AN ABSTRACT OF THE THESIS OF

Ann L. Francis, for the Master of Science Degree in Chemistry, presented 12 July, 1982.

Title: Integral Heats of Solution for Cu(II) Halides in Water at 23 ± 1°C

Abstract approved: Charles Greenlief

Integral heats of solution have been measured at constant pressure as a function of concentration for copper(II) chloride dihydrate, copper(II) chloride, and copper(II) bromide in water at 23 ± 1°C, by the method of solution calorimetry. The heat of solution at infinite dilution for each halide is obtained graphically by linear extrapolation of enthalpy vs. $m^{1/2}$ curves.

Data for $CuCl_2$ compare well with enthalpy data in the literature; $CuCl_2$ results are also in excellent agreement with temperature derivatives of activity and osmotic coefficient data from the literature, the two sets of data being correlated via the relative apparent molal enthalpy.

Dissolution of copper(II) halides in water at room temperature is an exothermic process. The enthalpy of solution decreases in absolute value with: 1) an increase in the waters of hydration of the crystalline salt; and, 2) a decrease in anionic charge density.

INTEGRAL HEATS OF SOLUTION
FOR CU(II) HALIDES
IN WATER AT 23 ± 1^{o}C

A Thesis
Presented to
the Department of Chemistry
EMPORIA STATE UNIVERSITY

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

---

by
Ann L. Francis
July 1982

Charles B. Creager

Approved for the Major Department

Harold E. Durst

Approved for the Graduate Council

To my Aunt Irene

ACKNOWLEDGEMENTS

I wish to acknowledge the entire staff of the Chemistry Department at *Emporia State University, who have so unselfishly given of their time* and attentions the past 5 years.

I also wish to express my appreciation to Dr. Alfred Ericson and Dr. Edward Rowe for their helpful suggestions and for their time invested in proofreading this paper.

I am deeply grateful to Dr. Charles Greenlief for his continual efforts and advice toward, not only this project, but my education in general; I especially wish to thank him for his perpetual patience.

I thank my parents, brothers and sisters, children and husband for their moral support. A special note of appreciation must be given to my Aunt Irene Nelson, whose "timely contributions" have helped make my continued education a reality, and to whom this manuscript is dedicated with love.

PREFACE

This thesis describes in detail the method and procedures used to obtain accurate heat of solution data at constant pressure for three Cu(II) halides in water, and the analysis and interpretation of these data. Results of preliminary investigations of several other copper salts have also been included, with suggestions for further study of these compounds.

It is beyond the scope of the manuscript to present a complete theoretical review of enthlapy of solution and electrolyte solutions. Rather, a brief description of pertinent concepts has been combined with selected references to introduce the reader to these theories.

CONTENTS

SECTION PAGE

LIST OF TABLES

LIST OF FIGURES

FIGURE PAGE

SECTION 1

INTRODUCTION

1.1 Enthalpy and Classical Thermodynamics

The concepts of classical thermodynamics are not predicated upon molecular theory; rather, they are based upon the assumption that a discreet value can be reproducibly measured for any macroscopic property, such as temperature, pressure, volume or heat capacity.[1] This is distinctly advantageous in that as our knowledge of molecular structure changes, thermodynamic concepts remain unaltered.

This study is concerned with determination of a thermodynamic, macroscopic property, enthalpy; thus, all discussion of the structures of compounds used,[2] of the solvent system[3] and electrolyte solutions is deemed unnecessary and has been excluded from this paper.

The thermodynamic quantity, enthalpy (H) of a system is defined as:

$$H = E + PV \qquad (1\text{-}1)$$

E being the internal energy of the system at pressure P and volume V. It was once a popular misconception that the value of an effected enthalpy change (ΔH), could serve as the criterion of spontaneity[4] for a chemical process. Although this notion has long since been disproven, it can yet be utilized within certain limitations: if the magnitude of ΔH is large its sign can be used to predict the feasibility of a reaction. Enthalpy values are also of great utility in the determination of the temperature dependence of a reaction's equilibrium constant.[5]

This study involves the quantitative determination of the heat effect which accompanies the process of dissolving a solid in a liquid solvent, i.e., the enthalpy of solution.

1.2 Reasons for Study

Consider the mixing of solute and solvent to form a solution. One of the conditions in order for a solution to be described as ideal is that its enthalpy of mixing is zero for all temperatures.[6] Although the ideal solution is not known to exist in nature, some solutions do closely approximate ideal behavior.[7] Normally, however, a heat of mixing, due to solute-solvent interactions (and solute-solute interactions at higher concentrations), is observed.

Our understanding of these interactions is meager. Through comparison of heats of solution of similar solutes in a single solvent system, one can make deductions as to the nature and extent of solute-solvent interactions.

Inorganic copper compounds were selected as solutes, as they have been relatively ignored in thermodynamic literature.[8]

Water was the solvent of choice for this study; future investigations will utilize non-aqueous systems, and/or water-alcohol systems.

The copper salts used were, in general, 2-1 electrolytes. The information obtained with these compounds is of value, as most electrolyte data in the literature are for 1-1 electrolytes.

SECTION 2

THEORETICAL INTERPRETATIONS OF THE ENTHALPY OF SOLUTION

2.1 Standard States, Activity and Osmotic Coefficients

When an ionic compound is dissolved in a polar medium such as water, the resulting solution consists of a distribution of ions, each surrounded by solvent.[9] Because the ions can migrate under the influence of an electric field, ionic solutions are known as electrolyte solutions.[10]

In extremely dilute solution, the distance between ions is so large that ion-ion interactions are virtually non-existent. Repulsive and attractive forces between the ions become very important, however, as the solution becomes more concentrated. It then becomes important to refer to the "effective" concentration, or mean activity,[11,12,13,14] of each species in the solution:

$$\alpha_{\pm} = \gamma_{\pm} m_{\pm} \qquad (2\text{-}1)$$

where $m = (m_+^{\nu+} m_-^{\nu-})^{1/\nu}$, and the mean activity coefficient, $\gamma_\pm$, is equal to: $\gamma_\pm = (\gamma_+^{\nu+} \gamma_-^{\nu-})^{1/\nu}$. ν_+ is the number of cations and ν_- the number of anions; $\nu = \nu_+ + \nu_-$.

To insure consistency, standard reference states must arbitrarily be designated for solvent and solute. Standard states[15] referred to (and used for the solvent and solute respectively) in this paper are:

Solvent standard state--pure solvent at the same temperature and pressure as the solution;

Solute standard state--the limiting state in which $\gamma_{\pm}$ approaches unity, as concentration approaches zero.

Note that in the limit of infinite dilution, the activity of the solute approaches its molal concentration.

For a very dilute solution, activity coefficients vary only slightly from unity. It becomes convenient, therefore, to refer to α values for the solvent on the basis of their deviations from unity. The osmotic coefficient, ϕ, of an electrolyte solution is defined:[16]

$$\phi = - \frac{1000 \ln \alpha_s}{M_s \sum_i \nu_i m_i} \qquad (2\text{-}2)$$

where α_s is the activity of the solvent, and M_s, the molar mass of the solvent; ν_i and m_i refer to individual ionic species and thier molalities, respectively.

2.2 Enthalpy of Solution

When a solid is dissolved in a solvent, heat is both absorbed and released. Energy is necessarily absorbed as bonds between ions in the crystal lattice are broken; during solvolysis of the ions, however, new bonds are formed and heat is released. Depending upon the net sum of these two heat quantities, a dissolution reaction may be either endothermic (heat absorbed) or exothermic (heat released).[17]

Let the symbol Q denote the quantity of heat transferred. By convention, a positive valued Q will represent the heat evolved in an exothermic reaction, and a negative Q, the heat absorbed, or an endothermic reaction.[18]

When solute and solvent (at the same initial temperature) are mixed, the resulting heat effect is manifested as a change in the temperature of the solution.[19] This rise or fall in temperature (ΔT), serves as a convenient tool for quantitative determination of the value Q (Section 2.3), and hence, a means for eventual evaluation of the nature and extent of solute-solvent interaction. Assuming the heat capacity, C, of the system is known, the temperature change which occurs can be used to calculate the quantity Q:[20]

$$Q = \Delta T \cdot C \qquad (2\text{-}3)$$

where $\Delta T = T_{final} - T_{initial}$. The integral heat (or enthalpy) of solution is then:[21]

$$\Delta H = -Q/n_2 \qquad (2\text{-}4)$$

where n_2 = moles of solute (ΔH is usually expressed in kJ/mole or kcal/mole). Note that if heat is liberated, the temperature would rise and Q would be positive; the enthalpy change would then be negative.

The value of ΔH for a dissolution reaction is a function of solute concentration.[22] Due to interactions between solute and solvent molecules, the observed heat effect is not directly proportional to the amount of solute present (Figure 1).

Because enthalpy is a relative term (absolute enthalpies cannot be determined), it is necessary to choose some reference state. The usual choice is that of the infinitely dilute solution.[23]

Consider the mixing of n_2 mole of salt (M-X) with n_1 moles of water (The subscripts 1 and 2 will refer heaeafter to solvent and solute, respectively.):

$$n_2\ \text{M-X}_{(\text{solid})} + n_1\ H_2O \longrightarrow n_2\ \text{M-X}_{(\text{aqueous, m})} \qquad (2\text{-}5)$$

(m denotes the molality of the resulting solution). The enthalpy changes which occur can be written in terms of both components:

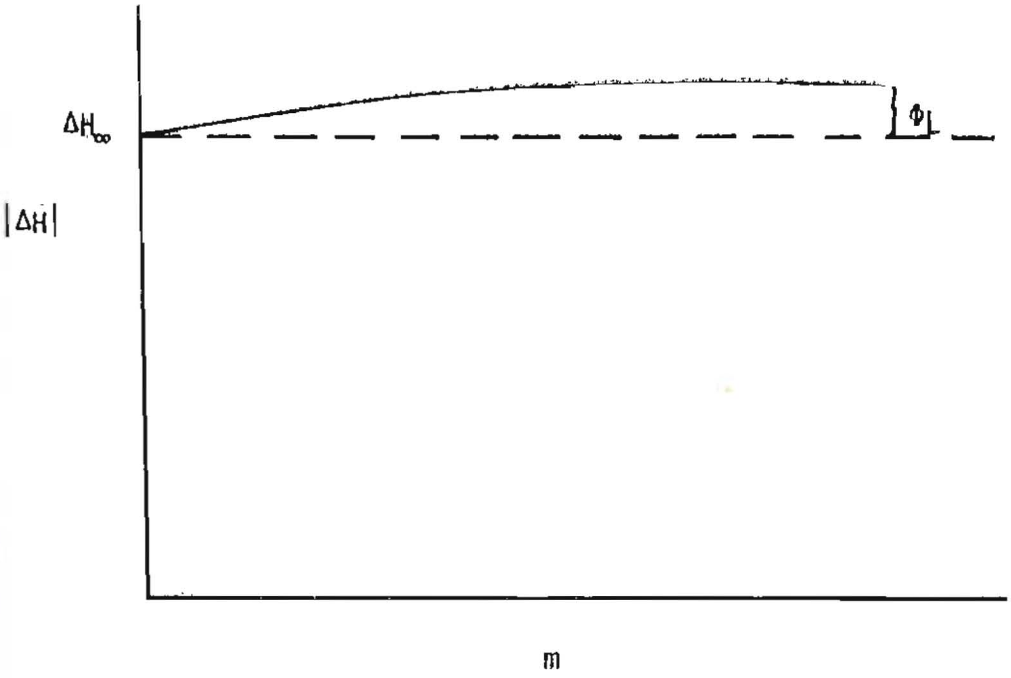
$$\Delta H = H_{\text{final}} - H_{\text{initial}} = n_1\bar{H}_1 + n_2\bar{H}_2 - (n_1H_1 + n_2H_2) \qquad (2\text{-}6)$$

where H_1 and H_2 are the enthalpies of the pure materials, and $\bar{H}_1$ and $\bar{H}_2$ the the partial molal enthalpies of each component in the solution. It is often convenient to attribute all changes in the enthalpy to the solute. Thus, we introduce an artifact, the apparent relative molal enthalpy of the solute, ΦL. The enthalpy change $\bar{H}_1 - H_1$ can be attributed solely to the solvent; its value, at zero concentration is ΔH_∞, the heat of solution at infinite dilution. The apparent relative molal enthalpy, ΦL, is then defined:[24]

$$\Phi L = (\Delta H - \Delta H_\infty)/n_2 \ . \qquad (2\text{-}7)$$

If the integral heat of solution is determined at several concentrations and its absolute value plotted as a function of m, the type of relationship as is shown in Figure 1 will be observed. The enthalpy curve can be extrapolated to zero concentration to give ΔH_∞, and ΦL is easily obtained at any concentration. ΦL is always small in magnitude, when compared to ΔH.

Figure 1: Integral heat of solution as a function of concentration. The curve ends when the solution reaches saturation.


ΔH∞
|ΔH|
Φ_L
m

2.3 Principles of Solution Calorimetry

Calorimetry is concerned with the direct evaluation of the energy changes which occur with all physical and chemical processes. According to the first law of thermodynamics, the energy of any system is a single-valued function of its state. Thermochemistry involves the study of the energy changes which accompany a given change in state.[25]

The problem at hand is to determine the enthalpy change, ΔH, or energy change, ΔE, which accompanies a given isothermal change in the state of a system. ΔH and ΔE are state functions, that is, their values depend only upon the initial and final states, and not upon the pathway between these states. Therefore, it is not necessary to carry out this change isothermally; it is more practical to use a two-step process:[26]

I. An adiabatic change in state with the appropriate products and a change in temperature;

II. Addition or removal of heat from the system until the temperature is the same as that of the original reactants.

In terms of equations:

$$\text{I.}\quad A_{(T_1)} + S_{(T_1)} \longrightarrow B_{(T_2)} + S_{(T_2)} \qquad (2\text{-}8)$$

$$\text{II.}\quad B_{(T_2)} + S_{(T_2)} \longrightarrow B_{(T_1)} + S_{(T_1)} \qquad (2\text{-}9)$$

$$\text{I + II.}\quad A_{(T_1)} \longrightarrow B_{(T_1)} \qquad (2\text{-}10)$$

where A is equal to the reactants used and B represents the products formed. T_1 and T_2 refer to temperatures of the system. S denotes the parts of the reaction vessel which are always at the same temperature as the products or reactants.

The beauty of this two-step process is that the heat, Q, for step I is zero (adiabatic process). Q for step II can be measured directly. Or, if the heat capacity of the system is known, Q_{II} can be calculated from the resulting temperature change in step I, and step II can be eliminated.[27]

Whether one directly evaluates ΔH or ΔE depends upon how one carries out the process. ΔE results from measurements at constant volume, ΔH from those at constant pressure. In any case,

$$\Delta H = \Delta E + \Delta(PV) \tag{2-11}$$

For condensed phases, the $\Delta(PV)$ term is negligible; hence:

$$\Delta H \simeq \Delta E \tag{2-12}$$

Although calorimetric determinations are based on temperature measurements, one nearly always measures work quantities in the form of electrical energies.[28] The fundamental quantities for measuring electrical energy are:

potential X current X time
= absolute volts X absolute amperes X seconds
= absolute Joules.

The heat capacity. C, of the system is determined by introducing a known quantity of heat into the system. C can then be calculated:

$$C = Q\,(T_2 - T_1)\ . \tag{2-13}$$

It is assumed throughout this study that C is constant over the small temperature range considered.

2.4 Debye-Huckel Theory

2.4.1 Debye-Huckel Limiting Law Equations

The behavior of an electrolyte solution can be expressed approximately by:[29]

$$\begin{aligned} \Phi L &= \Delta H - \Delta H_\infty \\ &= (2/3)(2.303)\ R\ T^2\ \frac{d\ A\gamma}{d\ T}\ \nu |\ z_+\ z_-\ |\ I^{1/2} \end{aligned} \tag{2-14}$$

where R is the gas constant and T the temperature in degrees Kelvin; z_+ and z_- represent the charges of the solute cation and anion, respectively. I is the ionic strength of the solution:

$$I = (1/2)\sum_i z_i^2\ m_i \tag{2-15}$$

$A\gamma$, the Debye-Huckel constant, has the value 0.511 $(\mathrm{kg/mole})^{1/2}$ for aqueous solution at 298.15 K. This constant is derived[30] from considerations of the solvent dielectric constant, density, and temperature (see Table 1). Once the temperature coefficients of these variables are evaluated, one obtains the Debye-Huckel Limiting Law:[31]

$$\Phi L\ (\mathrm{cal/mole}) = 239\ \nu\ |\ z_+\ z_-\ |\ I^{1/2} \tag{2-16}$$

TABLE 1

DEBYE-HUCKEL COEFFICIENTS AT 25°C[a,b]

Coefficient	Equation	Numerical Value
$A\gamma$ /(mole$^{1/2}$kg$^{-1/2}$)	$(2\pi N_o \rho_w/1000)^{1/2}(e^2/DkT)^{3/2}$	0.511
A_ϕ /(mole$^{1/2}$kg$^{-1/2}$)	$(1/3)(2\pi N_o \rho_w/1000)^{1/2}(e^2/DkT)^{3/2}$	0.392
A_H/(kg$^{1/2}$cal mole$^{-3/2}$)	$(6RT^2)(\partial A_\phi/\partial T)_{P,m}$ $= -9A_\phi RT^2[1/T + (\partial \ln D/\partial T)_{P,m} + \alpha_w/3]$	698

N_o = Avagadro's number

ρ_w = density of water

D = static dielectric constant of pure water

k = Boltzmann's constant

e = absolute electronic charge

$\alpha_w = (\ \ln V/\ T)_p$ = isobaric coefficient of thermal expansion of water

[a] Coefficients are evaluated for water as solvent.

