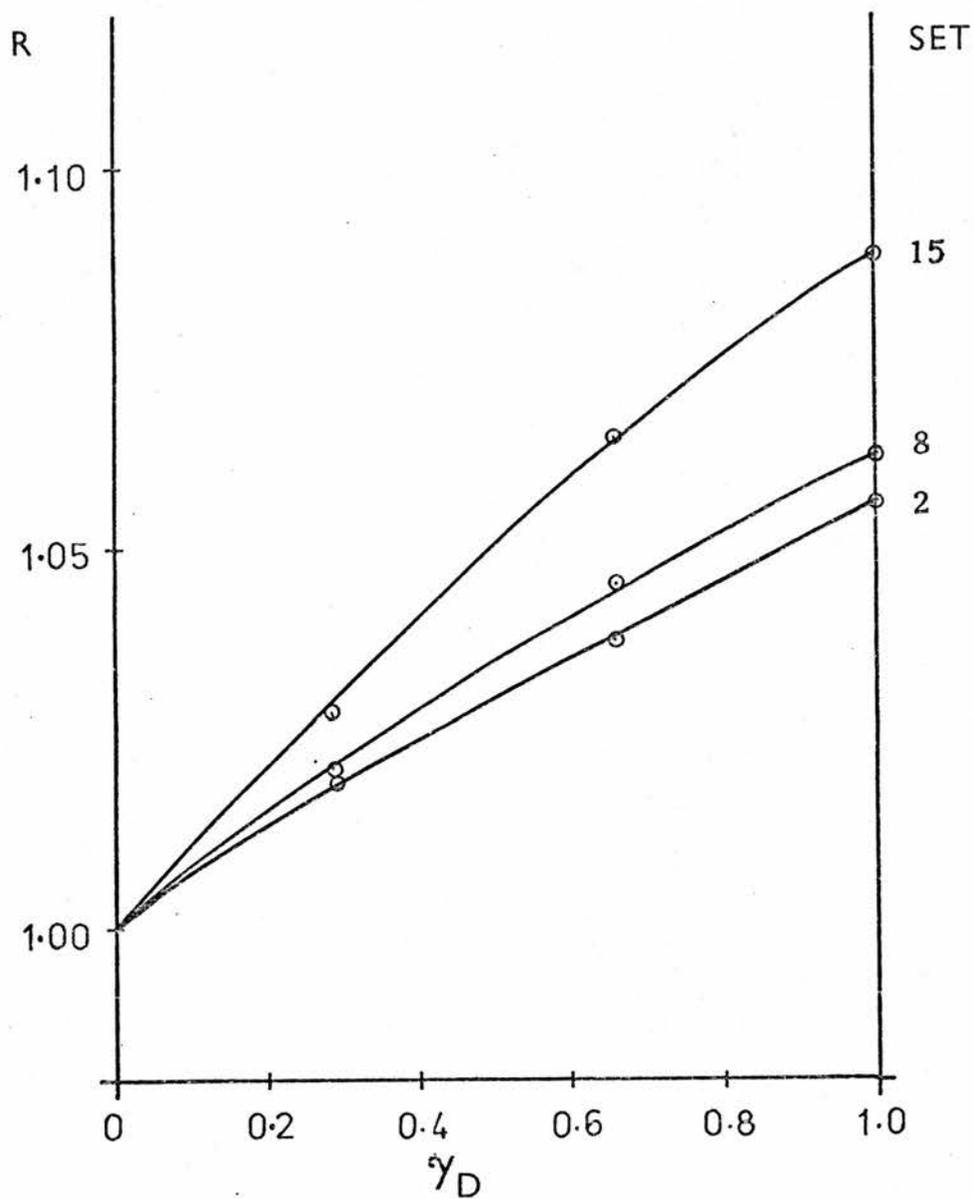


Fig. 4.5 Isopiestic ratio, $R = M_C / (m_C + m_D)$, against ionic fraction, $y_D = m_D / (m_C + m_D)$, of magnesium chloride for the system $\text{CaCl}-\text{MgCl}_2-\text{H}_2\text{O}$ at 45°C .

in appropriate units, of the quantity of energy to the amount of the given reaction or process.

The modern calorimetric method consists principally in measuring the amount of electrical energy necessary to duplicate (exothermic process) or nullify (endothermic process) the thermal effect accompanying a physical or chemical process; that is why it is convenient to express the data in units of electrical energy.

For a process that is exothermal, the heat evolved by a measured amount of the given chemical reaction or process is used to take the calorimeter system from its initial state I and temperature, T_i , to its final state F and temperature, T_f . With another kind of experiment, with the same calorimeter system at the same initial state, the heat evolved by a measured amount of electrical energy is used to take the calorimeter system from the same initial state I and temperature, T_i to the same final state F and temperature, T_f . In this way a direct equivalence between the measured amount of chemical reaction and the measured amount of electrical energy is obtained.

In practice it is difficult to obtain exactly the same rise of temperature in all experiments but with the fixed calorimeter system described, the amount of electrical or chemical energy added to the calorimeter can be so regulated that the differences in the rise of temperature in the various experiments will be less than a few per cent of the total rise.

If the process is an endothermal one, that is, one that absorbs heat energy as it takes place, then a measured quantity of electrical energy is added to the calorimeter system in an amount just sufficient to maintain the temperature constant,

balancing the energy absorbed by the reaction or process as it proceeds. The initial and final states of the calorimeter system are the same and the calorimeter neither absorbs nor gives up energy. Now, a direct equivalence (except for sign) is obtained between the measured amount of electrical energy and the measured amount of the given reaction or process.

In the chemical part of the thermochemical investigation, it is necessary first to secure that the process occurring is the specified one, and second, to measure with the necessary accuracy the amount of the given reaction or process that occurs in each experiment. Because of the numerous types of chemical processes, a wide variety of calorimeters have been designed.

In general, calorimeters may be classified according to whether they are isothermal or non-isothermal. The most used have been of the non-isothermal type, in which the heat quantities are estimated by the temperature changes they produce. Non-isothermal calorimeters are operated either under adiabatic conditions, or with constant-temperature environment.

The basis of the adiabatic method is the maintenance of zero thermal head throughout the experiment to eliminate heat exchange between the calorimeter and its environment. The observation of the smooth calorimeter-temperature-time curve, which is needed for the evaluation of the heat-leakage correction in the ordinary methods, is replaced in the adiabatic method by a manual or automatic adjustment of the jacket temperature.

In the constant-temperature environment method, the calorimeter is completely enclosed by a jacket of uniform temperature, and this defines the thermal head between the calorimeter and its

surroundings. The jacket may be an ordinary water thermostat or one containing a liquid, such as an electrolyte of low thermal conductivity (for ordinary temperature), or a relatively massive metal shield (which serves for low or high temperatures).

The calorimeter and its surroundings should be at uniform and measurable temperatures, so that heat losses can accurately be evaluated and corrected for. The heat exchange between the calorimeter and its surrounding jacket has several causes: for example, those which depend chiefly on the temperature difference between the calorimeter and the jacket (thermal head) such as conduction by solid connections between them, convection and conduction by gases, radiation. The thermal leakage from the calorimeter may in part also be due to evaporation from the calorimeter.

Thermal leakage through solid connections, such as supports and electrical connections should be made very small compared with that due to other causes. Evaporation should be eliminated as completely as possible. If the thermal head does not exceed a few degrees (and in the experiments described here it is much less than this, never exceeding 0.5 K), heat exchange due to radiation and gas conduction follows Newton's law. Then, if T is the calorimeter temperature at the time t and T_j is the jacket temperature

$$\frac{dT}{dt} = K (T_j - T)$$

where K is the leakage modulus of the system.

The radiation contribution to the leakage modulus is minimized by having the outside surface of the calorimeter and the

inside surface of the jacket highly polished. The conduction contribution may be decreased by evacuating the space between the calorimeter and jacket or by using a vacuum jacketed glass container as the calorimeter itself, but in the present work the space between the submerged calorimeter itself and the thermostat was not evacuated and simply acted as an air jacket.

4. 2. 2 Equipment

The apparatus employed in this work was slightly modified from that described by Jones and Williams (87).

The calorimeter used, fig. 4.6, is based upon the constant environment type and consisted of an inner reaction vessel and an outer shielding vessel of copper. The system was suspended in a thermostat bath controlled to $\pm 0.0005^\circ$ (LKB 7602 controller on 7603 bath). The inner or reaction vessel was a very thin plastic drinking cup which gave better results than the thick glass beaker employed in preliminary work. It was attached to a lid by two rubber bands. This lid was suspended from a top plate by chimneys. A large threaded ring and six clamping screws secured the top plate to the outer vessel via an O-ring seal, O. All surfaces of the outer vessel were coated with shiny nickel.

The chimneys allowed admission of the following probes:

Calibration heater, A	Burette tip, D
Heat detector, B	Pipette (occasionally), E
Stirrer (and cooler), C	

The electrical calibration heater was made of 5 cm of resistance wire (22.38Ω), looped twice and attached to leads which are threaded up a 1.5 mm diameter quartz tube. The wires were insulated by two coats of Araldite resin. The voltage across

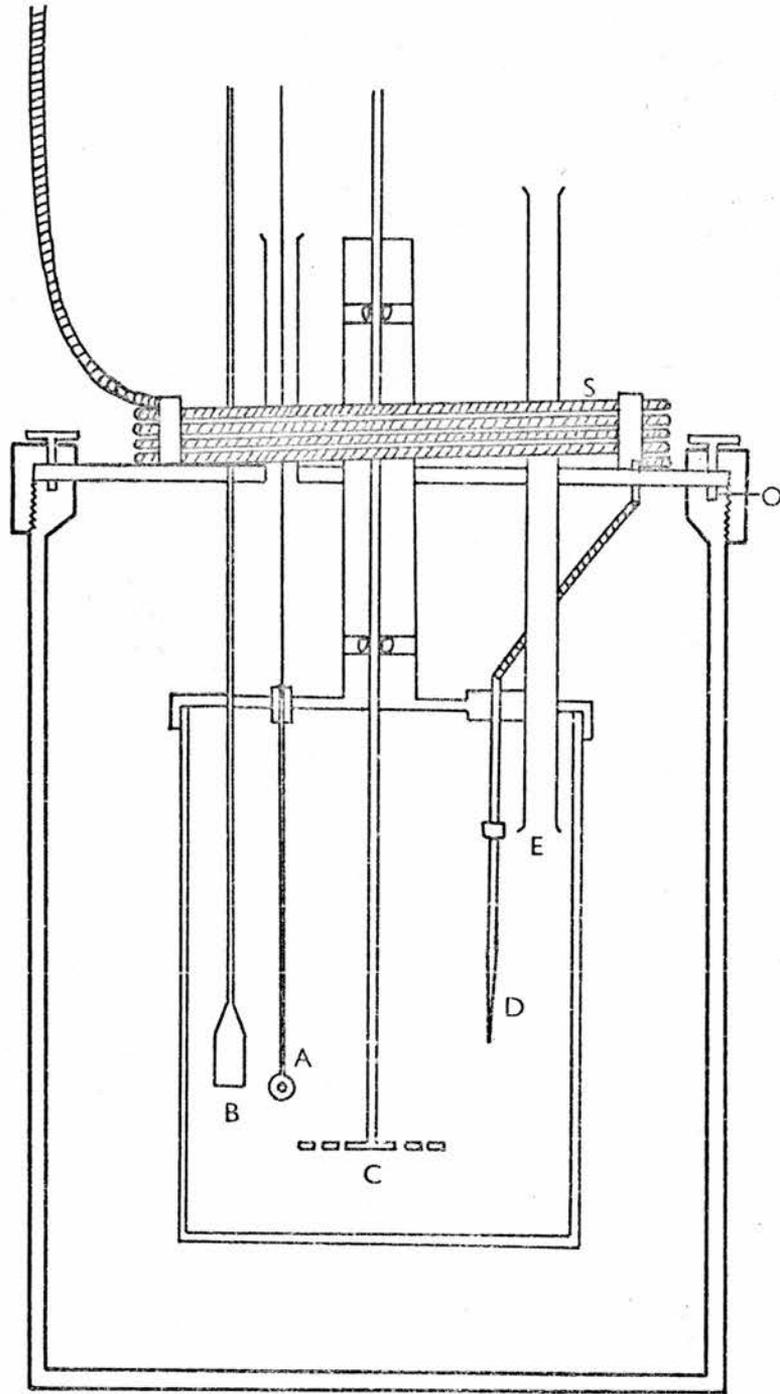


Fig. 4.6 The Calorimeter

the heater was measured on a digital voltmeter (Solartron IM 1420.2). The current passing through the heater also passed through a 10000 Ω standard resistance; the voltage across this standard was measured to give the current in the heater. The time for which the heating current flowed was automatically recorded on a 0.02s stopwatch (Jaquet 309e).

The temperature change was measured with a Hewlett-Packard 2801A quartz thermometer to 0.0001 $^{\circ}$ at 18s intervals, and printed out on a Hewlett-Packard printer 562A.

To agitate the solution a vibro-stirrer was used since it had smaller heat of stirring corrections than a paddle stirrer. The stirrer disc, a flat circular plate of 2.5 cm diameter and 1 mm thick polytetrafluoroethylene containing 10 holes of 1 mm diameter, was screwed onto a hollow stainless steel tube. The tube was connected indirectly to a vibro-motor (Chemap AP, EI) via a see-saw. The tube was also the means of introducing a stainless steel rod, supercooled in liquid nitrogen to adjust the temperature of the reaction vessel if necessary.

The solvent was added to the solution from a 10 ml piston burette (Metrohm AG, B274) through a thin glass burette tip. The solvent was prewarmed in a spiral nylon tube, S, (Portex SFD Nylon C, 10 ml capacity) on top of the vessel, immersed beneath the water level in the thermostat.

Chimney E allowed introduction of a pipette to remove solution after five or six additions of solvent.

4.2.3 Materials

Reagents of the same quality as in the isopiestic experiments were used in the calorimetric measurements. The stock solutions

were also prepared as described in section 4.1.4.

To prepare the mixed solutions, a known volume of stock solutions was weighed.

4.2.4 Procedure

The calorimeter and solutions were maintained at 20 °C in the thermostatted calorimeter room. The reaction vessel was charged with 100 ml of solution prepared by weight from the stock solutions. The assembled system was immersed in the thermostat overnight without stirring, to equilibrate at 25 °C. The vibro-stirrer was then switched on and after 30 min the experiments were started. These consisted of electrical heater calibrations and solvent additions, alternately.

During all the partial molar enthalpy measurements described here, only addition of the solvent, water, was made. The experiments were carried out in the following manner: an approximately 10 min "fore" period, a calibration heating, a 10 min "aft" period, addition of a known volume of solvent, a 10 min period, a calibration heating, et until 20 or 30 ml of water had been added. The "aft" period of one experiment was the "fore" period of the next except when the system temperature differed markedly from its equilibrium value, when adjustments were made with the cold stainless steel rod or the heater.

The amount of solvent added varied from 0.1 to 5 ml, depending on the changes of temperature expected. The complete experiment was finished when the reaction vessel contained 130 ml of solution. Then some solution was taken out, e.g. 50 ml, and distilled water, e.g. 20 ml, added to make 100 ml of a new initial solution. The solutions which were taken from the reaction vessel were weighed, and the amount of water added was measured in the

piston burette; its weight was calculated from the density of water at 25°C. In this way, the concentration of the new initial solution was exactly known.

The experiment always began with solution of approximately 6 mol kg⁻¹ (total "molality as defined in chapter 3)

4. 2. 5 Treatment of experimental data

The temperature readings for any experiment were plotted against time and an approximate T was obtained (an example is shown in fig 4.7). The corrected values were obtained by squares method by computer programme (Appendix 1) using the method described by Coops, Jessup, and Van Ness(88) which can be summarized as follows:

Observation of temperature and time is divided into three periods:

- (i) an initial period (ab in fig 4.7) in which the temperature change of the calorimeter is due entirely to heat transfer between calorimeter and surroundings (thermal leakage) and heat of stirring.
- (ii) a main period (bc in fig 4.7) in which the principal part of the temperature rise takes place as a result of the addition of electrical energy, or addition of solvent (also in this latter case there could be a temperature decrease).
- (iii) a final period (cd in fig 4.7) in which the temperature change of the calorimeter is again due entirely to thermal leakage and heat of stirring.

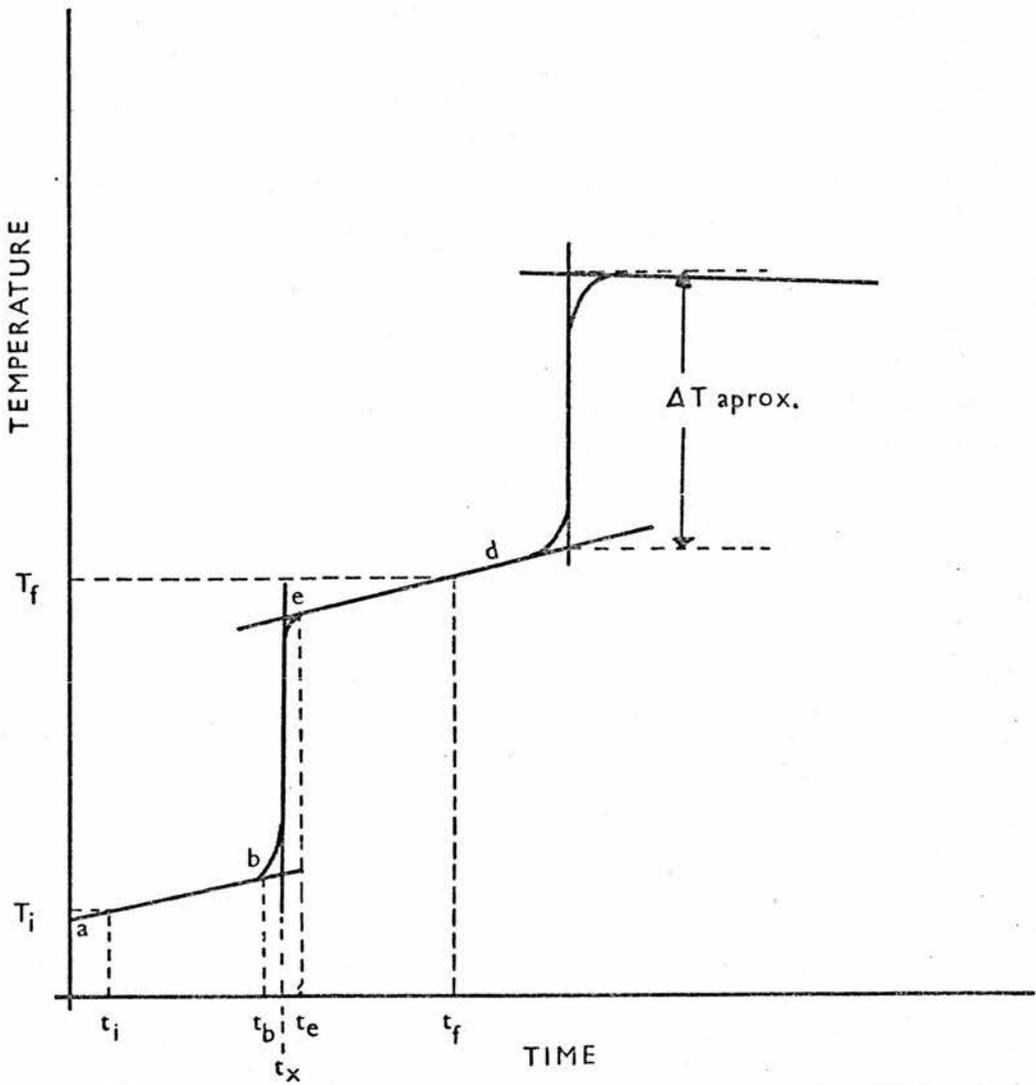


Fig. 4.7 Time-temperature curve for a calorimetric experiment

Let the temperature of the calorimeter at the beginning and end, respectively, of the main period be T_b and T_e . Then the observed temperature rise may be taken as

$$T_e - T_b \quad (4.7)$$

But this must be corrected for heat of stirring and thermal leakage. This correction is calculated from the observations of time and temperature, on the assumption that the rate of the temperature rise of the calorimeter due to heat of stirring is constant, and the rate of temperature rise due to thermal leakage is proportional to the difference between the temperatures of calorimeter and jacket (Newton's law of cooling).

The corrected temperature rise is given by

$$\Delta T_{\text{corr}} = T_{e_{\text{corr}}} - T_{b_{\text{corr}}} + \Delta \theta \quad (4.8)$$

where

$$T_{\text{corr}} = (1/n) \sum_{r=1}^n T_r \pm [(n-1)/2] g \quad (4.9)$$

with

T_r is the r th temperature reading of the initial or final period in a series of n observations at equally spaced times, and

$$g = 6 \frac{(n-1)(T_n - T_1) + (n-3)(T_{n-1} - T_2) + \dots}{n(n^2 - 1)} \quad (4.10)$$

represents the average change in temperature per interval for that period,

and

$$\Delta \theta = - [u + k (T_j - T)] (t_e - t_b) \quad (4.11)$$

or

$$\Delta \theta = - k (T_\infty - T_m) (t_e - t_b) \quad (4.12)$$

or

$$\Delta \theta = - [s_f + k (T_f - T_m)] (t_e - t_b) \quad (4.13)$$

In these expressions

u is the rate of the temperature rise of the calorimeter due to heat of stirring

k the cooling constant of the calorimeter

T_j the temperature of the jacket

T the temperature of the calorimeter

T_∞ is the temperature when $(dT/dt) = 0$

and

$$T_m = \left\{ \sum_{r=2}^{n-1} T_r + \frac{T_b + T_e}{2} \right\} \frac{1}{n-1} \quad (4.14)$$

is the average temperature.

The plus and minus sign in eqn (4.9) is used in calculating T_b from the data of the initial period and T_e from the data of the final period, respectively.

With the joules (=voltage x amperes x time) calculated and the values of ΔT , the calibrations of the apparatus for effective thermal capacity for each experiment between 100 and 130 ml, were carried out. This was also done by a least squares method included in the previous programme.

The temperature difference due to additions was also corrected for small differences between the temperatures of the water added and the solution.

4. 2. 6 Experimental results

The systems $\text{NaCl}-\text{CaCl}_2-\text{H}_2\text{O}$, $\text{CaCl}_2-\text{MgCl}_2-\text{H}_2\text{O}$, and $\text{NaCl}-\text{MgCl}_2-\text{H}_2\text{O}$ have been studied by the calorimetric method at 25°C .

4. 2. 6. 1 The system $\text{NaCl}-\text{CaCl}_2-\text{H}_2\text{O}$

The calorimetric data for the two binary systems are given in tables 4.5 and 4.6. The first column gives the molality of the solutions and the second column the corresponding partial molar enthalpy of water.

The data for the ternary systems are given in tables 4.7, 4.8, 4.9, 4.10, and 4.11. In these tables the first column gives the molality, m_A , of sodium chloride; the second column gives the molality, m_B , of calcium chloride; and the third column gives the partial molar enthalpy of water of the mixed solutions.

Plots of partial molar enthalpy of water against molality are shown in figs. 4.8, 4.9, and 4.10.

TABLE 4.5
 PARTIAL MOLAR ENTHALPY OF WATER, \mathcal{H}_3 , IN SODIUM
 CHLORIDE SOLUTIONS AT 25°C

m/mol kg ⁻¹	$\mathcal{H}_3/\text{Jmol}^{-1}$	m/mol kg ⁻¹	$\mathcal{H}_3/\text{Jmol}^{-1}$
5.5351	65.99	1.8992	39.52
5.2025	78.29	1.8148	37.06
4.9076	85.44	1.7376	35.07
4.6444	89.49	1.6666	32.67
4.4080	91.55	1.2625	21.27
4.3100	92.43	1.2018	19.17
4.1802	91.87	1.1466	11.41
4.0579	91.45	1.0502	14.12
4.0007	93.38	1.0078	12.34
3.8337	89.66	0.7656	10.00
3.8079	88.97	0.7290	11.34
3.6168	87.01	0.6958	5.117
3.4439	84.41	0.6655	5.644
3.2868	81.36	0.6377	5.268
3.1434	79.16	0.6122	5.166
2.8375	69.28	0.4656	2.371
2.6974	65.33	0.4435	4.155
2.5705	61.52	0.4233	2.426
2.4550	58.93	0.2002	-0.0469
2.2498	50.99	0.1000	-0.1033
2.0940	41.70		
1.9918	36.76		

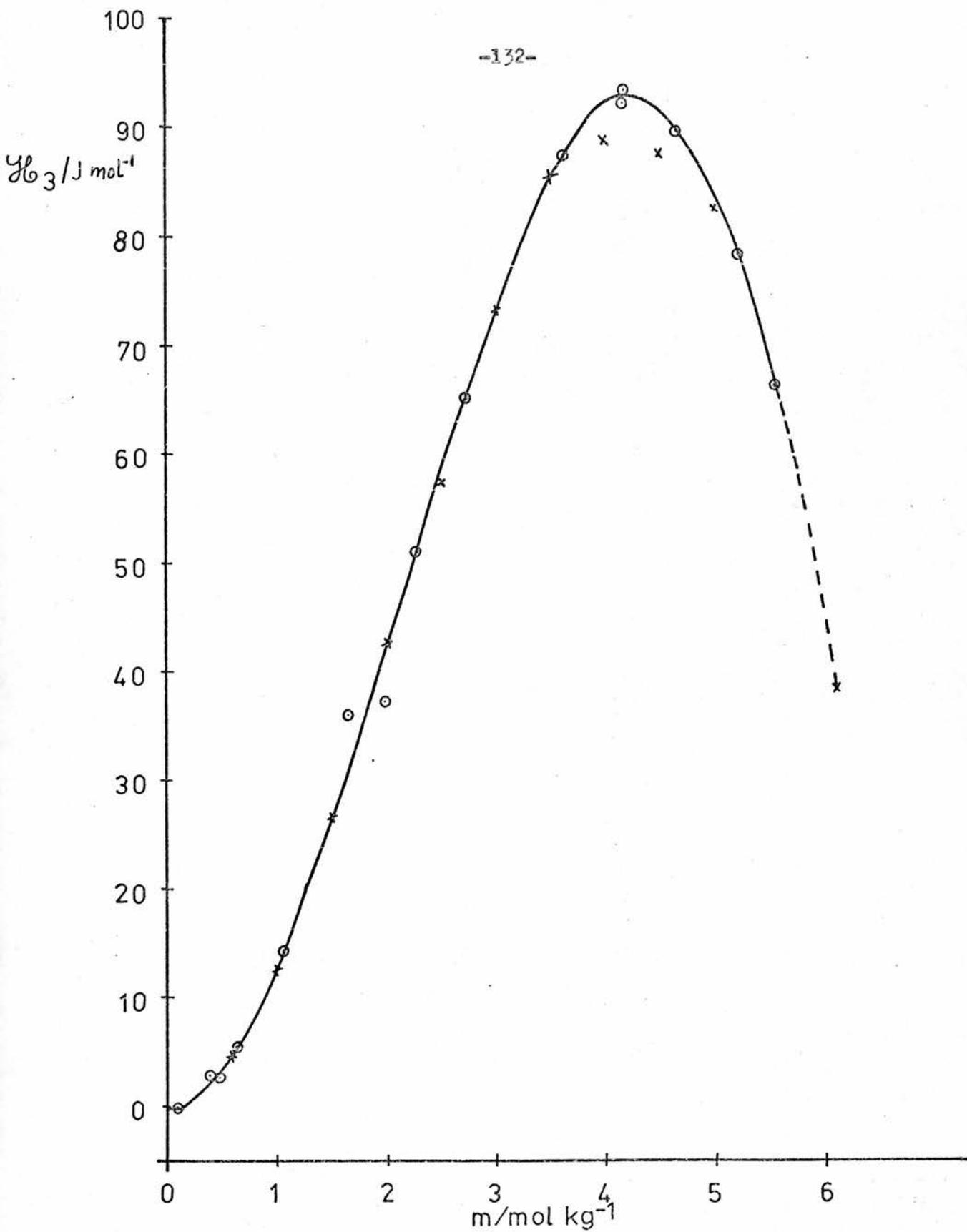


Fig. 4.8 Partial molar enthalpy of water in sodium chloride solutions at 25°C
 — and \circ Experimental values
 \times Robinson's values

