6-30-1975

The thermodynamics of electrolytic solutions

Eric Robert Bixon
New Jersey Institute of Technology

Recommended Citation

Bixon, Eric Robert, "The thermodynamics of electrolytic solutions" (1975). *Theses*. 2111.
https://digitalcommons.njit.edu/theses/2111

THE THERMODYNAMICS OF
ELECTROLYTIC SOLUTIONS

BY

ERIC R. BIXON

A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE
OF
MASTER OF SCIENCE IN CHEMICAL ENGINEERING
AT
NEW JERSEY INSTITUTE OF TECHNOLOGY

Newark, New Jersey

1975

ABSTRACT

The thermodynamic properties of solutions of electrolytes may be accurately determined by the measurement of the activity of the solvent. When the solute is nonvolatile, this quantity may be obtained from measurements of the lowering of the vapor pressure caused by the presence of the dissolved solute.

An experimental method has been devised to measure this effect using a semi-conventional Othmer Still. The experimental apparatus has been constructed and evaluated. Data has been obtained for the vapor pressure lowering of methanol due to the presence of dissolved electrolyte for five different electrolyte-methanol systems. An extrapolation technique was developed to make use of the data at higher concentrations for extrapolation to infinite dilution. This technique has been applied to the five systems to give the activity coefficients for each system as a function of concentration.

APPROVAL OF THESIS

THE THERMODYNAMICS OF ELECTROLYTIC SOLUTIONS

BY

ERIC R. BIXON

FOR

DEPARTMENT OF CHEMICAL ENGINEERING

BY

FACULTY COMMITTEE

APPROVED:

NEWARK, NEW JERSEY

JUNE, 1975

ACKNOWLEDGEMENTS

Deep appreciation is extended to Dr. D. Tassios for his guidance and understanding in carrying out the completion of this project. Sincere gratitude is also extended to Max Bixon and Juan Toscano for their aid in developing the experimental equipment. Recognition is also extended to the faculty and staff of New Jersey Institute of Technology for their aid in completing this project.

TABLE OF CONTENTS

PAGE

Abstract i
Approval Page ii
Acknowledgements iii
Table of Contents iv
List of Figures vi
List of Tables vii
Preface 1

Experimental

A. Objective 2
B. Method 2
C. Description of Apparatus 2
D. Reagents and Chemicals 8
E. Procedure 9

Theory

Part I: Thermodynamic Concepts . . . 12
Part II: Electrostatic Interactions . . 18

Results and Discussion

A. Experimental Results 26
B. Correlation of Experimental Results . 33
C. Conclusions 35
Nomenclature 74

TABLE OF CONTENTS (cont'd)

PAGE

Appendices:

A. Calculation of A_γ 77

B. Sensitivity of the quantity $(1 - \phi)/m^{1/2}$ to errors in Pressure Measurement . . 78

C. 79

D. Derivation of Equation (55) . . . 80

E. Data Sources 81

F. Discussion of the Standard State . . 83

G. Integration involved in the Gibbs Duhem Equation 84

Literature Cited 85

LIST OF FIGURES

PAGE

FIGURE I Distilling Apparatus 3

FIGURE II Experimental Set-Up 5

FIGURE III Lithium Chloride in Methanol (ΔP Plot) 61

FIGURE IV Sodium Iodide in Methanol (ΔP Plot) 62

FIGURE V Sodium Hydroxide in Methanol (ΔP Plot) 63

FIGURE VI Calcium Chloride in Methanol (ΔP Plot) 64

FIGURE VII Copper Chloride in Methanol (ΔP Plot) 65

FIGURE VIII Lithium Chloride in Methanol ($(1-\phi)/m^{1/2}$ Plot) . . . 66

FIGURE IX Sodium Iodide in Methanol ($(1-\phi)/m^{1/2}$ Plot) . . . 67

FIGURE X Sodium Hydroxide in Methanol ($(1-\phi)/m^{1/2}$ Plot) . . . 68

FIGURE XI Calcium Chloride in Methanol ($(1-\phi)/m^{1/2}$ Plot) . . . 69

FIGURE XII Copper Chloride in Methanol ($(1-\phi)/m^{1/2}$ Plot) . . . 70

FIGURE XIII $-\delta$ VS. molality for a 1-1 electrolyte 71

FIGURE XIV $-\delta'$ VS. molality for a 1-2 electrolyte 72

FIGURE XV Activity Coefficients of the Solvent for the system Lithium Chloride in Methanol 73