[b] L.F.Silvester and K.S. Pitzer, "Thermodynamics of Electrolytes. X. Enthalpy and the Effect of Temperature on the Activity Coefficients," J. Soln. Chem., 7, 327 (1978).

the units of the numerical coefficient being cal mole$^{-3/2}$ kg$^{1/2}$. This relationship has been proven valid, and may be used to guide one's extrapolations to zero concentration; however, it is valid only in the limit of infinite dilution, where short-range interactions become unimportant. It is recommended that this relationship be used only at or below concentrations of 0.001 m;[32] in general, 1-1 electrolytes (non-associating) adhere most closely to this predicted behavior. Failure of an electrolytic solution to conform to the limiting law at very low concentrations usually indicates ion-association.

The limiting law equation and its refined forms which follow ". . . are not derived from any detailed molecular model, but rather are based upon general [thermodynamic] arguments."[33] Its derivation is based upon the "primitive model"[34] of an electrolyte solution: ions are treated as hard, charged spherical objects; the solvent, which holds the ions apart, is treated as a structureless continuum, characterized only by its dielectric constant. This model is far from realistic--it can serve only as a crude approximation in the limit of zero concentration.

The Debye-Huckel theory assumes that the behavior of strong electrolytes in dilute solution can be adequately described on the basis of: 1)complete dissociation, and, 2), an adequate consideration of the effects of interionic attractions.[35] In its limiting form, only the long-range effects of Coulombic attractions are considered.

A rather lengthy, in-depth discussion of the history and derivation of both the extended and limiting Debye-Huckel equations can be found in Harned and Owen,[36] or Robinson and Stokes.[37] A more readable rendition is that of Lewis and Randall.[38] Without delving into the complexities of these derivations, it is sufficient to say that the equations came about as the result of application of the Poisson-Boltzmann equation to the Debye treatment of the interionic attraction theory.[39]

The limiting law, as used for prediction of mean activity or osmotic coefficients is:

$$\log \gamma_{\pm} = - A_{\gamma} \nu \mid z_{+} z_{-} \mid I^{1/2} \qquad (2\text{-}17)$$

$$1 - \phi = - A_{\phi} \nu \mid z_{+} z_{-} \mid I^{1/2} \qquad (2\text{-}18)$$

Values of the Debye-Huckel coefficients are listed in Table 1.

2.4.2 Debye-Huckel Extended Law Equations

It now becomes appropriate to introduce a more refined version of the Debye-Huckel equations:

$$\log \gamma_{\pm} = - A_{\gamma} \nu \mid z_{+} z_{-} \mid \frac{I^{1/2}}{1 + b\, I^{1/2}} + m\, B^{\gamma}_{MX} \qquad (2\text{-}19)$$

$$1 - \phi = - A_{\phi} \nu \mid z_{+} z_{-} \mid \frac{I^{1/2}}{1 + b\, I^{1/2}} + m\, B^{\phi}_{MX} \qquad (2\text{-}20)$$

where b = 1.2 and is constant for all electrolytes. This extended form of the Debye-Huckel law can be used at higher concentrations than can its limiting form. It is also appropriate for use with polyvalent electrolytes or mixed electrolyte solutions.

The terms within these equations relate to three types of interactions:[40]

1). The limiting term: $A \nu \mid z_+ z_- \mid I^{1/2}$, deals with Coulombic interactions between the ions and their ion atmospheres.

2). $1 + b\, I^{1/2}$ relates to repulsions.

3). mB is essentially a second virial coefficient. This term may be thought of as a "specific effect" term, as it encompasses all first-order effects due to short-range interactions, such as direct interaction between ions, or interactions due to solvent influences. All temperature contributions of the $1 + b\, I^{1/2}$ term are also contained with mB.

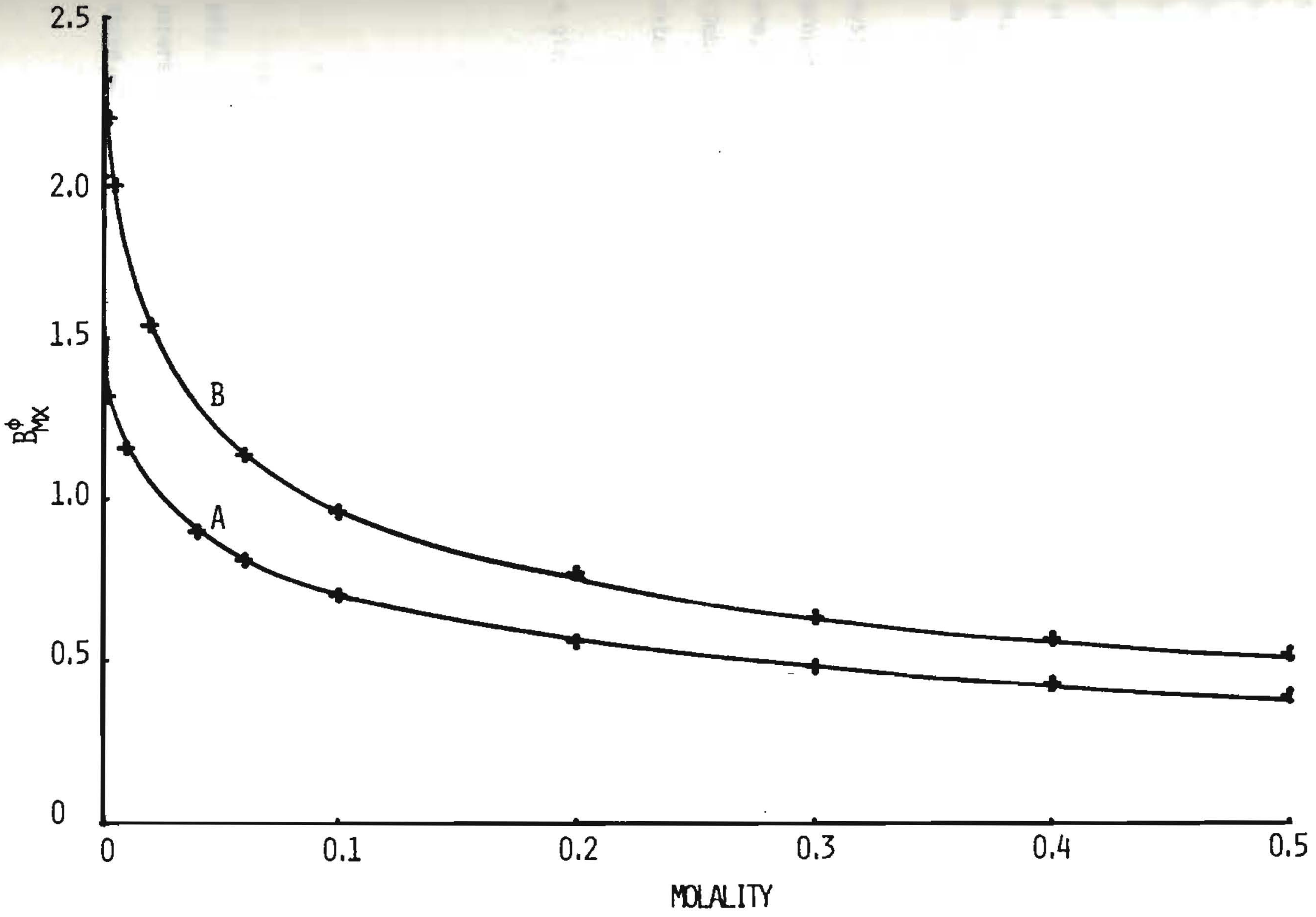
Figure 2 is a plot of B^{ϕ}_{MX} as a function of m for both $CuCl_2$ and $CuBr_2$ in H_2O at 25°C, as calculated from a critical compilation[41] of values of ϕ(refer to Table AI). Note that B^{γ}_{MX} might be similarly calculated from $\gamma_{\pm}$ values (also listed in Table AI), and plotted in a similar fashion.

.4.3 Semi-empirical Equations Based Upon Debye-Huckel Theory

To derive empirical equations which would allow accurate calculations of thermodynamic properties of an electrolyte solution would require knowledge of all interactions which occur within said

Figure 2: Behavior of the second virial coefficients (of the osmotic coefficient expression) with molality, for $CuCl_2$ and $CuBr_2$ in water at 25°C (Data can be found in Table AI).

A = $CuCl_2$
B = $CuBr_2$
[Units of B^{ϕ}_{MX} are $moles^{-1}kg$]


2.5
2.0
1.5
1.0
0.5
0
B^{ϕ}_{MX}
B
A
0
0.1
0.2
0.3
0.4
0.5
MOLALITY

solution. Unfortunately, 2-body and 3-body interaction approximations often prove insufficient, and it becomes necessary to consider the complex mathematics of many-body interactions. An alternative approach is the use of semi-empirical relationships for the prediction of the properties. Although there exist numerous examples[42,43] of this type of approach in the literature, only one will be discussed in this paper, as it has been used as a thermodynamic-based consistency check on the data obtained with the Parr 1451 Solution Calorimeter.

Pitzer[44] and co-workers have proposed a convenient and effective system of equations which allow calculations of any thermodynamic property of electrolyte and mixed electrolyte solutions. The equations are, as previously stated, semi-empirical: although based on theory (Debye-Huckel), the parameters--unique to each solute--can be determined solely through experimentation.

Consideration of the short-range interactions which occur within a given electrolyte solution is accomplished via:

1). three second virial coefficient factors, $\beta^{(o)}$, $\beta^{(1)}$, and $\beta^{(2)}$, which relate to both ion pair (M-X, M-M, X-X) interactions, and indirect forces arising from the solvent;

2). a third virial coefficient, C_{MX}, which accounts for triple ion interactions.

The equations which follow will refer to 2-1 (or 1-2) electrolytes only. It is recommended that the reader refer to the series of papers by Pitzer[45] and co-workers for the specific treatment of these equations in the case of other valence-type electrolytes.

$\beta^{(2)}$ terms have been eliminated, as they are necessary only for analysis of 2-2 or higher valence-type electrolytes. C_{MX}, important only at high concentrations, will also be ignored.

$\gamma_\pm$ and ϕ for an electrolyte solution may be expressed as:

$$\ln \gamma_\pm = - | z_M z_X | \frac{A\gamma}{3} \left[\frac{I^{1/2}}{1 + b\, I^{1/2}} + (2/b)\ln(1 + b\, I^{1/2}) \right] + m \frac{2\nu_M\nu_X}{\nu} \left[2\, \beta^{(o)} + \frac{2\beta^{(1)}}{\alpha I^2}\left[1 - \left(1 + \alpha I^{1/2} - \frac{\alpha^2 I}{2}\right) \exp\{-\alpha I^{1/2}\}\right]\right] + \,.\,.\,.\,.\,. \qquad (2\text{-}21)$$

$$\phi - 1 = - | z_M z_X | A_\phi \frac{I^{1/2}}{1 + bI^{1/2}} + m \frac{2\nu_M\nu_X}{\nu} \left[\beta^{(o)} + \beta^{(1)} \exp\{ -\alpha I^{1/2}\}\right] + \,.\,.\,. \qquad (2\text{-}22)$$

where $b = 1.2$ and $\alpha = 2.0$ (for most electrolytes).

The total excess Gibbs Free Energy, G^{ex}, can be expressed by:

$$G^{ex} = G^{observed} - G^{ideal}$$

$$= n_w\, \nu\, m\, R\, T\, (1 - \phi + \ln\gamma_\pm) \qquad (2\text{-}23)$$

where n_w = the number of kilograms of solvent, R the gas constant, and T, the temperature in degrees Kelvin.

The relative enthalpy, ΔH, of solution can be written in terms of the Gibbs energy:

$$\Delta H = - T^2 \left[\frac{\partial(G^{ex}/T)}{\partial T}\right]_{P,m}$$

$$= \nu \; m \; R \; T^2 \left[[\partial\phi/\partial T]_{P,m} - [\partial \ln\gamma_{\pm}/\partial T]_{P,m}\right] \qquad (2\text{-}24)$$

Taking the appropriate derivatives, one finds for the apparent relative molal enthalpy:

$$\Phi L = \nu|z_M z_X|(A_H/3b)\ln(1 + bI^{1/2}) - 2\,\nu_M\nu_X\,RT^2\left[m\,B^L_{MX} + \ldots\,.\right] \qquad (2\text{-}25)$$

where A_H is the Debye-Huckel coefficient for enthalpy.

$$B^L_{MX} = (\partial B_{MX}/\partial T)_{P,m} \qquad (2\text{-}26)$$

and

$$B^L_{MX} = \beta^{(o)} + \frac{2\beta^{(1)}}{\alpha^2 I}\left[1 - (1 + \alpha I^{1/2})\exp\{-\alpha I^{1/2}\}\right] + \ldots\,. \qquad (2\text{-}27)$$

The coefficients $\beta^{(o)}$ and $\beta^{(1)}$ are determined by a least square fit of activity or osmotic coefficient data, for a specific solute at a specific temperature. Note that to evaluate the enthalpy expression, one must have information on the behavior of these parameters as a function of temperature. The temperature derivatives are obtained by least squares best fit to enthalpy data. The utility of these equations is further exemplified in Section 8.2.

SECTION 3

INSTRUMENTATION

3.1 Mass Balances

All masses of water were weighed directly into a tared Dewar on an O'HAUS Triple Beam balance (2610 gm capacity).

Solid samples were weighed on a Model B6 METTLER Gram-a-matic Analytical balance:

Capacity	100 gm
Optical Range	115 mg
Readability	0.01 mg
Precision	±0.01 mg

3.2 The PARR 1451 Solution Calorimeter

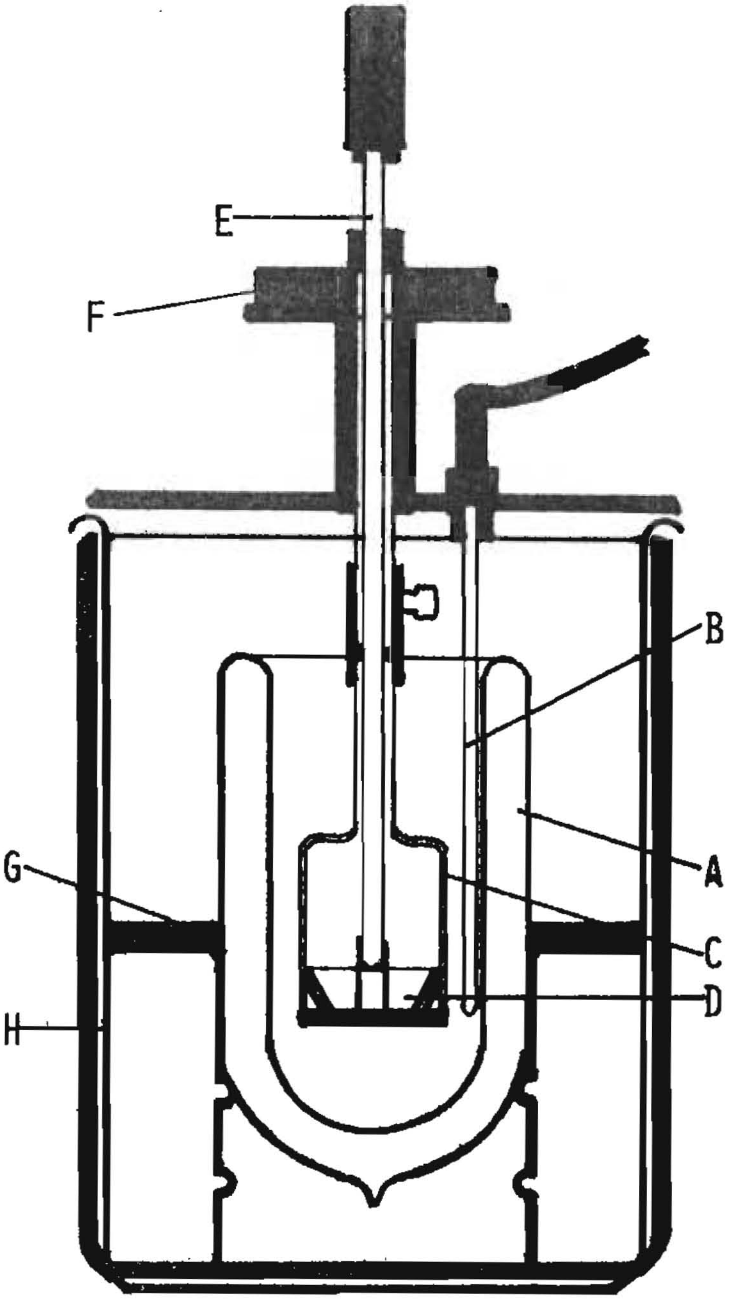
3.2.1 Description of Apparatus

The 1451 Solution Calorimeter is designed for the convenient measurement of heat evolved or absorbed during a chemical reaction in liquid medium.