TABLE 4.6
 PARTIAL MOLAR ENTHALPY OF WATER, \mathcal{H}_3 , IN CALCIUM
 CHLORIDE SOLUTIONS AT 25°C

$m/\text{mol kg}^{-1}$	$-\mathcal{H}_3/\text{J mol}^{-1}$	$m/\text{mol kg}^{-1}$	$-\mathcal{H}_3/\text{J mol}^{-1}$	$m/\text{mol kg}^{-1}$	$-\mathcal{H}_3/\text{J mol}^{-1}$
5.5585	2291	3.9271	745.2	2.5822	225.9
5.5459	2292	3.7951	670.4	2.5419	210.8
5.3750	2036	3.7873	619.4	2.5080	206.5
5.3632	2048	3.7788	657.8	2.4550	197.8
5.2033	1845	3.6244	569.5	2.4041	188.3
5.1922	1852	3.6167	575.9	2.3554	178.2
5.0421	1694	3.4751	486.3	2.3086	165.6
5.0317	1687	3.4679	503.5	2.2636	160.4
4.8907	1487	3.3375	435.7	2.2203	152.7
4.8809	1516	3.3309	445.8	2.1786	146.1
4.7480	1400	3.2105	390.5	2.1385	138.1
4.7388	1379	3.2044	397.4	2.0998	132.6
4.6664	1302	3.0984	369.6	2.0588	125.7
4.6566	1265	3.0870	351.8	2.0054	118.6
4.6460	1323	3.0215	342.9	1.9446	109.6
4.4524	1099	2.9701	311.0	1.8785	100.2
4.4427	1091	2.9099	304.6	1.8080	91.69
4.2654	959.3	2.8354	276.9	1.7425	84.08
4.2565	952.5	2.7798	273.1	1.6758	76.64
4.0934	868.6	2.7250	249.5	1.6082	69.59
4.0852	849.6	2.6736	246.4	1.5459	63.51
4.9348	775.3	2.6229	224.0	1.4882	59.16

Table continued

$m/\text{mol kg}^{-1}$	$-\mathcal{H}_3/\text{J mol}^{-1}$	$m/\text{mol kg}^{-1}$	$-\mathcal{H}_3/\text{J mol}^{-1}$
1.4347	54.81	0.6143	12.28
1.3801	49.17	0.5908	11.42
1.3247	46.37	0.5691	10.64
1.2736	42.96	0.5489	10.61
1.2264	39.08	0.5283	8.95
1.1824	36.08	0.5074	9.13
1.1376	33.97	0.4880	8.86
1.0921	32.15	0.4701	8.13
1.0502	24.40	0.4534	7.50
1.0113	27.31	0.4364	8.05
0.9753	25.59	0.4031	6.64
0.9385	24.01	0.3883	5.78
0.9011	22.34	0.3605	5.66
0.8666	16.96	0.3330	5.49
0.8346	19.54	0.3094	4.56
0.8049	18.09	0.2978	4.51
0.7746	17.14	0.2557	3.12
0.7438	16.44	0.2460	2.50
0.7154	15.62	0.2273	2.72
0.6890	14.49	0.2112	2.21
0.6645	12.93	0.1148	1.50
0.6396	12.82	0.0986	0.993

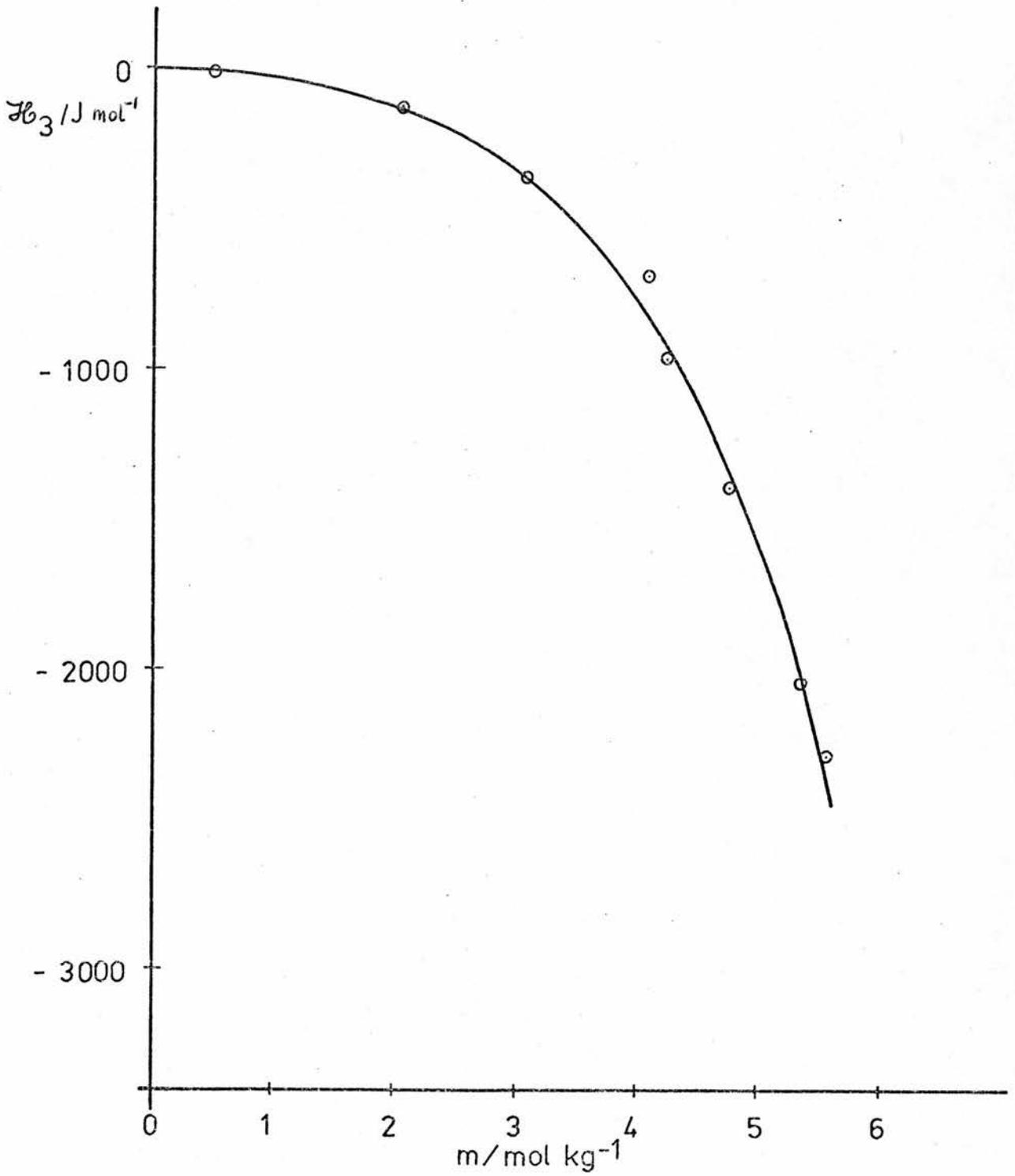


Fig. 4.9 Partial molar enthalpy of water in calcium chloride solutions at 25°C

TABLE 4.7

PARTIAL MOLAR ENTHALPY OF WATER, H_3 , IN SODIUM
CHLORIDE-CALCIUM CHLORIDE SOLUTIONS AT 25°C

$$x_B = \frac{3m_B}{m_A + 3m_B} = 0.3370$$

$\frac{m_A}{\text{mol kg}^{-1}}$	$\frac{m_B}{\text{mol kg}^{-1}}$	$H_3/\text{J mol}^{-1}$	$\frac{m_A}{\text{mol kg}^{-1}}$	$\frac{m_B}{\text{mol kg}^{-1}}$	$H_3/\text{J mol}^{-1}$
4.3808	0.7421	-31.62	1.2046	0.2041	18.43
4.1551	0.7039	-11.90	1.1557	0.1958	17.37
3.9516	0.6694	4.86	0.9900	0.1677	12.67
3.7671	0.6382	4.59	0.9424	0.1597	11.30
3.5837	0.6070	25.43	0.8992	0.1523	10.51
3.4021	0.5763	33.88	0.8597	0.1456	9.977
3.2380	0.5485	37.94	0.8236	0.1395	9.161
3.0891	0.5232	42.18	0.7904	0.1339	8.881
2.9408	0.4982	43.12	0.6005	0.1017	3.908
2.7938	0.4733	45.41	0.5719	0.0969	3.034
2.6607	0.4507	45.15	0.5458	0.0925	3.195
2.5398	0.4303	45.26	0.5221	0.0884	3.136
2.4191	0.4098	42.63	0.5003	0.0847	2.608
2.2994	0.3895	42.66	0.4803	0.0813	1.859
2.1910	0.3712	40.97	0.4122	0.0698	1.680
2.0924	0.3545	39.78	0.3926	0.0665	2.812
2.0022	0.3392	38.63	0.3748	0.0635	1.482
1.9195	0.3252	37.08	0.3585	0.0607	1.547
1.4502	0.2457	24.56	0.3436	0.0582	1.434
1.3799	0.2338	22.64	0.3299	0.0559	1.491
1.3160	0.2230	20.89			
1.2579	0.2131	19.44			

TABLE 4.8
 PARTIAL MOLAR ENTHALPY OF WATER, H_3 , IN SODIUM
 CHLORIDE-CALCIUM CHLORIDE SOLUTIONS AT 25°C

$$x_B = \frac{3m_B}{m_A + 3m_B} = 0.4547$$

$\frac{m_A}{\text{mol kg}^{-1}}$	$\frac{m_B}{\text{mol kg}^{-1}}$	$H_3/\text{J mol}^{-1}$	$\frac{m_A}{\text{mol kg}^{-1}}$	$\frac{m_B}{\text{mol kg}^{-1}}$	$H_3/\text{J mol}^{-1}$
3.9045	1.0955	-70.39	1.0458	0.2934	12.67
3.8986	1.0938	-69.70	0.9957	0.2793	12.04
3.7229	1.0445	-49.13	0.9501	0.2666	10.78
3.5624	0.9995	-32.91	0.9086	0.2549	9.887
3.3951	0.9525	-16.00	0.8705	0.2442	9.053
3.2229	0.9042	- 3.513	0.8354	0.2344	8.779
3.0674	0.8606	5.707	0.7987	0.2241	7.527
2.9262	0.8210	13.00	0.7606	0.2134	7.121
2.7974	0.7849	17.71	0.7259	0.2037	6.083
2.6795	0.7518	21.93	0.6653	0.1867	4.881
2.2846	0.6410	29.98	0.6387	0.1792	4.982
2.1719	0.6094	30.28	0.4863	0.1364	2.041
2.0697	0.5807	29.82	0.4632	0.1300	1.149
1.9768	0.5547	29.80	0.4423	0.1241	0.6593
1.8918	0.5308	29.23	0.4232	0.1187	0.3314
1.8138	0.5089	28.40	0.4056	0.1138	-0.1018
1.7222	0.4860	26.87	0.3895	0.1093	-0.2940
1.6477	0.4624	25.47			
1.5712	0.4409	24.07			
1.5014	0.4213	23.33			
1.4376	0.4034	22.16			
1.3789	0.3869	21.04			

TABLE 4.9
 PARTIAL MOLAR ENTHALPY OF WATER, H_3 , IN SODIUM
 CHLORIDE-CALCIUM CHLORIDE SOLUTIONS AT 25°C

$$x_B = \frac{3m_B}{m_A + 3m_B} = 0.5971$$

$\frac{m_A}{\text{mol kg}^{-1}}$	$\frac{m_B}{\text{mol kg}^{-1}}$	$H_3/\text{J mol}^{-1}$	$\frac{m_A}{\text{mol kg}^{-1}}$	$\frac{m_B}{\text{mol kg}^{-1}}$	$H_3/\text{J mol}^{-1}$
2.6850	1.3264	-69.21	1.1399	0.5631	8.480
2.5747	1.2719	-59.56	1.0981	0.5425	8.956
2.4731	1.2217	-48.09	1.0593	0.5233	8.042
2.3792	1.1753	-37.55	0.8438	0.4169	4.801
2.2921	1.1323	-29.21	0.8112	0.4008	4.155
2.2037	1.0887	-21.04	0.7810	0.3858	3.717
2.1143	1.0445	-14.27	0.7529	0.3720	3.729
2.0319	1.0038	-9.582	0.7268	0.3591	2.128
1.9557	0.9661	-5.994	0.7002	0.3459	1.150
1.8850	0.9312	-2.497	0.6731	0.3325	1.724
1.8131	0.8957	1.407	0.6481	0.3202	1.987
1.7403	0.8597	2.554	0.6249	0.3087	2.033
1.6732	0.8266	4.494	0.6033	0.2981	1.572
1.6110	0.7958	6.402	0.5813	0.2872	0.569
1.5533	0.7673	7.511	0.5589	0.2761	1.358
1.4946	0.7383	9.073	0.5381	0.2659	0.5715
1.4351	0.7089	8.802	0.5189	0.2564	0.1469
1.3801	0.6818	8.472	0.4470	0.2208	0.2547
1.3292	0.6567	9.741	0.3458	0.1709	0.2240
1.2820	0.6334	9.232	0.1102	0.0544	0.4892
1.2338	0.6095	9.649			
1.1850	0.5854	7.526			

TABLE 4.10
 PARTIAL MOLAR ENTHALPY OF WATER, H_3 , IN SODIUM
 CHLORIDE-CALCIUM CHLORIDE SOLUTIONS AT 25°C

$$x_B = \frac{3m_B}{m_A + 3m_B} = 0.8155$$

$\frac{m_A}{\text{mol kg}^{-1}}$	$\frac{m_B}{\text{mol kg}^{-1}}$	$H_3/\text{J mol}^{-1}$	$\frac{m_A}{\text{mol kg}^{-1}}$	$\frac{m_B}{\text{mol kg}^{-1}}$	$H_3/\text{J mol}^{-1}$
1.5504	2.2841	-236.9	0.7285	1.0726	-24.99
1.5256	2.2476	-220.3	0.7011	1.0325	-19.89
1.5013	2.2119	-221.1	0.6734	0.9918	-18.83
1.4781	2.1776	-194.9	0.6477	0.9541	-18.52
1.4480	2.1333	-182.7	0.6240	0.9191	-17.09
1.4056	2.0708	-166.4	0.6019	0.8866	-16.36
1.3522	1.9921	-151.6	0.5192	0.7646	-10.91
1.3027	1.9192	-140.3	0.4988	0.7346	-10.35
1.2528	1.8452	-111.1	0.4800	0.7069	- 9.921
1.2020	1.7704	-103.8	0.4625	0.6812	- 9.125
1.1551	1.7014	- 92.90	0.4463	0.6573	- 8.637
1.1118	1.6375	- 81.31	0.4276	0.6298	- 7.139
1.0716	1.5783	- 73.55	0.4070	0.5995	- 6.517
1.0306	1.5181	- 63.75	0.3883	0.5719	- 5.564
0.9891	1.4572	- 56.95	0.3712	0.5468	- 6.942
0.9509	1.4009	- 50.78	0.2813	0.4142	- 4.743
0.9155	1.3489	- 45.09	0.2678	0.3944	- 3.860
0.8827	1.3005	- 41.15	0.2556	0.3763	- 4.755
0.8493	1.2509	- 33.84	0.2444	0.3599	- 4.403
0.8155	1.2007	- 30.81			
0.7843	1.1547	- 28.64			
0.7554	1.1121	- 26.18			

TABLE 4.11

PARTIAL MOLAR ENTHALPY OF WATER, H_3 , IN SODIUM
CHLORIDE-CALCIUM CHLORIDE SOLUTIONS AT 25°C

$$x_B = \frac{3m_B}{m_A + 3m_B} = 0.9046$$

$\frac{m_A}{\text{mol kg}^{-1}}$	$\frac{m_B}{\text{mol kg}^{-1}}$	H_3/Jmol^{-1}	$\frac{m_A}{\text{mol kg}^{-1}}$	$\frac{m_B}{\text{mol kg}^{-1}}$	H_3/Jmol^{-1}
1.0644	3.3637	-558.3	0.5422	1.7132	-82.41
1.0536	3.3295	-553.4	0.5209	1.6460	-74.10
1.0328	3.2636	-520.6	0.5013	1.5839	-67.41
1.0124	3.1991	-474.0	0.4830	1.5263	-62.20
0.9978	3.1530	-460.7	0.4641	1.4665	-56.01
0.9789	3.0934	-435.4	0.4447	1.4051	-50.53
0.9607	3.0359	-414.1	0.3341	1.0560	-24.46
0.9390	2.9673	-389.3	0.3177	1.0039	-22.74
0.9160	2.8948	-354.8	0.3027	0.9568	-20.56
0.8961	2.8319	-334.0	0.2892	0.9138	-18.72
0.8770	2.7716	-314.9	0.2768	0.8746	-16.23
0.8588	2.7139	-297.9	0.2002	0.6325	-9.930
0.8412	2.6585	-281.4	0.1904	0.6017	-9.669
0.8244	2.6054	-266.1	0.1815	0.5737	-9.137
0.8044	2.5421	-249.2	0.1735	0.5482	-8.348
0.7369	2.3291	-190.0	0.1661	0.5249	-7.294
0.7137	2.2555	-174.4	0.1594	0.5035	-9.662
0.6918	2.1865	-160.8	0.1362	0.4305	-5.282
0.6713	2.1216	-148.3	0.1296	0.4096	-5.545
0.6519	2.0604	-138.9	0.1236	0.3907	-6.604
0.6336	2.0027	-128.2	0.1181	0.3734	-4.852
0.5652	1.7861	-91.80	0.1131	0.3575	-4.055

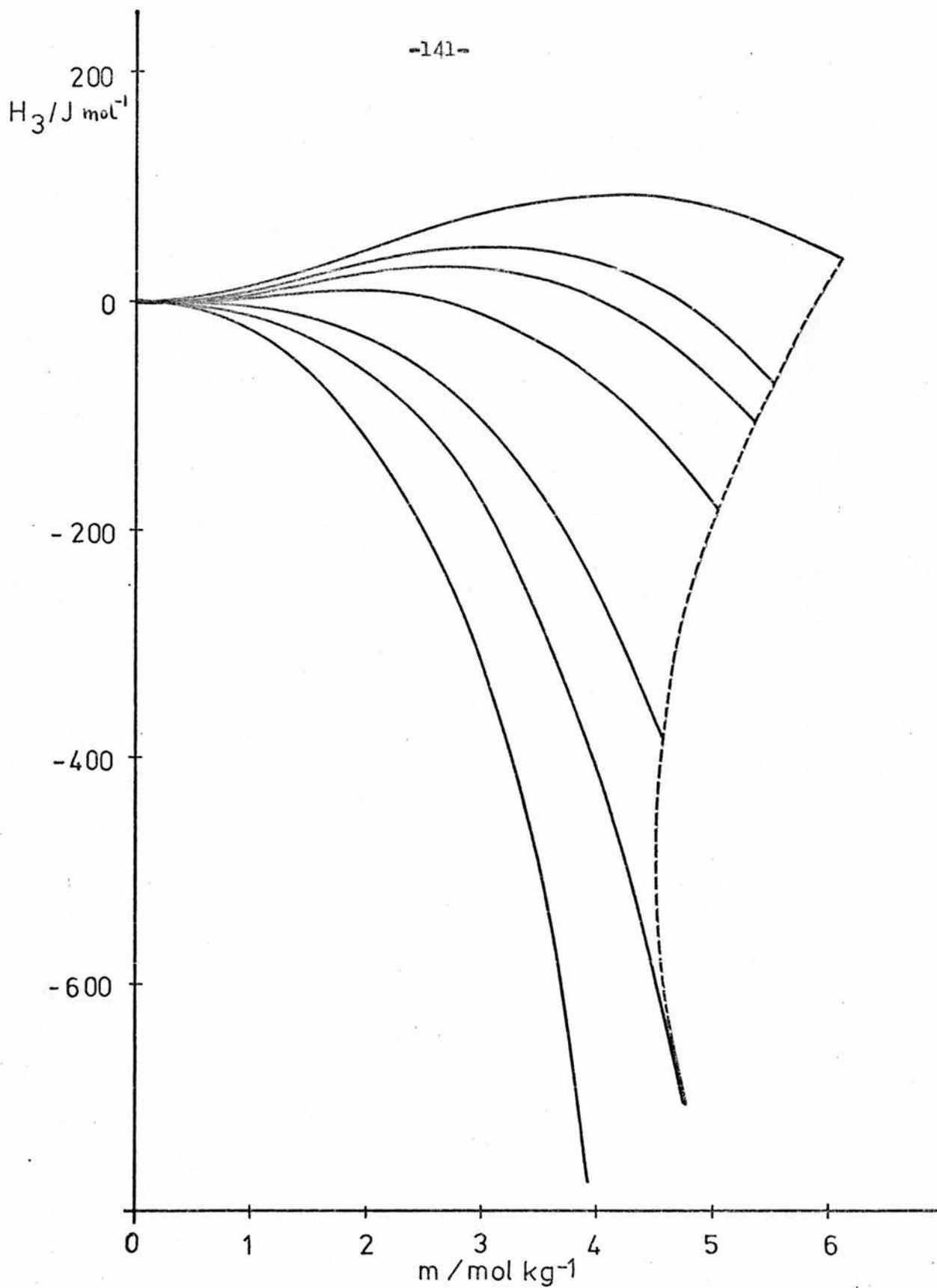


Fig. 4.10 Partial molar enthalpy of water against $(m_A + m_B) = m$
for the system $\text{NaCl}-\text{CaCl}_2-\text{H}_2\text{O}$ at 25°C

4. 2. 6. 2 The system $\text{CaCl}_2\text{-MgCl}_2\text{-H}_2\text{O}$

The calorimetric data for the binary system $\text{CaCl}_2\text{-H}_2\text{O}$ is given in table 4.6 (section 4. 2. 5. 1) and for the binary system $\text{MgCl}_2\text{-H}_2\text{O}$ is given in table 4.12. The first column of this latter table gives the molality, M_c , of magnesium chloride; and the second column the corresponding partial molar enthalpy of water.

The data for the ternary systems are given in tables 4.13, 4.14, and 4.15. In these tables the first column gives the molality, m_B , of calcium chloride; the second column gives the molality, m_c , of magnesium chloride; and the third column gives the partial molar enthalpy of water of the mixed solutions.

Calorimetric data at constant partial molar enthalpy of water are given in table 4.16. The third column gives the molality, M_B , of the reference calcium chloride solution, and the fourth and fifth columns give the molalities of calcium chloride, m_B , and magnesium chloride, m_c , in the mixed solutions. The second column gives the values of the partial molar enthalpy of water for each set of solutions.

Plots of partial molar enthalpy of water against molality are shown in fig 4.11.

Calorimetric data at constant partial molar enthalpy of water are given in table 4.16. The third column gives the molality, M_B , of the reference calcium chloride solution, and the fourth and fifth column give the molalities of calcium chloride, m_B , and magnesium chloride, m_c , in the mixed solutions. The second column gives the values of the partial molar enthalpy of water for each set of solutions.