LIST OF TABLES

PAGE

Vapor Pressure of Pure Water . . . . Table I 37

Vapor Pressure of Pure Methanol . . . . . . Table II 37

Literature Data for Sodium Chloride and Water at 100°C . . . . . . Table III-A 38

Experimental Data for Sodium Chloride and Water at 100°C. . . . . . . Table III-B 38

Old Data for Sodium Iodide and Methanol . . . Table IV-A 39

New Data for Sodium Iodide and Methanol . . . Table IV-B 40

Old Data for Lithium Chloride and Methanol . . Table V-A 41

New Data for Lithium Chloride and Methanol . . Table V-B 42

Data for Sodium Hydroxide and Methanol . . . Table VI 43

Data for Calcium Chloride and Methanol . . . Table VII 44

Data for Copper Chloride and Methanol . . . . Table VIII 45

Parameters of Equation 55 for ten 1-1 Salts in Water . . . . . . Table IX 46

Values of B in Equations 56 and 57 for Ten 1-1 Salts in Water . . . . . . Table X 47

Values of B for 1-2 Salts in Water . . . . Table XI 48

Values of B' in Equation 58 for 1-1 Salts in Water . . . . . . Table XII 49

Values of B' for 1-2 Salts in Water . . . . Table XIII 50

Values of B' for 1-2 Salts in Water To I = 6 . . . . . . Table XIV 51

Activity Coefficients of Lithium Chloride in Methanol at 24.88°C. . . . . . . Table XV 52

Activity Coefficients of Sodium Iodide in Methanol at 24.88°C. . . . . . . Table XVI 53

Activity Coefficients of Sodium Hydroxide in Methanol at 24.88°C. . . . . . . Table XVII 54

Activity Coefficients of Calcium Chloride in Methanol at 24.88°C. . . . . . . Table XVIII 55

LIST OF TABLES (cont'd)

		PAGE
Activity Coefficients of Copper Chloride and Methanol at 24.88°C.	Table XIX	56
Comparison of Literature and Experimental Values for $\gamma_{\pm}$ of Lithium Chloride in Methanol. . .	Table XX	57
Experimental Values of $\gamma_{solvent}$ for Lithium Chloride in Methanol	Table XXI	58
Literature Values of $\gamma_{solvent}$ for Lithium Chloride in methanol	Table XXII	59
Comparison of Literature and Experimental Values of $\gamma_{solvent}$ of Lithium Chloride in Methanol.	Table XXIII	60

PREFACE

Electrolytic solutions have been investigated and studied by physical chemists and engineers for many years. A number of models have been devised to describe the interactions between solute and solvent molecules -- the most famous being that proposed by Debye and Huckel in 1923.

A number of thermodynamic quantities have been utilized to quantitatively describe these interactions. The properties of primary interest in this investigation are the activity of the solvent, and the osmotic and activity coefficients of the solute.

Several methods exist to experimentally determine these quantities and, in general, two or more of these methods are combined to obtain a set of best values for these properties. This project investigates the application of an experimental technique that can determine these properties without the aid of other experimental measurements.

EXPERIMENTAL

A. Objective

The purpose of the experimental apparatus was to accurately determine the activity of a solvent in the presence of a dissolved solute at various concentrations. Five different electrolytes were chosen as solutes and methanol was chosen as the solvent. The data was taken isothermally at 24.88°C by the measurement of the vapor pressure of each electrolytic solution.

B. Method

A solution of a given electrolyte was boiled at 24.88°C in the distilling apparatus (See Figure I). This was accomplished in a modified Othmer still by adjusting the pressure over the solution while continually adding heat. The still featured continuous recirculation of the condensed vapor phase. After a certain time, about thirty to sixty minutes, the steady state condition characteristic of equilibrium was obtained and the solution pressure was measured using a cathetometer to read a mercury manometer.