In the 1451 system (refer to Figure 3), one reactant (liquid) is held in a glass Dewar flask, while the other (either solid or liquid) is sealed in a sample glass cell which rotates within the liquid medium. The Dewar is situated within a stainless steel chamber which is covered with a plastic lid (not airtight). A thermistor probe, inserted through the lid, is positioned parallel

Figure 3: The Parr 1451 Solution Calorimeter

A. Glass Dewar
B. Thermistor Probe
C. Glass Sample Cell
D. Teflon Sample Dish
E. Glass Push Rod
F. Geared Drive
G. Dewar Spacer Ring
H. Stainless Steel Air Can



PARR 1451 SOLUTION CALORIMETER

to the rotating cell, its tip being nearly at the bottom of the Dewar, and well under the surface of the liquid medium.

Three 115/120 volt, 50/60 Hz grounded outlets are required for power cords to the stirring motor, thermometer bridge, and recorder. A ground wire should be run from the grounding terminal on the bridge to a similar terminal on the recorder.

For best results, the calorimeter should be placed in a draft-free area in a room with minimal temperature changes.

Calorimetric measurements can be made conveniently at room temperature and atmospheric pressure for systems producing 2-1000 thermochemical calories (8.4-4800 absolute Joules).

The rotating sample cell will hold up to 20 ml liquid, or approximately 3 gms solid. However, solid samples of one gram or less are recommended to insure that neither the heat capacity nor the ionic strength of the system undergoes significant change when reactants are mixed. The Dewar flask requires 90-120 ml of liquid to adequately cover the rotating sample cell. The sample cell is allowed to rotate until reactants are thermally equilibrated. Reaction can then be initiated by depressing a push rod assembly which opens the sample cell immersed in the liquid medium.

The thermistor probe is connected to a Wheatstone bridge (hereafter referred to as the "bridge"), which is read by a potentiometric strip chart recorder[46] (Fischer RecordAll Series 5000). All temperature changes are recorded as they occur within the calorimeter in the form of a thermogram (a plot of temperature as a function of time).

Probe and bridge are so designed as to respond linearly within the range of 20-30°C, a 100 microvolt change in output corresponding to a temperature change of exactly 0.001°C. Thus, temperatures can be read directly from the chart paper if plotted on a 10, 100, or 1000 millivolt chart. The following relationships apply:

Thermometer Output	Temperature changes/°C
100 microvolts (0.0001 V)	0.001
10 millivolts (0.010 V)	0.100
100 millivolts (0.100 V)	1.000
1000 millivolts(1.000 V)	10.00

The bridge can be balanced to a zero output at any temperature between 20-30°C, and a temperature recording range selected:

Recorder Voltage Setting/Volts	Full-Scale Temperature Range/°C
0.010	0.10
0.100	1.00
1.000	10.0

.2.2 Method of Calibration

Standardization of a calorimeter involves use of a controlled chemical reaction for which the amount of heat evolved or absorbed is well-established. From a known energy input, the energy equivalent of the calorimeter can be determined.

For standardization of the 1451 Solution Calorimeter,[47] solid

TRIS (tris[hydroxymethyl]aminomethane, or THAM) is dissolved in 0.1 N HCl, a reaction which is known to release 58.738 calories per gram TRIS. Resulting temperature changes (ΔT) are used to determine a mean calorimeter constant, e, by the following method.

Calculation of the known energy input, Q:

$$Q/\text{calories} = m\,[\,58.738 + 0.3433\,(25 - T_{rxn}) \qquad (3\text{-}1)$$

where m = mass of TRIS in grams and

T_{rxn} = temperature (^{o}C) at 63% of reaction.

The term: $0.3433\,(25 - T_{rxn})$ adjusts the heat of reaction to any temperature above or below the 25^{o}C reference temperature.

Calculation of the energy equivalent (calorimeter and contents), e:

$$e/\text{cal}\ ^{o}C^{-1} = Q\,/\,\Delta T \qquad (3\text{-}2)$$

Calculation of the energy equivalent of the empty calorimeter, e':

$$e'/\text{cal}\ ^{o}C^{-1} = e - (100.00)(0.99894) \qquad (3\text{-}3)$$

The term: 100.00 refers to the weight in grams of 0.10 N HCl used in the calorimeter.

The term: 0.99894 is the specific heat of 0.10 N HCl.

SECTION 4

PURITY OF MATERIALS

4.1 Water

Distilled water was passed through a Barnstead Bantam Demineralizer once to give the deionized water used as solvent in this study. It was assumed that any impurities in the deionized water would cause negligible error in the experimental results; therefore, no attempt was made to determine either quantity or identity of these impurities.

4.2 Tris[hydroxymethyl]aminomethane

TRIS crystals were obtained directly from Parr Instrument Co., Moline, Ill. The quality of this compound (as stated on the label was such that a 0.50 ± 0.01 gm sample would release 58.82 ± 0.08 cal/gm when dissolved in 100.00 ml 0.1 N HCl at 25°C.

Although reportedly stable towards light, air, and moisture, at least one source reports that TRIS has a shelf life of only six months.[48]

4.3 Cupric Halides

Copper (II) halides were obtained from Sigma Chemical Corporation. Elemental analysis[49] is given in Table 2. All elemental analysis figures are believed to be accurate to ± 1%. Cu and Fe were determined

TABLE 2

ELEMENTAL ANALYSIS OF $CuCl_2 \cdot 2H_2O$ and $CuBr_2$

Compound	weight percent found	weight percent theory	element
$CuCl_2 \cdot 2H_2O$	36.6	37.3	Cu
	41.2	41.6	Cl
	0.005	----	Fe(trace)
	22.2	21.2	H_2O(by difference)
$CuBr_2$	27.5	28.4	Cu
	72.0	71.5	Br

by A.A; Cl and Br were determined by titration.

No elemental analysis is available for $CuCl_2$, as it was prepared in the lab from the dihydrate (Section 5.2).

4.4 Other Copper Compounds

As data for these compounds (see Section 6) have not been subjected to analytical evaluation, a discussion of their purities is rendered irrelevant.

SECTION 5

PROCEDURES AND EXPERIMENTAL TECHNIQUES

5.1 Calibration of the Calorimeter

TRIS was stored in a dessicator over $CaCl_2$ at room temperature. Samples (0.500 ± 0.001 gms) were weighed directly into dry Teflon pans, glass sample cells being snapped over these. 100.0 ± 0.1 gm of 0.1 N HCl was weighed into a tared Dewar flask.

A minimum of 15 minutes was allowed for the calorimeter and its contents to reach thermal equilibrium; a trace was made of the exothermic dissolution of TRIS. Chart speed was 1 inch per minute; recorder voltage was 0.10 volt.

The Dewar flask, sample cells, Teflon pans, and push rods were washed in a detergent solution, rinsed with water, then acetone, and dried between trials.

For greater consistency, all trials were made with the same 0.1 N HCl solution (33 ml conc HCl/4 L deionized H_2O), as the heat evolved during the dissolution of TRIS is dependent upon hydrogen ion concentration. In fact, TRIS will absorb heat during dissolution at neutral pH.

Glass sample cells were cleaned every 2 week with a dichromate cleaning solution (32 gms $Na_2Cr_2O_7$/ 1 L conc H_2SO_4).

It was necessary to determine two calorimeter constants, as two Dewar flasks were used. The mean e values of the standardization data are:

System I: $e_I = 0.5040 \pm 0.0041$ kJ/^oC

System II: $e_{II} = 0.5038 \pm 0.0031$ kJ/^oC

Within experimental error these two numbers are the same (see Section 7.1). Individual values of e are listed in Table AII.1.

5.2 Heats of Solution of Copper(II) Chloride Dihydrate, Copper(II) Chloride, and Copper(II) Bromide in Water

Approximate solute sample sizes, which were found to be the most practical for this apparatus, are listed in Table 3. All samples were dissolved in 100.00 ± 0.10 gms deionized H_2O, and the resulting temperature changes recorded.

$CuCl_2 \cdot 2H_2O$ solid samples were prepared by grinding $CuCl_2 \cdot 2H_2O$ rocks (Sigma Chemical Corp.) with mortar and pestle, no more than six hours prior to analysis.

$CuCl_2$ solid samples were prepared by heating ground dihydrate crystals at 100 ± 5^oC for a minimum of 12 hours (weight loss was 21.18%; theoretical weight loss = 21.13%). Because of the hygroscopic nature of this compound, it was necessary to store the major portion of it in the oven (at 100 ± 5^oC), removing it long enough to weigh two samples. Yellow-brown $CuCl_2$ crystals would begin turning blue ($CuCl_2 \cdot 2H_2O$) within 15 minutes of air exposure.

$CuBr_2$ solid was heated in the oven at 100 ± 5^oC two hours prior to analysis, to insure dryness (weight loss was 0.25%). Samples were

TABLE 3

SUITABLE CONCENTRATION RANGES FOR CU(II) HALIDE SAMPLES

Compound and Mol. wt.	Weight Range (gm)	Molality Range	Voltage Scale
$CuCl_2 \cdot 2H_2O$	0.04 - 0.30	0.003 - 0.018	0.01
(170.47)	0.75 - 1.75	0.044 - 0.100	0.10
$CuCl_2$	0.01 - 0.14	0.001 - 0.010	0.01
(134.33)	0.14 - 0.80	0.010 - 0.060	0.10
$CuBr_2$	0.06 - 0.28	0.003 - 0.012	0.01
(223.31)	0.48 - 0.71	0.021 - 0.032	0.10

weighed two at a time from a large quantity of the dry bromide; the major portion of the bromide was then returned to the oven. After seven hours in the oven bromide crystals began to turn white, at which point they were discarded. It was not possible to measure heats of solution at concentrations greater than 0.035 molal, as the solid $CuBr_2$ particles tended to clump, resulting in uneven, imcomplete dissolution.

5.3 Recommendations

Greater care should have been taken with anhydrous samples, especially $CuCl_2$. During transfers between oven, sample cells and calorimeter, it would have been more appropriate to transport this compound in a dessicator. To further insure the integrity of their anhydrous conditions, $CuCl_2$ and $CuBr_2$ should be stored over phosphorus pentoxide rather than calcium chloride.

At times it was necessary to speed the drying process of sample cells and Teflon pans. The Teflon pans dry quite nicely in a 100°C oven. However, it is not recommended that glass sample cells be heated to any extent. Heating these cells in the oven resulted in shrinkage of the plastic stems to the point that they would no longer fit onto the metal shaft of the stirring drive. This necessitated grinding down the metal shaft before further trials could be made.

Great care was taken to quickly wipe all spills and to dispose of solutions immediately after use, as copper(II) solutions are corrosive in nature. $CuBr_2$ was noted to be extremely corrosive in its solid form, as it destroyed the plating on a metal spatula upon contact; it is recommended that only porcelain spatulas be used for transferring samples of this compound. It is further suggested that a paper or cloth mask be worn during the pulverizing of the dihydrate compound, as the invisible dust which forms is quite irritating to the mucous membranes.

SECTION 6

PRELIMINARY INVESTIGATIONS OF OTHER COPPER COMPOUNDS

6.1 Copper(II) Sulfates

The deep blue, deliquescent crystals of the pentahydrate compound were found to dissolve in H_2O endothermically, to form a pale green solution. Although $CuSO_4 \cdot 5H_2O$ is quite soluble in water (16.4gm/100cc),[51] dissolution of finely ground crystals was accomplished only with excessive stirring. The calorimeter's stirring system was inadequate for dissolving a reasonable amount of this compound.

Both the monohydrate and anhydrous sulfates were prepared by heating the pentahydrate:

$$CuSO_4 \cdot 5H_2O \xrightarrow{110^oC} CuSO_4 \cdot H_2O \text{ (bluish-white powder)}$$

(weight loss = 27.9%; theoretical weight loss = 28.8%)

$$CuSO_4 \cdot 5H_2O \xrightarrow{150^oC} CuSO_4\text{(anhy) (white powder)}$$

(weight loss = 35.9%; theoretical weight loss = 36.1%)

Neither of these compounds could be analyzed in the calorimeter. Upon addition to H_2O, both the monohydrate and anhydrous crystals underwent exothermic reaction to form the large, deep blue pentahydrate compound, which is slow to dissolve.

6.2 Copper(I) Halides

Neither of these compounds was soluble in water, as the Cu^+ ion is unstable in aqueous solution:[52]

$$2\ Cu^+ \xrightarrow{H_2O} Cu^{2+} + Cu^0$$

Addition of the yellow-green CuCl powder to H_2O resulted in a green precipitate which turned to turquoise after five minutes. The solubility of CuCl in water is 0.0062 gm/100cc.[53]

Solubility in water of the white-green powder CuBr is given in the literature as "very slightly soluble". When this powder was added to water, there were no observable changes; the solid remained as a precipitate.

Both CuCl and CuBr are known to be quite soluble in HCl solutions, their solubilities increasing with Cl^- concentration.[54] It is therefore recommended that a study be made of the heats of solution of these two compounds in HCl solution. This would involve prior determination of the heats of solution of one or more of the Cu(II) halides in an identical HCl solution.

6.3 Copper(II) Nitrate Trihydrate

Time did not permit a detailed study of the heats of solution of this compound. It was found to be quite easily analyzable with the 1451 calorimeter. Blue-green, deliquescent $Cu(NO_3)_2 \cdot 3H_2O$ crystals were found to undergo endothermic dissolution in water to form a blue-green solution. An average value obtained for the heat of solution (weight of solute range = 1.5 - 2 gms) is 0.4 kJ/mole.

6.4 Copper(II) Perchlorate Hexahydrate

These deep blue deliquescent crystals were easily soluble in water. Dissolution was endothermic, a 0.5 gm sample producing approximately a -0.05°C change in a 100 ml solution. This is a relatively small temperature change (and must be measured at 0.01 volts); it is probable that data for this compound are in great error, and thus it has been rejected. The enthalpy of solution is approximately 20 kJ/mole for a 0.5 gm sample. Note that to collect data a 0.10 volts, one would need to start with solute samples of two grams or greater.

SECTION 7

ANALYSIS OF THE EXPERIMENTAL DATA

7.1 Estimation of the Error in Molality

Molality (moles solute / kg solvent) was the concentration scale of choice for this study for two reasons:

1). the error involved in measuring 100 ml samples of water (at 25°C) by volume was estimated to be ±0.3 ml (relative error = 3×10^{-3}), whereas, measuring the water by weight introduces an estimated relative error of 3×10^{-4};

2). more importantly, molality is a temperature-independent property.

Error in the variable m was first estimated. Because the measurement m is a function of M (molecular weight of the solute), S (mass of the solvent), and E (mass of the solute), the error in m can be expressed:

$$\frac{\Delta m}{m} = \left[\left(\frac{\Delta M}{M}\right)^2 + 2\left(\frac{\Delta E}{E}\right)^2 + 2\left(\frac{\Delta S}{S}\right)^2 \right]^{1/2} , \qquad (7\text{-}1)$$

the factor 2 being included for both S and E as these quantities are measured by difference.