TABLE 4.12

Partial Molar Enthalpy of Water, H_3 , in
Magnesium Chloride Solutions at 25 °C

$M_c/\text{mol kg}^{-1}$	$H_3/\text{J mol}^{-1}$
4.8560	-1507
4.4014	-1242
4.0228	-1023
3.5846	- 793.1
3.2300	- 617.8
2.9393	- 490.9
2.6965	- 410.0
2.1197	- 241.9
1.9162	- 190.8
1.7484	- 153.9
1.2558	- 78.05
1.1381	- 64.55
1.0406	- 55.21
0.9585	- 47.10
0.7603	- 29.57
0.7235	- 26.82
0.6901	- 25.45
0.6597	- 21.64
0.6319	- 20.55
0.6063	- 20.52
0.4487	- 3.430
0.4033	- 2.027
0.3746	- 3.258

TABLE 4.13

Partial Molar Enthalpy of Water, H_3 , in
Calcium Chloride-Magnesium Chloride Solutions at 25 °C

$$x_c = \frac{m_c}{m_B + m_c} = 0.2496$$

m_B /mol kg ⁻¹	m_c /mol kg ⁻¹	H_3 /J mol ⁻¹
3.8004	1.2640	-2182
3.7960	1.2625	-2328
3.5902	1.1941	-2353
3.2326	1.0752	-1699
2.9393	0.9773	-1293
2.6957	0.8966	- 958.6
2.4004	0.7985	- 620.4
2.1673	0.7209	- 517.5
1.9755	0.6571	- 391.4
1.8148	0.6037	- 300.1
1.4223	0.4731	- 174.9
1.2874	0.4282	- 133.3
1.1759	0.3911	- 103.7
1.0321	0.3600	- 94.18
0.8488	0.2823	- 52.61
0.8074	0.2635	- 47.43
0.7699	0.2561	- 42.83
0.7357	0.2447	- 42.92
0.7044	0.2343	- 36.07
0.6756	0.2247	- 33.72
0.5103	0.1697	- 19.99
0.4855	0.1615	- 18.19
0.4630	0.1540	- 16.49
0.4425	0.1472	- 15.16
0.4155	0.1382	- 8.985
0.3001	0.0999	- 1.334

TABLE 4.14

Partial Molar Enthalpy of Water, H_3 , in
Calcium Chloride-Magnesium Chloride at 25 °C

$$x_c = \frac{m_c}{m_B + m_c} = 0.5109$$

$m_B/\text{mol kg}^{-1}$	$m_c/\text{mol kg}^{-1}$	$H_3/\text{J mol}^{-1}$
1.6889	1.7639	-719.5
1.5233	1.5910	-556.5
1.3873	1.4489	-411.3
1.2736	1.3301	-370.7
0.9995	1.0438	-218.2
0.9039	0.9440	-172.4
0.8250	0.8617	-133.2
0.7585	0.7925	-111.7
0.5898	0.6160	- 64.40
0.5611	0.5860	- 59.37
0.5350	0.5588	- 53.56
0.5113	0.5340	- 49.13
0.4895	0.5113	- 46.78
0.3452	0.3606	- 23.42
0.3285	0.3431	- 21.70
0.3133	0.3272	- 19.70
0.2995	0.3127	- 18.69
0.2868	0.2995	- 17.78
0.1979	0.2067	- 2.475
0.1651	0.1809	- 0.8803

TABLE 4.15

Partial Molar Enthalpy of Water in
Calcium Chloride-Magnesium Chloride Solutions at 25 °C

$$x_c = \frac{m_c}{m_B + m_c} = 0.7580$$

$m_B/\text{mol kg}^{-1}$	$m_c/\text{mol kg}^{-1}$	$H_2/\text{J mol}^{-1}$
1.2777	4.0014	-1652
1.2120	3.7956	-1929
1.1504	3.6026	-1342
1.0442	3.2700	-1184
0.9559	2.9936	- 713.1
0.7677	2.4041	- 585.9
0.6991	2.1891	- 464.6
0.6417	2.0094	- 384.2
0.5051	1.5819	- 226.3
0.4569	1.4458	- 180.6
0.4152	1.3004	- 147.0
0.3821	1.1966	- 123.1
0.3000	0.9393	- 72.99
0.2854	0.8936	- 65.83
0.2721	0.8522	- 44.25
0.2601	0.8144	- 55.99
0.2491	0.7799	- 52.16
0.2390	0.7482	- 48.59
0.1808	0.5663	- 28.29
0.1721	0.5389	- 26.03
0.1642	0.5141	- 24.89
0.1570	0.4915	- 23.00
0.1009	0.3158	- 4.849
0.0918	0.2874	- 2.656

TABLE 4.16

Mixed Solutions of CaCl_2 and MgCl_2 Having The Same Partial

Molar Enthalpy Of Water As The Reference

Solution of Molality M_B

Set	$H_3/\text{J mol}^{-1}$	$M_B/\text{mol kg}^{-1}$	$m_B/\text{mol kg}^{-1}$	$m_c/\text{mol kg}^{-1}$
1	1000	4.3205	2.7252	0.9064
			1.0096	3.1621
			0.	3.9790
2	800	3.9856	2.5572	0.8506
			0.9721	3.0448
			0.	3.5979
3	600	3.6770	2.3548	0.7832
			1.5669	1.6367
			0.7883	2.4692
4	400	3.2320	0.	3.1935
			1.9891	0.6616
			1.3559	1.4164
5	200	2.4683	0.6529	2.0450
			0.	2.6665
			1.5008	0.4992
			0.9052	0.9455
			0.4789	1.4999
			0.	1.9521

Table Continued

Set	H_2/J_{mol}	$M_B/mol\ kg^{-1}$	$m_B/mol\ kg^{-1}$	$m_C/mol\ kg^{-1}$
6	100	1.8785	1.1197	0.5724
			0.7164	0.7485
			0.3443	1.0785
			0.	1.3934
7	50	1.3892	0.8281	0.2754
			0.5162	0.5395
			0.2757	0.8655
			0.	0.9895
8	20.	0.8873	0.5103	0.1697
			0.3133	0.5272
			0.1477	0.4626
			0.	0.5975
9	10	0.5386	0.4200	0.1397
			0.2409	0.2516
			0.1169	0.3660
			0.	0.5078

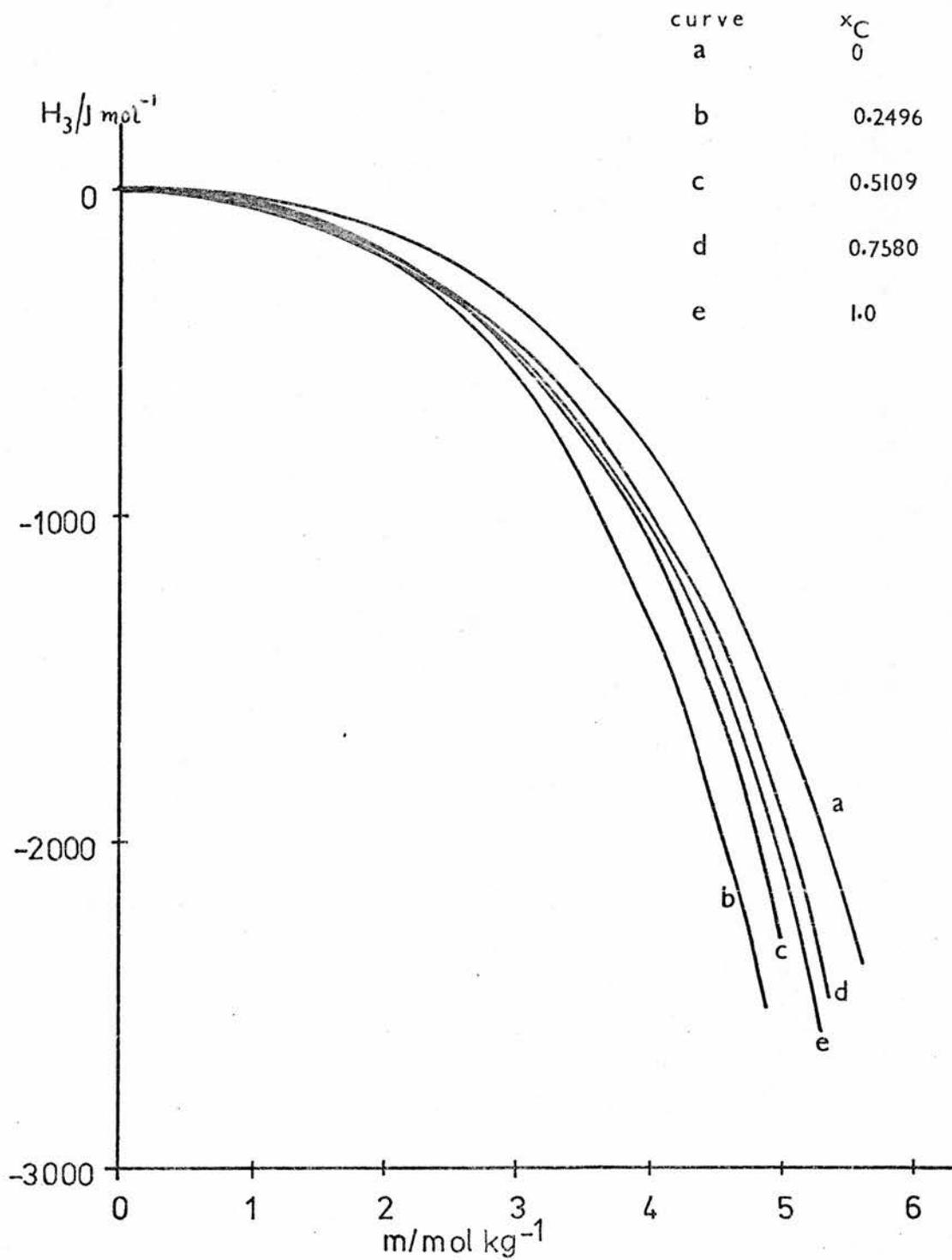


Fig. 4.11 Partial molar enthalpy of water against total molality for the system $\text{CaCl}_2\text{-MgCl}_2\text{-H}_2\text{O}$ at 25°C

4.2.6.3 The system NaCl-MgCl₂-H₂O

The calorimetric data for the binary systems are given in table 4.5 (section 4. 2. 5. 1) and table 4.12 (section 4. 2. 5. 2).

The data for the ternary systems are given in tables 4.17, 4.18, and 4.19. In these tables the first column gives the molality, m_A , of sodium chloride; the second column gives the molality, m_C , of magnesium chloride; and the third column gives the partial molar enthalpy of water of the mixed solutions.

Plots of partial molar enthalpy of water against molality are shown in Fig.4.12.

TABLE 4.17

Partial Molar Enthalpy of Water, H_3 , in
Sodium Chloride-Magnesium Chloride Solutions at 25 °C

$$x_B = \frac{\bar{z}m_B}{m_A + \bar{z}m_B} = 0.2713$$

$m_A/\text{mol kg}^{-1}$	$m_B/\text{mol kg}^{-1}$	$H_3/\text{J mol}^{-1}$
4.9408	0.6132	-58.95
4.7869	0.5941	-45.44
4.5294	0.5622	-20.18
4.2724	0.5303	- 4.793
4.0430	0.5018	7.059
3.8370	0.4762	17.22
3.6510	0.4532	24.67
3.4822	0.4322	11.66
2.5226	0.3131	4.340
2.3351	0.2961	8.542
2.2619	0.2803	18.57
1.2852	0.1595	16.20
1.2232	0.1518	14.46
1.1669	0.1448	13.24
1.1155	0.1384	12.40
0.7362	0.0913	4.494
0.7010	0.0870	3.731
0.6399	0.0794	1.253
0.4319	0.0536	0.1182
0.4110	0.0511	- 0.2791
0.3920	0.0488	- 0.6177
0.3747	0.0465	- 0.5694

TABLE 4.18

Partial Molar Enthalpy of Water, H_3 , in
Sodium Chloride-Magnesium Chloride Solutions at 25 °C

$$x_B = \frac{\bar{m}_B}{m_A + \bar{m}_B} = 0.4806$$

$m_A/\text{mol kg}^{-1}$	$m_B/\text{mol kg}^{-1}$	$H_3/\text{J mol}^{-1}$
4.0251	1.2416	-135.5
3.8179	1.1777	-132.7
3.6212	1.1170	-118.0
3.4438	1.0623	-103.9
3.2130	0.9911	- 69.85
3.0024	0.9262	- 58.35
2.2500	0.6941	- 6.774
2.1383	0.6596	- 3.027
1.9933	0.6149	8.343
1.2726	0.3925	6.211
1.2108	0.3735	5.856
1.1037	0.3404	13.61
0.7101	0.2191	8.338
0.6463	0.1994	8.597
0.4075	0.1257	7.639
0.3711	0.1145	7.655
0.2344	0.0723	7.795
0.2136	0.1383	5.465

TABLE 4.19

Partial Molar Enthalpy of Water, H_3 , in
Sodium Chloride-Magnesium Chloride Solutions at 25 °C

$$x_B = \frac{3m_B}{m_A + 3m_B} = 0.8409$$

$m_A/\text{mol kg}^{-1}$	$m_B/\text{mol kg}^{-1}$	$H_3/\text{J mol}^{-1}$
1.8818	3.3159	-647.5
1.7875	3.1497	-620.6
1.6932	2.9836	-526.7
1.5316	2.6988	-404.5
1.3982	2.4637	-311.9
1.0866	1.9149	-185.5
0.9785	1.7243	-148.5
0.8899	1.5631	-119.6
0.6043	1.0649	- 55.24
0.5748	1.0128	- 46.50
0.5274	0.9292	- 34.76
0.3359	0.5921	- 19.55
0.3196	0.5632	- 17.89
0.3048	0.5371	- 16.76
0.2912	0.5133	- 15.76
0.1868	0.3293	0.2646
0.1700	0.2996	3.077
0.0971	0.1882	6.243
0.0884	0.1713	4.599
0.0811	0.1572	7.308
0.0750	0.1452	5.591

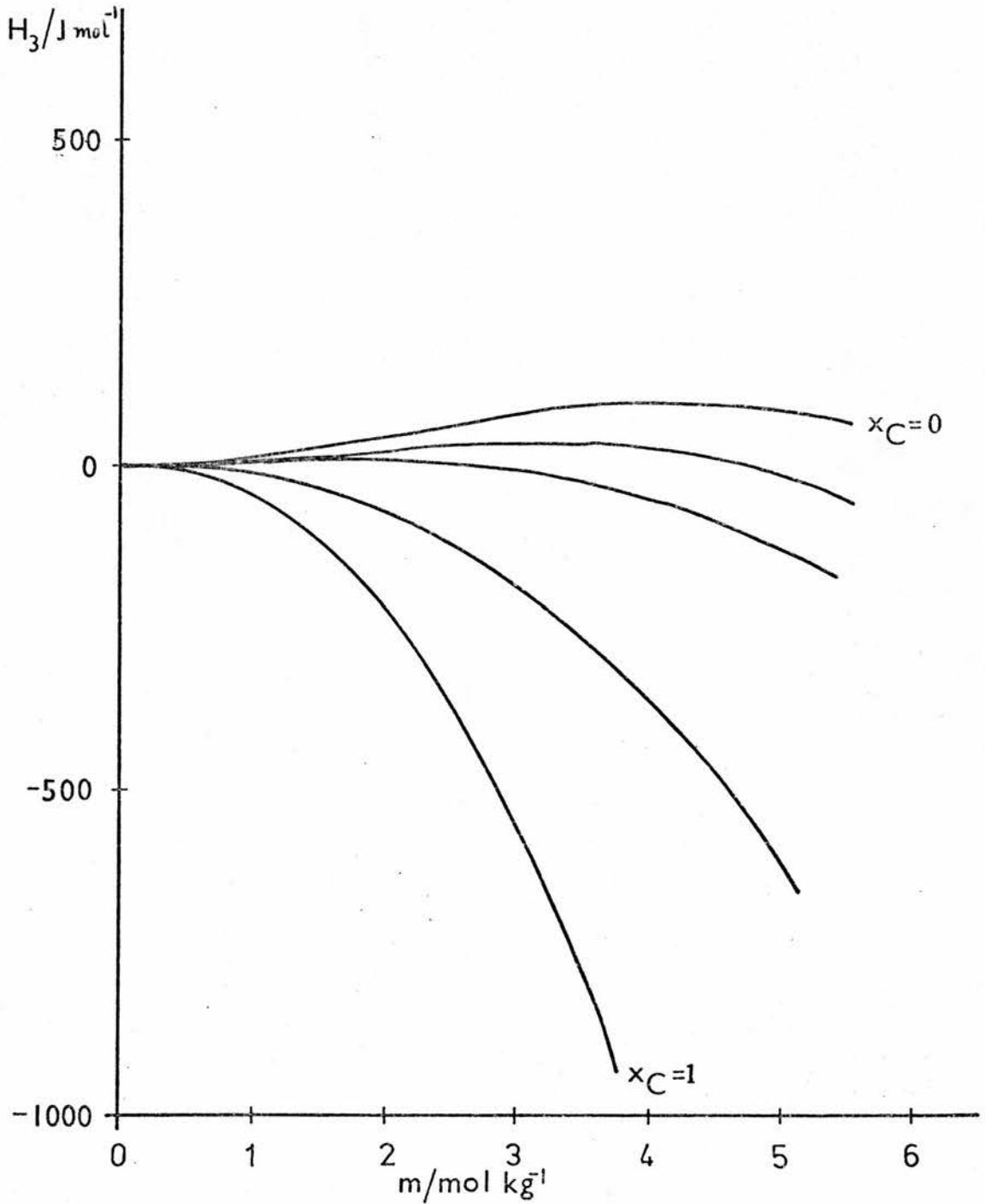


Fig. 4.12 Partial molar enthalpy of water, H_3 , against molality, $m=m_A+m_C$, for the system $\text{NaCl-MgCl}_2\text{-H}_2\text{O}$ at 25°C .

CHAPTER 5

RESULTS AND DISCUSSION

Introduction

The primary objective of this thesis, as was previously mentioned, was directed towards the application for the first time of the method, which McKay and Perring developed for activity coefficients of the solute components of a ternary system, to other partial molar quantities such as partial molar enthalpies. The corresponding equations, deduced here, for these partial molar quantities were already presented in Chapter 3 of this thesis.

Once having obtained the equation which theoretically allowed the computation of the partial molar enthalpies of each solute component in the mixture by measurements of only the partial molar enthalpy of the solvent, it was convenient to test their utility in practical work. With this purpose, the system sodium chloride-calcium chloride-water, due to its important role in some natural salt deposits, was chosen (for study at 25°C).

As the results on this system showed that the method could be successfully applied to ternary mixtures of electrolyte solutions, numerical values of the partial molar enthalpy of each component in the presence of the other, obtained by this new form of the McKay-Perring method, and the procedure for obtaining them, will be presented in some detail in this chapter. The isopiestic results for this system, at 45°C, will also be presented here. The purpose of this latter study was only for appreciating the differences with temperature which could be expected in the activity coefficients of sodium chloride in the mixtures.

The system $\text{NaCl}-\text{CaCl}_2-\text{H}_2\text{O}$, studied here, is part of the more

complex four component system $\text{NaCl}-\text{CaCl}_2-\text{MgCl}_2-\text{H}_2\text{O}$, which can be considered to be formed by the ternary system already mentioned and the ternary systems sodium chloride-magnesium chloride-water and calcium chloride-magnesium chloride-water. The possibility of extending the treatment, in later investigations, to these more complex systems was the reason for obtaining the experimental data for the three component systems sodium chloride-magnesium chloride-water and calcium chloride-magnesium chloride-water in addition to the first system studied.

Even though the study of these latter two systems is not really included as a central part of this work, a brief discussion of their treatment by this new method will also be presented during the course of this chapter.

5. 2 Isoopiestic Results

In the isopiestic measurements, the ternary solutions were equilibrated with both binary solutions. In this section, results for the binary system $\text{CaCl}_2-\text{H}_2\text{O}$ and the ternary system $\text{NaCl}-\text{CaCl}_2-\text{H}_2\text{O}$ will be presented. Also some brief discussion of the systems $\text{NaCl}-\text{MgCl}_2-\text{H}_2\text{O}$ and $\text{CaCl}_2-\text{MgCl}_2-\text{H}_2\text{O}$ will be given. No previous studies of these systems at 45°C have been reported.

5. 2. 1 The system $\text{CaCl}_2-\text{H}_2\text{O}$

Osmotic and activity coefficients for this system were obtained from the isopiestic equilibration of calcium chloride solutions with sodium chloride solutions as reference.

The values of the experimental osmotic coefficient were calculated with the relation

$$\phi_B = \frac{v_A m_A}{v_B m_B} \phi_A$$

In this particular case $\nu_A = 2$ and $\nu_B = 3$, and then

$$\phi_{\text{CaCl}_2} = \frac{2 m_{\text{NaCl}}}{3 m_{\text{CaCl}_2}} \phi_{\text{NaCl}} \quad (5.1)$$

The molalities of sodium and calcium chloride are those given in table 4.1, i.e., those values represented by M_A and m_B , this latter corresponding to the case $m_A = 0$ in that table. To obtain the values for the osmotic coefficient of sodium chloride at each particular molality, the data given by Harned(89) and by Vlasov (90) were fitted to the relation proposed by Lietzke and Stoughton (49) written in the following form

$$\phi = 1 - \frac{I}{\nu_j m_j} \left\{ \frac{2S}{A^3 I} \left[(1 + AI^{\frac{1}{2}}) - 2 \ln(1 + AI^{\frac{1}{2}}) - (1 + AI^{\frac{1}{2}})^{-1} \right] + BI + CI^2 + DI^3 \right\} \quad (5.2)$$

The value of the limiting slopes S at 45°C was interpolated from the data given by Silvester and Pitzer (59), and was taken as $S=1.21725$. The A parameter was fixed at 1.47186 by considering that the parameter interpreted as the average distance of closest approach, \bar{a} , does not depend on temperature. In this manner the least-squares fit of eqn.(5.2) gave

$$B = 0.029119$$

$$C = 0.009158$$

$$D = -0.0007201 \quad \text{for NaCl}$$

Once having obtained the values of ϕ_{NaCl} , the experimental osmotic coefficients of calcium chloride were calculated using eqn.(5.1). These values were used to fit eqn. (5.2); the parameter A was fixed at 1.63462. The corresponding least-squares fit gave

$$B = 0.053545$$

$$C = 0.006753$$

$$D = - 0.0001705 \quad \text{for } \text{CaCl}_2.$$

The experimental and calculated values of the osmotic coefficient of calcium chloride are given in table 5.1. Also the activity coefficients of calcium chloride were calculated by using the parameters B, C, and D previously obtained. The following relation was used:-

$$\ln \gamma_{\pm} = - \frac{2S}{1 + AI^{1/2}} + (2B)I + (3/2 C)I^2 + (4/3 D)I^3 \quad (5.3)$$

The values of the osmotic and activity coefficients of CaCl_2 , which seem not to have been reported at 45 °C, are given at rounded concentrations in table 5.2. They are given up to 5 mol kg⁻¹ but the highest experimental concentration was only 3 mol kg⁻¹.

TABLE 5.1

Osmotic Coefficients Of Calcium

Chloride At 45°C

$m/\text{mol kg}^{-1}$	$\phi_{(\text{exp})}$	$\phi_{(\text{Calc})}$
0.3600	0.890	0.889
0.3735	0.892	0.892
0.3958	0.896	0.896
0.4972	0.918	0.919
0.7916	1.000	0.994
1.0232	1.057	1.059
1.2131	1.114	1.116
1.4784	1.200	1.200
1.4933	1.204	1.205
1.6089	1.245	1.244
1.6168	1.247	1.246
1.8492	1.328	1.326
1.9300	1.357	1.355
2.2112	1.452	1.453
2.6499	1.631	1.623
2.7865	1.683	1.682
2.7928	1.688	1.685
2.8209	1.699	1.696
2.8563	1.712	1.711
2.8990	1.723	1.723
2.9340	1.741	1.742
2.9579	1.751	1.752
2.9822	1.760	1.762
3.0057	1.770	1.772

TABLE 5.2
Osmotic And Activity Coefficients
Of CaCl_2 at 45°C

$m/\text{mol kg}^{-1}$	ϕ	γ_{\pm}
0.1	0.851	0.511
0.2	0.859	0.466
0.3	0.876	0.449
0.4	0.898	0.444
0.5	0.920	0.445
1.0	1.053	0.499
1.2	1.112	0.538
1.4	1.175	0.585
1.6	1.241	0.643
1.8	1.309	0.711
2.0	1.380	0.792
2.5	1.569	1.061
3.0	1.769	1.464
3.5	1.979	2.065
4.0	2.194	2.960
4.5	2.411	4.29
5.0	2.628	6.25

5.2.2 The system NaCl-CaCl₂-H₂O

From the isopiestic vapour pressure measurements made on the ternary system sodium chloride-calcium chloride-H₂O, the activity coefficient of sodium chloride in the presence of the other salt has been calculated by using the McKay-Perring method.

By introducing the isopiestic ratio, R, into the McKay - Perring equation, the activity coefficient of sodium chloride in the mixtures is given by the relation.

$$\ln \gamma_A = \ln \Gamma_A + \ln R + \int_0^{M_A \phi_A} \left\{ -\frac{y_B}{M_A} \left(\frac{\partial R}{\partial y_B} \right)_{a_w} + \frac{R-1}{M_A} \right\} d(M_A \phi_A) \quad (5.4)$$

in the same notation as previously (chapter 3 and 4).

The molalities M_A and M_B of the binary systems sodium chloride and calcium chloride, and the molalities m_A and m_C of sodium chloride and calcium chloride in the ternary system were given in table 4.1. The values of the ionic fraction, y_B , of calcium chloride and those of the isopiestic ratio, R, were given in table 4.2.

The isopiestic ratio, R, was found to be of the form

$$R = 1 - ay_B - by_B^2 \quad (5.5)$$

The values of the parameters a and b obtained by the least squares method are given in the fourth and fifth columns of table 5.3.

It was shown that if the isopiestic ratio can be represented by the relation (5.5), then the integral term in the McKay - Perring equation reduces to :

$$y_B^2 \int_0^{M_A \phi_A} (b/M_A) d(M_A \phi_A) \quad (5.6)$$

The sixth column of the table 5.3 gives the values of b/M_A and fig. 5.1 shows the plot of b/M_A against $M_A \phi_A$. The smooth curve is that of the equation:-

$$b/M_A = - 0.00043 + 0.00081 (M_A \phi_A) - 0.000066 (M_A \phi_A)^2 \quad (5.7)$$

There is some scatter of the points in figure 5.1 because it is not easy to get precise values of the b coefficient, especially for the more dilute solutions. The best fit was found to be when sets 1 to 5 and 11 were eliminated.

The integral in eqn (5.6) becomes

$$y_B^2 \left[- 0.00043 + 0.000405 (M_A \phi_A) - 0.000033 (M_A \phi_A)^2 \right] M_A \phi_A \quad (5.8)$$

The values of the integrals, multiplied by 0.4343, to convert to decadic logarithms, are given in the seventh column of table 5.3.

The activity coefficients of sodium chloride at 45°C in some mixtures of the system sodium chloride-calcium chloride-water are given in table 5.4, fifth column. The first column of this table gives the molality of the reference solution of sodium chloride, the second column gives the molality of the mixture which is in isopiestic equilibrium with the reference solution of molality M_A , the third column gives the logarithm of the ratio between the activity coefficient of sodium chloride in the mixture and its activity coefficient in the binary solution. Figure 5.2 shows the plot of this relation against the molality, $m = m_A + 1.5 m_B$, at ionic fractions equal to 0.2402 and 0.6421.

The activity coefficient of calcium chloride in the mixtures

are given by

$$\log \gamma_B = \log \Gamma_B + \log R' + \frac{(1-\gamma_B)^2}{2.303} \int_0^{M_A \phi_A} (b/M_A) d(M_A \phi_A) \quad (5.9)$$

The table 5.5 gives the values of the isopiestic ratios $R' = M_B/m$ and the values of the activity coefficients, γ_B , of calcium chloride in the mixtures.

In figure 5.3 the plots of the activity coefficients of sodium chloride and calcium chloride in the ternary system $\text{NaCl}-\text{CaCl}_2-\text{H}_2\text{O}$ against the total molality of the mixture, at constant ionic fraction, are shown. It can be noted that both curves intercept at approximately 2.3 mol kg^{-1} showing a more rapid increase in the activity coefficient of calcium chloride.

In the region of low concentrations where molality and mole fraction are proportional to each other, the extent to which the activity coefficient differ from unity is a measure of the deviations from ideality in the solution. The extrapolation of the curves on fig. 5.3 towards zero concentration will show minima in both curves, that of calcium chloride being below that of sodium chloride. That is, the activity coefficient of calcium chloride decreases more rapidly with increasing concentration, at low concentrations, than the activity coefficient of sodium chloride, which is in accordance with the Debye - Hückel theory due to the higher charge of the calcium ion. At higher concentrations, however, the activity coefficient of calcium chloride will increase more rapidly, largely due to its higher capacity for hydration.

Comparison of the values of the activity coefficients of each of the two salts in the ternary system with their values in the binary systems shows that the activity coefficient of sodium chloride

varies only slightly. It may be concluded that the addition of calcium chloride has only slight effect on the activity coefficient of sodium chloride, but that the addition of sodium chloride has considerable effect on the activity coefficient of calcium chloride.

The system $\text{NaCl}-\text{CaCl}_2-\text{H}_2\text{O}$ at 25°C was investigated by Robinson and Bower (91). They reported an activity coefficient of 0.829 for sodium chloride in a mixture of total ionic strength 4.5 mol kg^{-1} and ionic fraction 0.8944. At the same ionic strength and ionic fraction here, at 45°C , the value 0.831 was obtained by interpolation. The change in the activity coefficient over the 20K interval is only 0.002.