C. Description of Apparatus

The experimental apparatus is designed to control the temperature of a boiling solution to within ± .05°C while maintaining a constant pressure accurate to within ± .1 mm Hg. The apparatus is pictured schematically in Figure II. The essential features are outlined below:

1. The distilling apparatus is pictured in Figure I .

FIGURE I DISTILLING APPARATUS

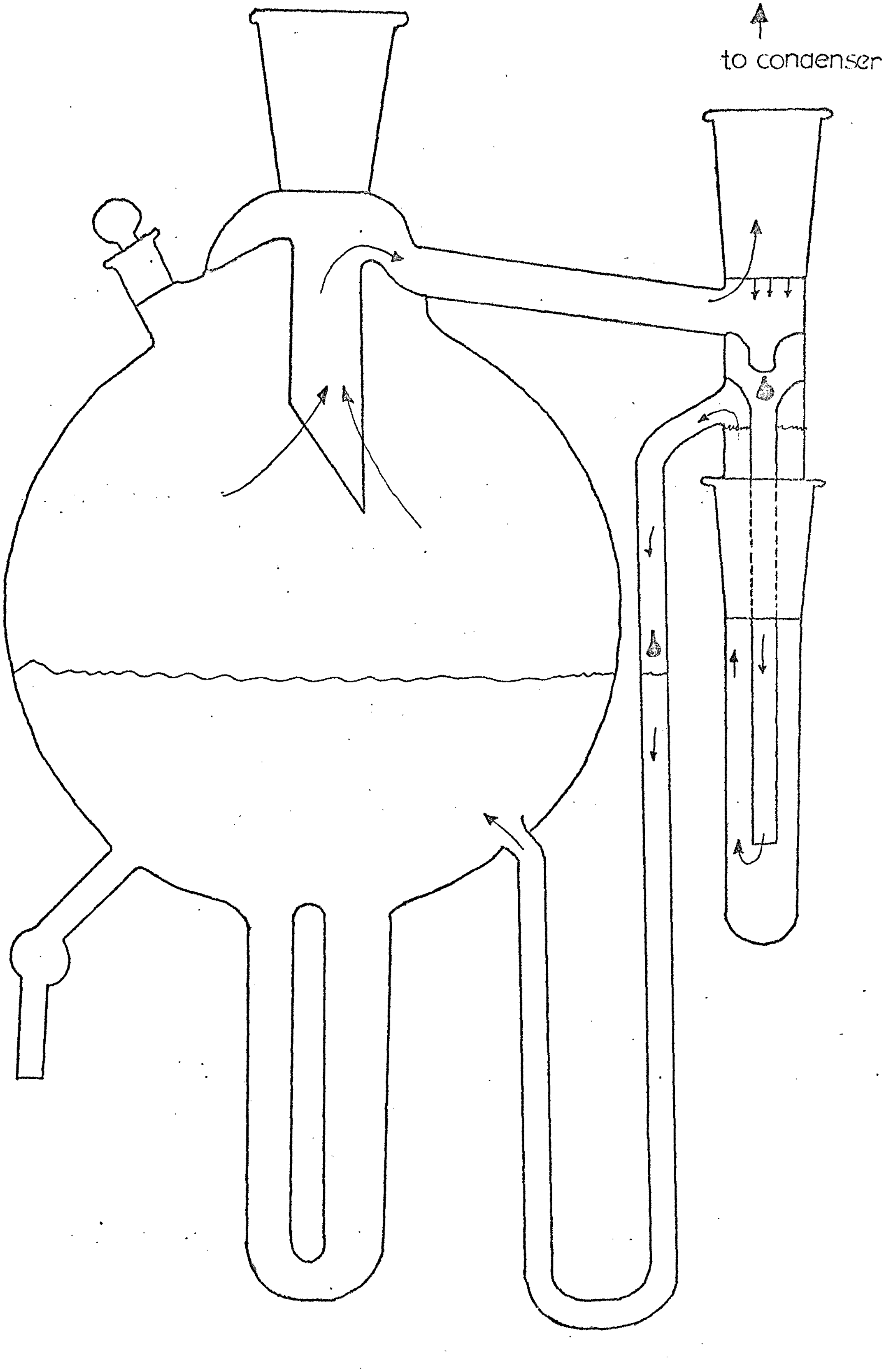
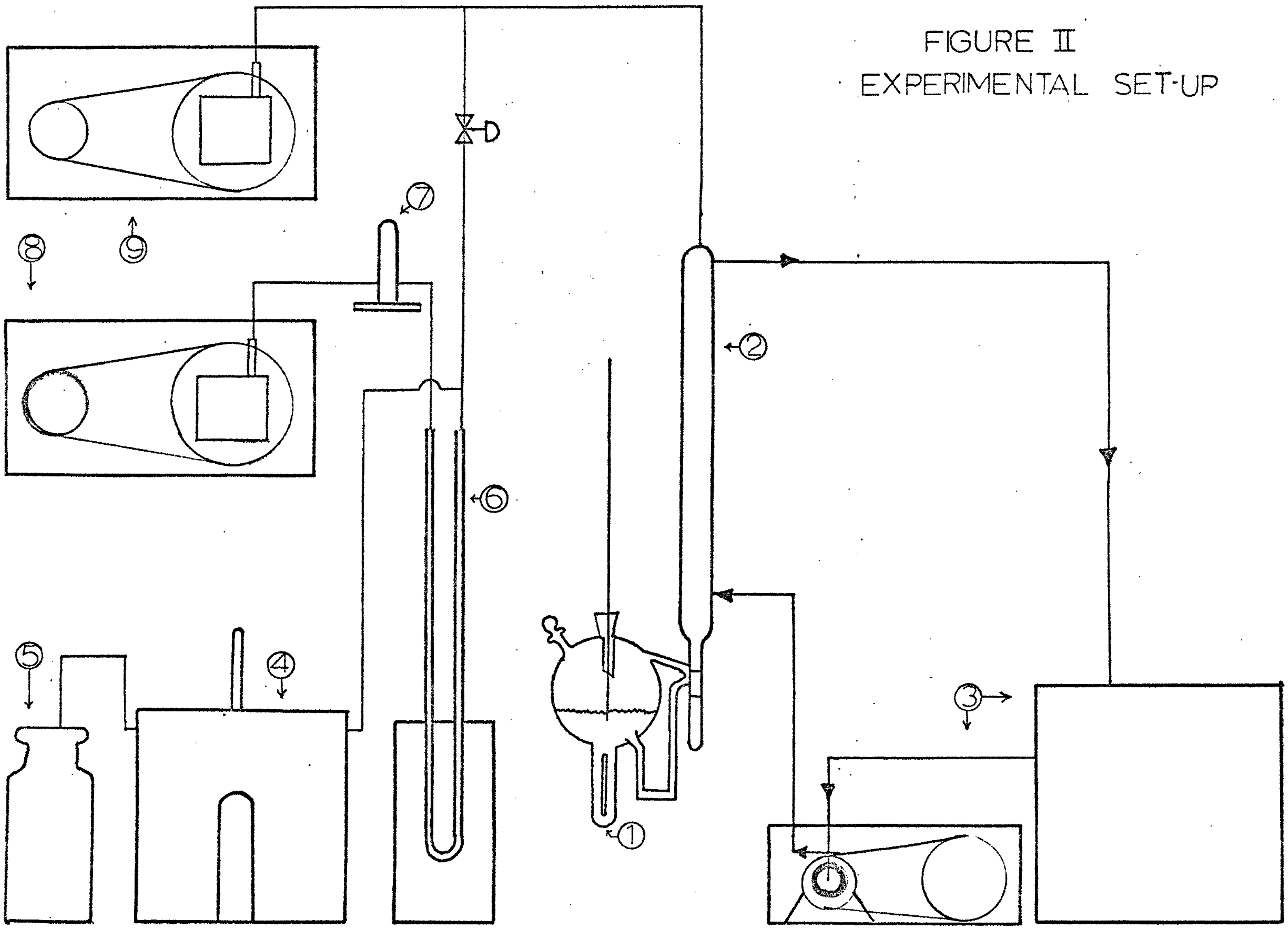