The quantity M is well-established, thus $\left(\frac{\Delta M}{M}\right)^2$ is essentially zero. ΔE and ΔS are estimates of the weight variations observed daily during weighings of solute and solvent samples, respectively. Values designated for E and S are typical weights of a Teflon pan and a solvent-filled Dewar:

$$\left(\frac{\Delta m}{m}\right) = \left[2\left(\frac{\Delta E}{E}\right)^2 + 2\left(\frac{\Delta S}{S}\right)^2\right]^{1/2} \tag{7-2}$$

$$= \left[2\left(\frac{0.00020}{7.2}\right)^2 + 2\left(\frac{0.30}{380}\right)^2\right]^{1/2}$$

$$= \left[(1.5 \text{ X } 10^{-9}) + (1.2 \text{ X } 10^{-6})\right]^{1/2}$$

$$= 1.1 \text{ X } 10^{-3}$$

Error in molality is obviously dependent upon measurement of the solvent weight. Estimated errors in m and $m^{1/2}$ are:

molality	Δ m	$m^{1/2}$	$\Delta\ m^{1/2}$
0.0025	0.000003	0.05	0.0017
0.0100	0.000011	0.10	0.0033
0.0500	0.000055	0.22	0.0074

Although Δm appeared to be insignificant, $\Delta m^{1/2}$ could not be ignored. A series of weight measurements was then made to obtain a more accurate estimate of the errors in m and $m^{1/2}$:

	Variable	Measurement
(E)	weight of Teflon pan (20 measurements)	7.35202 ± 0.00010 gms
(S)	weight of Dewar + 100 gms water (50 measurements)	378.07 ± 0.19 gms

Use of standard deviation and mean values in the error expression reflects virtually no change in the quantity $2(\frac{\Delta E}{E})^2$

$$(\frac{\Delta m}{m}) = \left[2(\frac{\Delta E}{E})^2 + 2(\frac{\Delta S}{S})^2\right]^{1/2}$$

$$= \left[(1.3 \times 10^{-9}) + (2 \times 10^{-7})\right]^{1/2}$$

$$= 4.5 \times 10^{-4}$$

Note that the term $2(\frac{\Delta S}{S})^2$ has decreased by a factor of 25. Best estimates of the error in m and $m^{1/2}$ are shown below. These errors are essentially negligible when compared to errors in the enthalpy (Section 7.2).

molality	Δ m	$m^{1/2}$	$\Delta m^{1/2}$
0.0025	0.000002	0.050	0.0014
0.0100	0.000008	0.100	0.0028
0.0500	0.000040	0.220	0.0088

7.2 Error in the Integral and Apparent Relative Molal Enthalpies

The molar integral heat of solution, ΔH, was determined for each salt sample (the appropriate calorimeter constant, e_I or e_{II}, was used for each calculation rather than an average value. ΔH values are shown in Tables AII.2 - AII.4. The temperature at 63% of reaction is also listed for each trial.

ΔH quantities for the solution of each cupric halide have been grouped according to molality; a mean enthalpy and its standard deviation, $\sigma_{\Delta H}$, were determined at each concentration (Table AII.5-7).

The relative standard deviation values in percent $(s = \frac{\sigma_{\Delta H}}{\text{mean}} \times 100)$ are listed in these tables, as well as estimates, $\sigma'_{\Delta H}$, of the error which could reasonably be expected from the given precision of the instrument.

All data were then re-examined, and those groups with $s > 5\%$ were checked for obvious outlying results. In only three cases was it possible to reject a measurement on the basis of the Q test.[55] For greater than 90% of the suspect cases, retention of data was indicated; consideration was given to reporting the median (denoted by * in the tables) of such groupings rather than the mean, as the number of data points in each grouping was small (2-7).

$-\Delta H$ vs. m and $-\Delta H$ vs. $m^{1/2}$ were plotted for $CuCl_2 \cdot 2H_2O$, $CuCl_2$ and $CuBr_2$, using those data points with less than 3.5% deviation from the mean. The enthalpy was found to behave more linearly as a function of $m^{1/2}$ (see Figures 4-6). Data at concentrations below $m^{1/2} = 0.013$ could not be retained for $CuCl_2 \cdot 2H_2O$ due to the great error incurred by using the instrument at 0.01 volts; $CuCl_2$ data at concentrations less than $m^{1/2} = 0.16$ were also suspect and were rejected for the same reason. $CuBr_2$ data (though obtained at 0.01 volts) were retained as: 1). the s% was less than 3 in most cases; and 2). it was difficult at best to obtain data at 0.10 volts, due to failure of the larger amounts of solute required to dissolve completely.

Figure 4: The integral heat of solution for $CuCl_2 \cdot 2H_2O$ in water as a function of $m^{1/2}$ (23 ± $1^{o}C$).

correlation coefficient = -0.98230

slope/kJ $kg^{1/2}$ $mole^{-3/2}$ = -12.3

y-intercept/kJ $mole^{-1}$ = -23.0 = ΔH_{∞}

(Data in Tables AII.5 and AIII.1)

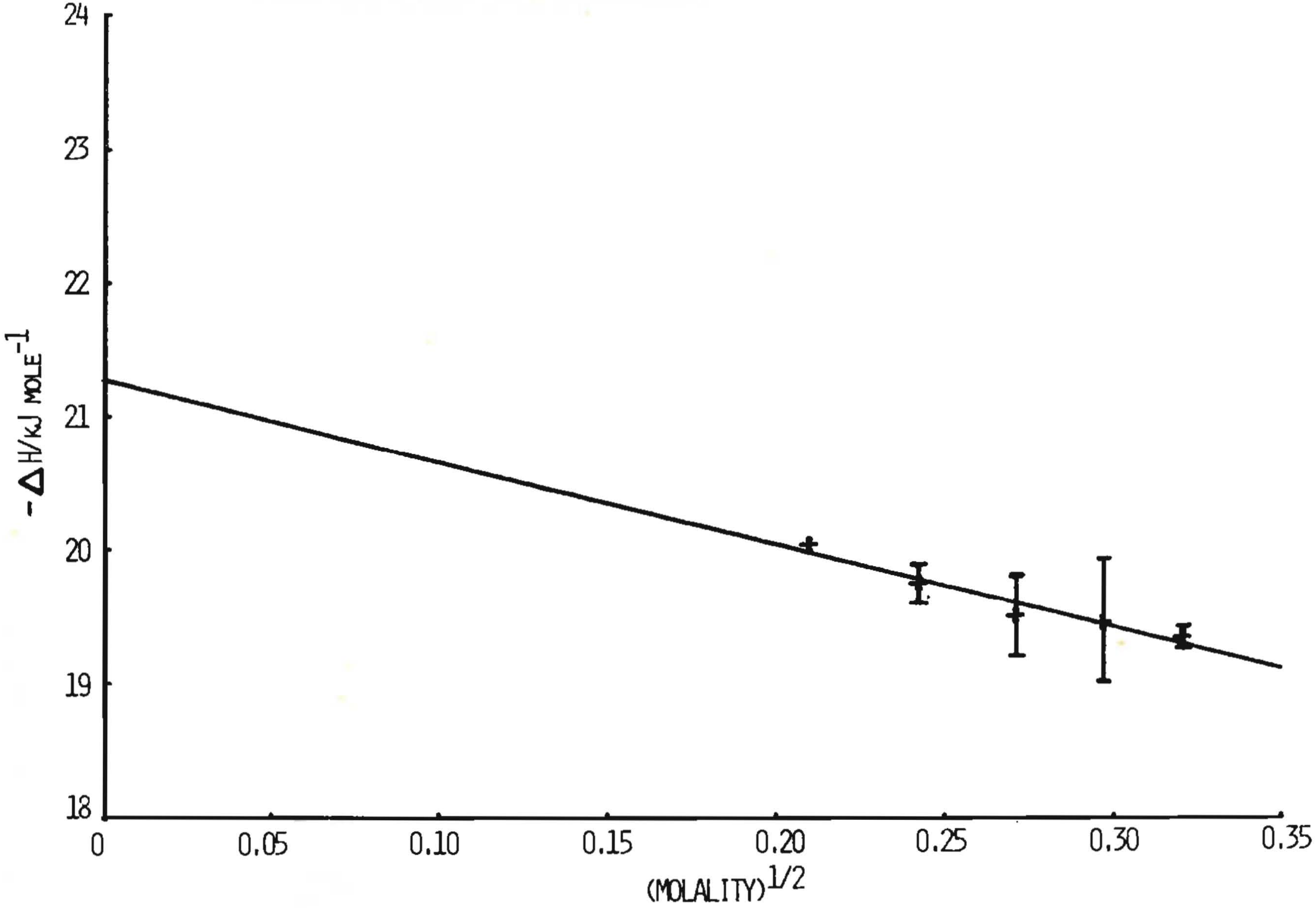

24
23
22
21
20
19
18
$-\Delta H/\mathrm{kJ\ mole}^{-1}$
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
$(\mathrm{MOLALITY})^{1/2}$

Figure 5: The integral heat of solution for $CuCl_2$ in water as a function of $m^{1/2}$ (23 ± 1°C).

correlation coefficient = -0.88199

slope/kJ $kg^{1/2}$ $mole^{-3/2}$ = -7.69

y-intercept/kJ $mole^{-1}$ = -49.1 = ΔH_{∞}

(Data in Tables AII.6 and AIII.1)

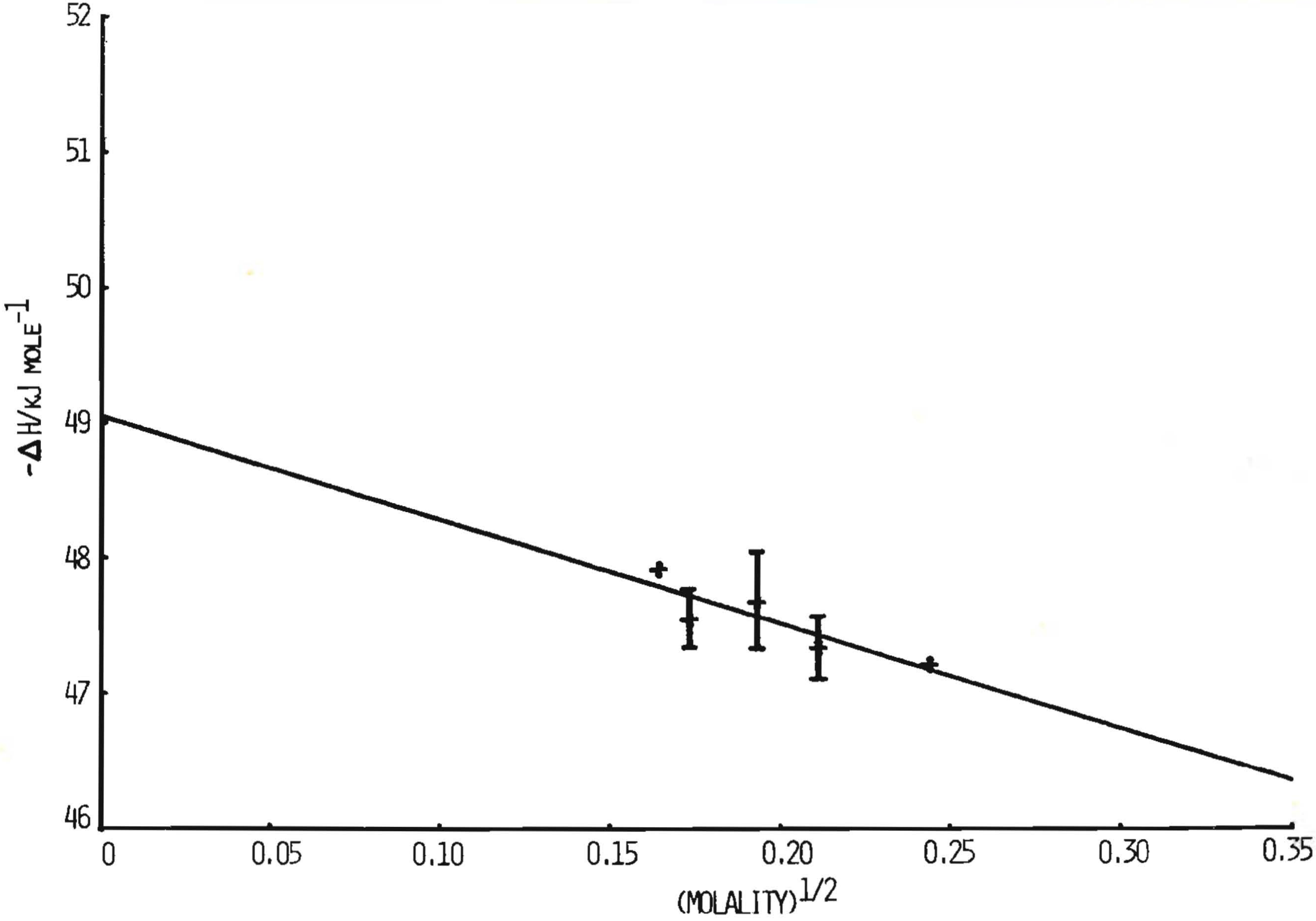

52
51
50
49
48
47
46
$-\Delta H/\text{kJ mole}^{-1}$
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
$(\text{MOLALITY})^{1/2}$

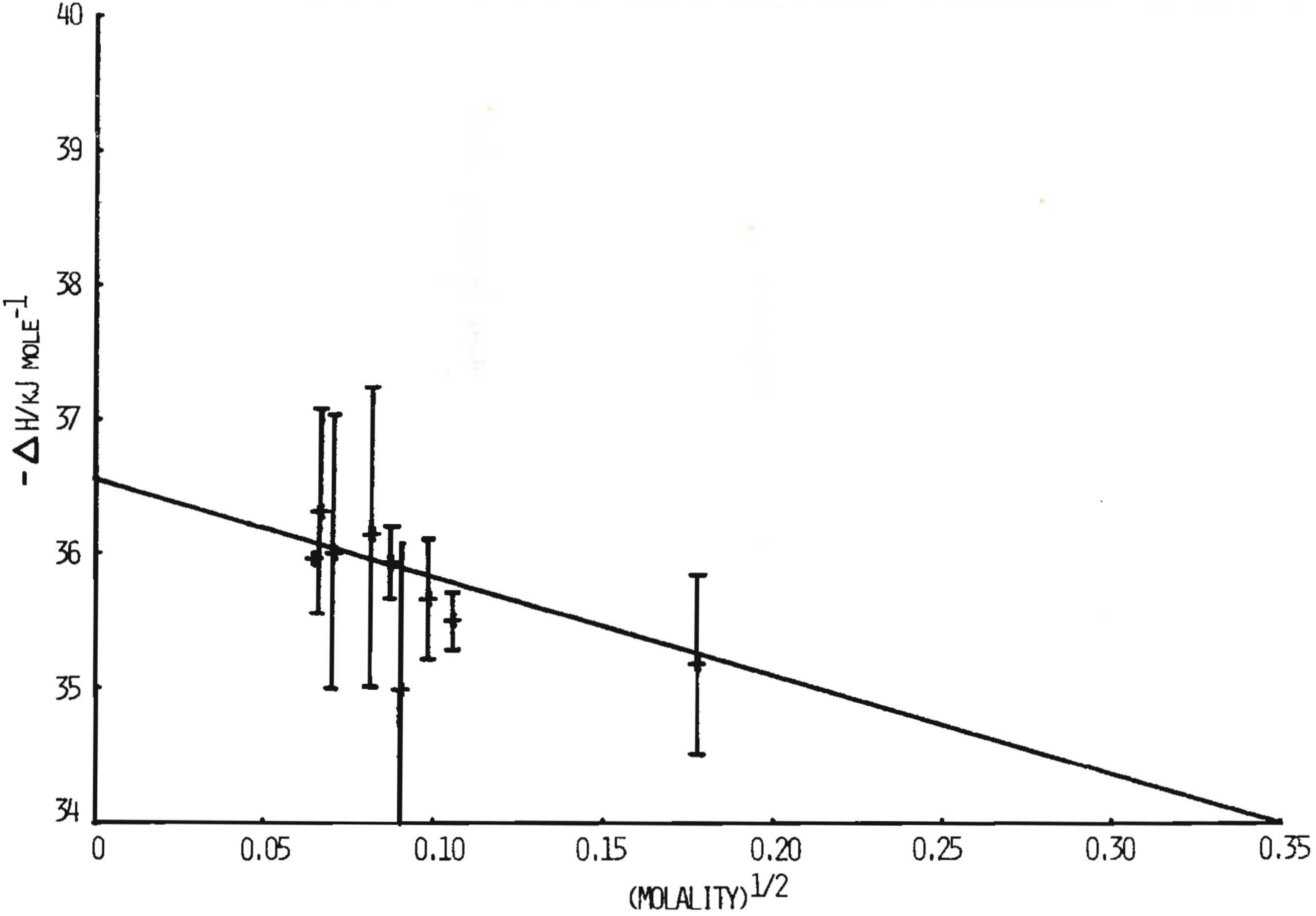
Figure 6: The integral heat of solution for $CuBr_2$ in water as a function of $m^{1/2}$ (23 ± 1^oC).

correlation coefficient = -0.89214

slope/kJ $kg^{1/2}$ mole $^{-3/2}$= -8.94

y-intercept/kJ mole^{-1} = -36.7 = ΔH_∞

(Data in Tables AII.7 and AIII.1)


40
39
38
37
36
35
34
- Δ H/KJ MOLE^{-1}
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
(MOLALITY)$^{1/2}$

SECTION 8

RESULTS

8.1 Experimental Results

$-\Delta H$ vs. $m^{1/2}$ curves were extrapolated to zero concentration (linear least squares analysis) to obtain ΔH_∞ for each halide in water at 23 ± 1°c (Figure 7, Table AIII.1, and Section 8.3).