TABLE 5.3
Values of the parameters of eqn.(5.5) and of the integral in eqn. (5.6)

Set	$H_A / \text{mol kg}^{-1}$	$H_A \phi_A / \text{mol kg}^{-1}$	a	b	b/H_A	INT*
1	0.5213	0.4206	0.0436	-0.0093	-0.0197	-0.00005
2	0.5417	0.5000	0.0395	-0.0075	-0.0135	-0.00005
3	0.5758	0.5320	0.0257	0.0036	0.0062	-0.00005
4	0.7369	0.6846	0.0148	-0.0197	-0.0026	-0.00005
5	1.2491	1.1879	-0.0210	-0.0513	-0.0251	0.00001
6	1.6673	1.6223	-0.0878	0.0158	0.0009	0.0001
7	2.0531	2.0279	-0.1216	0.0015	0.0007	0.0003
8	2.5354	2.6604	-0.1691	0.0032	0.0012	0.0006
9	2.6154	2.6965	-0.1694	0.0017	0.0006	0.0006
10	2.8671	3.0047	-0.1936	0.0053	0.0019	0.0003
11	2.8839	3.0252	-0.2178	0.0270	0.0093	0.0003
12	3.3990	3.5345	-0.2352	0.0073	0.0023	0.0012
13	3.5804	3.9277	-0.2455	0.0036	0.0024	0.0014
14	4.2170	4.8158	-0.2737	0.0027	0.0007	0.0021
15	5.3194	6.4843	-0.3507	0.0123	0.0023	0.0036
16	5.6648	7.0357	-0.3669	0.0116	0.0020	0.0041
17	5.6860	7.0734	-0.3710	0.0136	0.0024	0.0041
18	5.7594	7.1877	-0.3720	0.0108	0.0019	0.0042
19	5.9509	7.3370	-0.3771	0.0114	0.0019	0.0043
20	5.9597	7.5152	-0.3820	0.0112	0.0019	0.0045
21	6.0483	7.6632	-0.3863	0.0119	0.0020	0.0046
22	6.1127	7.7692	-0.3887	0.0109	0.0018	0.0047
23	6.1753	7.8735	-0.3947	0.0140	0.0023	0.0048
24	6.24	7.9810	-0.3939	0.0096	0.0015	0.0049

$$*INT = 0.4343 \int_0^{H_A \phi_A} \frac{H_A \phi_A}{(b/H_A)} d(H_A \phi_A)$$

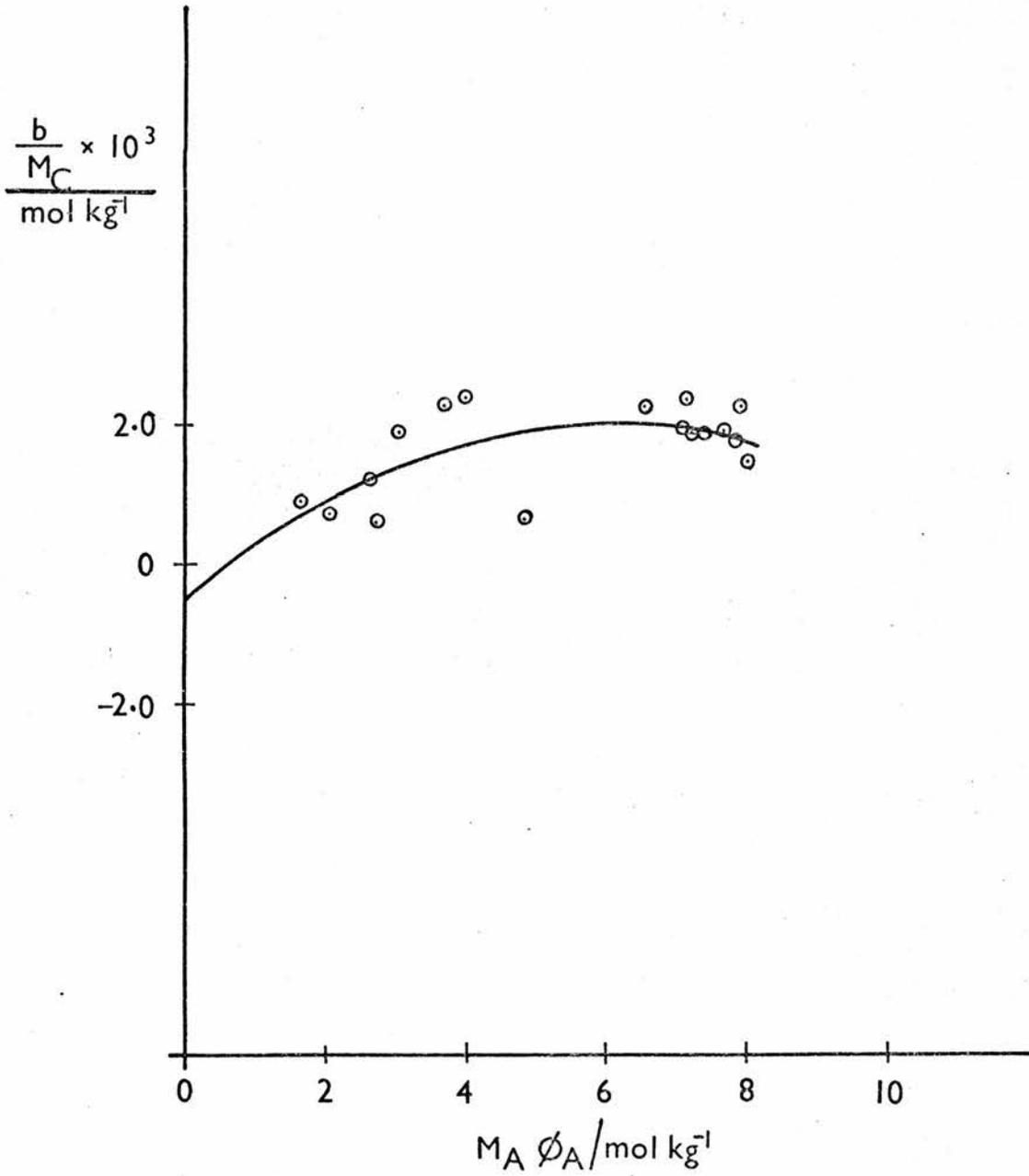


Fig. 5.1 b/M_A against $M_A \phi_A$ for the system NaCl-CaCl₂-H₂O at 45°C

TABLE 5.4
Activity Coefficients of Sodium Chloride In
The System NaCl-CaCl₂-H₂O At 45°C

$N_A/\text{mol kg}^{-1}$	$m/\text{mol kg}^{-1}$	y_B	$\log \gamma_A/\Gamma_A$	γ_A
0.5213	0.5283	0.2222	-0.00402	0.659
	0.5317	0.5958	-0.00990	0.660
0.5417	0.5487	0.2223	-0.00367	0.668
	0.5516	0.5959	-0.00924	0.660
0.5758	0.5815	0.2222	-0.00257	0.667
	0.5839	0.5958	-0.00729	0.660
0.7369	0.7438	0.2222	-0.00118	0.661
	0.7384	0.5959	-0.00298	0.658
1.2491	1.2420	0.2402	0.00294	0.660
	1.2161	0.6420	0.01132	0.673
1.6673	1.6327	0.2403	0.00903	0.677
	1.5795	0.6421	0.02358	0.700
2.0381	1.9801	0.2403	0.01247	0.695
	1.8918	0.6421	0.03250	0.728
2.5854	2.4851	0.2403	0.01724	0.729
	2.3343	0.6421	0.04451	0.776
2.6154	2.5138	0.2403	0.01732	0.731
	2.3600	0.6421	0.04479	0.779
2.8671	2.7177	0.2918	0.02373	0.757
	2.5532	0.6417	0.05036	0.805
2.8839	2.7334	0.2918	0.02591	0.762
	2.5440	0.6386	0.05267	0.810
3.3990	3.2206	0.2403	0.02357	0.794
	2.9642	0.6421	0.05987	0.863

Table 5.4 Continued

$M_A/\text{mol kg}^{-1}$	$m/\text{mol kg}^{-1}$	y_B	$\log \gamma_A/\Gamma_A$	γ_A
3.5804	3.5835	0.2403	0.02477	0.810
	3.1018	0.6421	0.05282	0.884
4.2170	3.9006	0.2918	0.03344	0.831
	3.5944	0.6417	0.07072	0.960
5.3194	4.9111	0.2403	0.03508	0.996
	4.3586	0.6421	0.08788	1.125
5.6648	5.2092	0.2403	0.03667	1.038
	4.6026	0.6421	0.09188	1.179
5.6860	5.2267	0.2403	0.03703	1.041
	4.6115	0.6421	0.09251	1.183
5.7594	5.2925	0.2403	0.03719	1.050
	4.6658	0.6421	0.09319	1.194
5.8509	5.5710	0.2403	0.03767	1.062
	4.7264	0.6421	0.09432	1.209
5.9597	5.4667	0.2403	0.03812	1.075
	4.8007	0.6421	0.09549	1.227
6.0483	5.5400	0.2403	0.03853	1.086
	4.8643	0.6421	0.09640	1.241
6.1127	5.5955	0.2403	0.03881	1.095
	4.9083	0.6421	0.09714	1.252
6.1753	5.6495	0.2403	0.03929	1.103
	4.9467	0.6420	0.09809	1.263
6.24	5.7082	0.2403	0.03934	1.111
	4.9936	0.6420	0.09865	1.273

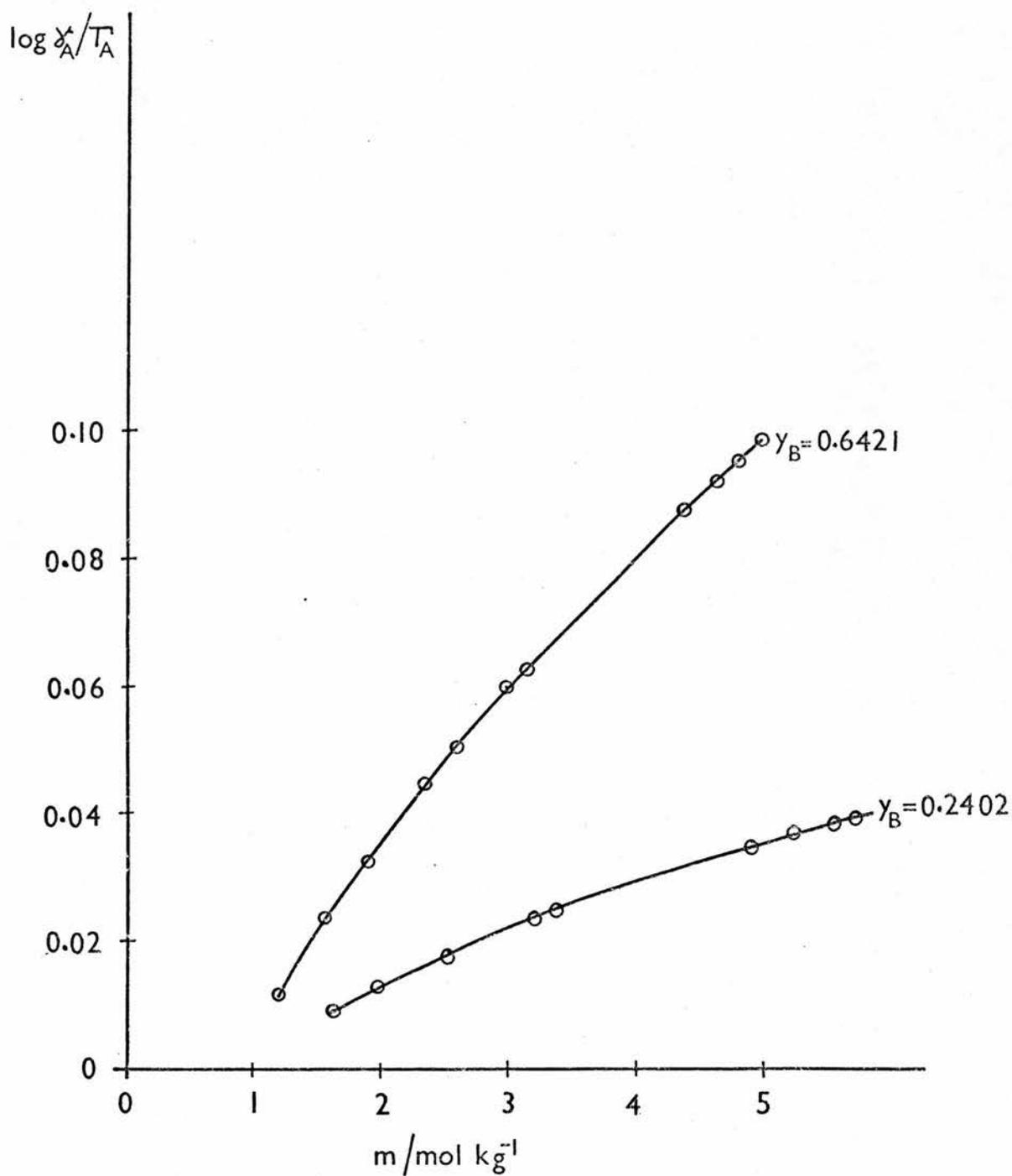


Fig. 5.2 $\log \gamma_A/T_A$ against molality for sodium chloride in the system $\text{NaCl}-\text{CaCl}_2-\text{H}_2\text{O}$ at 45°C

TABLE 5.5
 Activity Coefficients of CaCl_2
 in the System $\text{NaCl}-\text{CaCl}_2-\text{H}_2\text{O}$ at 45 °C

Set	$M_B/\text{mol kg}^{-1}$	$m/\text{mol kg}^{-1}$	R^1	$\log \gamma_B/T_B$	γ_B
1	0.5400	0.5317	1.0156	0.00671	0.456
		0.5283	1.0221	0.00946	0.459
2	0.5603	0.5213	1.0359	0.01527	0.465
		0.5516	1.0153	0.00630	0.459
		0.5487	1.0211	0.00904	0.461
3	0.5937	0.5417	1.0343	0.01460	0.467
		0.5339	1.0168	0.00723	0.463
		0.5815	1.0210	0.00900	0.465
4	0.7458	0.5758	1.0311	0.01325	0.469
		0.7384	1.0100	0.00431	0.476
		0.7433	1.0027	0.00114	0.473
5	1.1874	0.7569	1.0121	0.00517	0.477
		1.2161	0.9764	-0.01037	0.523
		1.2420	0.9560	-0.01954	0.512
6	1.5348	1.2491	0.9506	-0.02199	0.509
		1.5795	0.9717	-0.01246	0.606
		1.6327	0.9400	-0.02681	0.587
7	1.8197	1.6673	0.9205	-0.03588	0.575
		1.8918	0.9619	-0.01683	0.692
		1.9801	0.9190	-0.03651	0.661
8	2.2176	2.0381	0.8928	-0.04895	0.642
		2.3348	0.9498	-0.02229	0.864
		2.4851	0.8924	-0.04909	0.812
12	2.7738	2.5854	0.8577	-0.06606	0.781
		2.9642	0.9358	-0.02866	1.200
		3.2206	0.8613	-0.06415	1.106
14	3.3168	3.3990	0.8161	-0.08706	1.049
		3.5944	0.9228	-0.03462	1.703
		3.9006	0.8503	-0.06937	1.572
		4.2170	0.7865	-0.1022	1.458

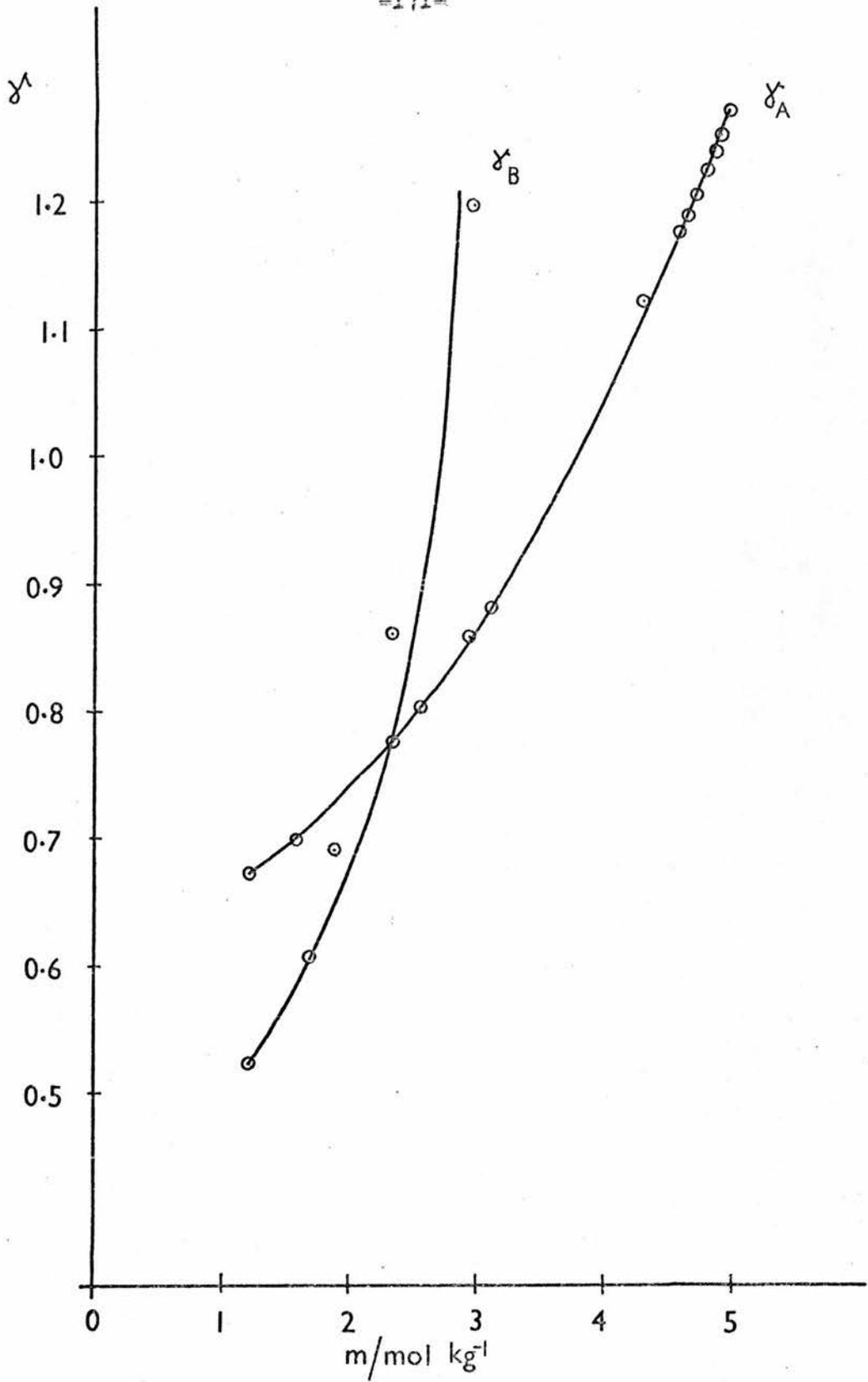


Fig. 5.3 Activity coefficient of NaCl in sodium chloride - calcium chloride solutions at 25°C against $m = m_A + 1.5 m_B$, at constant $x_B = 0.6421$

5.2.3 The system $\text{CaCl}_2\text{-MgCl}_2\text{-H}_2\text{O}$

The values of the molalities M_C and M_D of the binary aqueous systems containing calcium chloride or magnesium chloride are given in table 4.3. In the same table the values of the molalities m_C and m_D of calcium chloride and magnesium chloride in the mixed ternary solution in isopiestic equilibrium with these binary solutions are given. In table 4.2 the values of the ionic fraction of magnesium chloride defined as

$$y_D = m_C / (m_C + m_D)$$

and the isopiestic ratio are presented.

It may be assumed that the isopiestic ratio has also the form

$$R = 1 - ay_D - by_D^2 \quad (5.10)$$

Values of the parameters a and b are given in table 5.6. The sixth column of this table gives also the value of b/M_C needed for the evaluation of the integral term of the McKay-Perring equation, which is now written

$$y_D^2 \int_0^{M_C \phi_C} \frac{M_C \phi_C}{(b/M_C) + (M_C \phi_C)} d(M_C \phi_C) \quad (5.11)$$

A plot of b/M_C against $M_C \phi_C$ is shown in fig 5.4. The curve has been represented by the equation

$$b/M_C = 0.004986 - 0.000958 (M_C \phi_C) + 0.00195 (M_C \phi_C)^2 \quad (5.12)$$

even though a straight line could also have been taken; but the term to be evaluated has a very small numerical value and some uncertainty can therefore be tolerated in the exact form of the curve in fig 5.4.

Now the integral (5.11) becomes

$$y_D^2 \left[0.004986 - 0.000479 (M_C \phi_C) + 0.00065 (M_C \phi_C)^2 \right] M_C \phi_C \quad (5.13)$$

The values of the integral term, multiplied by 0.4343, to convert to decadic logarithms are given in table 5.6. The ratio between the activity coefficient of calcium chloride in the mixtures and its activity coefficient in the binary solution is shown in table 5.7. The activity coefficient of calcium chloride is increased by the addition of magnesium chloride while the activity coefficient of magnesium chloride is decreased by the addition of calcium chloride.

The same system at 25 °C was also reported by Robinson and Bower (92): they found that at constant total ionic strength the logarithm of the activity coefficient of either salt is, to a close approximation, a linear function of the concentration of the other salt. This was the first 2:2 system studied by the isopiestic method and since then only a few more of this kind have been reported.

TABLE 5.6

Values Of The Parameters Of Eqn (5.10)
And The Integral Term in Eqn (5.11)

Set	$M_c / \text{mol kg}^{-1}$	$M_c \phi_c / \text{mol kg}^{-1}$	a	b	b/M_c	INT*
1	0.5496	0.5122	-0.0843	0.0296	0.0163	0.0012
2	0.5537	0.5166	-0.0641	0.0083	0.0046	0.0012
3	0.5721	0.5366	-0.0849	0.0260	0.0149	0.0012
4	0.6092	0.5775	-0.0501	0.0005	0.0003	0.0013
5	0.6920	0.6705	-0.0628	0.0113	0.0078	0.0015
6	0.9416	0.9755	-0.0699	0.0043	0.0040	0.0021
7	1.3315	1.5322	-0.0528	0.0067	0.0039	0.0032
8	1.3495	1.5641	-0.0732	0.0104	0.0140	0.0032
9	1.4306	1.6953	-0.0764	0.0019	0.0027	0.0035
10	1.4592	1.7423	-0.0603	0.0170	0.0248	0.0036
11	1.4737	1.7670	-0.0799	0.0170	0.0250	0.0036
12	1.7787	2.3159	-0.0337	0.0342	0.0680	0.0048
13	1.7800	2.3176	-0.0862	0.0153	0.0072	0.0048
14	2.3965	3.6666	-0.0973	0.0180	0.0431	0.0079
15	3.2450	6.0746	-0.1101	0.0205	0.0665	0.0145

* INT = $0.4343 \int_0^{M_c \phi_c} (b/M_c) d(M_c \phi_c)$

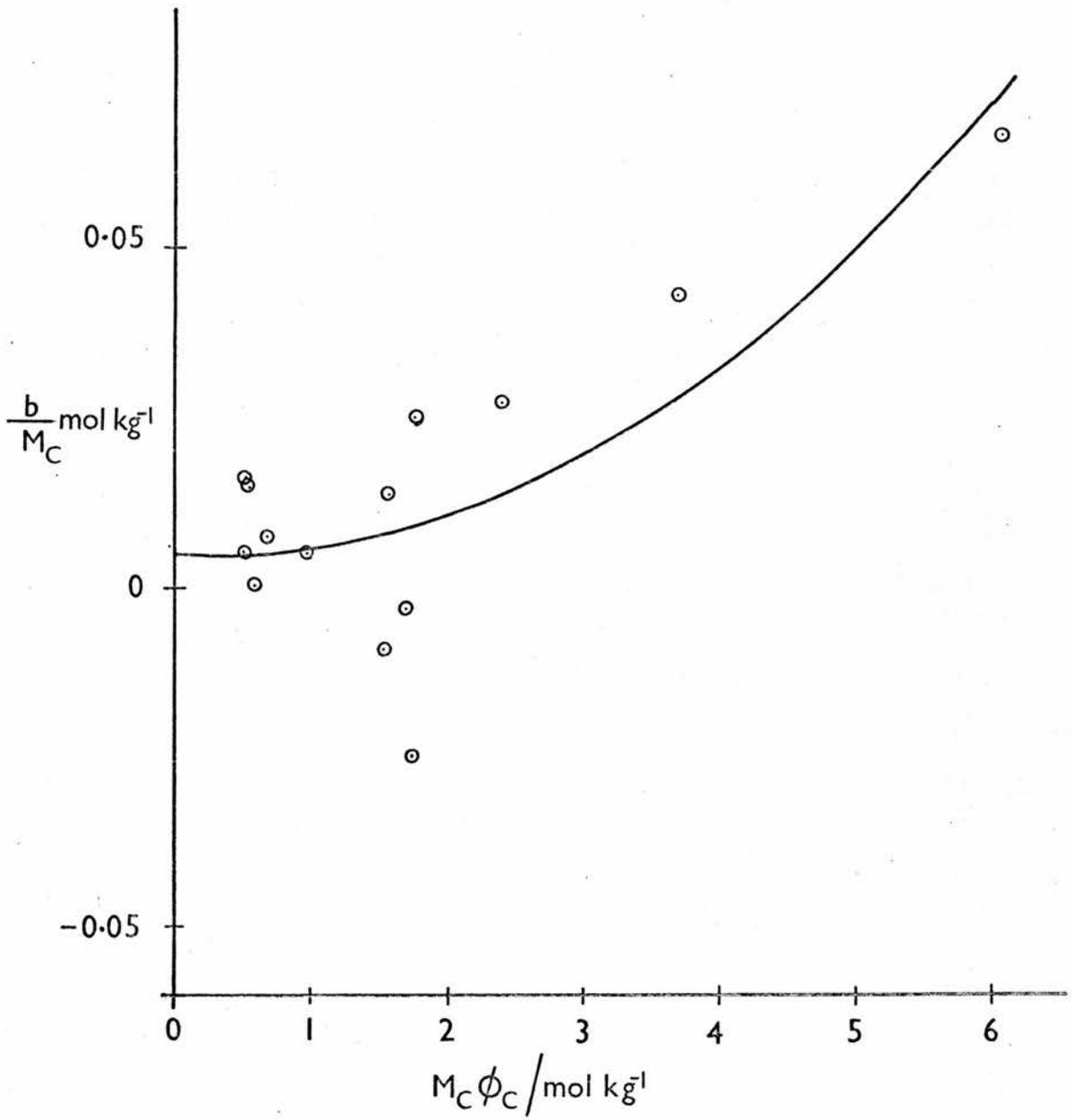


Fig. 5.4 b/M_C against $M_C \phi_C$ for the system $\text{CaCl}_2\text{-MgCl}_2\text{-H}_2\text{O}$ at 45°C

TABLE 5.7
 Activity Coefficient Ratios of Calcium Chloride
 In Calcium Chloride-Magnesium Chloride-Water
 Solutions At 45°C

Set	$M_c/\text{mol kg}^{-1}$	$m/\text{mol kg}^{-1}$	γ_D	$\log \gamma_c/r_c$
1	0.5496	0.5366	0.2987	0.00981
		0.5278	0.6612	0.01372
2	0.5537	0.5425	0.2986	0.00803
		0.5341	0.6611	0.01701
3	0.5721	0.5624	0.2987	0.00998
		0.5541	0.6613	0.01956
4	0.6092	0.5993	0.2987	0.00654
		0.5906	0.6612	0.01467
5	0.6920	0.6798	0.2986	0.00775
		0.6677	0.6612	0.01627
6	0.9416	0.9257	0.2987	0.00900
		0.9007	0.6613	0.02020
7	1.3315	1.3115	0.2987	0.00735
		1.2815	0.6613	0.01755
8	1.3495	1.3248	0.2988	0.00927
		1.2901	0.6613	0.02002
9	1.4306	1.3986	0.2984	0.01019
		1.3596	0.6610	0.02550
10	1.4592	1.4299	0.2986	0.00879
		1.3958	0.6612	0.02161
11	1.4737	1.4439	0.2986	0.00994
		1.4074	0.6612	0.02086
12	1.7787	1.7532	0.2987	0.00608
		1.7170	0.6612	0.01796
13	1.7800	1.7417	0.2986	0.01090
		1.6912	0.6612	0.02341
14	2.3965	2.3969	0.2986	0.01244
		2.2644	0.6612	0.02732
15	3.3450	3.1560	0.2986	0.01455
		3.0426	0.6612	0.03320

5.3 Calorimetric results

In this section the calorimetric results for ternary systems NaCl-CaCl₂-H₂O, NaCl-MgCl₂-H₂O, and MgCl₂-CaCl₂-H₂O, at 25°C, will be presented. Some results for the binary systems NaCl-H₂O and CaCl₂-H₂O will also be included.

5.3.1 The systems NaCl-H₂O and CaCl₂-H₂O

Even though these systems have been widely studied, direct measurements of the partial molar enthalpy of water were made on them, because they were necessary for the study of the ternary systems. The results of these measurements were also employed to calculate the partial molar enthalpy of sodium chloride to compare the result with those previously reported.

Table 5.8 shows the values of the partial molar enthalpies of each component in the aqueous binary system. The partial molar enthalpy of water in each system was determined experimentally and the partial molar enthalpies of sodium chloride and that of calcium chloride were obtained by the Gibbs-Duhem relation

$$H_i = -55.508 \int_c^m \frac{1}{m} d\mathcal{H}_3$$

where i represents NaCl or CaCl₂, \mathcal{H}_3 is the partial molar

enthalpy of water and the molality of the sodium chloride or calcium chloride solution.

The agreement between the values obtained, for sodium chloride, in this work and those reported by Robinson (93) and by Craft and Van Hook (94) is excellent. Also the values obtained for the partial molar enthalpy of calcium chloride in the binary system $\text{CaCl}_2\text{-H}_2\text{O}$ are in good agreement with those which have been reported (95) although only up to 2 mol kg^{-1} . It appears that values have not previously been reported beyond this concentration for this system.

TABLE 5.8

Partial Molar Enthalpies of Each Component
in the Systems NaCl-H₂O and CaCl₂-H₂O at 25 °C

m	NaCl		CaCl ₂	
	H_3/Jmol^{-1}	$H_{\text{NaCl}}/\text{Jmol}^{-1}$	H_3/Jmol^{-1}	$H_{\text{CaCl}_2}/\text{Jmol}^{-1}$
0.5	3.0	- 63.6	- 2.4	3927
1.0	12.3	- 779.3	- 5.5	5204
1.5	28.0	-1477.	- 9.0	6592
2.0	43.0	-1943	-13.1	8700
2.5	60.0	-2345	-19.5	10780
3.0	74.5	-2634	-26.8	13140
3.5	85.3	-2816	-35.3	15970
4.0	91.3	-2909	-46.8	20160
4.5	90.7	-2899	-60.0	24240
5.0	83.6	-2763	-75.7	29760

5.3.2 The system NaCl-CaCl₂-H₂O

This system has been the first system studied with the new form of the McKay-Perring method, which has been developed in Chapter 3 of this thesis. It was found that it could be treated only by the constant total molality method, because there were practically no ranges of equal partial molar enthalpy of water in the binary aqueous systems, the effects being characteristically of opposite sign.

The following definitions are made for applying the equations.

m_A, m_B are the molalities of sodium chloride and calcium chloride, respectively, in a solution containing both these salts.

m is any convenient linear combination of the form

$$m = k_A m_A + k_B m_B$$

x_B is the mole fraction of calcium chloride in the mixture of sodium chloride and calcium chloride.

$$x_B = k_B m_B / m$$

H_A, H_B are the partial molar enthalpies of sodium chloride and calcium chloride, respectively, in the mixed solution.

\mathcal{H}_A is the partial molar enthalpy of sodium chloride in a solution containing sodium chloride only, at the same m as the mixed solution.

\mathcal{H}_B is the partial molar enthalpy of calcium chloride in a solution containing only calcium chloride at the same m as the mixed solution.

$\mathcal{H}_{3(A)}, \mathcal{H}_{3(B)}$ are the partial molar enthalpies of water in solutions containing sodium chloride only and calcium chloride only, respectively.

H_3 is the partial molar enthalpy of water in the mixed solution.

Using these definitions, the partial molar enthalpies of each component in the mixed solutions, as has been shown in

Chapter 3, become

$$H_A = \mathcal{H}_A + \frac{k_A}{0.018} \int_0^m \left\{ \frac{1}{m^2} \left(\frac{\partial H_3}{\partial \ln x_B} \right)_m - \frac{1}{m} \left(\frac{\partial [H_3 - \mathcal{H}_{3(A)}]}{\partial m} \right)_{x_B} \right\} dm \quad (5. 14)$$

and

$$H_B = \mathcal{H}_B + \frac{k_B}{0.018} \int_0^m \left\{ \frac{1}{m^2} \left(\frac{\partial H_3}{\partial \ln x_A} \right)_m - \frac{1}{m} \left(\frac{\partial [H_3 - \mathcal{H}_{3(B)}]}{\partial m} \right)_{x_A} \right\} dm \quad (5. 15)$$

The application of eqns (5. 14) and (5. 15) requires a knowledge of \mathcal{H}_A (or \mathcal{H}_B). They can be obtained directly from tables of partial molar enthalpy of sodium chloride (or calcium chloride) in its own solution, or can be determined from the experimental values of $\mathcal{H}_{3(A)}$ (or $\mathcal{H}_{3(B)}$) using the Gibbs-Duhem equation, as has been done here. The partial molar enthalpies of water in the pure solutions and in the mixtures can be obtained directly from calorimetric measurements, starting with concentrated solutions and adding water to them.

Once having the values of \mathcal{H}_3 at different m 's and x_B 's one must obtain the value of the integral term in eqn (5. 14). To evaluate this integral term it is convenient to find an analytical expression for H_3 and $[H_3 - \mathcal{H}_{3(A)}]$. The analytical expression of H_3 as a function of x_B and m is also linked with the choice of the constants k_A and k_B as has previously been mentioned (Chapter 3).

CHOICE OF k_A AND k_B

In order to generalize the equations to systems of any charge type, the quantity

$$m = k_A m_A + k_B m_B$$

is defined, where k_A and k_B are constants. These must be chosen to give the most suitable representation of the system.

An attempt to do this was to put the total molality of the solution, m , simply equal to the sum of the individual molalities of the components, that is, putting $k_A = k_B = 1$. A plot of H_3 versus x_B at constant $m = m_A + m_B$ is shown in Fig. 5.5. The curve-fitting to a polynomial

$$H_3 = J + Kx_B + Lx_B^2 + \dots$$

by a least-squares method was not successful within the limits of experimental error, even adding more terms to the quadratic equation.

Keeping $k_A = 1$, the value of k_B was changed. The values $k_B = 0.5$ and $k_B = 1.5$ were tried but the fit of the experimental values was not better than the previous with $k_B = 1$. The best that can be said is that the derived equation led to approximately the right order of magnitude at moderate concentrations, but at high concentrations they suffered great deviations, especially at low molar fractions.

Having always those values of k_A and k_B in mind, other functions (fig. 5.5 a) like

$$\frac{H_3 - H_3^0}{H_3^0} = f(mx_B)$$

and

$$F = (H_3 - H_3^0) / x_B m^2$$

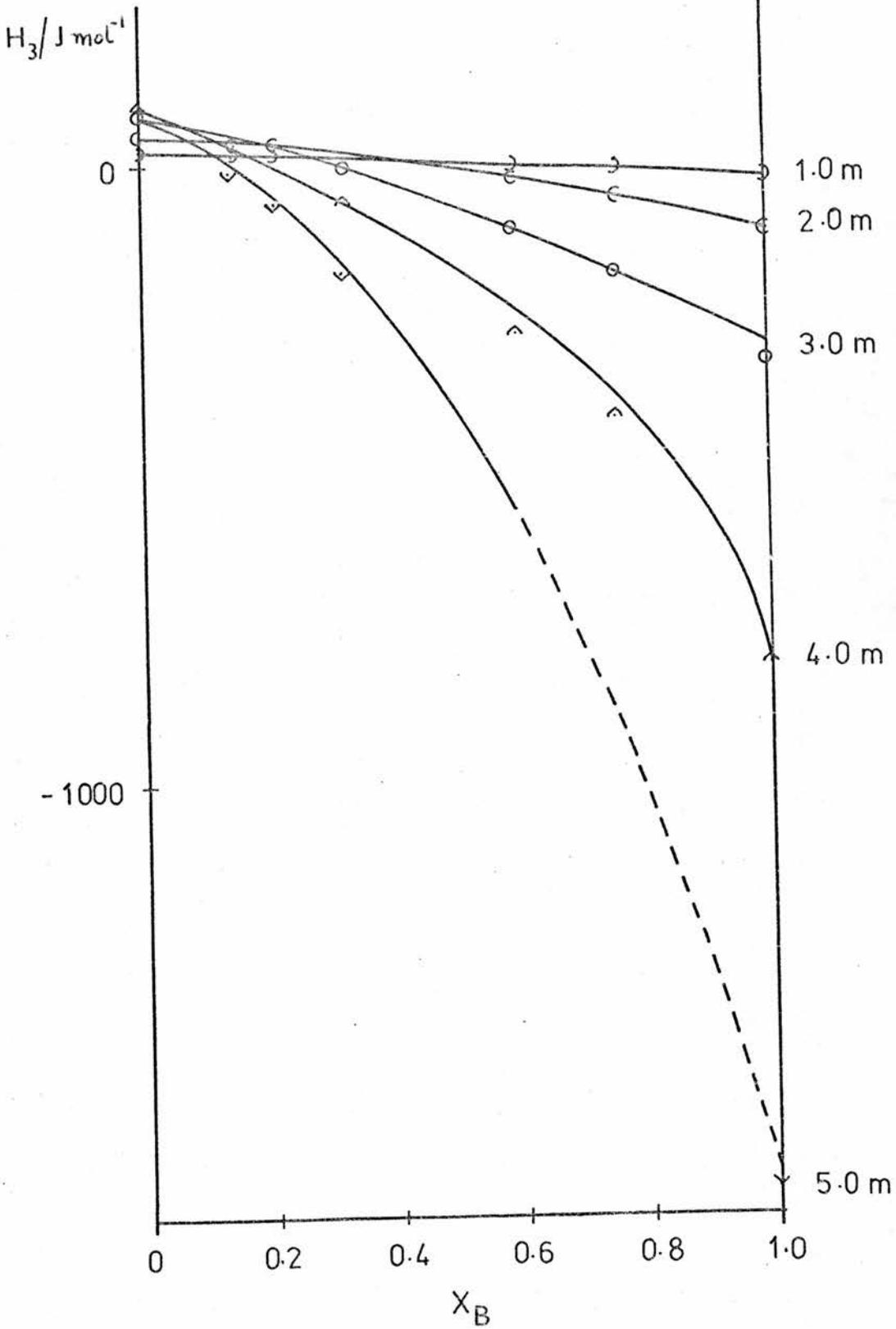


Fig. 5.5 Partial molar enthalpy of water in sodium chloride - calcium chloride solutions at 25°C. ($k_A = k_B = 1$)

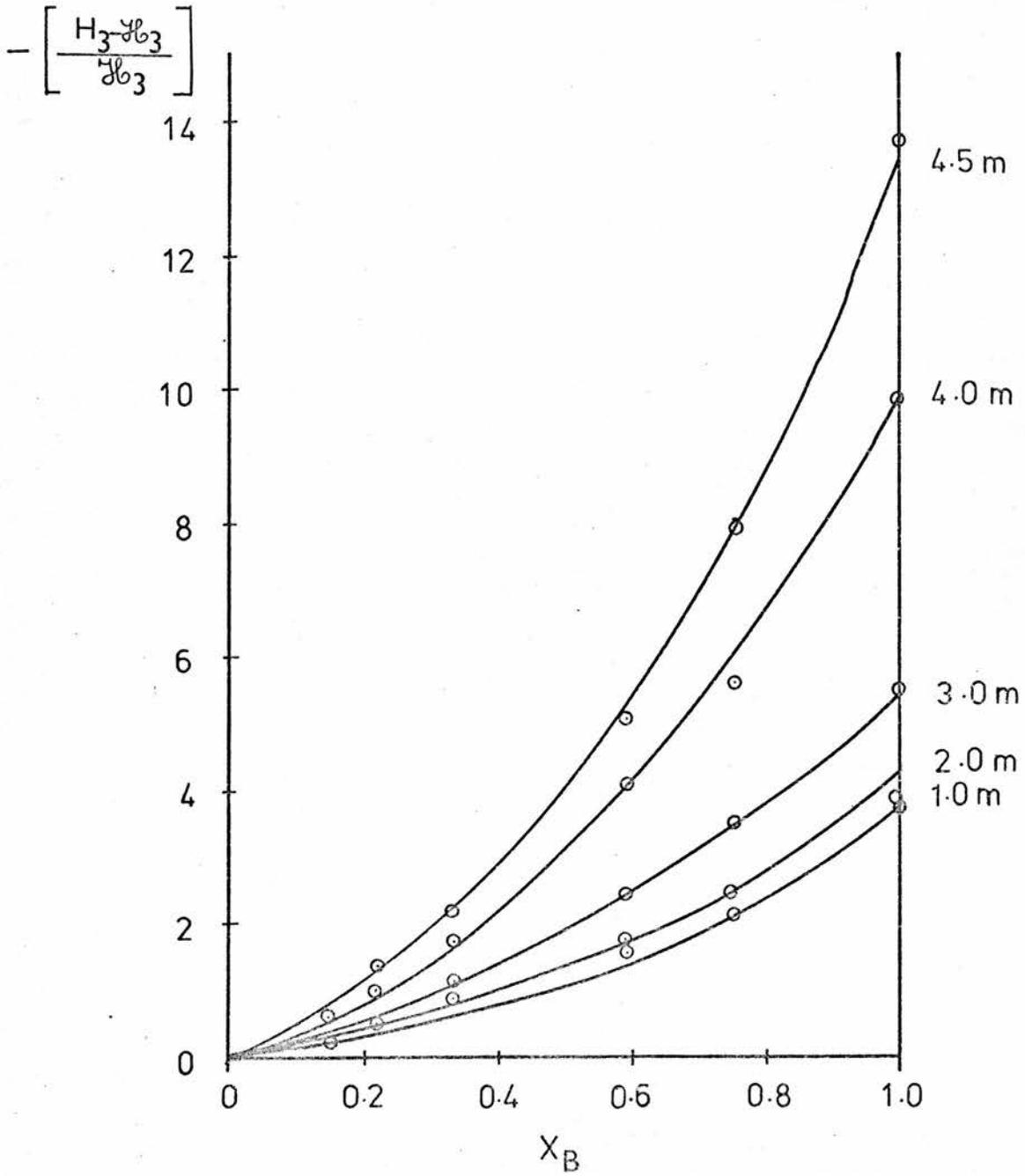


Fig. 5.5a Sodium chloride - calcium chloride solutions
at 25°C. ($k_A = k_B = 1$)

were tried but none of them reproduced in an adequate way the experimental values of H_3 .

$$\text{Although the function } H_3 = J + Kx_B + Lx_B^2$$

with $k_A = k_B = 1$ did not satisfy all the experimental values, it was found to be the best of those which were first tried. That is why it was decided to investigate the properties that the parameters J, K, L would have and their dependence on m if one could be found.

By definition at $x_B = 0$, $H_3 = J = \mathcal{H}_3$, that is, J represented the partial molar enthalpy of water in the binary solution of component A in water. The parameters K and L were both functions of m and both were equal to zero at $m = 0$. K was found to be of the form $Dm + Em^2$, and L varied exponentially with m, making it difficult to evaluate the integral term at the limits.

It was finally decided to try a new value of k_B . Because the ionic strength of the solution is $I = m_A + 3m_B$, it was thought that k_B could be made to equal 3, so that $m = I$. Plots of H_3 versus x_B (figs. 5.6, 5.7, 5.8, and 5.9) were drawn in this way, at constant $m = I$. It was observed that in this case the dependence was linear within the limits of experimental error.

The fitting of the experimental data to a first-degree polynomial by the least-squares method, may be expressed as

$$H_3 = \alpha + \beta x_B \quad (5.16)$$

where

$$\alpha = \bar{H}_3(A) \quad (5.17)$$

$$\beta = \bar{H}_3(B) - \bar{H}_3(A) \quad (5.18)$$

and both are function of m . Table 5.9 shows the values of the experimental H_3 and those calculated by eqn.(5.16).

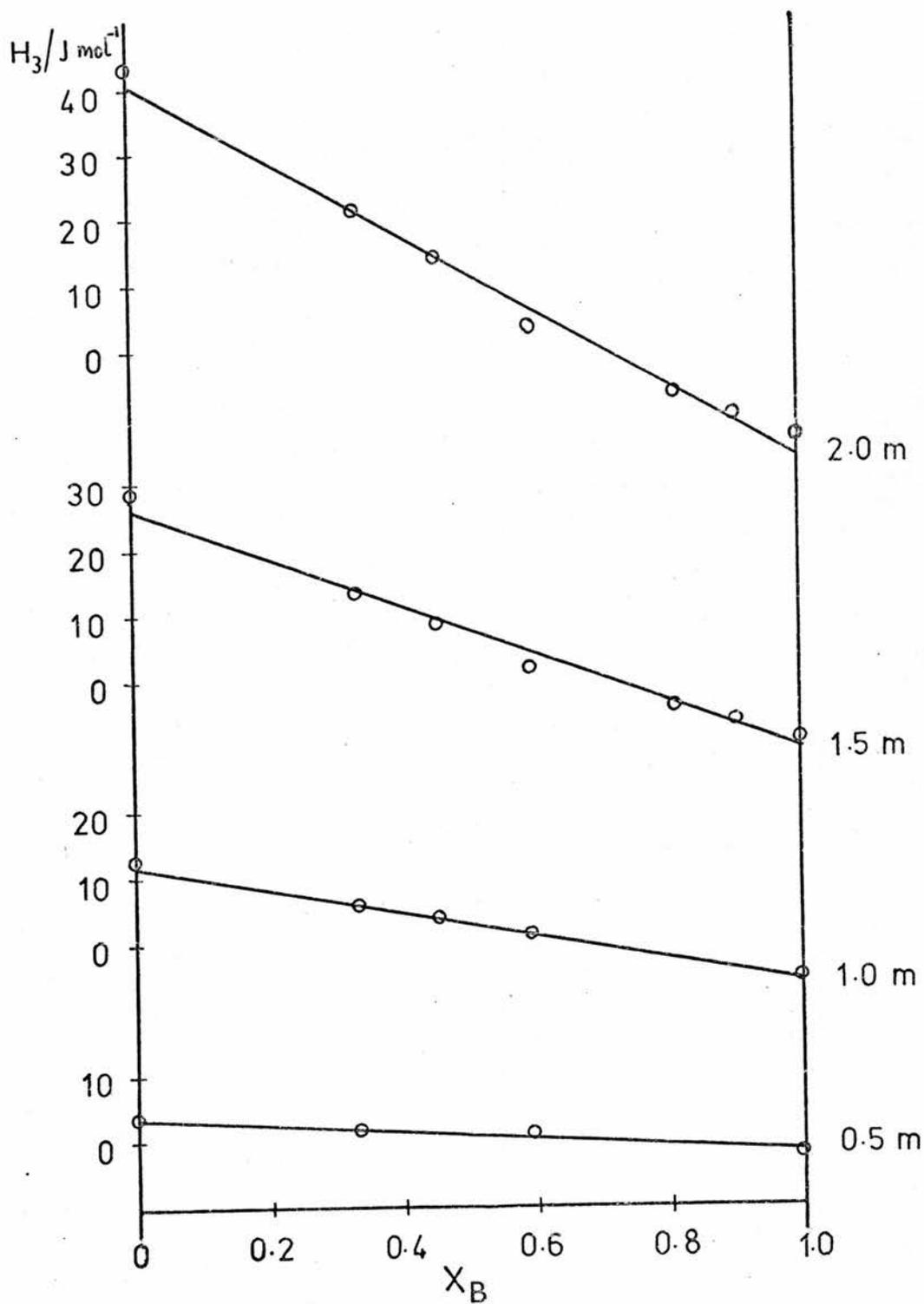


Fig. 5.6 Partial molar enthalpy of water against mole fraction of $CaCl_2$ at constant $m=1$, in $NaCl-CaCl_2-H_2O$ solutions, at $25^\circ C$

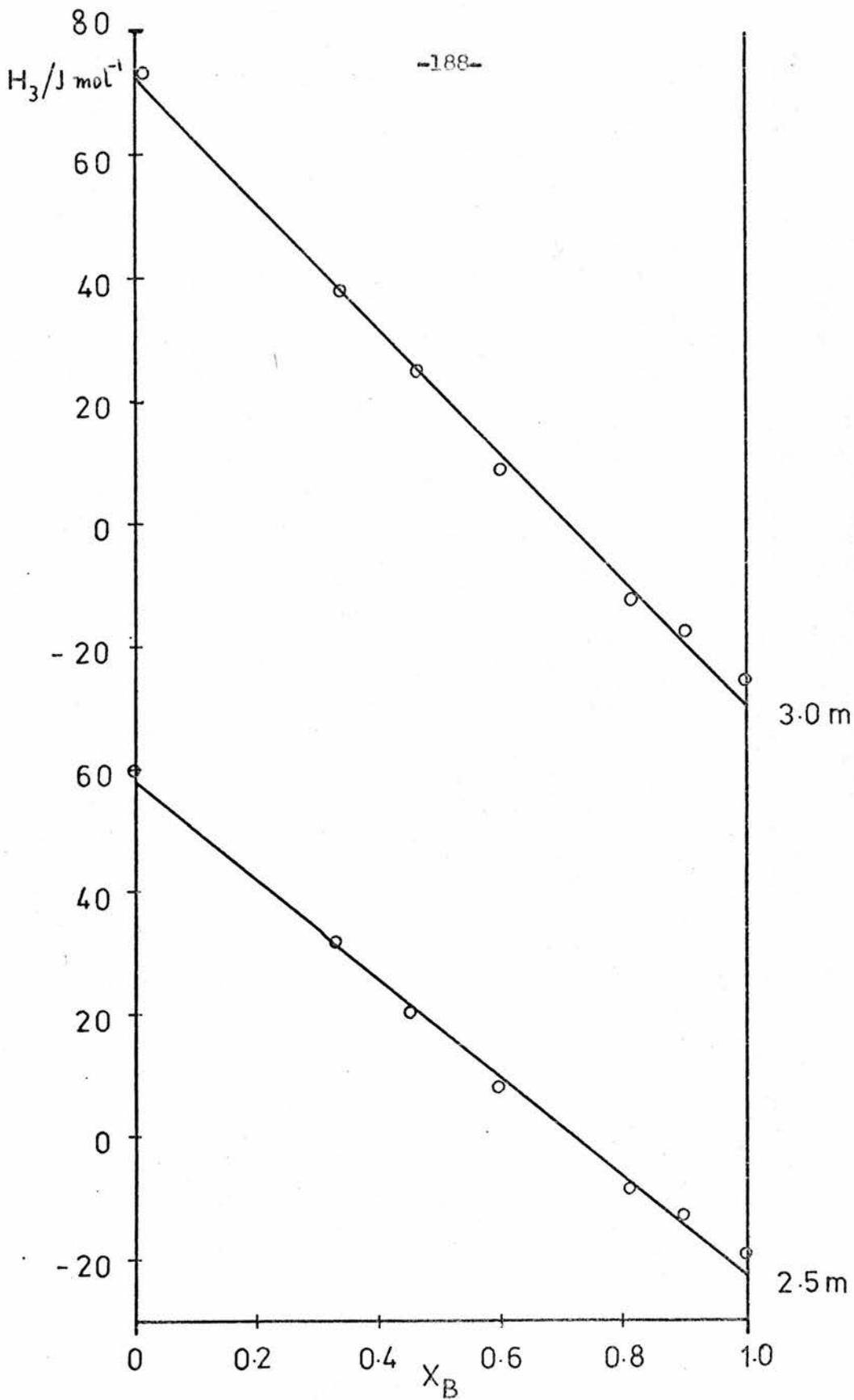


Fig. 5.7 Partial molar enthalpy of water against mole fraction of CaCl_2 at constant $m=I$, in $\text{NaCl-CaCl}_2\text{-H}_2\text{O}$ solutions, at 25°C

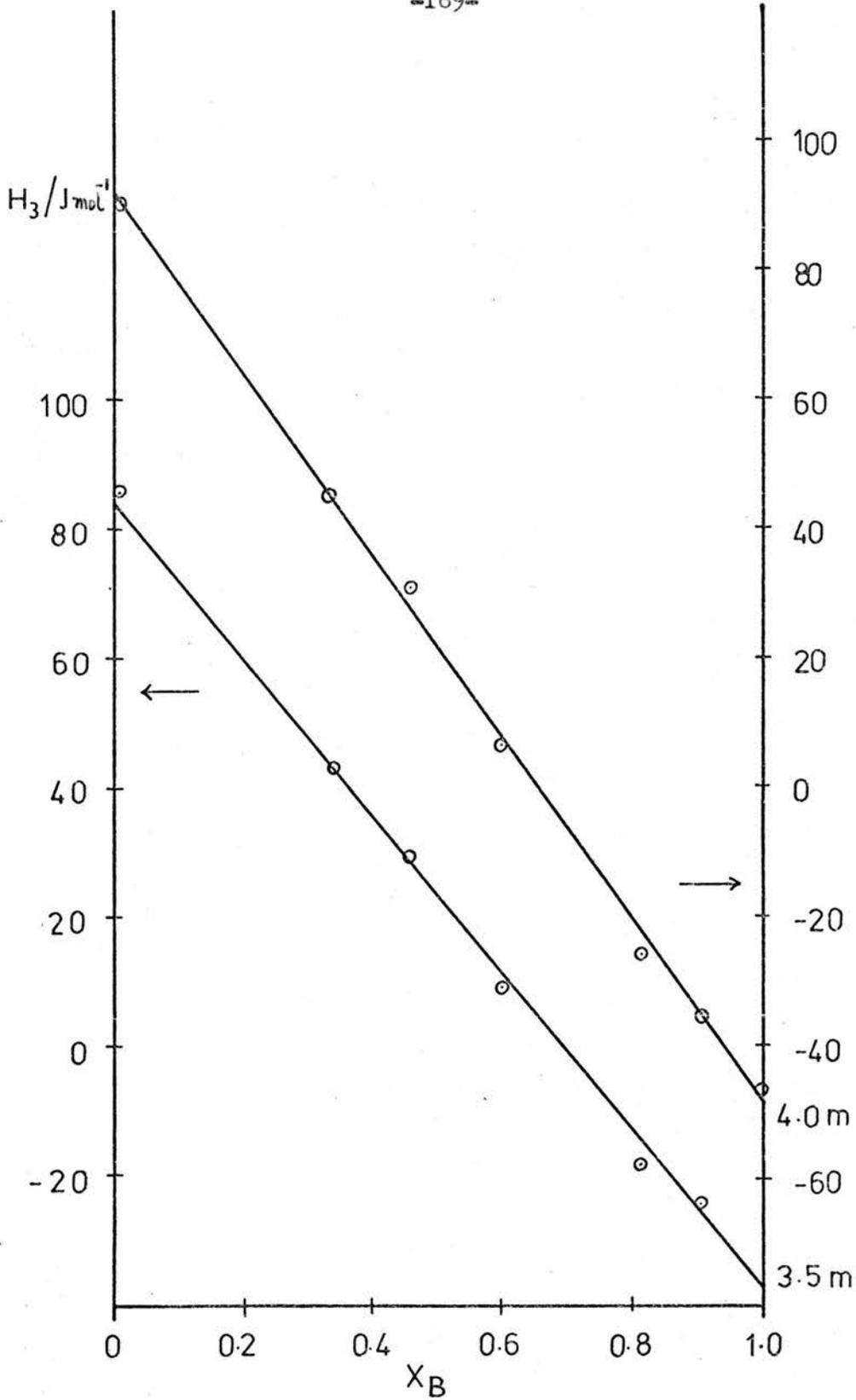


Fig. 5.8 Partial molar enthalpy of water against mole fraction of CaCl_2 at constant $m=1$, in $\text{NaCl}-\text{CaCl}_2-\text{H}_2\text{O}$ solutions, at 25°C