ΦL values (Figure 8) were calculated (as per equation 2-7), and are listed in Table AIII.2. Note: ΔH values used to calculate ΦL were read directly from the experimental curve (Figure 7). Error bars were acquired from the information in Tables AII.5-7.

Also shown in Figure 8 (and listed in Table AIII.2) is ΦL as calculated by the Debye-Huckel limiting law for a 2-1 electrolyte in H_2O at 25°C (Section 2.4.1).

No temperature corrections have been made for the experimental enthalpy data. Reaction temperatures have been reported as 23 ± 1°C.

8.2 Comparison of Experimental Results with Literature Data

2.1 Direct Comparison

Figure 9 (Table AIII.3) is a plot of $-\Delta H$ vs. $m^{1/2}$ (obtained in this study for $CuCl_2$), as compared to the data for heats of solution of this same compound (in water at 25°C) determined by Partington and Soper[56] in 1929. Enthalpy data from the literature have been converted to

Figure 7: Integral heats of solution for $CuCl_2 \cdot 2H_2O$, $CuCl_2$, and $CuBr_2$ in water at 23 ± 1°C.

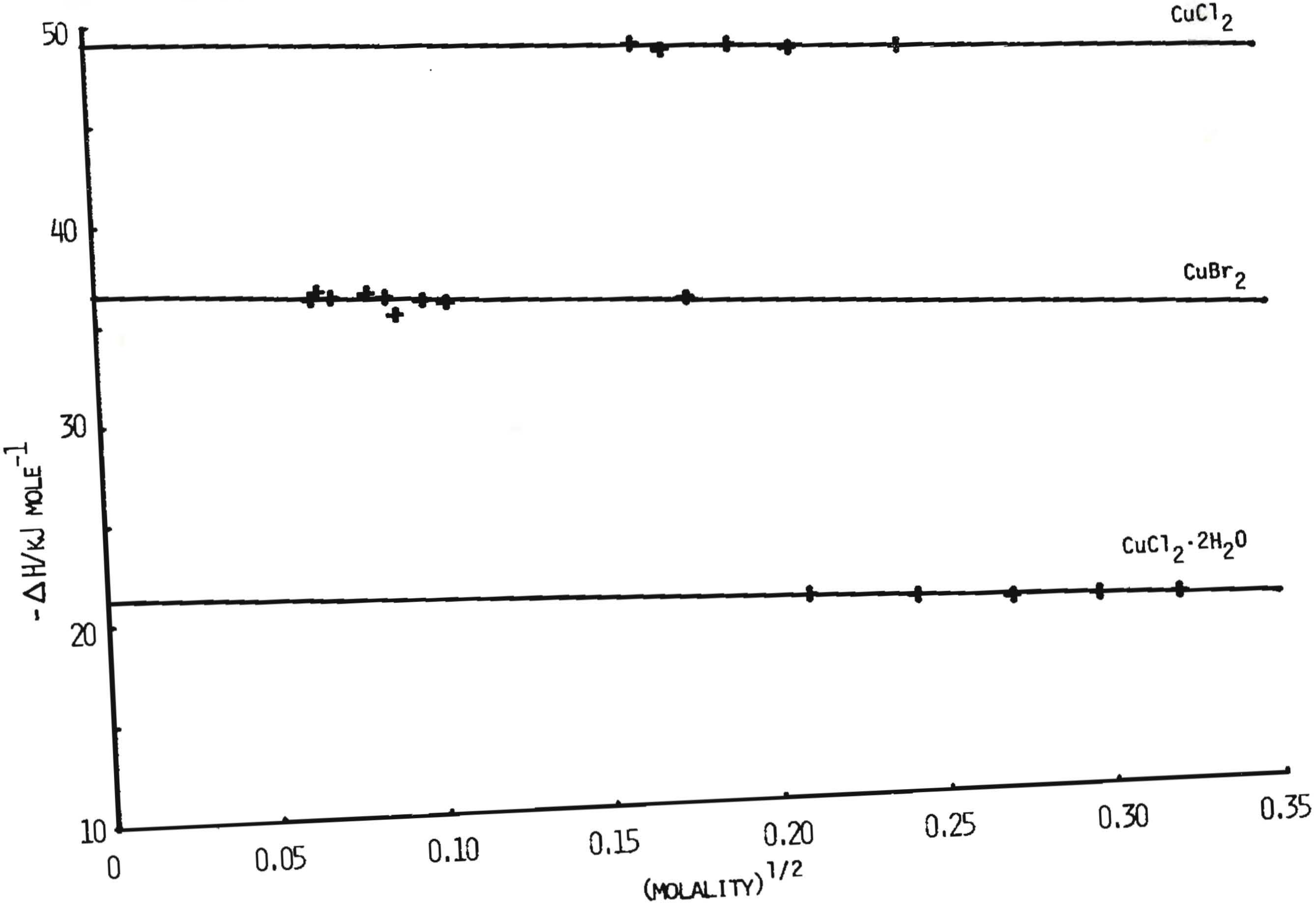

CuCl$_2$
CuBr$_2$
CuCl$_2$·2H$_2$O
50
40
30
20
10
$-\Delta H$/kJ mole^{-1}
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
(molality)$^{1/2}$

Figure 8: Relative apparent molal enthalpies as a function of $m^{1/2}$ in water.

——————— Experimental (23 ± 1°C)

A. $CuCl_2 \cdot 2H_2O$

B. $CuBr_2$

C. $CuCl_2$

●———————● Debye Huckel Limiting Law (25°C)

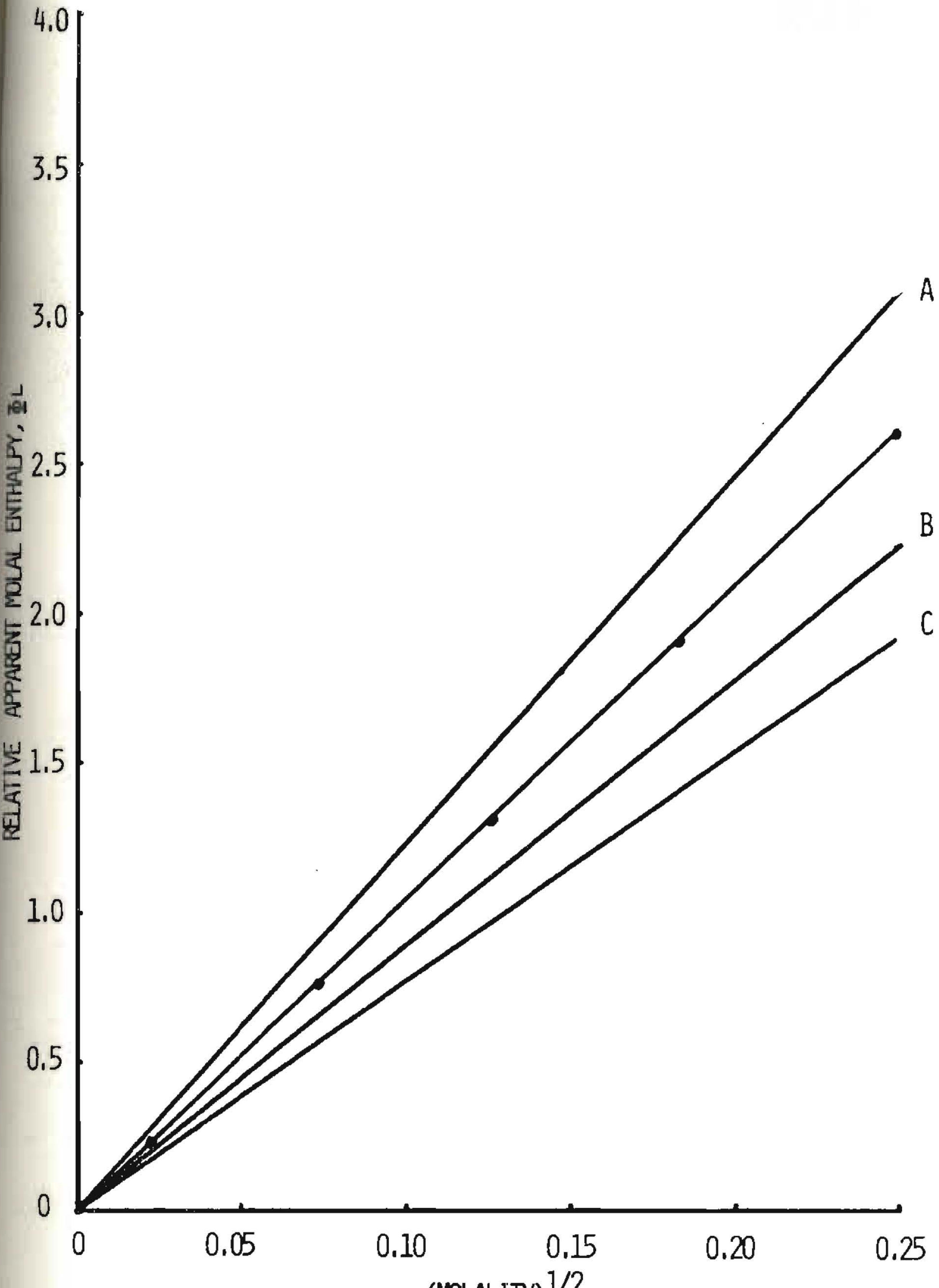
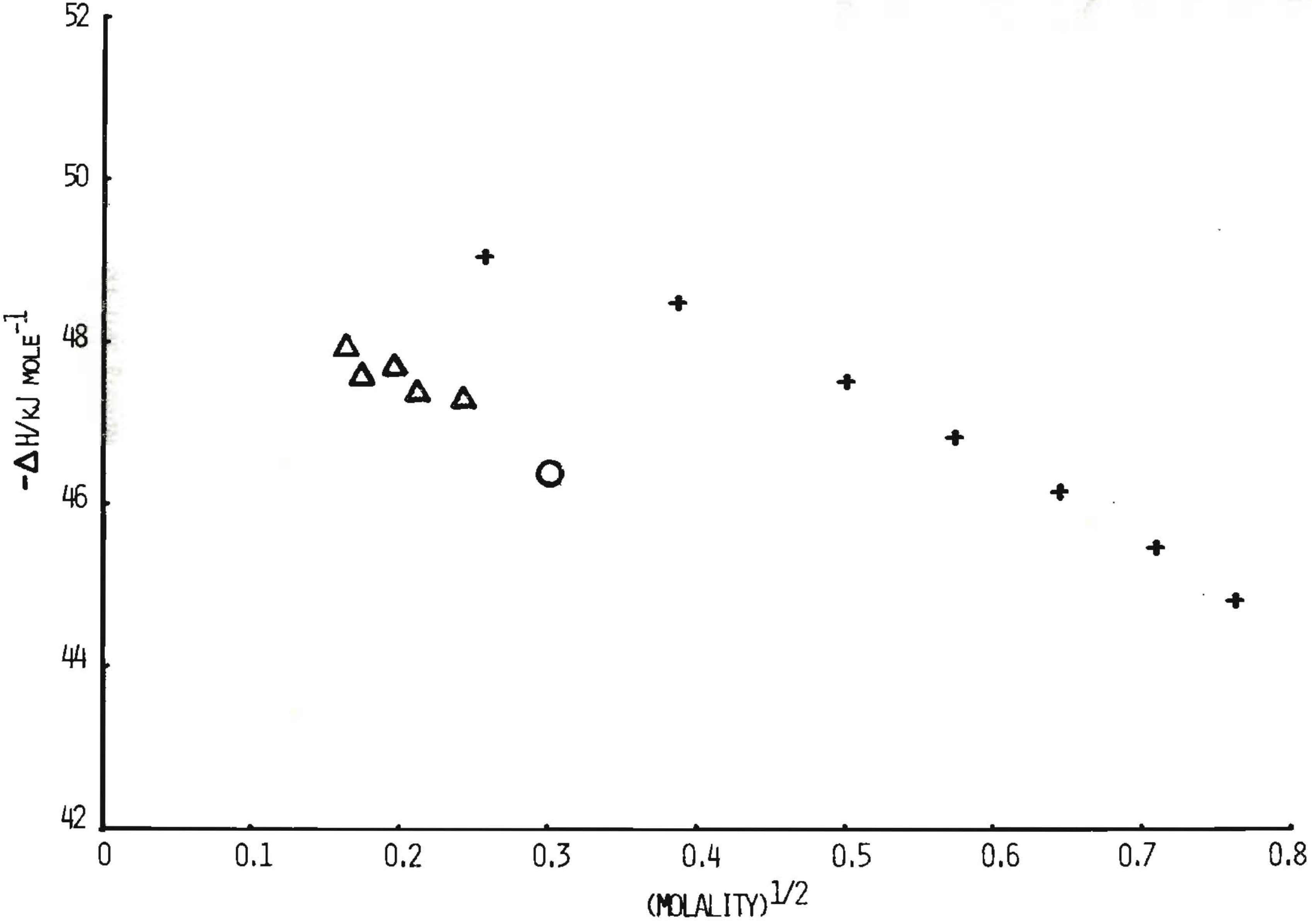

RELATIVE APPARENT MOLAL ENTHALPY, Φ_L
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
A
B
C
0
0.05
0.10
0.15
0.20
0.25
(MOLALITY)$^{1/2}$

Figure 9: Heats of Solution for $CuCl_2$ in water.

✚	Literature data from J.R. Partington (at 25°C)--(Table AIII.3)
○	Literature value--J. Thomsen (18°C)--(Table AIII.3)
△	Experimental data--(23 ± 1°C)--(Table AIII.1)


52
50
48
46
44
42
$-\Delta H$/KJ MOLE^{-1}
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
(MOLALITY)$^{1/2}$

kJ/mole, and concentration has been expressed in terms of $m^{1/2}$. Also shown in this figure is one enthalpy value at one concentration for $CuCl_2$ in water at 18°C, reported by J. Thomsen.[57] Note that Partington's data were obtained at such high concentrations that the enthalpy does not behave linearly with $m^{1/2}$.

No enthalpy data could be found in the literature for $CuBr_2$ or $CuCl_2 \cdot 2H_2O$.