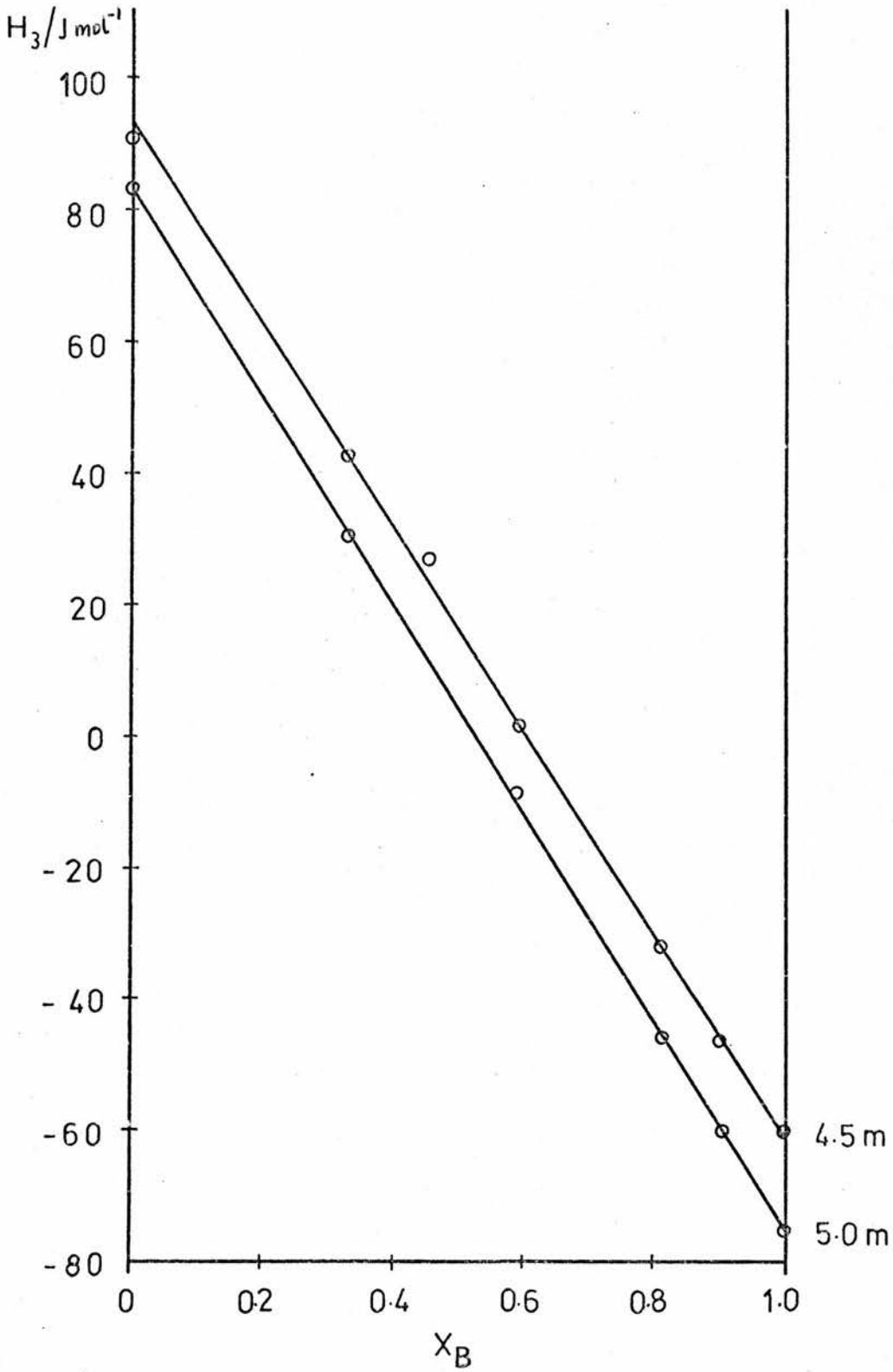


Fig. 5.9 Partial molar enthalpy of water against mole fraction of CaCl_2 at constant $m=1$, in $\text{NaCl}-\text{CaCl}_2-\text{H}_2\text{O}$ solutions, at 25°C

TABLE 5.9

PARTIAL MOLAR ENTHALPY OF WATER VERSUS
 MOLAR FRACTION OF Ca Cl_2 AT CONSTANT IONIC
 STRENGTH IN SODIUM CHLORIDE-CALCIUM CHLORIDE SOLUTIONS AT 25°C

$m = I$	x_B	H_3 (exp)/ J mol^{-1}	H_3 (calc)/ J mol^{-1}
0.5	0.0000	3.0	3.3
	.3370	1.5	1.5
	.5971	0.2	0.2
	1.0000	- 2.4	- 1.9
1.0	0.0000	12.3	11.8
	.3370	5.5	5.8
	.4597	3.1	3.7
	.5971	1.2	1.2
1.5	1.0000	- 5.5	- 5.9
	0.0000	28.0	26.0
	.3370	13.0	13.6
	.4597	8.0	9.1
	.5971	1.6	4.0
	.8155	- 4.5	- 4.0
	.9046	- 6.6	- 7.3
2.0	1.0000	- 9.0	-10.8
	0.0000	43.0	40.7
	.3370	21.2	21.6
	.4597	13.7	14.7
	.5971	3.7	6.9
	.8155	- 6.9	- 5.5
	.9046	- 9.7	-10.6
	1.0000	-13.1	-16.0

Table continued

$m = I$	x_B	H_3 (exp)/J $_{mol}^{-1}$	H_3 (calc)/J $_{mol}^{-1}$
2.5	0.0000	60.0	58.5
	.3370	32.2	31.4
	.4547	20.5	21.5
	.5971	7.3	10.4
	.8155	- 9.1	- 7.2
	.9046	-13.1	-14.3
	1.0000	-19.5	-22.0
	3.0	0.0000	74.5
.3370		38.4	38.3
.4597		25.1	25.7
.5971		8.6	11.7
.8155		-13.2	-10.6
.9046		-18.1	-19.7
1.0000		-26.8	-29.5
3.5		0.0000	85.3
	.3370	42.7	43.0
	.4597	29.3	28.1
	.5971	8.2	11.3
	.8155	-18.4	-15.3
	.9046	-24.4	-26.1
	1.0000	-35.3	-37.7

Table continued

m = I	x_B	H_3 (exp)/Jmol ⁻¹	H_3 (calc)/Jmol ⁻¹
4.0	0.0000	91.3	92.1
	.3370	45.2	44.6
	.4597	30.3	27.4
	.5971	6.4	8.0
	.8155	-25.4	-22.8
	.9046	-35.7	-35.3
	1.0000	-46.8	-48.7
	4.5	0.0000	90.7
.3370		42.8	41.6
.4597		26.7	22.8
.5971		1.4	1.8
.8155		-32.2	-31.7
.9046		-46.9	-45.3
1.0000		-60.0	-59.9
5.0		0.0000	83.6
	.3370	30.7	30.6
	.5971	- 8.7	-10.9
	.8155	-46.2	-45.7
	.9046	-60.3	-59.9
	1.0000	-75.7	-75.1

now equation (5.16) may be written

$$H_3 = \mathcal{H}_{3(A)} + \beta x_B \quad (5.19)$$

then

$$\left(\frac{\partial H_3}{\partial x_B} \right)_m = \beta \quad (5.20)$$

and

$$\left(\frac{\partial H_3}{\partial \ln x_B} \right)_m = \beta x_B \quad (5.21)$$

Also from eqn (5.19)

$$\left(\frac{\partial (H_3 - \mathcal{H}_{3(A)})}{\partial m} \right)_{x_B} = x_B \frac{\partial \beta}{\partial m} \quad (5.22)$$

By replacing the values of $(\partial H_3 / \partial \ln x_B)_m$ and $[\partial (H_3 - \mathcal{H}_{3(A)})]_{x_B}$

obtained in eqn (5.21) and (5.22) into eqn (5.14), with $k_A = 1$, the following equation is obtained

$$H_A - \mathcal{H}_A = \frac{1}{0.018} \int_0^m \left\{ \frac{1}{m^2} \beta x_B - \frac{1}{m} \frac{d\beta}{dm} x_B \right\} dm \quad (5.23)$$

The variation of the parameter β with m is shown in fig 5.10. The circles represent the experimental values of β and the full line the β values calculated with the $\mathcal{H}_{3(A)}$ and $\mathcal{H}_{3(B)}$ obtained with eqn (5.16). The variation of β with m is given by

$$\beta = am + bm^2 + cm^3 \quad (5.24)$$

The values of the constants a , b , and c were calculated by a least-squares method which gives

$$a = -3.7889$$

$$b = -16.7649$$

$$c = 2.2307$$

For obtaining these values, the β 's obtained from eqn (5.16) were

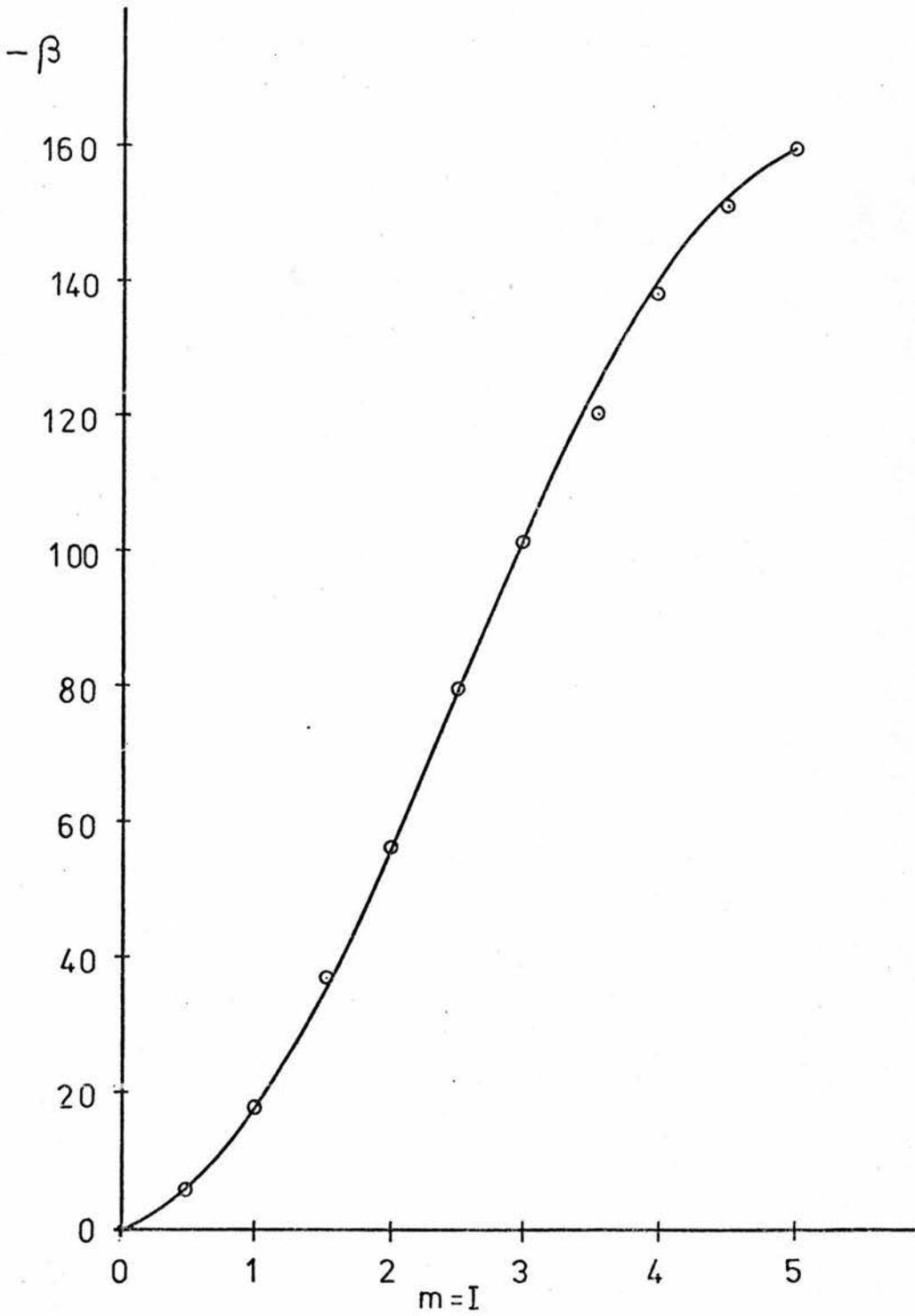


Fig. 5.10 Value of the parameter β for the system sodium chloride - calcium chloride - water, at 25°C

— β calculated from eqn.(5.16) \circ β experimental

Thus

$$\beta = - 3.7889 m - 16.7649 m^2 + 2.2307 m^3 \quad (5.25)$$

The values of the experimental β 's and those obtained from eqn (5.16) and eqn(5.25) are given in table 5.10

From eqn. (5.24) one obtains

$$\frac{d\beta}{dm} = a + 2b m + 3c m^2 \quad (5.26)$$

By introducing eqns. (5.24) and (5.26) into eqn. (5.23), this latter becomes

$$H_A - \gamma_A = \frac{1}{0.018} \int_0^m \left\{ - x_B (b + 2 cm) dm \right\} \quad (5.27)$$

or, on integration at constant x_B ,

$$H_A = \gamma_A - \frac{1}{0.018} x_B (bm + cm^2) \quad (5.28)$$

In table (5.9) the values of the integral

$$\int_0^m (b + cm) dm = bm + cm^2$$

are given.

For the partial molar enthalpy of the second solute in the mixture, that is for CaCl_2 , one has eqn (5.15)

$$H_B - \gamma_B = \frac{k_B}{0.018} \int_0^m \left\{ \frac{1}{m^2} \left(\frac{\partial H_3}{\partial \ln x_A} \right)_m - \frac{1}{m} \left(\frac{\partial (H_3 - \gamma_{3(B)})}{\partial m} \right) \right\} dm$$

But

$$H_3 = \alpha + \beta x_B = \gamma_{3(A)} + \beta x_B \quad (5.19)$$

and

$$\beta = \gamma_{3(B)} - \gamma_{3(A)} \quad (5.18)$$

Then $\gamma_{3(A)} = \gamma_{3(B)} - \beta$ (5.29)

Also $x_A + x_B = 1$ (5.30)

Hence $H_3 = \gamma_{3(B)} - \beta x_A$ (5.31)

By taking the appropriate derivatives with respect to x_A and m one obtains

$$\left(\frac{\partial H_3}{\partial \ln x_A} \right)_m = -\beta x_A \quad (5.32)$$

and

$$\left(\frac{\partial (H_3 - \gamma_{3(B)})}{\partial m} \right)_{x_A} = - \frac{d\beta}{dm} x_A \quad (5.33)$$

By introducing eqns (5.24), (5.32), and (5.33) into eqn (5.15), one gets

$$H_B - \gamma_B = \frac{k_B}{0.018} \int_0^m x_A (b + 2 cm) dm \quad (5.34)$$

on integration at constant x_A , with $k_B = 3$, the following relation is obtained

$$H_B = \gamma_B + \frac{3 x_A}{0.018} (b m + c m^2) \quad (5.35)$$

Table 5.11 gives the values of the differences between the partial molar enthalpy of sodium chloride in the ternary mixture and in the binary one, $(H_A - \gamma_A)$, at rounded ionic strengths and different mole fractions of calcium chloride; and table 5.12 gives the values of the partial molar enthalpy of sodium chloride H_A , in the mixtures calculated from eqn (5.28). Figures 5.11 and

5.12 show plots of the partial molar enthalpy of sodium chloride against mole fraction of calcium chloride at constant ionic strength, and against the ionic strength at constant mole fraction, respectively.

In tables 5.13 and 5.14 the differences ($H_B - \mathcal{H}_B$) and the values of H_B for calcium chloride respectively are shown. Figures 5.13 and 5.14 show plots of the partial molar enthalpy of calcium chloride against mole fraction of sodium chloride at constant ionic strength, and against ionic fraction at constant mole fraction, respectively.

Consistency between calorimetric and isopiestic data.

For the complete description of any of the ternary systems it will ultimately be necessary to show that the changes in activity coefficient with temperature satisfy the thermodynamic equation

$$\frac{d \ln \gamma_i}{dT} = - \frac{L_i}{RT^2}$$

Preliminary explorations along these lines have not been entirely satisfactory, even for the binary systems. Using the accepted values of L_i and γ_i in the literature. For example, at 4.0 mol kg⁻¹, the L_{NaCl} values quoted by Robinson (93), and Craft and Van Hook(94) would require a change in $\log \gamma_{\pm}$ for NaCl about twice that actually observed, and similar discrepancies have been found in the ternary system.

It is not yet clear whether such inconsistencies can be traced to errors in the calorimetric or the isopiestic technique; but, since the observed changes in $\log \gamma_{\pm}$ with temperature are in any case very small, it seems most probable that the enthalpies of dilution, being more directly determined, give a much more reliable estimate of the small variation in $\log \gamma_{\pm}$

to be expected over a moderate temperature range. It is therefore concluded that, although some refinement may still be possible in the numerical treatment of the experimental values by the McKay-Perring method, the calorimetric estimates are probably fairly reliable and could be used to estimate small changes in $\log \gamma_{\pm}$ with temperature.

TABLE 5.10

Values of the parameter $\beta = [(\mathcal{H}_3)_B - (\mathcal{H}_3)_A] / J$
 for the system Na Cl-Ca Cl₂-H₂O at 25°C

m = I	$-\beta_{\text{exp}}$	$-\beta_{\text{calc}}^{(a)}$	$-\beta_{\text{calc}}^{(b)}$	$\int_0^m (c)$
0.5	5.4	5.2	5.8	- 7.8
1.0	17.8	17.7	18.3	-14.5
1.5	37.0	36.8	35.9	-20.1
2.0	56.1	56.7	56.8	-24.6
2.5	79.5	80.5	79.4	-28.0
3.0	101.3	102.2	102.0	-30.2
3.5	120.6	121.8	123.0	-31.4
4.0	138.1	140.8	140.6	-31.4
4.5	150.7	153.1	153.3	-30.3
5.0	159.3	159.5	159.2	-28.1

(a) β calculated with eqn. (5.16)

(b) β calculated with eqn. (5.25)

(c) $\int_0^m \{ (b + cm) \} dm = bm + cm^2$

TABLE 5.11

Partial molar enthalpies of Na Cl, H_A , in sodium chloride-calcium chloride solutions less the partial molar enthalpies of Na Cl, \mathcal{H}_A , in its own solutions, at 25°C

I	$(H_A - \mathcal{H}_A) / \text{J mol}^{-1}$				
	$x_B = 0.3370$.4547	.5971	.8155	.9046
0.5	146.0	197.0	258.7	353.4	392.0
1.0	271.5	366.3	481.0	659.9	728.7
1.5	376.3	507.7	666.8	910.6	1010.1
2.0	460.6	621.4	816.0	1114.5	1236.3
2.5	524.2	707.3	928.8	1268.6	1407.2
3.0	565.4	762.9	1001.8	1368.2	1517.7
3.5	587.9	793.2	1041.6	1422.6	1578.0
4.0	587.9	793.2	1041.6	1422.6	1578.0
4.5	567.3	765.4	1005.1	1372.8	1522.7
5.0	526.1	709.8	932.1	1273.1	1412.2

TABLE 5.12

Partial molar enthalpy of Na Cl in sodium chloride
 -calcium chloride solutions at 25°C

I	$H_A/J \text{ mol}^{-1}$				
	$x_B = 0.3370$.4547	.5971	.8155	.9046
0.5	77	128	190	285	323
1.0	- 508	- 413	- 299	- 123	- 51
1.5	-1101	- 969	- 808	- 566	- 467
2.0	-1482	-1322	-1127	- 828	- 707
2.5	-1821	-1638	-1426	-1076	- 938
3.0	-2069	-1871	-1632	-1266	-1116
3.5	-2228	-2023	-1774	-1393	-1238
4.0	-2321	-2116	-1867	-1486	-1331
4.5	-2332	-2134	-1894	-1526	-1376
5.0	-2237	-2053	-1831	-1490	-1351

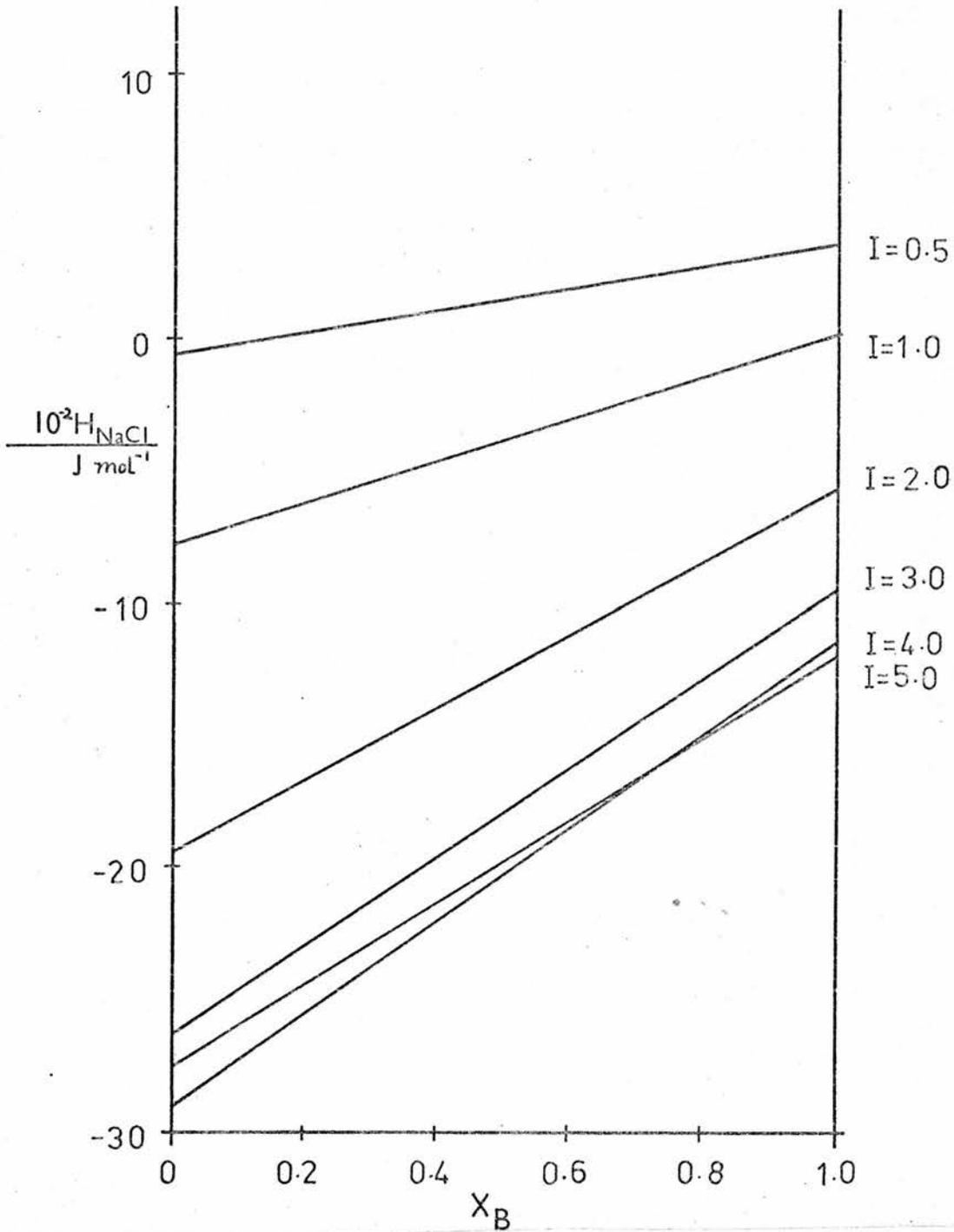


Fig. 5.11 Partial molar enthalpy of NaCl in sodium chloride - calcium chloride solutions against mole fraction of CaCl_2 at constant ionic strength, at 25°C

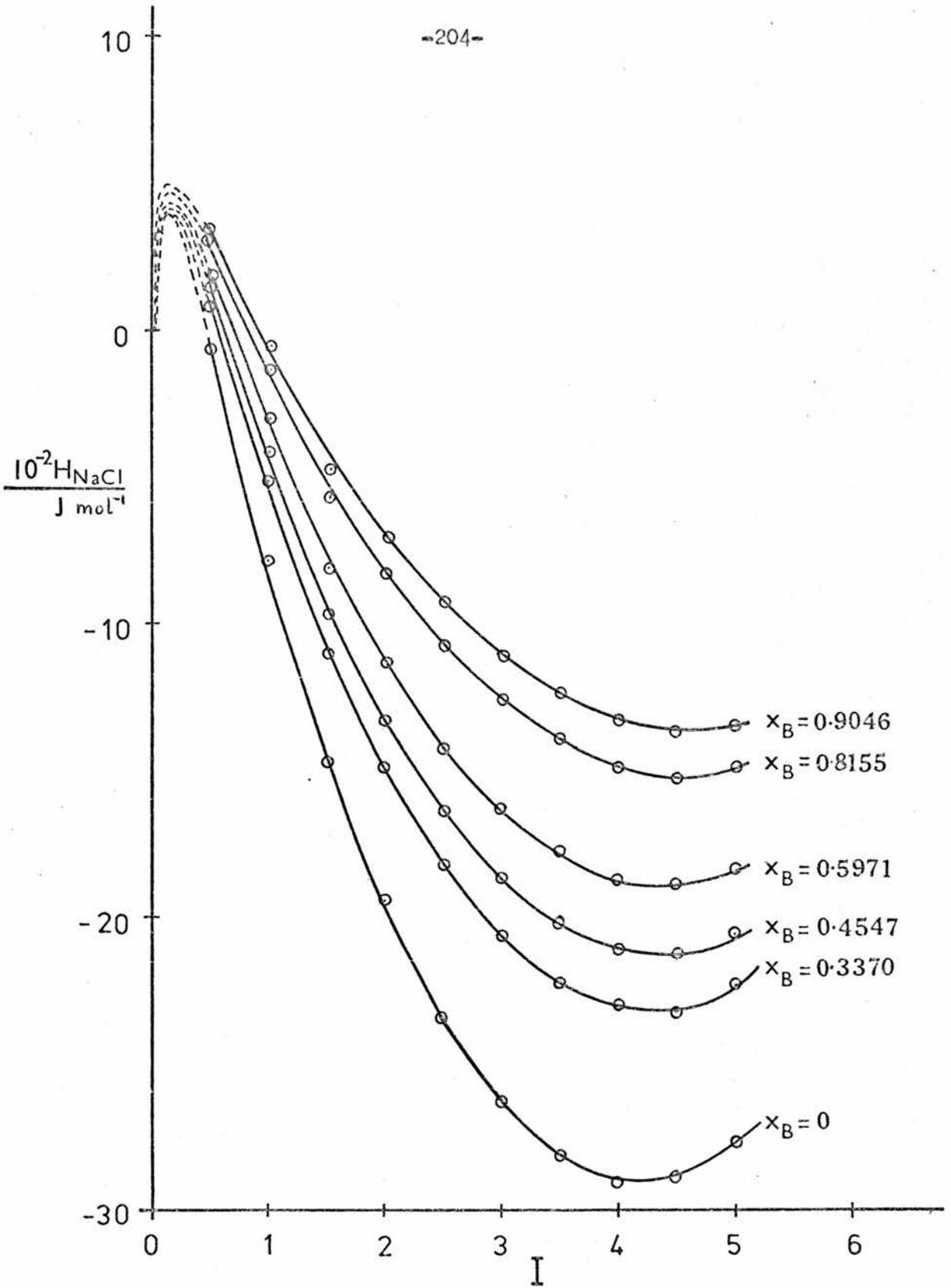


Fig. 5.12 Partial molar enthalpy of NaCl in sodium chloride - calcium chloride solutions against ionic strength at constant x_{CaCl_2} at 25°C

TABLE 5.13

Partial molar enthalpies of CaCl_2 , H_B , in sodium chloride-calcium chloride solutions less the partial molar enthalpies of CaCl_2 , \mathcal{H}_B , in its own solutions at 25°C

I	$(H_B - \mathcal{H}_B) / \text{J mol}^{-1}$					
	$x_A = 0.8000$.6630	.5453	.4029	.1845	.0954
0.5	-1040	- 862	- 709	- 524	- 240	- 124
1.0	-1933	-1602	-1318	- 974	- 446	- 230
1.5	-2680	-2221	-1827	-1350	- 618	- 320
2.0	-3280	-2718	-2236	-1652	- 756	- 391
2.5	-3733	-3094	-2545	-1880	- 861	- 445
3.0	-4027	-3337	-2745	-2028	- 929	- 480
3.5	-4187	-3470	-2854	-2108	- 966	- 499
4.0	-4187	-3470	-2854	-2108	- 966	- 499
4.5	-4040	-3348	-2754	-2035	- 932	- 482
5.0	-3747	-3105	-2554	-1887	- 864	- 447

TABLE 5.14

Partial molar enthalpy of Ca Cl_2 in sodium
chloride-calcium chloride solutions at 25°C

I	$H_B / \text{J mol}^{-1}$					
	$x_A = 0.8000$.6630	.5453	.4029	.1845	.0954
0.5	1776	1954	2107	2292	2576	2692
1.0	1438	1769	2053	2397	2925	3141
1.5	1247	1706	2100	2577	3309	3607
2.0	1073	1635	2117	2701	3597	3962
2.5	1045	1684	2233	2898	3917	4333
3.0	1177	1867	2459	3176	4275	4724
3.5	1480	2197	2813	3559	4701	5168
4.0	1942	2659	3275	4021	5163	5630
4.5	2552	3244	3838	4557	5660	6110
5.0	3548	4190	4741	5408	6431	6848

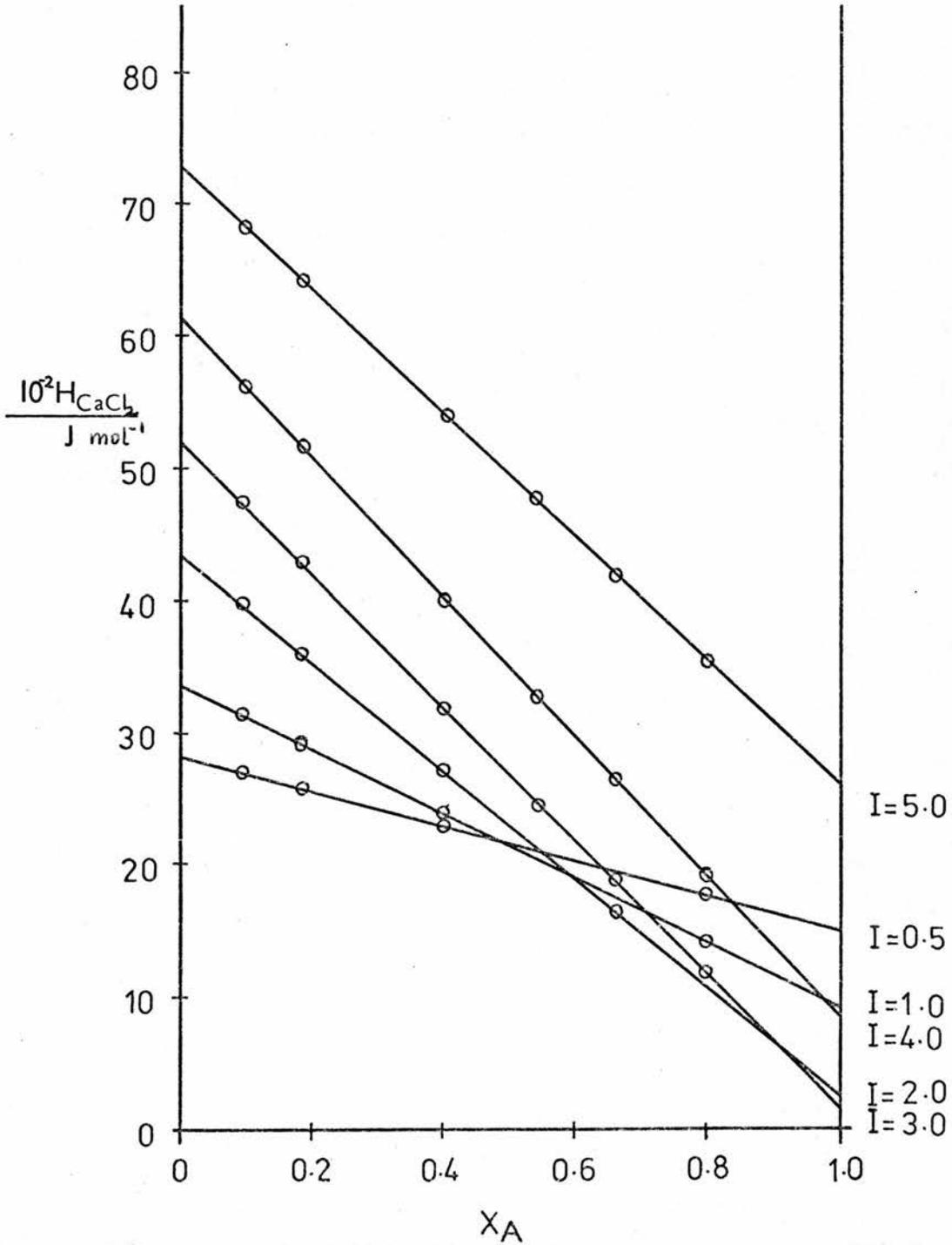


Fig. 5.13 Partial molar enthalpy of $CaCl_2$ in sodium chloride - calcium chloride solutions against mole fraction of NaCl at constant ionic strength, at $25^\circ C$

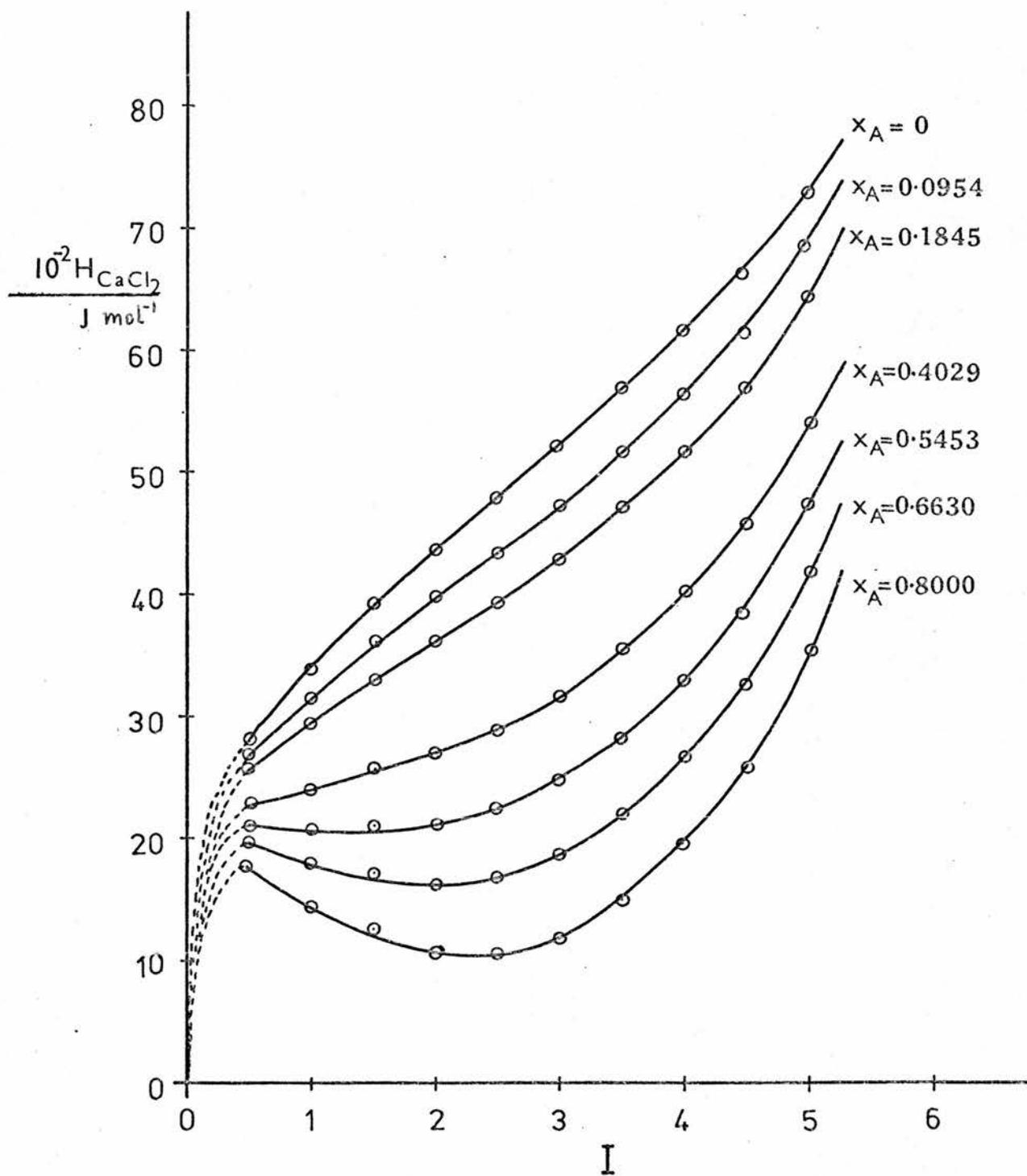


Fig. 5.14 Partial molar enthalpy of $CaCl_2$ in sodium chloride - calcium chloride solutions against ionic strength at constant x_{NaCl} , at $25^\circ C$

5. 3. 3 The system NaCl-MgCl₂-H₂O

The system sodium chloride-magnesium chloride-water is similar to the sodium chloride-calcium chloride-water system in that the partial molar enthalpy values of water in the binary systems are characteristically of opposite sign. Thus the NaCl-MgCl₂-H₂O system could only be treated by the constant total molality method.

Table 5.15 gives the values of the partial molar enthalpy of water at different mole fractions but constant total molality (or ionic strength). Figure 5.15 shows that the variation of the partial molar enthalpy of water at constant molality is a linear function of the mole fraction. Then

$$H_3 = \alpha + \beta x_c$$

where

α is equal to the partial molar enthalpy of water of the binary reference solution, and

β is equal to the difference between the partial molar enthalpies of water of the two binary solutions.

Figure 5.16 shows the variation of the parameter β with the molality m . The analytical expression of β as a function of n will allow the computation of the integral term in the relation for obtaining the partial molar enthalpy of each solute in the mixtures, just as has been done for the system NaCl-CaCl₂-H₂O.

TABLE 5.15

Partial Molar Enthalpy Of Water For Various
Molar Fractions Of Magnesium Chloride
At Constant Ionic Strength In Sodium
Chloride-Magnesium Chloride Solutions At 25°C

$n/\text{mol kg}^{-1}$	x_c	H_2/Jmol^{-1}
1.0	0.	12.3
	0.2713	4.3
	0.4806	8.1
	0.8409	3.5
	1.0000	1.2
2	0.	43.0
	0.2713	16.6
	0.4806	12.7
	0.8409	- 17.8
	1.0000	- 22.5
3	0.	74.5
	0.4806	7.0
	0.8409	- 30.8
	1.0000	- 51.2
	4	0.
0.2713		7.6
0.4806		1.7
0.8409		- 62.4
1.0000		- 90.0
5	0.	83.6
	0.2713	24.1
	0.4806	- 30.5
	0.8409	- 98.3
	1.0000	-141.0

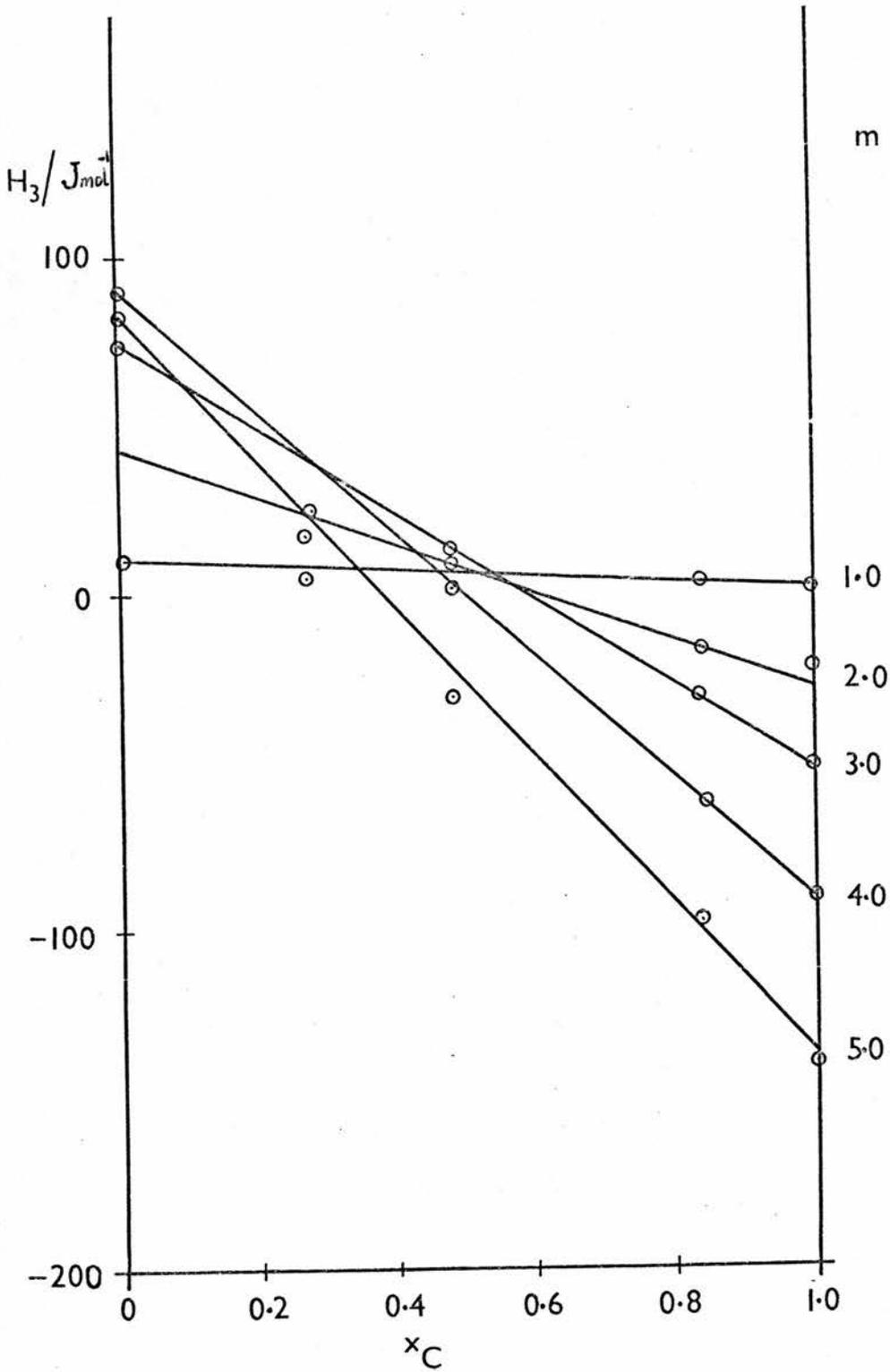


Fig. 5.15 Partial molar enthalpy of water in the system $NaCl-MgCl_2-H_2O$ at constant ionic strength, at 25 C

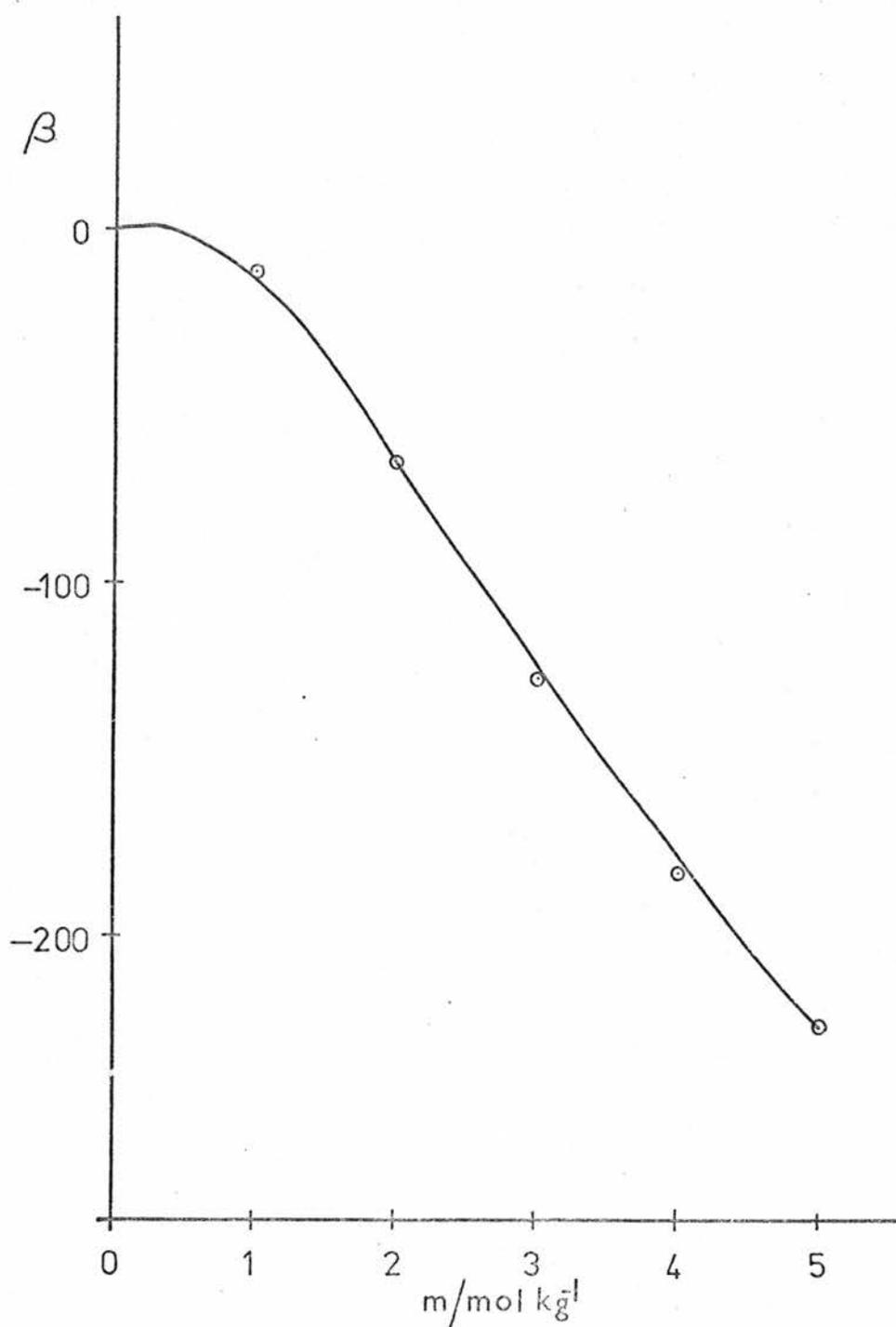


Fig. 5.16 Value of the parameter for the system
 $\text{NaCl-MgCl}_2\text{-H}_2\text{O}$

5. 3. 4 The system $\text{CaCl}_2\text{-MgCl}_2\text{-H}_2\text{O}$

The experimental values of the partial molar enthalpy of water in the ternary solutions seem to show characteristic peculiarities. Their values are very close to those of the binary system $\text{MgCl}_2\text{-H}_2\text{O}$ up to approximately 3 mol kg^{-1} and at higher concentrations they show deviations outside the limits of both binary systems.

However, the partial molar enthalpy of water, in both binary systems and in the ternary solutions, did run in the same direction, which indicates that the system $\text{CaCl}_2\text{-MgCl}_2\text{-H}_2\text{O}$ could be treated by either of the two methods described in chapter 3, thus differing importantly from the other two systems, i.e. $\text{NaCl-CaCl}_2\text{-H}_2\text{O}$ and $\text{NaCl-MgCl}_2\text{-H}_2\text{O}$, which could only be treated by the constant total molality method. For this 2:2 system therefore, the method using the constant partial molar enthalpy of water has been tried.

In this latter method the partial molar enthalpy of calcium chloride, H_B , in the ternary system, is given by

$$H_B - \mathcal{H}_B = \frac{1}{0.018} \int_0^{H_3} \left\{ -\frac{1}{m^2} \left(\frac{\partial m}{\partial \ln x_c} \right) - \frac{1}{m} + \frac{1}{M_B} \right\} d H_3 \quad (5.36)$$

where

\mathcal{H}_B is the partial molar enthalpy of the reference solution, i.e. the binary aqueous solution of calcium chloride.

M_B is the molality of the reference solution.

$m = m_B + m_C$ is the molality of the mixed solution which has the same partial molar enthalpy as the reference solution of molality H_B .

$x_c = n_c / (n_B + n_c)$ is the mole fraction of magnesium chloride in the mixture of molality m .

H_3 is the partial molar enthalpy of water.

The variation of the molality m (for constant H_3) with the mole fraction x_c is shown in fig 5.17. It can be noted that this is almost constant except in the region of low mole fraction where it suffers a sharp deviation. In the range in which m is independent of x_c at constant H_3 ,

$$\left(\frac{\partial m}{\partial \ln x_c} \right)_H = x_c \left(\frac{\partial m}{\partial x_c} \right)_{H_3} = 0$$

Hence eqn (5.36) becomes

$$H_B - \mathcal{H}_B = \frac{1}{0.018} \int_0^{H_3} \left\{ -\frac{1}{m} + \frac{1}{M_B} \right\} d H_3$$

and the problem reduces to finding an analytical expression for the term $(-1/m + 1/M_B)$ with the partial molar enthalpy of water.

It can be appreciated from the curves in fig 4.11, the two binary systems and the ternary mixture itself in this case show rather small differences in solvent partial molar enthalpies. This example therefore serves better as a specific case in which the calorimetric behaviour is similar to that of the well-known isopiestic solvent activity results, rather than as a system which is well adapted for the extraction of partial molar enthalpy values for the other components.

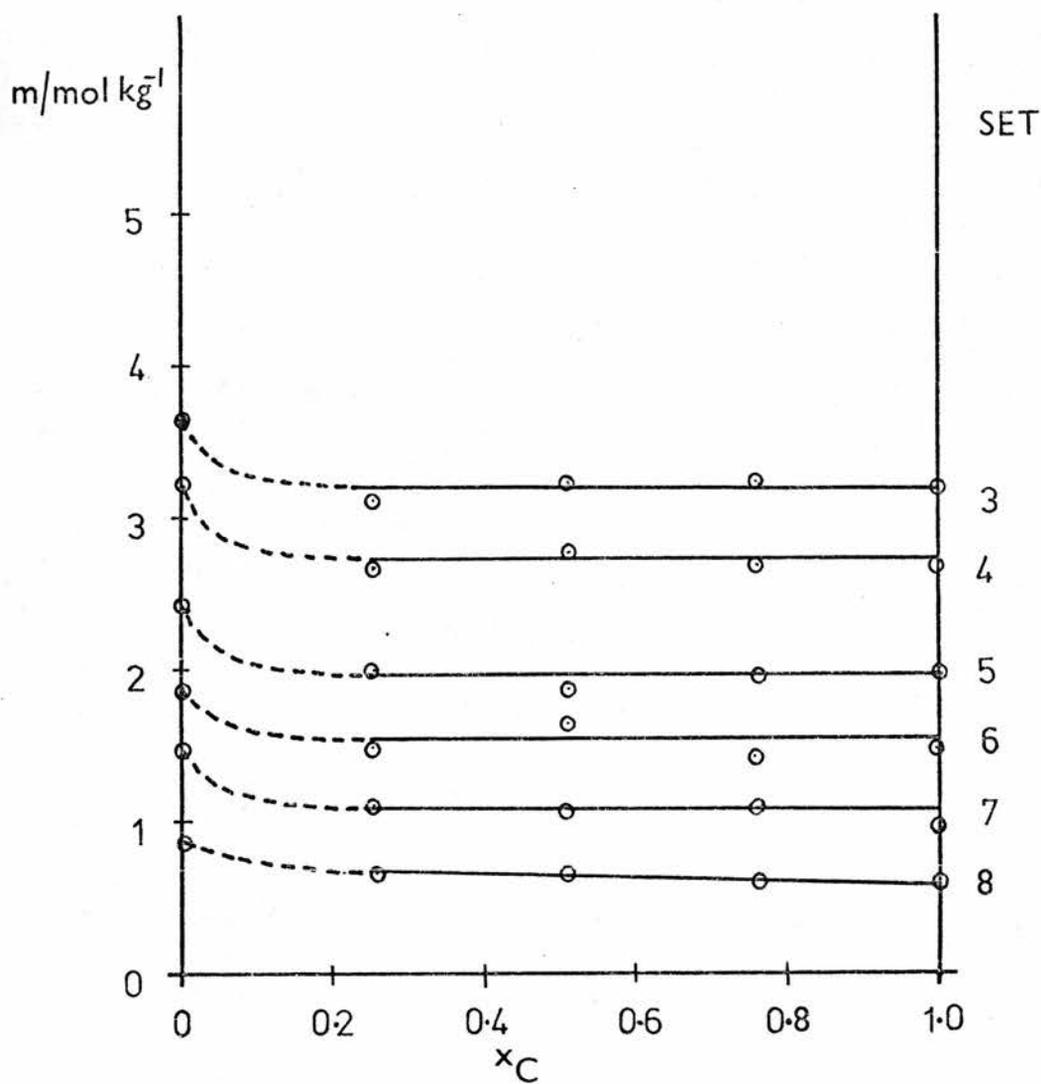


Fig. 5.17 Total molality against mole fraction of magnesium chloride at constant partial molar enthalpy of water

REFERENCES

1. T.F. Young and M.B. Smith, J. Phys. Chem., 1954, 58: 716.
2. T.F. Young, Y.C. Wu, and A.A. Krawetz, Discuss. Faraday Soc., 1957, 24: 37, 77, 80.
3. Y.C. Wu, M.B. Smith, and T.F. Young, J. Phys. Chem., 1965, 69: 1868, 1873.
4. R.H. Wood and H.L. Anderson, J. Phys. Chem., 1956, 70, 992.
5. A.K. Covington, T.H. Lilley, and R.A. Robinson, J. Phys. Chem., 1968, 72: 2759.
6. H.A.C. McKay, Discuss. Faraday Soc., 1957, 24: 76.
7. G. Scatchard, Chem. Rev., 1956, 19: 309
8. G. Scatchard, J. Am. Chem. Soc., 1961, 83: 2636.
9. G. Scatchard, J. Am. Chem. Soc., 1968, 90: 3124;
1969, 91: 2410.
10. K.S. Pitzer, Acc. Chem. Res., 1977, 10: 371.
11. K.S. Pitzer, J. Phys. Chem., 1973, 77: 268
12. L.F. Silvester and K.S. Pitzer, J. Phys. Chem., 1977, 81: 1822.
13. G. Scatchard and R.G. Breckenridge, J. Phys. Chem. 1954, 58: 596.
14. H.A.C. McKay, Nature, 1952, 169: 464.
15. H.A.C. McKay and J.K. Perring, Trans. Faraday Soc., 1953, 49: 163.
16. H.A.C. McKay, Trans. Faraday Soc., 1953, 49: 237.
17. W.J. Angersinger, J. Phys. Chem., 1954, 58: 792.
18. F.J. Millero, Chem. Rev., 1971, 71: 147 - 176.
19. F.J. Millero, Deep-Sea Res., 1973, 20: 101.
20. F.J. Millero, in The Sea, E. Goldberg, editor, Willey and Sons. Vol 5, 1974.
21. G. Tammann, Z. Anorg. Allgem. Chem., 1926, 158: 1.
22. R.A. Horne, Science, 1970, 168: 151.
23. W.C. Roentgen, Ann. Phys. Chim. (Wied), 1892, 45: 91.