Experimental values for $\Phi L(CuCl_2)$ have been summarized in Figure 10, and are compared to values from Partington's data (Table AIII.3). ΦL_I data were calculated using Partington's extrapolated value of -49.58 kJ/mole as ΔH_∞. ΦL_{II} data were obtained on the basis of Silvester and Pitzer's extrapolated ΔH_∞ of -50.76 kJ/mole.[58]

.2.2 Indirect Comparison

Refer to Section 2.4.3 for relevant equations. B^L_{MX} (the second virial coefficient of the enthalpy expression) and ΦL were evaluated at various concentrations (Table AIII.4) for $CuCl_2$ in water at 25°C, via the temperature derivatives of $\beta^{(o)}$ and $\beta^{(1)}$ reported by Silvester and Pitzer:[59,60]

Enthalpy Equation Parameters

$CuCl_2$ at 25°C

$(4/3)\dfrac{\partial\beta^{(o)}}{\partial T} \times 10^3$	$(4/3)\dfrac{\partial\beta^{(1)}}{\partial T} \times 10^3$	max m
-3.62	11.3	0.6

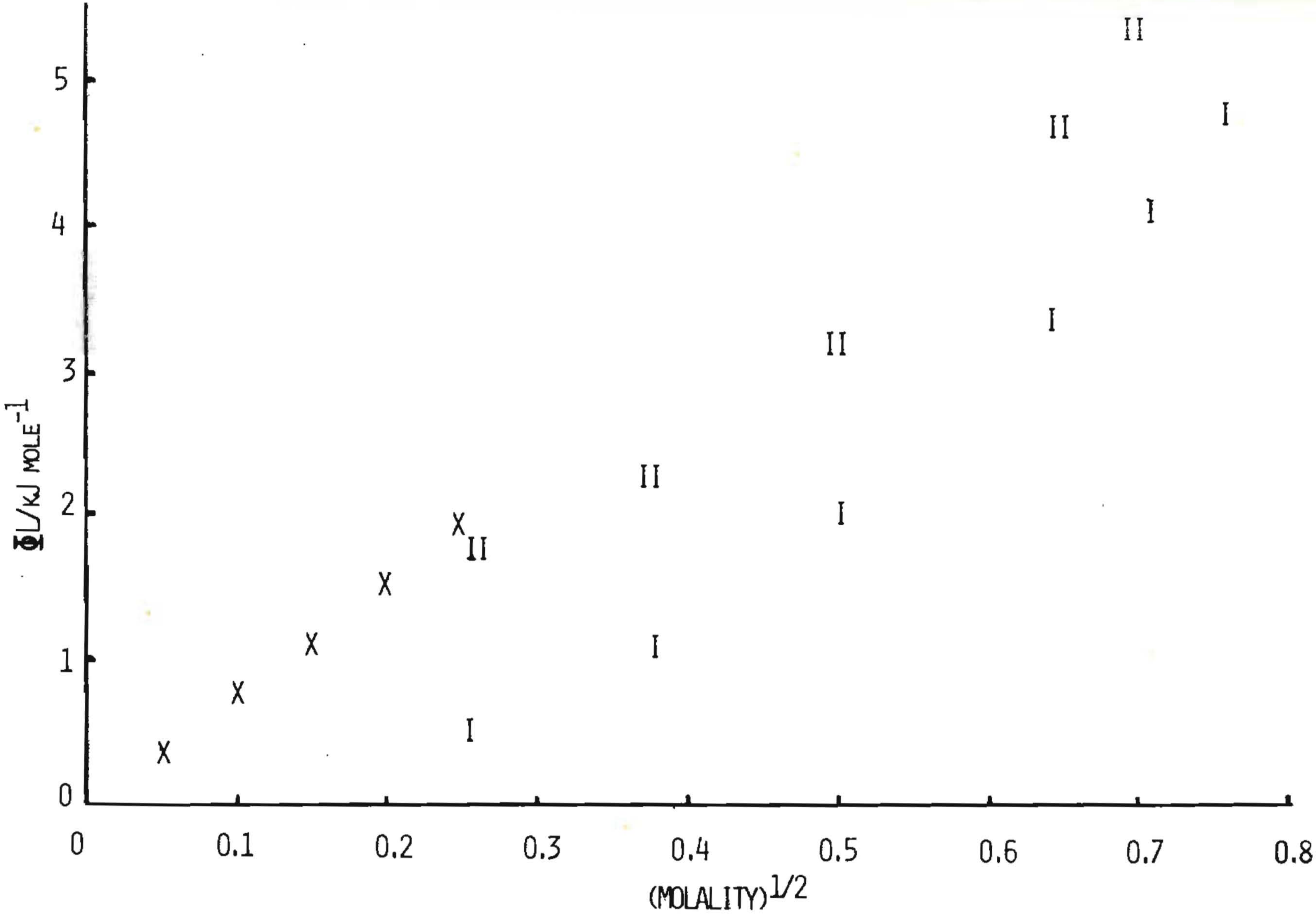
A TRS-80 Radio Shack Computer Program was written to generate B^L_{MX} and

Figure 10: Relative apparent molal enthalpy as a function of $m^{1/2}$ for $CuCl_2$ in water.

X Experimental data--23 ± 1°C (Table AIII.2)

I Partington/Soper data--25°C (Table AIII.3)

II Partington/Soper data--25°C (Table AIII.3)


ΦL/KJ MOLE^{-1}
0
1
2
3
4
5
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
(MOLALITY)$^{1/2}$

ΦL at varied concentrations. This program has been included as Appendix IV.

Figure 11 is a plot of B^L_{MX} as a function of m for $CuCl_2$ in H_2O at 25°C. Figure 12 compares ΦL(as a function of $m^{1/2}$) values generated by Pitzer's semi-empirical equation with ΦL determined in this study.

8.3 Discussion of Results

Experimentally determined enthalpies of solution at infinite dilution are:

	ΔH_∞/kJ $mole^{-1}$
$CuCl_2 \cdot 2H_2O$	-23.0
$CuCl_2$	-49.1
$CuBr_2$	-36.7

All three halides were found to possess a negative ΔH_∞ in water. According to the convention adopted earlier (Section 2.2), a negative enthalpy (exothermic reaction) results when heat released by hydrolysis of the ions exceeds that absorbed during disruption of the crystal lattice. That ΔH_∞ is less negative for the dihydrate than for $CuCl_2$ further exemplifies this concept, in that $CuCl_2 \cdot 2H_2O$ is partially hydrolyzed prior to dissolution; therefore, the heat effect of ion hydrolysis is lessened.

A decrease in the net heat liberated is also observed when one compares $\Delta H_\infty[CuCl_2]$ and $\Delta H_\infty[CuBr_2]$ One might expect $CuBr_2$ to exhibit the lesser (in absolute magnitude) enthalpy: the Br^- ion being much

Figure 11: Variation of the second virial coefficient of the apparent relative molal enthalpy expression, B^L_{MX}, with molality for $CuCl_2$ in water at 25^oC (Table AIII.4).

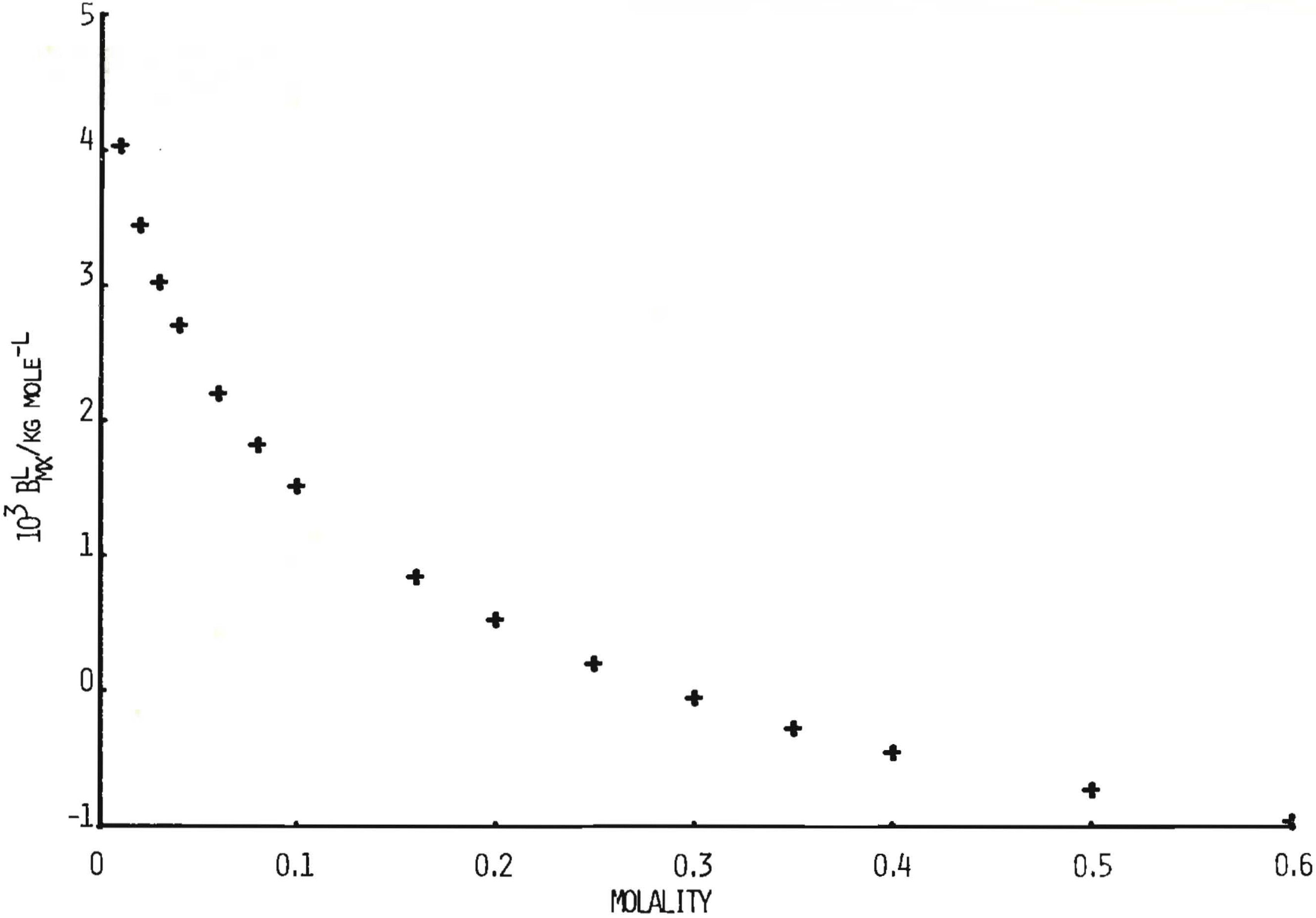
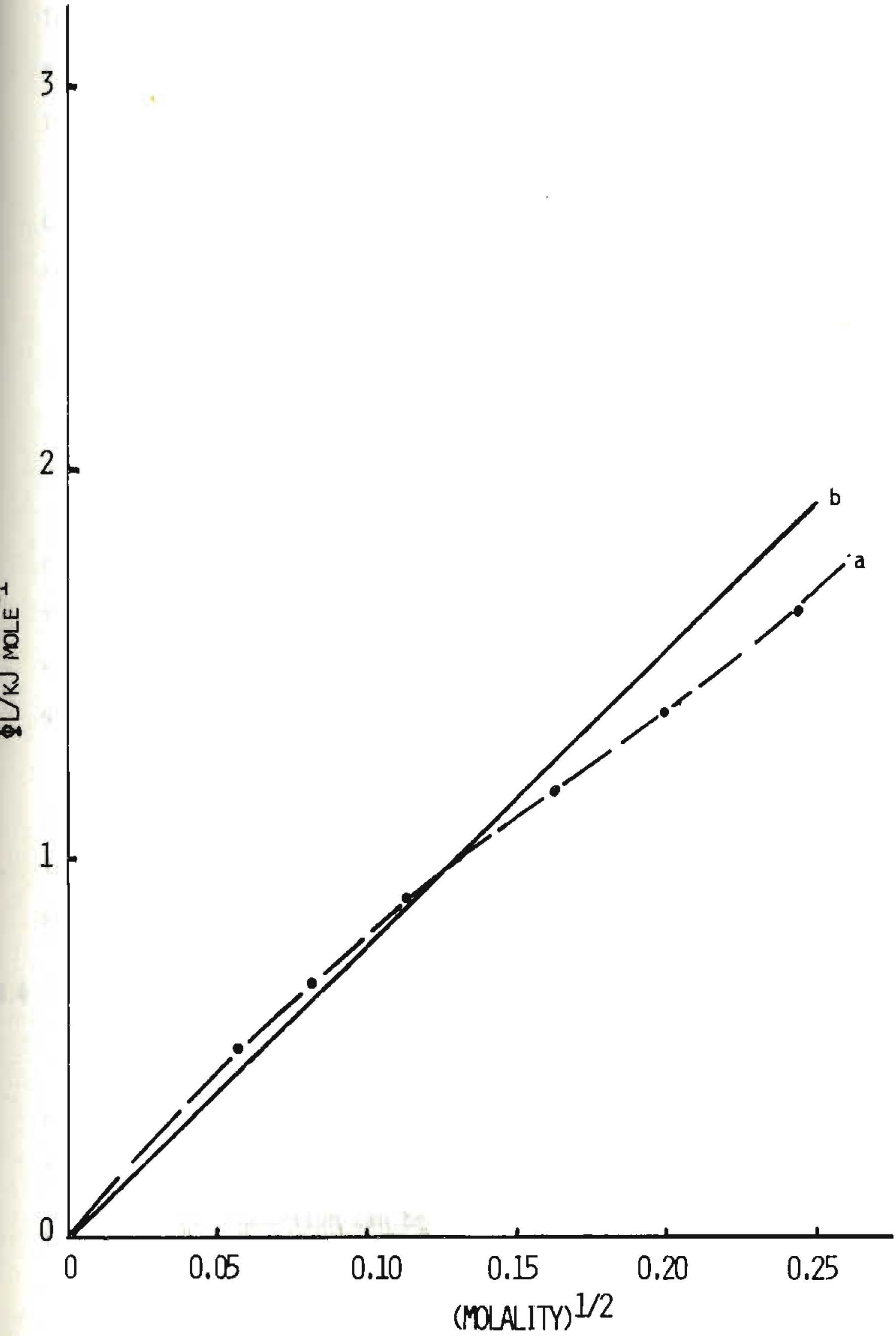

5
4
3
2
1
0
-1
$10^3 B^L_{MX}$/KG MOLE^{-L}
0
0.1
0.2
0.3
0.4
0.5
0.6
MOLALITY

Figure 12: Relative apparent molal enthalpy for $CuCl_2$ in water as a function of $m^{1/2}$.

●—— — —● Calculated from the temperature derivatives of $\beta^{(o)}$ and $\beta^{(1)}$, as reported by Pitzer and Silvester.

———— Experimental data determined in this study.

(Refer to Tables AIII.2 and AIII.4 for corresponding data.)


ΦL/KJ MOLE^{-1}
3
2
1
0
0
0.05
0.10
0.15
0.20
0.25
(MOLALITY)$^{1/2}$
a
b

larger than Cl^-, possesses a lower charge density, and thus would not attract as many solvent molecules. The experimental results conformed to expectations.

Although quantitative data was not obtained for $Cu(NO_3)_2 \cdot 3H_2O$ and $Cu(ClO_4)_2 \cdot 6H_2O$, enough information was obtained to approximate ΔH_∞ for each compound:

	ΔH_∞/kJ mole
$Cu(NO_3)_2 \cdot 3H_2O$	$\approx + 0.4$
$Cu(ClO_4)_2 \cdot 6H_2O$	$\approx + 20$

In comparing $\Delta H_\infty[CuCl_2]$ and $\Delta H_\infty[Cu(NO_3)_2 \cdot 3H_2O]$, one sees the effects of 1), three waters of hydration in the crystal structure, and, 2), an increase in anion size. It is impossible to separate the two effects without information[61] for anhydrous copper(II) nitrate, but note that dissolution is now an endothermic process.

Further down the scale we find the enthalpy of solution for the perchlorate hexahydrate compound; again we observe the effects of increases in anion size and number of waters of hydration in the crystal structure.

8.4 Quality of the Data

Copper(II) chloride anhydrous and dihydrate data are believed to be reasonably accurate, as no data outside 3.5% relative standard deviation (Section 7.2) were retained.

A direct comparison can be made between experimentally determined and literature values reported for $\Delta H_{\infty}[CuCl_2]$ in water(from Section 8.2.1):

	$\Delta H_{\infty}[CuCl_2]$ kJ $mole^{-1}$
experimental (23 ± 1^oC)	-49.1
Partington (25^oC)	-49.58
Silvester and Pitzer(25^oC)[62]	-50.76

Figure 12 is a plot of ΦL for $CuCl_2$ vs. $m^{1/2}$. Curve "a" was calculated from the temperature derivatives of $\beta^{(o)}$ and $\beta^{(1)}$ (Section 8.2.2). Curve "b" is of the experimental data determined in this study. We find excellent agreement between the two curves.

Although experimental $CuBr_2$ data appear to be consistent with that of $CuCl_2$ and $CuCl_2 \cdot 2H_2O$ (see Figure 8), they must be taken with a grain of NaCl: most measurements were made at 0.01 volts, where error was found to be great (Section 7.2).

SECTION 9

SUMMARY

9.1 Conclusions

Integral heats of solution, ΔH, were measured at constant pressure for Cu(II) salts in water (at $23 \pm 1^{\circ}C$) as a function of concentration by the method of solution calorimetry. ΔH_{∞}, the integral heat of solution at infinite dilution, was determined by linear least squares extrapolation of ΔH vs. $m^{1/2}$ curves for copper(II) chloride dihydrate, copper(II) chloride, and copper(II) bromide. Relative results between these three compounds conformed with what one might reasonably predict (Section 8.3).

The calorimetric method was found to give accurate results when used within certain limitations (Section 7.2).
Experimental results for copper(II) chloride were in excellent agreement with activity and osmotic coefficient information from the literature; the two sets of data were correlated via, the quantity ΦL, the relative apparent molal enthalpy.

9.2 Importance of the Study

Data such as that obtained in this study is of importance to the thermodynamic literature. The state of the art is such that, although critical compilations of enthalpy data exist for 1-1 electrolytes,[63] data for higher valence-type electrolytes is rare. Furthermore, the enthalpy, osmotic and activity coefficient compilations[64] which are available for both the 1-1 and higher valence electrolytes contain only data for electrolytes in water at 25°C. It is possible to extend these data to different temperatures and pressures, providing heat capacity information and partial molar volume data are available, and providing the enthalpy is well-determined at 25°C.

Information of this type is also of importance in filling in the gaps left by theory. Reality (either fortunately, or unfortunately) often departs rather severely from our theoretical expectations. Refer to Figure 8. The Debye-Huckel curve (limiting law) takes into account ion charges only (Section 2.4), The experimental ΦL curves, although all do converge eventually, clearly illustrate that outside the limit of infinite dilution, effects are being exerted by something other than ionic charges. Even with the introduction of size factors and first-order effect parameters into the equations(Section 2.4.2), we still find theory to be somewhat lacking. Obviously there is a real need for more information, so that we might gain more insight into the thermodynamics of electrolyte solutions.

.3 Suggestions for Further Studies

Much more heat of solution data is needed for many more copper salts. Had time permitted, heats of solution for CuCl, $CuCl_2 \cdot 2H_2O$, $CuCl_2$, $CuBr_2$ and CuBr would have been measured in HCl solution at 25°C. Such information would illustrate the effects of a decrease in charge density of the cation. Heats for solution could also be compared for the Cu(II) compounds in H_2O and HCl.

To obtain more information as to how waters of hydration will affect heats of solution, one might make calorimetric measurements of a series: studies of $Cu(NO_3)_2$, $Cu(NO_3)_2 \cdot 3H_2O$, and $Cu(NO_3)_2 \cdot 6H_2O$, or $CuSO_4$, $CuSO_4 \cdot H_2O$, and $CuSO_4 \cdot 5H_2O$, for example, would be worthwhile.

Also of great value would be enthalpy data for dissolution of copper salts in aqueous-alcohol and non-aqueous systems.

Were the equipment available, enthalpy information for copper salts might be obtained at temperatures other than $25^\circ C$.

Data obtained from any one of the above-mentioned studies would make welcomed contributions to the literature.

REFERENCES

1. I.M. Klotz and R.M. Rosenberg, "Chemical Thermodynamics, Basic Theory and Methods," 3rd ed, Benjamin/Cummins Publishing Co., Menlo Park, CA (1974), pp. 3-5.

2. For crystalline structures of copper salts mentioned in this study, refer to: J.C. Bailer, Ed., "Comprehensive Inorganic Chemistry," Vol. 3, Pergamon Press Ltd., Oxford (1973), pp. 22-41.

3. For a description of the structure of water: G.H. Nancollas, "Interactions in Electrolyte Solutions," Elsevier Publishing Co., Amsterdam (1966), Chapter 1.

4. Klotz and Rosenberg, "Chemical Thermodynamics," p.5.

5. Klotz and Rosenberg, "Chemical Thermodynamics," p.5.

6. P.W. Atkins, "Physical Chemistry," W.H. Freeman and Co., San Francisco, CA (1978), p. 210.

7. Atkins, "Physical Chemistry", p. 209.

8. An intradepartmental research project involving copper compounds has been proposed by the Chemistry faculty at Emporia State University.

9. Atkins, "Physical Chemistry," p. 20.

10. Atkins, "Physical Chemistry," p. 20.

11. H.S. Harned and B.B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold Publishing Co., N.Y., NY (1958), p. 6.

12. Atkins, "Physical Chemistry," p. 312.

13. Klotz and Rosenberg, "Chemical Thermodynamics," p. 322.

14. Ricardo M. Pytkowicz, "Activity Coefficients in Electrolyte Solutions," Vol. 1, C.R.C Press Inc., Boca Raton, Florida (1979), p. 11.

15. Pytkowicz, "Activity Coefficients in Electrolyte Solutions," Vol. 1, p. 9.

16. Pytkowicz, "Activity Coefficients in Electrolyte Solutions," Vol. 1, p. 11.

17. Atkins, "Physical Chemistry," pp. 113-115.

18. The reader must be aware, when examining thermodynamic data in the literature as to which convention is being used. Quite often, a text will adopt the opposite convention, i.e., that a negative Q represents heat evolved.

19. Atkins, "Physical Chemistry," pp. 113-115.

20. D.P. Shoemaker, C.W. Barland, and J.I. Steinfeld, "Experiments in Physical Chemistry," 3rd ed, McGraw-Hill Book Co., N.Y., NY (1974), p. 164.

21. Shoemaker et. al., "Experiments in Physical Chemistry," p. 162.

22. Shoemaker et. al., "Experiments in Physical Chemistry," p. 163.

23. Pytkowicz, "Activity Coefficients in Electrolyte Solutions," p. 21.

24. Klotz and Rosenberg, "Chemical Thermodynamics," p. 278.

25. Weissberger, "Techniques of Organic Chemistry," Vol. 1, 3rd ed, Interscience Publishers Inc., N.Y., NY (1959), p. 526.

26. Shoemaker, et.al., "Experiments in Physical Chemistry," p. 131.

27. Shoemaker, et.al., "Experiments in Physical Chemistry," p. 132.

28. Weissberger, "Techniques of Organic Chemistry," p. 531.

29. Shoemaker, et.al., "Experiments in Physical Chemistry," p. 157.

30. Atkins, "Physical Chemistry," pp. 314-323. Derivation of A can be found in most general physical chemistry texts.

31. Shoemaker, et.al., "Experiments in Physical Chemistry," p. 157.

32. Thermodynamics cannot tell us at what concentration we will find adherence to this law. It can tell us that as we approach infinite dilution, the solution will eventually behave in the predicted manner.

33. G.N. Lewis and M. Randall, "Thermodynamics," 2nd ed, McGraw-Hill Book Co., Inc., N.Y., NY (1961), p. 347.

34. Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," pp. 42-58.

35. Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Chapter 2.

36. Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," pp. 42-58.

37. R.A. Robinson and R.H. Stokes, "Electrolyte Solutions," 2nd ed, Butterworths, Londond (1968), p. 74-68.

38. Lewis and Randall, "Thermodynamics," pp. 332-348.

39. Lewis and Randall, "Thermodynamics," pp. 332.

40. Lewis and Randall, "Thermodynamics," Chapter 25.

41. R.N. Goldberg, "Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: Bi-Valent Compounds of Pb, Cu, Mn and U," J. Phys, & Chem. Ref. Data, 8, 1005 (1979).

42. Pytkowicz, "Activity Coefficients in Electrolyte Solutions," Vols. 1 and 2.

43. Lewis and Randall, "Thermodynamics," Appendix 4.

44. L.F. Silverster and K.S. Pitzer, "Thermodynamics of Electrolytes. X. Enthalpy and the Effect of Temperature on the Activity Coefficients," J. Soln Chem., 7, 327-337 (1978).

45. Most of the papers in this series are listed in the reference section of: Silvester and Pitzer, J. Soln. Chem.,7.

46. Recorder requirements are: an internal impedance of greater than 100 ohms, and plotting ranges of 1, 100, and 100 millivolts full scale.

47. "Instructions for the 1451 Solution Calorimeter,"Parr Instruments, p. 17. The method for analysis of thermograms is also given in this manual.

48. This information was obtained from a Parr Solution Calorimeter salesman. No reference was made to this on the label, however.

49. Lot analyses (not listed on labels) were obtained from Sigma Chemical Corporation by telephone.

50. Additional information on these compounds is given in: "The Merck Index, An Encyclopedia of Chemicals and Drugs," Merck and Co., Inc., Rathway, NJ.

51. "Handbook of Chemistry and Physics," 48th ed., C.P. Weast, Ed., Chemical Rubber Co., Cleveland, OH (1968), pp. B-176.

52. "Comprehensive Inorganic Chemistry," p. 26.

53. "Handbook of Chemistry and Physics," pp. 22-25.

54. "Comprehensive Inorganic Chemistry," pp. 22-25.

55. D.A. Skoog and D.M. West, "Analytical Chemistry, and Introduction," 2nd ed, Holt, Rinehart and Winston, Inc., N.Y., NY (1974), p. 44.

56. J.R. Partington and W.E. Soper, "The Heats of Solution of Some Salts in Water and Ethyl Alcohol Solutions," *Philosophical Magazine and Journal of Science* (1929), 237.

57. J. Thomsen, as cited by Partington and Soper, *Phil. Mag. & J. Science* (1929), 237.

58. Silvester and Pitzer, *J. Soln. Chem.*, *7*, 335.

59. Silvester and Pitzer, *J. Soln. Chem.*, *7*, 333.

60. Parameters (not utilized in this manuscript) for the activity and osmotic coefficient expressions for $CuCl_2$ and $Cu(NO_3)_2$ in water at 25^oC are listed in Table VI of : K.S. Pitzer and G. Mayorga, "Thermodynamics of Electrolytes II. Activity and Osmotic Coefficients for Strong Electrolytes with One or Both Ions Univalent," *Journal of Physical Chemistry*, *77*, 2300 (1973).

61. Such information does exist-- heats of solution values are listed for several Cu(II) salts in "Lange's Handbook of Chemistry," 11th ed, McGraw-Hill Book Co. (1961) p. 9-109.

62. Silvester and Pitzer, *J. Soln. Chem.*, *7*, 335. The value: -50.76 kJ/mole for ΔH_∞ $[CuCl_2]$ was actually obtained by a linear least squares extrapolation of Partington's data.

63. "Thermal Properties of Aqueous Uni-univalent Electrolytes," *National Standard Reference Data Series*, *N.B.S.2* (Washington D.C.: U.S. Gov. Printing Office, 1965).

64. In general, refer to *Phys. & Chem. Ref. Data*. This journal makes available current primary data in the fields of Physics and Chemistry.

APPENDIX I

Literature Data for use with the Debye-Huckel Extended Law

TABLE AI

SECOND VIRIAL COEFFICIENTS[a] FOR THE OSMOTIC COEFFICIENT EXPRESSION[b]

$CuCl_2$, $CuBr_2$ at 25°C

		$CuCl_2$			$CuBr_2$	
m	γ	ϕ	B^{ϕ}_{MX}	γ	ϕ	B^{ϕ}_{MX}
0.001	0.8873	0.9616	1.340	0.8895	0.9628	2.240
0.002	0.8487	0.9481	1.320	0.8526	0.9504	2.180
0.003	0.8216	0.9386	1.300	0.8271	0.9418	2.100
0.004	0.8003	0.9311	1.280	0.8071	0.9351	2.030
0.005	0.7826	0.9248	1.250	0.7907	0.9296	1.970
0.006	0.7674	0.9195	1.240	0.7767	0.9250	1.920
0.008	0.7423	0.9105	1.280	0.7536	0.9175	1.840
0.010	0.7217	0.9033	1.160	0.7350	0.9115	1.770
0.020	0.6538	0.8796	1.404	0.6743	0.8931	1.540
0.030	0.6124	0.8659	0.960	0.6382	0.8834	1.400
0.040	0.5831	0.8567	0.901	0.6130	0.8776	1.290
0.060	0.5427	0.8453	0.814	0.5791	0.8717	1.140
0.080	0.5153	0.8390	0.752	0.5569	0.8698	1.040
0.100	0.4952	0.8356	0.705	0.5411	0.8700	0.963
0.200	0.4415	0.8358	0.561	0.5036	0.8846	0.774
0.300	0.4183	0.8466	0.484	0.4938	0.9076	0.636
0.400	0.4066	0.8605	0.432	0.4953	0.9338	0.570
0.500	0.4007	0.8754	0.395	0.5033	0.9614	0.524
0.600	0.3982	0.8906	0.366	0.5155	0.9900	0.490
0.700	0.3980	0.9056	0.342	0.5309	1.0189	0.464
0.800	0.3992	0.9203	0.323	0.5490	1.0479	0.442
1.000	0.4046	0.9485	0.291	0.5911	1.1049	0.409

[a] The above second virial coefficients have been calculated at different concentrations from osmotic coefficient data tabulated in R.N. Goldberg's "Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: Bi-univalent Compounds of Pb, Cu, Mn and U," J. Phys. & Chem. Ref. Data, 1005 (1979).

[b] The osmotic coefficient expression for a 2-1 electrolyte:

$$\phi - 1 = -2A \frac{I^{1/2}}{1 + b\, I^{1/2}} + (4/3)\, m\, B^{\phi}_{MX}$$

where b = 1.2 and A_{ϕ} = 0.3910 at 25°C. B^{γ}_{MX} can be similarly evaluated at each concentration from the activity coefficient data in this table.

APPENDIX II

Experimental Data

TABLE AII.1

ENERGY EQUIVALENTS OF CALORIMETER AND CONTENTS

mass TRIS (gms)	T_{rxn} (^{o}C)	ΔT (^{o}C)	Q (cal)	e_o (kJ/^{o}C)
		SYSTEM I		
0.49885	20.7110	0.2450	30.03597	0.5129
0.49977	20.4300	0.2500	30.13957	0.5027
0.49991	20.5100	0.2500	30.13428	0.5043
0.50004	21.1770	0.2490	30.02762	0.5046
0.50009	20.1779	0.2490	30.10033	0.5058
0.50036	20.8050	0.2520	30.11074	0.4999
0.50009	20.6760	0.2520	30.11664	0.5000
0.50014	20.5060	0.2500	30.14883	0.5046
0.50002	21.4300	0.2490	29.98299	0.5038
0.50016	20.1610	0.2500	30.03757	0.5027
0.50038	20.7850	0.2530	30.11538	0.4980
0.49991	20.7150	0.2510	30.39910	0.5067
0.50002	24.4560	0.2420	29.46356	0.4094
0.50030	24.1730	0.2470	29.51273	0.4999
0.49986	22.6360	0.2440	29.76644	0.4104
0.50016	22.2470	0.2490	29.85110	0.5016
0.50040	22.0180	0.2500	29.90477	0.5005
		SYSTEM II		
0.49997	22.3520	0.2480	29.82174	0.5031
0.49990	23.1690	0.2470	29.67735	0.5027
0.49956	22.2700	0.2490	29.81347	0.5010
0.50044	23.3990	0.2440	29.66990	0.5088
0.50024	22.8130	0.2470	29.75868	0.5041
0.50076	22.5890	0.2480	29.82812	0.5032
0.50032	22.8820	0.2450	29.75158	0.5081
0.50000	23.1420	0.2460	29.68793	0.5049
0.50035	22.8950	0.2470	29.57113	0.5040
0.50023	22.7640	0.2500	29.76650	0.4982

TABLE AII.2

HEATS OF SOLUTION FOR $CuCl_2 \cdot 2H_2O$ IN WATER AT 23 ± 1°C

Molality	$-\Delta H/kJmole^{-1}$	T_{rxn}	Molality	$-\Delta H/kJmole^{-1}$	T_{rxn}	Molality	$-\Delta H/kJmole^{-1}$	T_{rxn}
0.073319	19.10	22.8720	0.087995	19.12	21.0350	0.102675	19.38	23.2640
0.043981	20.05	21.9680	0.102636	19.29	22.9800	0.073329	19.78	23.5190
0.058664	19.92	22.0390	0.102654	19.39	23.7100	0.088011	19.80	22.9190
0.073326	19.65	22.3800	0.058658	16.67	23.4720	0.044014	20.03	23.0730
0.073334	19.50	22.4510	0.058675	19.65	22.0840	0.017249	21.30	22.3081
0.014078	21.62	22.9992	0.010828	21.97	22.6204	0.012267	21.08	22.5289
0.004059	21.23	23.0394	0.017581	21.21	23.3011	0.012868	21.46	23.4326
0.002796	21.62	23.3998	0.007811	22.06	24.2706	0.002595	22.14	23.9375
0.002986	21.43	24.3027	0.003942	21.10	23.9704	0.003268	23.40	23.6979
0.003615	21.47	23.8215	0.003767	25.69	23.9219	0.004772	20.91	23.6606
0.006124	21.31	23.5966	0.003311	22.07	24.3371	0.0030056	22.75	24.3076
0.003364	23.37	21.4003	0.003570	21.17	20.5765	0.003969	18.41	20.5864
0.006130	23.02	20.6953	0.003043	19.71	20.9543	0.002818	21.10	22.1075
0.007836	21.81	21.9822	0.003338	22.20	22.2532	0.004037	24.72	21.7796
0.002589	25.19	22.2737	0.003053	22.78	22.2410	0.009624	23.61	20.9006
0.004027	23.03	22.7633	0.004035	24.35	22.8528	0.017237	21.22	23.1469
0.017270	21.76	23.1987	0.007122	22.07	23.0180	0.012277	22.16	23.0369
0.004779	21.72	23.0134	0.003647	21.84	23.0280	0.009594	22.48	23.0376
0.002583	21.47	23.0004	0.002599	17.44	22.3094	0.002625	16.71	22.4782

TABLE AII.2 (continued)

Molality	$-\Delta H/\mathrm{kJmole}^{-1}$	T_{rxn}	Molality	$-\Delta H/\mathrm{kJmole}^{-1}$	T_{rxn}	Molality	$-\Delta H/\mathrm{kJmole}^{-1}$	T_{rxn}
0.003319	21.56	22.4012	0.003321	20.94	22.3763	0.003319	21.87	22.4066
0.003637	22.31	22.3270	0.003628	20.01	22.2938	0.003587	22.05	22.4079
0.017563	21.66	22.4340	0.017541	21.29	22.5640	0.010841	21.75	22.6424
0.004774	20.58	22.1703	0.004772	21.96	22.0058	0.003319	21.40	21.6377
0.003293	20.05	21.7972	0.009647	21.00	21.5676	0.009608	21.66	21.2903
0.005339	21.70	21.1382	0.005363	22.18	21.8751	0.005344	21.31	20.8423