24. J.A. Pople, Proc. Roy. Soc. Lond., 1951, A205: 163.
25. J.D. Bernal and R.H. Fowler, J.Chem. Phys. 1933, 1: 515
26. R.P. Marchi and H. Eyring, J. Phys. Chem., 1964, 68: 221
27. O. Ya. Samoilov, Structure of aqueous solutions and the Hydration of Ions. Consultants Bureau, New York, 1965.
28. H.S. Frank, Federataion Proc., 1965, 24, No2, Part 3.
29. B.P. Fabricand, S.S. Goldberg, R. Leifer, and S.G. Ungar, Mol. Phys., 1963 - 64, 7: 425.
30. F.J. Millero, in Water and aqueous solutions: Structure, Thermodynamics, and Transport processes. R.A. Horne, editor, Wiley-Interscience, 1971.
31. H.S. Frank and W.Y. Wen, Discuss. Faraday Soc., 1957, 24: 133.
32. H. Eigen and E. Wicke, J. Phys. Chem., 1954, 58: 702.
33. J.L. Kavanau, Water and solute-water interactions. San Francisco: Holden-Day, 1964.
34. D. Eisenberg and W. Kauzmann, The structure and properties of water, Oxford, University Press., 1969.
35. R.A. Horne, Water and aqueous solutions: Structure, Thermodynamics, and Transport processes. Wiley-Interscience, 1971.
36. H. Eyring and R.P. Marchi, J. Chem. Educ., 1963, 40: 562.
37. R.M. Diamond, J. Phys. Chem., 1963, 67: 2513.
38. R.W. Stoughton, Ann. Rev. Phys. Chem., 1965, 16: 297.
39. N. Bjerrum, Z. Elektrochem., 1907, 24: 259.
40. P. Debye and E. Hückel, Physik. Z., 1923, 24: 185.
41. E. Hückel, Physik. Z., 1925, 26: 93.
42. E.A. Guggenheim, Phil. Mag., 1935, 19: 558 - 643.
43. E. Glueckauf, in The structure of Electrolyte solutions, ed. W.J. Hamer, Wiley, New York, 1959.
44. M.H. Lietzke, R.H. Stoughton, and R.H. Fuoss, Proc. Natl. Acad. Sci. (US), 1968, 59: 39.

45. G. Scatchard, *Physik. Z.*, 1932, 33: 22.
46. G. Scatchard, *Chem. Rev.*, 1936, 19: 309.
47. L. Onsager, *Chem. Rev.*, 1933, 13: 73.
48. P. Van Rysselberghe and S. Eisenberg, *J. Am. Chem. Soc.*, 1939, 61: 3030, [1940, 62: 451].
49. M.H. Leitske and R.H. Stoughton, *J. Phys. Chem.*, 1962, 66: 508.
50. N. Bjerrum, *Kgl. Danske Videnskab Selskab, Mat-Fys. Medd.*, 1926, No 9, 7.
51. R.A. Robinson and R.H. Stokes, *Electrolyte Solutions*. Butterworths Scientific Publication, London, 2nd ed., 1955.
52. E. Glueckauf, *Trans. Faraday Soc.*, 1955, 51: 1235.
53. N. Bjerrum, *Z. Physik. Chem.*, 1926, 119: 145.
54. T.H. Gronwald, V.K. La Mer, and K. Sandved, *Physik. Z.*, 1928, 29: 358.
55. E. Lange and J. Mixner, *Physik. Z.*, 1929, 30: 670.
56. H.S. Harned and J.C. Hecker, *J. Am. Chem. Soc.*, 1933, 55: 4838.
57. H.S. Harned and R.W. Ehlers, *J. Am. Chem. Soc.*, 1933, 55: 2179.
58. R.H. Stoughton and M.H. Lietzke, *J. Chem. Eng. Data*, 1965, 10: 254.
59. F.L. Silvester and K.S. Pitzer, *J. Phys. Chem.*, 1977, 81: 1822.
60. J.H. Bronsted, *J. Am. Chem. Soc.*, 1922, 44: 877.
61. E.A. Guggenheim, *Trans. Faraday Soc.*, 1966, 62: 3446.
62. H.S. Harned and B.B. Owen, *The Physical Chemistry of Electrolyte Solutions*. 3rd ed. Reinhold Publishing Corporation, New York, 1957.
63. H.S. Harned and R.A. Robinson, *Multicomponent Electrolyte Solutions*. Oxford: Pergamon Press.
64. R.A. Robinson and V.E. Bower, *J. Res. NBS (Phys. and Chem.)*, 1965, 69A (1): 19.
65. E. Glueckauf, H.A.C. McKay, and A.R. Mathieson, *J. Chem. Soc.*, 1949, S299.
66. G. Scatchard, *J. Am. Chem. Soc.* 1961, 83: 2636.

67. Y.C. Wu, R.M. Rush, and G. Scatchard, J. Phys. Chem., 1968, 72: 4048
68. K.S. Pitzer and J.J. Kim, J. Am. Chem. Soc., 1974, 96: 57.
69. K.H. Khoo, C.Y. Chan, and T.K. Lim, Faraday I, 1978, 74: 837.
70. K.H. Khoo, T.K. Lim, and C.Y. Chan, Faraday I, 1978, 74: 2037.
71. R.H. Wood and H.L. Anderson, J. Phys. Chem. 1966, 70: 1877.
72. H.A.C. McKay, Trans. Faraday Soc., 1952, 48: 1103
73. B.B. Owen and T.F. Cooke, J. Am. Chem. Soc., 1937, 59: 2273.
74. H de Vries, Footnote ref 79.
75. W.R. Bousfield, Trans. Faraday Soc., 1917, 13: 401.
76. D.A. Sinclair, J. Phys. Chem., 1933, 37: 495.
77. R.A. Robinson and D.A. Sinclair, J. Am. Chem. Soc., 1934, 56: 1830.
78. R.A. Robinson, J. Am. Chem. Soc., 1935, 57: 1161.
79. G. Scatchard, W.J. Hamer, and S.E. Wood, J. Am. Chem. Soc., 1938, 60: 3061.
80. Ch. H. Mason, J. Am. Chem. Soc., 1938, 60: 1638.
81. R.A. Robinson, Trans. Faraday Soc., 1939, 35: 1217.
82. A.V. Luck'yanov, Siberian Chem. Journal, 1967, 67: 707.
83. O.D. Bonner, Ch. F. Jordan, R.H. Arisman, and J.H. Bednarek, J.Chem. Thermodynamics, 1976, 8: 1173.
84. O.D. Bonner, J. Chem. Thermodynamics, 1976, 8: 1167
85. B.A. Phillips and G.M. Watson with W.A. Felsing, J. Am. Chem Soc., 1942, 64: 244.
86. R. Mallison, Thesis Ph.D. University of Edinburgh, 1975.
87. A.D. Jones and D.R. Williams, J. Chem. Soc., 1970 (A), 3138.
88. J. Coops, R.S. Jessup, and K. Van Ness, in F.D. Rossini, ed., Experimental Thermochemistry. Interscience Publishers, Inc., New York.
89. H.S. Harned, in Gmelin Handbuch der Anorg. Chem. Syst. Nr. 28, 1961

90. Yu. G. Valasov, Russ. J. Phys. Chem., 1965, 37: 1399
91. R.A. Robinson and V.E. Bower, J. Res. NBS (Phys. and Chem.), 1966, 70A (4): 313.
92. R.A. Robinson and V.E. Bower, J. Res. NBS (Phys. and Chem), 1966, 70A (4): 305.
93. R.A. Robinson, J. Am. Chem. Soc., 1932, 54: 1311.
94. Q.D. Craft and W.A. Van Hook, J. Soln. Chem., 1975 4 (11): 923.
95. G.N. Lewis and H. Randall, Thermodynamics, 2nd ed., McGraw-Hill series in advance chemistry
96. J. O'M. Bockris, Quart. Rev. (London), 1949, 3: 173.

APPENDIX 1

EXECUTION.

```

L.00001 C LATEST UPDATE 20 JCT 77 , 21 JCT 77 (IMPLICIT & VOLWAT(.7) 1.11 WRITE607
L.00002 C LATEST UPDATE 3 NOV 77 JOULES PER MOLE H2O ADDED , READ AMSALT
L.00003 C 21 NOV 77 AMSALT WGTWAT : 5.12.77 AMSALB & CALCN
L.00004 C IMPLICIT REAL*8 (A-H,O-Z)
L.00005 C DIMENSION READNG(2000),T(2000),IREAD(2000),INC(2000),D(2000),
L.00006 C I CALHN(40),VOLCAL(40),AMDJ(40)
L.00007 C JIJ USED AS A LOOP COUNTER INDEX AT LINE 227
L.00008 C JIJ=0
L.00009 C NI IS USED AS A LOOP COUNTER AT LINE 208
L.00010 C NI=1
L.00011 C READ(5,554)(D(I),I=1,80)
L.00012 C READ(5,554)(D(I),I=81,160)
L.00013 C WRITE(6,6666) (D(I),I=1,80)
L.00014 C WRITE(6,6666) (D(I),I=81,160)
L.00015 C 6666 FORMAT(14 ,80A1)
L.00016 C 554 FORMAT(30A1)
L.00017 C READ (5,500) AMSALT,WGTWAT,VOLIN, AMSALB
L.00018 C 500 FORMAT(F7.5,F9.4,F7.2,F7.5)
L.00019 C READ(5,555)NEND
L.00020 C READ(5,555)(IREAD(I),INC(I),I=1,NEND)

L.00021 C WRITE(6,5656)(IREAD(I),INC(I),I=1,NEND)
L.00022 C5656 FORMAT(1H ,20(12,1X,11))
L.00023 C5555 FORMAT(14)
L.00024 C READ(5,5555) MM
L.00025 C WRITE(6,5969) MM
L.00026 C6969 FORMAT(1H ,14)
L.00027 C MMM=0
L.00028 C IP= 1
L.00029 C CALL RDA(NSTART,NN,NNN,N,THERMU,BASE,VOLWAT,WETEMP,VOLT,AMP,SEC,
L.00030 C - MM,MMM,IP,VOLCA,EXPV)
L.00031 C ICOUNT = 1
L.00032 C MMM=1
L.00033 C IP = 2
L.00034 C CALL RDA(NSTART,NN,NNN,N,THERMU,BASE,VOLWAT,WETEMP,VOLT,AMP,SEC,
L.00035 C - MM,MMM,IP,VOLCA,EXPV)

```

```

L.00036 C WRITE(6,2) NSTART,NN,NNN,N,THERMO,BASE,VOLWAT,WETEMP,VOLT,AMP,SEC
L.00037 C 1,MM,MMM,VOLCA,EXPV0
L.00038 L.00038 2 FORMAT(1H, ' FTR SUBROUTINE ',4I4,7F10.5,2I4/2F8.2)
L.00039 L.00039 MMM=MMM+1
L.00040 L.00040 IF(NSTART.NE.0) GO TO 11
L.00041 L.00041 ICOUNT = ICOUNT +1
L.00042 L.00042 MMM = 1
L.00043 L.00043 GO TO 5
L.00044 L.00044 11 IF(ICOUNT.EQ.1) GO TO 9
L.00045 L.00045 GO TO 10
L.00046 L.00046 9 IF(VOLWAT.EQ.0.0) GO TO 20
L.00047 L.00047 GO TO 5
L.00048 L.00048 10 IF(ICOUNT.EQ.3) GO TO 1005
L.00049 L.00049 IF(VOLWAT.NE.0.0) GO TO 20
L.00050 L.00050 GO TO 5
L.00051 L.00051 20 CONTINUE
L.00052 L.00052 DU 1400 I=1,N
L.00053 L.00053 1400 READNG(I) = 0.000000
L.00054 L.00054 3 FORMAT(4I4,F8.4,F12.7)
L.00055 L.00055 666 FORMAT(14,20I4)
L.00056 L.00056 555 FORMAT(20( 12,I1))
L.00057 L.00057 WRITE(6,567) NSTART,NN,NNN,N,THERMU,BASE
L.00058 L.00058 667 FORMAT(1H, '//, ' ANALYSIS WAS TAKEN OVER THE RANGE',/ ,1H ,
L.00059 L.00059 1,NSTART = ,I4,/ ,1H , 'NN = ,I4,/ ,1H , 'NNN = ,I4,/ ,1H , 'N =
L.00060 L.00060 2 ,I4,/ ,1H , 'THERMOSTAT TEMPERATURE = ,F10.5,/ ,1H , 'BASE TEMPERAT
L.00061 L.00061 3URE FOR THIS DATA WAS = ,F10.5)
L.00062 L.00062 DO 1110 I=NSTART,N
L.00063 L.00063 IF(INC(I).EQ. 0)GO TO 700
L.00064 L.00064 IF (INC(I).EQ. 1)GO TO 701

L.00065 IF (INC(I).EQ. 2)GO TO 702
L.00066 L.00066 IF(INC(I).EQ. 3)GO TO 703
L.00067 L.00067 IF(INC(I).EQ.4) GO TO 704
L.00068 L.00068 IF(INC(I).EQ.5) GO TO 710
L.00069 L.00069 IF(INC(I).EQ.9) GO TO 705
L.00070 L.00070 IF (INC(I).EQ.8) GO TO 706
L.00071 L.00071 IF(INC(I).EQ.7) GO TO 707

```

```

L.00072 IF (INC(I).EQ.6) GO TO 708
L.00073 READNG(I)=IREAD(I)*1.0D-04 + BASE
L.00074 GO TO 1110
L.00075 BASE = BASE + 0.0100
L.00076 READNG(I) = IREAD(I)*1.0D-04 + BASE
L.00077 GO TO 1110
L.00078 BASE = BASE + 0.0200
L.00079 READNG(I) = IREAD(I)*1.0D-04 + BASE
L.00080 GO TO 1110
L.00081 BASE = BASE + 0.0300
L.00082 READNG(I)= IREAD(I)*1.0D-04 + BASE
L.00083 GO TO 1110
L.00084 BASE = BASE - 0.0100
L.00085 READNG(I)=IREAD(I)*1.0D-04 + BASE
L.00086 GO TO 1110
L.00087 BASE = BASE - 0.0200
L.00088 READNG(I) = IREAD(I)*1.0D-04 + BASE
L.00089 GO TO 1110
L.00090 BASE= BASE - 0.0300
L.00091 READNG(I)=IREAD(I)*1.0D-04+BASE
L.00092 GO TO 1110
L.00093 BASE = BASE - 0.0400
L.00094 READNG(I)=IREAD(I)*1.0D-04 + BASE
L.00095 GO TO 1110
L.00096 BASE = BASE + 0.0400
L.00097 READNG(I) = IREAD(I) * 1.0D-04 + BASE
L.00098 GO TO 1110
L.00099 BASE = BASE + 0.0500
L.00100 READNG(I) = IREAD(I) * 1.0D-04 + BASE
L.00101 GO TO 1110
L.00102 CUNTINUE
L.00103 WRITE(6,61) (READNG(IY),IY=NSTART,N)
L.00104 DJ 1000 I=NSTART,N
L.00105 T(I) = READNG(I)
L.00106 FORMAT(1H,10F12.4)
L.00107 AN = NN- NSTART + 1 + 1
L.00108 NI = NN +1

```



```

L.00148          SUMTT = 0.0
L.00149 C TO CALCULATE SIGMA TEMPERATURE
L.00150 DO 102 IJJ = NNN,N
L.00151 SUMTT = SUMTT + T(IJJ)
L.00152 AAAN = N - NNN + 1

L.00153 TCORBB = (SUMTT/AAAN)+((AAAN-1.0)/2.0)*GG
L.00154 TCOREE = (SJMTT/AAAN)-((AAAN-1.0)/2.0)*GG
L.00155 WRITE(6,67)TCOREE
L.00156 FORMAT(IH,'CORRECTED TEMPERATURE AT THE END OF THE MAIN PERIOD
L.00157 1,POINT NNN, WAS = ',F10.5)
L.00158 WRITE(6,68)TCORBB
L.00159 FORMAT(IH,'CORRECTED TEMPERATURE AT THE END OF THE EXPT,
L.00160 1 POINT N = ',F10.5)
L.00161 C TO CALCULATE AK = K PAGE 31
L.00162 GF = (TCORBB - TCOREE)/((AAAN - 1.0)*18.0)
L.00163 TF = TCOREE + (TCORBB - TCOREE)/2.0
L.00164 AK = (GI - GF)/(TF - TI)
L.00165 U = GF + AK*(TF - THERMJ)
L.00166 TINF1 = (GF/AK) + TF
L.00167 TINF2 = (GI*TF - GF*TI)/(GI - GF)
L.00168 LN = NN + 1
L.00169 M = NNN - 1
L.00170 TMSUM = 0.0
L.00171 DO 103 IK = LN,M
L.00172 TMSUM = TMSUM + T(IK)
L.00173 DN = NNN - NN
L.00174 C EQUATION 10 PAGE 32
L.00175 TMEAN = (TMSUM + (TCOR3+TCOREE)/2.0)/DN
L.00176 TIME = 18.0*(NNN - NN)
L.00177 C EQN 7 PAGE 32
L.00178 DELTE1 = -(U+AK*(THERMO-TMEAN))*TIME
L.00179 C EQ 8 PAGE 32
L.00180 DELTE2 = -AK*(TINF1 - TMEAN)*TIME
L.00181 C EQ 9 PAGE 32..
L.00182 DELTE3 = -(GF+AK*(TF-TMEAN))*TIME

```

```

L.00183 DELTC1 = TCUREE - TCORB + DELTE1
L.00184 DELTC2 = TCOREE - TCORB + DELTE2
L.00185 DELTC3 = TCOREE - TCORB + DELTE3
L.00186 WRITE(6,600) DELTC1
L.00187 WRITE(6,600) DELTC2
L.00188 WRITE(6,600) DELTC3
L.00189        600  FORMAT(1H, 'CORRECTED TEMPERATURE RISE = ',F10.5)
L.00190        601  WRITE(6,601)N,NN,NN,SI,TI,B8N,NJ,JN,NL,SUMA,CN,GG,TCORBB,TCOREE,
L.00191        C    IGF,TF,AK,U,TINF1,TINF2,TMEAN,DELTE1,DELTE2,DELTE3
L.00192        C    FOPMAT(1H, ,I4,3F10.4,3I6,/,7F10.6,/,7F10.6,/,F10.6)
L.00193        C
L.00194        C
L.00195        C
L.00196        IF(VOLWAT.EQ.0.0) GO TO 1020

L.00197        IF(N1.EQ.1) GO TO 950
L.00198        GO TO 951
L.00199        C  REMOVE GO TO 1020 WHEN PROGRAMME COMPLETED
L.00200        950  SPHT = 1.00
L.00201        DENSTY = 0.997069
L.00202        DO 4000 I =1,NIJ
L.00203            SUMX = SUMX + VOLCAL(I)
L.00204            SUMY=SUMY + CALBN(I)
L.00205            SUMXY = SUMXY + VOLCAL(I)*CALBN(I)
L.00206            SUMXX = SUMXX + VOLCAL(I)* VOLCAL(I)
L.00207            SUMY2 = SUMY2 + AMDJ(I)
L.00208            SUMXY2 = SUMXY2 + VOLCAL(I)*AMDJ(I)
L.00209            AN= I
L.00210        CONTINUE
L.00211        SLOPE = (SUMX*SUMY-AN*SUMXY)/(SUMX*SUMX-AN*SUMXX)
L.00212        CONST = (SUMX*SUMY-SJMY*SUMXX)/(SUMX*SUMX-AN*SUMXX)
L.00213        SLOPE2 = (SUMX*SUMY2 - AN*SUMXY2)/(SUMX*SUMX-AN*SUMXX)
L.00214        CONST2 = (SUMX*SUMY2 - SUMY2*SUMXX)/(SUMX*SUMX-AN*SUMXX)
L.00215        951  N1 = N1 + 1
L.00216        WRITE(6,6662) SLOPE,CONST
L.00217        WRITE(6,6663) SLOPE2,CONST2

```

```

L.00218 C CALUSE = SLOPE2*(VOLWAT + EXPVO) + CONST2
L.00219 C GENJOU = DELTC1/CALUSE
L.00220 C WRITE(6,6664) GENJOU,EXPVO,VOLWAT
L.00221 6664 FORMAT(1H,'JJOULES GENERATED ON DILUTION =',F10.5/1H,'FOR INITIAL
L.00222 1 VOLUME OF SOLUTION IN CALORIMETER =',F10.2/1H,
L.00223 2 'VOLUME OF WATER ADDED =',F10.2,'ML')
L.00224 6662 FORMAT(1H,'THE SLOPE OF THE CALIBRATION GRAPH IS =',F10.4,'AND
L.00225 1THE CONSTANT (INTERCEPT) IS =',F10.4)
L.00226 6663 FORMAT(1H,'THE SLOPE OF THE GRAPH OF DEGREES/JOULE AGAINST
L.00227 1 VOLUME IS =',E14.8/1H,'AND THE CONSTANT IS =',E14.8)
L.00228 EXPCAL = SLOPE * EXPVO + CONST
L.00229 CALIB = EXPCAL
L.00230 WRITE(6,606) CALIB
L.00231 606 FORMAT(1H,'CALCULATED CALIBRATION FACTOR FOR THE CALORIMETER BEFO
L.00232 1RE ADDITION OF WATER =',F10.4)
L.00233 FITEMP = ((VOLWAT*DENSITY*SPHT)*WTEMP + (CALIB*TCORB))/((CALIB)+
L.00234 1 (VOLWAT * DENSITY * SPHT))
L.00235 CORNN = (FITEMP - TCORB)*(-1.0000)
L.00236 WRITE(6,603) CORNN
L.00237 603 FORMAT(1H,' CORRECTION FOR TEMP. RISE QUOTED ABOVE,I.E. ALLOWING
L.00238 1FOR TEMP OF THE ADDED WATER, IS ',F10.5/1H,'AND IS TO BE ADDE
L.00239 1D TO THE TEMPERATURE QUOTED ABOVE')
L.00240 CALUSE = SLOPE2*(VOLWAT + EXPVO) + CONST2

L.00241 IF(VOLWAT.LE.0.7) CORNN = 0.0
L.00242 GENJOU = (DELTC1 + CORNN)/CALUSE
L.00243 WRITE(6,6664) GENJOU,EXPVO,VOLWAT
L.00244 AJOMOL = (GENJOU*18.015)/(VOLWAT*DENSITY)
L.00245 CALMOL = AJOMOL/4.184
L.00246 C MCGLASHAN P23 RIC MONOGRAPH (15) 1968 4.184 JOULE/THERMOCHEM CAL
L.00247 WRITE(6,608) AJOMOL, CALMOL
L.00248 608 FORMAT(1H,'JJOULES GENERATED PER MOLE OF WATER ADDED =',F10.5/
L.00249 11H,'EQUIVALENT TO =',F10.5,' THERMUJCHEMICAL CALORIES PER MOLE
L.00250 2OF WATER ADDED')
L.00251 WGTWFI=WGTWAT+((EXPVO-VOLIN)+VOLWAT)*DENSITY
L.00252 AMULTY = (AMSALT*1000.00)/WGTWFI

```

```

L.00253 AMDLTB = (AMSALB * 1000.0)/WGTFI
L.00254 WRITE(6,699) WGTWFI,AMOLTY,AMOLTB
L.00255 699 FORMAT(1H,'FINAL WEIGHT OF WATER =',F10.4/1H,'FINAL MOLALITY
L.00256 1 OF A =',1X,F10.4/1H,'FINAL MOLALITY OF B =',1X,F10.4)
L.00257 GO TO 5
L.00258 C ARE PERFORMED BEFORE THE CALCULATIONS FOR THE DILUTION EXPERIMENTS
L.00259 1020 AJOLE = VJLT*AMP*SEC
L.00260 WRITE(6,607) AJOLE
L.00261 607 FORMAT(1H,'ELECTRICAL JOULES IN CALIBRATION = VIT = ',F10.5)
L.00262 JIJ = JIJ + 1
L.00263 AMDJ(JIJ) = DELTC1/AJOLE
L.00264 WRITE(6,604) AMDJ(JIJ)
L.00265 604 FORMAT(1H,'DEGREES TEMPERATURE RISE OF CALDRIMETER PER JOULE OF
L.00266 ELECTRICAL ENERGY = ',F10.6)
L.00267 C CALCULATE THE WATER EQUIVALENT OF THE CALDRIMETER
L.00268 VOLCAL(JIJ) =VOLCA
L.00269 CALBN(JIJ)=(AJOLE / 4.184)/DELTC1
L.00270 WRITE(6,605) CALBN(JIJ), VOLCAL(JIJ)
L.00271 605 FORMAT(1H,'CALIBRATION FACTOR IS = ',F10.6,' GRAMS OF WATER ,WIT
L.00272 1H VOLUME SOLUTION =',F10.3,' IN THE CALDRIMETER.')
L.00273 NIJ=JIJ
L.00274 GO TO 5
L.00275 1003 WRITE(6,602)
L.00276 602 FORMAT(1H,'PROBABLE ERROR EN VALOR DE N,NN,NNN.')
L.00277 1005 CALL EXIT
L.00278 END

```

EXECUTION.

```

C LATEST UPDATE 21 OCT 77 IMPLICIT
SUBROUTINE RDA(NI,NJ,NK,NL,TH,BA,VOL,WET,VJ,AM,SE,MM,MMM,IP,VOLCA,
1 EXPVO)
C IMPLICIT REAL*8 (A-H,O-Z)
C DOUBLE PRECISION BA,BBA
C DIMENSION II(40),JJ(40),KK(40),LL(40),TTH(40),BBA(40),VVOL(40),
1 WWET(40),VVO(40),AAM(40),SSE(40),VVOLCA(40),EEXPVO(40)
C IF (IP.EQ.2) GO TO 10
C READ(5,1)((II(M),JJ(M),KK(M),LL(M),TTH(M),BBA(M),VVOL(M),WWET(M),
1 VVO(M),AAM(M),SSE(M),VVOLCA(M),EEXPVO(M)),M=1,MM)
C WRITE(6,1) II(1),JJ(1),KK(1),LL(1),TTH(1),BBA(1)
C -VVOL(1),WWET(1),VVO(1),AAM(1),SSE(1),VVOLCA(1),EEXPVO(1)
1 FORMAT(4I4,F8.4,F9.4,F6.2,F8.4,F6.3,F8.5,F6.2,F7.2 / F7.2)
C RETURN
10 M=MMM
C WRITE(6,7) M
7 FORMAT(1H , THE VALUE OF M = , I4)
C NI=II(M)
C NJ=JJ(M)
C NK=KK(M)

NL=LL(M)
TH=TTH(M)
BA=BBA(M)
VOL=VVOL(M)
WET=WWET(M)
VJ=VVO(M)
AM=AAM(M)
SE=SSE(M)
VOLCA = VVOLCA (M)
EXPVO =EEXPVO(M)
C WRITE(6,6)NI,NJ,NK,NL,TH,BA,VOL,WET,VJ,AM,SE,VOLCA,EXPVO
6 FORMAT( , , 4I4,9F10.5)
C RETURN
END

```