TABLE AII.3

HEATS OF SOLUTION FOR $CuCl_2$ IN WATER AT 23 ± 1°C

Molality	$-\Delta H/kJmole^{-1}$	T_{rxn}	Molality	$-\Delta H/kJmole^{-1}$	T_{rxn}	Molality	$-\Delta H/kJmole^{-1}$	T_{rxn}
0.044669	47.16	23.1020	0.052122	48.15	23.4840	0.059457	47.21	23.7140
0.044671	47.49	23.6790	0.037198	47.41	23.5660	0.003789	34.31	24.1183
0.004536	47.33	22.6470	0.005235	42.74	22.4615	0.005908	41.28	22.4147
0.007467	41.16	22.9445	0.003963	47.05	22.8768	0.009449	45.00	23.0579
0.002624	32.27	23.6137	0.002854	29.84	23.6570	0.005552	44.29	24.0539
0.008974	43.47	23.8677	0.027034	47.91	24.1381	0.029800	47.69	24.4445
0.037435	47.93	24.5073	0.002201	35.94	24.3960	0.000926	34.82	24.4441
0.002821	27.87	23.2232	0.003158	42.77	22.9670	0.019347	47.40	23.1636
0.014644	47.15	23.1328	0.003709	41.31	23.1346	0.030314	47.38	23.3204
0.003854	46.55	21.8962	0.004598	31.34	21.4253	0.005191	40.67	20.4963
0.007459	45.00	20.7624	0.009000	78.49	20.8738	0.004374	47.81	20.7196
0.005590	47.15	20.5547	0.005615	44.33	22.7161	0.006317	42.91	22.9610
0.003879	47.16	22.8898	0.003088	41.25	22.4958	0.004568	39.49	23.5043
0.007523	46.09	23.2746	0.008222	42.96	23.1242	0.004391	45.10	22.5387
0.004373	42.06	22.5151	0.004392	44.75	22.3544	0.000886	34.70	22.1668
0.000943	26.72	22.1528	0.000952	28.58	22.3181	0.002232	27.31	22.1487
0.002223	41.27	22.1482	0.002651	37.83	22.0458	0.002606	21.19	22.1457
0.008974	46.94	22.2781	0.002815	40.64	22.2577	0.006323	38.02	22.3156

TABLE AII.3 (continued)

Molality	$-\Delta H$/kJmole^{-1}	T_{rxn}	Molality	$-\Delta H$/kJmole^{-1}	T_{rxn}	Molality	$-\Delta H$/kJmole^{-1}	T_{rxn}
0.002815	40.64	22.2577	0.006323	38.02	22.2156	0.010425	41.62	22.2875
0.010402	48.59	21.9389	0.006320	43.24	22.5855	0.002627	41.82	21.9043
0.002639	31.13	21.6469	0.002860	38.06	21.4658	0.002879	40.95	21.3427
0.003211	37.98	20.7208	0.003184	46.06	21.6002	0.002863	36.44	20.5544
0.002812	42.28	23.4488	0.00374	48.47	23.5308	0.003747	35.24	23.4426

TABLE AII.4

HEATS OF SOLUTION FOR $CuBr_2$ IN WATER AT 23 ± 1°C

Molality	$-\Delta H/kJmole^{-1}$	T_{rxn}	Molality	$-\Delta H/kJmole^{-1}$	T_{rxn}	Molality	$-\Delta H/kJmole^{-1}$	T_{rxn}
0.006671	35.96	23.4036	0.006818	37.11	23.4419	0.003023	33.34	22.9453
0.008859	36.41	22.9828	0.009629	35.96	23.2711	0.021512	35.86	23.1729
0.031682	35.63	23.1704	0.003702	35.26	23.1891	0.012393	36.15	22.9968
0.018074	35.41	23.0717	0.004462	35.57	22.8732	0.006328	35.44	22.7649
0.002691	37.26	22.9247	0.026619	35.78	22.9958	0.002761	36.50	22.0750
0.003028	38.44	22.2776	0.003031	31.59	22.0146	0.002848	32.20	22.0221
0.002852	37.63	21.9351	0.004979	35.33	22.1316	0.004394	36.16	22.2053
0.003587	35.83	22.1436	0.003554	35.02	22.2908	0.003401	32.45	22.3223
0.003385	36.77	22.4707	0.003132	32.34	22.5806	0.003161	33.32	22.5186
0.006761	34.43	20.6965	0.004546	36.37	20.8652	0.002438	36.49	20.8751
0.004513	37.19	20.0643	0.004035	34.85	21.9593	0.004470	36.30	20.6324
0.004491	36.89	21.3536	0.004490	37.41	22.0190	0.004445	36.37	20.9858
0.004526	35.28	22.4674	0.006728	36.24	23.4595	0.011196	35.72	22.7894
0.011213	35.26	22.2495	0.008926	35.51	23.4466	0.031331	34.72	22.3360
0.046663	34.76	22.8880	0.040340	35.45	22.6130	0.001661	31.53	23.3394
0.001661	31.53	23.3394	0.004256	35.86	23.4768	0.002360	27.10	24.0706
0.003576	32.54	24.1088	0.002408	32.42	24.1674	0.003985	32.48	24.1116
0.008104	34.81	24.1042	0.008559	35.49	24.1275	0.007293	36.05	24.0481
0.007631	35.18	24.0498	0.011230	35.53	24.0199	0.009830	35.35	24.1299

TABLE AII.4(continued)

Molality	$-\Delta H$/kJmole^{-1}	T_{rxn}	Molality	$-\Delta H$/kJmole^{-1}	T_{rxn}	Molality	$-\Delta H$/kJmole^{-1}	T_{rxn}
0.003965	33.28	24.0966	0.008282	35.16	24.1662	0.002644	31.62	24.1518
0.004232	34.99	24.1218	0.004243	37.04	24.2110	0.007663	36.68	23.7860
0.005123	36.67	23.7163	0.029160	35.72	24.3616	0.006696	36.94	24.1271
0.005962	38.02	24.2259						

TABLE AII.5

MEAN ENTHALPIES AND STANDARD DEVIATIONS

$CuCl_2 \cdot 2H_2O$

$m^{1/2}$	$-\Delta H$/kJ $mole^{-1}$	$\sigma_{\Delta H}$	s%	$\sigma'_{\Delta H}$
		SYSTEM I		
0.32040	19.35	0.06	0.3	0.077
0.29665	19.46	0.48	2.5	0.078
0.27079	19.51	0.30	1.5	0.078
0.24221	19.75	0.15	0.8	0.079
0.20976	20.04	0.01	0.1	0.080
		SYSTEM II		
0.13194	21.40	0.25	1.2	0.214
0.11078	21.62	0.76	3.5	0.216
0.10409	21.86	0.16	0.7	0.219
0.09832	22.19	1.13	5.1	0.222
0.08845	21.94	0.18	0.8	0.219
0.07828	22.17	1.21	5.5	0.222
0.06910	21.29	0.65	3.0	0.213
0.07313	21.73	0.44	2.0	0.217
0.06333	20.47	3.67	17.9	0.205
0.05759	20.70	1.31	6.0	0.217
0.06030	20.08	1.76	8.8	0.201
0.05509	21.67	1.45	6.7	0.217
0.05299	21.36	0.37	1.7	0.214
0.05097	20.65	3.61	17.4	0.207

TABLE AII.6

MEAN ENTHALPIES AND STANDARD DEVIATIONS

$CuCl_2$

$m^{1/2}$	$-\Delta H$/kJ mole^{-1}	$\sigma_{\Delta H}$	s%	$\sigma'_{\Delta H}$
		SYSTEM I		
0.10200	45.11	4.930	10.9	0.180
0.17337	47.54	0.219	0.46	0.190
0.19318	47.67	0.370	0.78	0.191
0.21135	47.33	0.230	0.49	0.189
0.24384	47.21	-----	----	0.188
0.16442	47.91	-----	----	0.192
		SYSTEM II		
0.07474	45.26	1.64	3.7	0.453
0.07220	41.71	1.46	3.5	0.417
0.07951	42.91*	2.92	6.9	0.414
0.08651	44.08	2.59	5.9	0.441
0.09473	45.21	2.45	5.4	0.452
0.06620	44.93	2.35	5.2	0.449
0.06135	40.12	5.70	14.2	0.401
0.06244	46.92	0.33	0.7	0.469
0.05128	32.85	7.82	23.9	0.329
0.06758	39.39	8.00	20.3	0.394
0.05332	36.58	5.65	15.4	0.366
0.05643	42.27	4.06	9.6	0.423
0.04710	34.84	7.04	20.3	0.348
0.03067	30.04	4.24	14.2	0.300

*median value

TABLE AII.7

MEAN ENTHALPIES AND STANDARD DEVIATIONS

$CuBr_2$

$m^{1/2}$	$-\Delta H$/kJ mole^{-1}	$\sigma_{\Delta H}$	s%	$\sigma'_{\Delta H}$
		SYSTEM II		
0.17751	35.18	0.64	1.8	0.141
0.10589	35.50	0.23	0.7	0.355
0.09443	35.47	1.34	3.8	0.355
0.09864	35.66	0.43	1.2	0.357
0.08745	35.93	1.06	2.9	0.359
0.07838	36.73	1.82	4.9	0.367
0.07107	36.00	0.95	2.6	0.360
0.09052	34.99	0.25	0.7	0.350
0.08206	36.14	1.07	3.0	0.361
0.06514	35.96	1.03	2.9	0.360
0.06701	36.31	0.73	2.0	0.363
0.05339	34.92	3.84	11.5	0.349
0.05046	32.98	4.10	12.4	0.330
0.06284	34.45	2.08	6.0	0.345
0.06004	34.66	1.46	4.2	0.347
0.05825	34.61	3.05	8.8	0.346
0.05545	33.81	2.69	8.0	0.338

APPENDIX III

Experimental and Literature Results

TABLE AIII.1

INTEGRAL HEATS OF SOLUTION AT 23 ± 1°C

$CuCl_2$		$CuBr_2$		$CuCl_2 \cdot 2H_2O$	
$m^{1/2}$	$-\Delta H$/kJ $mole^{-1}$	$m^{1/2}$	$-\Delta H$/kJ $mole^{-1}$	$m^{1/2}$	$-\Delta H$/kJ $mole^{-1}$
0.17337	47.54	0.17751	35.18	0.32040	19.35
0.19318	47.67	0.10589	35.50	0.29665	19.46
0.21135	47.33	0.09864	35.66	0.27079	19.51
0.16442	47.91	0.08745	35.93	0.24221	19.75
0.24384	47.21	0.07107	36.00	0.20976	20.04
		0.08206	36.14	0.13194	21.40
		0.06514	35.96	0.11078	21.62
		0.06701	36.31	0.10409	21.86
				0.08845	21.94

	$CuCl_2$	$CuBr_2$	$CuCl_2 \cdot 2H_2O$
Correlation coefficient	-0.88199	-0.89214	-0.98230
slope/ $kg^{1/2}$ $mole^{-3/2}$	-7.69	-8.94	-12.3
y-intercept = ΔH_∞ / kJ $mole^{-1}$	-49.1	-36.7	-23.0

TABLE AIII.2

APPARENT RELATIVE MOLAL ENTHALPIES IN WATER AT 23 ± 1°C

$m^{1/2}$	ΦL/kJ $mole^{-1}$ D.H.[a]	ΦL/kJ $mole^{-1}$ Experimental[b]		
		$CuCl_2$	$CuBr_2$	$CuCl_2 \cdot 2H_2O$
0.00	0.00	0.00	0.00	0.00
0.05	0.51	0.39	0.44	0.62
0.10	1.03	0.77	0.89	1.23
0.15	1.55	1.15	1.33	1.84
0.20	2.07	1.54	1.78	2.46
0.25	2.60	1.92	2.22	3.07
	slope/ kJ $kg^{1/2}$ $mole^{-3/2}$			
	10.40	7.68	8.88	12.28

[a] Debye-Huckel Limiting Law for a 2-1 electrolyte in water at 25°C.

[b] Values have been read off experimental curve, Figures 4, 5, and 6.

TABLE AIII.3

HEATS OF SOLUTION FOR $CuCl_2$ IN WATER AT 25°C

$m^{1/2}$	$-\Delta H$/kJ mole^{-1}	ΦL_I[b]/kJ mole^{-1}	ΦL_{II}[c]/kJ mole^{-1}
0.258	49.05	0.53	1.71
0.388	48.49	1.09	2.27
0.501	47.51	2.07	3.25
0.574	46.83	2.75	3.93
0.645	46.15	3.43	4.61
0.709	45.46	4.12	5.30
0.762	44.81	4.77	5.95
0.304[d]	46.36	3.22	4.40

[a] J.R. Partington and W.E. Soper, "Heats of Solution of Some Salts in Water and Ethyl Alcohol Solutions," Philosophical Magazine and Journal of Science: 237 (1929).

[b] calculated from Partington's extrapolated value of -49.58 kJ/mole for ΔH_∞.

[c] calculated from ΔH_∞ = -50.76 kJ/mole: Silvester, L.F., and K.S. Pitzer, Journal of Solution Chemistry, 7, 335 (1978).

[d] J. Thomsen, as cited by J.R. Partington (reference a).

TABLE AIII.4

APPARENT RELATIVE MOLAL ENTHALPIES[a] AND SECOND VIRIAL COEFFICIENTS[b] FOR $CuCl_2$ IN WATER AT 25°C

m	$m^{1/2}$	B^L_{MX}/kg mole^{-1}	ΦL/kJ mole^{-1}
0.00333	0.0577	0.00471	0.505
0.00667	0.0817	0.00432	0.678
0.01000	0.1000	0.00403	0.800
0.01333	0.1155	0.00380	0.897
0.01667	0.1291	0.00361	0.979
0.02000	0.1414	0.00344	1.051
0.02333	0.1528	0.00329	1.115
0.02667	0.1633	0.00315	1.174
0.03000	0.1732	0.00302	1.229
0.03333	0.1826	0.00291	1.279
0.03667	0.1915	0.00280	1.327
0.04000	0.2000	0.00270	1.373
0.05000	0.2236	0.00248	1.499
0.06000	0.2449	0.00220	1.613
0.07000	0.2646	0.00200	1.720
0.08000	0.2828	0.00182	1.821
0.10000	0.3162	0.00151	2.012
0.12000	0.3464	0.00125	2.195
0.14000	0.3742	0.00103	2.372
0.16000	0.4000	0.00084	2.547
0.20000	0.4472	0.00052	3.062
0.25000	0.5000	0.00020	3.319
0.30000	0.5477	-0.00005	3.748
0.35000	0.5916	-0.00027	4.179
0.40000	0.6323	-0.00045	4.612
0.50000	0.7010	-0.00073	5.484
0.60000	0.7746	-0.00096	6.364

---

[a] as calculated from semi-empirical equations proposed by Pitzer and co-workers, J.Soln.Chem.,7, 327-337(1978).

[b] Values for both the second virial coefficient and enthalpy were computer generated--see Appendix IV for program.

APPENDIX IV

Program for Generation of
Apparent Relative Molal Enthalpy

FIGURE 13

COMPUTER[a,b] PROGRAM FOR GENERATION OF B^{L}_{MX} AND ΦL

```
 10  REM "PROGRAM TO GENERATE B AND PHI FOR ANN FRANCIS"
 20  CLS
 30  A$="##.#####[[[["
 40  FOR I=.01 TO .50 STEP .01
 50  D=2.718281828459045235[(-2*(I[.5))
 60  E=(1+(2*(I[.5)))*D
 70  F=(1-E)
 80  G=(1/I)*F
 90  H=(-.002717(.0042375*G))
100  B=H
110  L=6*(698/3.6)
120  M=(LOG(1+(1.2*(I[.5))))*L
130  N=(4*1.987*298.15[2)*(I/3)*B)
140  O=M-N
150  R=I/3
160  Q=R[.5
170  LPRINTTAB(0);:LPRINT USING A$;R;
180  LPRINTTAB(15);:LPRINT USING A$;Q;
190  LPRINTTAB(30) I;
200  LPRINTTAB(40);:LPRINT USING A$;B;
210  LPRINTTAB(55);:LPRINT USING A$;O
220  NEXT I
230  END
```

[a] For use with a TRS-80 Radio Shack Computer and printer.

[b] Written by Mike Greenlief, Chemistry Dept., E.S.U., Spring, 1982.