FIGURE II

EXPERIMENTAL SET-UP

1. Distilling Apparatus
2. Condenser
3. Heat Exchanger
4. Manostat
5. Surge Tank
6. Manometer
7. McLeod Gauge
8. Manometer Vacuum Pump
9. System Vacuum Pump

FIGURE II
EXPERIMENTAL SET-UP



It consists of a round flask with an electrical heating tape wound around the bottom extension. The solution is boiled inside the flask and the vapors are driven out the top and condensed in the condenser. The condensed liquid droplets then fall into the catch tube and are carried up to the top of the reservoir. The liquid then overflows back into the boiling salt solution. In this manner continual recirculation of the condensed vapor phase is achieved. The arrows in Figure I indicate the direction of flow of the vapor and condensed liquid phases.

Since the vapor phase consists only of the condensed solvent, the solute being nonvolatile, equilibrium is characterized by a reservoir filled only with pure solvent. During the development of the experimental technique, it became evident that equilibrium could be more easily reached if the reservoir was kept filled with pure solvent, since this is a necessary condition for equilibrium.

2. The condenser consists of two eighteen inch glass condensers connected in series. It operates between -20°C to -60°C using a mixture of ethylene glycol and acetone as the cooling fluid. Dry ice is used to maintain the coolant temperature.

3. The heat exchanger consists of a coil of copper tubing immersed in the dry ice bath. The cooling fluid is pumped by an oberdorfer gear pump from a separate

reservoir through the condenser, through the copper tubing and then back into the reservoir. The need for a separate reservoir inside the ice bath is due to pumping difficulties caused by the carbon dioxide gas in the bath itself.

While designing the heat exchanger, it became evident that only a special pump could satisfactorilly pump such a low temperature coolant. Several major pump manufacturers were unable to offer any suggestions. Finally an engineer at Edward's Engineering Corporation pointed out an Oberdorfer gear pump that was pumping a fluid at similar temperatures. This type of pump fitted with teflon packing and seals was selected. The pump was powered by an electric motor fitted with a variable speed pulley and fan belt.

4. The Precision Micro-Set Manostat is the heart of the pressure control system. It is capable of controlling a maximum vaccuum of 3.0 mm of mercury with a control accuracy of ± .1 mm under ideal conditions. The Manostat operates on the principle of bleeding air into the system to control the vaccuum. The system is allowed to attain a vaccuum slightly higher than desired. This causes a solenoid valve to fire intermittently bleeding in small amounts of air into the system. Several needle valves allow this amount to be regulated until the desired pressure is achieved.

5. A twenty-five liter surge tank was installed in

series with the distilling apparatus and the Manostat. This volume was necessary in order to buffer the pressure fluctuations inherent in the operation of the Manostat.

6. The manometer used was a standard U-tube manometer with mercury used as the working fluid.

7. The McCleod gauge reads the pressure on the evacuated side of the manometer.

8. There are two separate vacuum pumps. The purpose of the first vacuum pump is to evacuate one side of the manometer. The purpose of the second vacuum pump is to evacuate the system to the desired pressure. The system pump is connected in series with one side of the manometer, the surge tank, the manostat and the distilling apparatus. These pumps are labeled (8) and (9) in Figure II.

D. Reagents and Chemicals

1. 'Baker Analyzed' Reagent Grade Sodium Hydroxide was used for the sodium hydroxide runs. The assay was 98.3% NaOH. The largest impurity present was sodium carbonate listed as .4%. Before each run an unknown impurity was filtered out with coarse grade filter paper. The other impurities were not listed on the label.

2. Two different types of lithium chloride were used in these experiments. The first brand used was from Fisher Scientific Company while the other brand was 'Baker Analyzed' Reagent Grade. Both grades were assayed as being 99.8% purity.

3. The cupric chloride was certifed anhydrous grade from Fisher Scientific. The impurities listed on the label totaled .06%.
4. The calcium chloride used was 'Baker Analyzed' Reagent Grade and was assayed at 98.4% purity.
5. The sodium iodide used was Mallinckrodt granular analytical reagent. The impurities listed on the label totaled .055%.
6. The silver nitrate was Certifed A.C.S. crystal from Fisher Scientific. Its purity was listed as being 99.9 %.
7. 'Electrically Purified' water was used in all aqueous solns.
8. The hydrochloric acid used was certified as .1000 normal by Harleco Chemicals.
9. Two different brands of methanol were used. The first brand was from Fisher Scientific Company and was certified as being 99.9 mole percent pure. The second type used was 'Baker Analyzed' Reagent and was listed as being 99.8% pure.
10. The indicators used were standard solutions of one molar potassium chromate for the Mohr titrations, and standard methyl red indicator for the sodium hydroxide determinations.

E. Experimental Procedure.

The experimental procedure varied from system to system but the basic methods and techniques were common to all systems. Before each electrolyte was run, a three quart batch of solvent of uniform properties was tested until its vapor pressure was determined to within ± .200 mm Hg. This was accomplished by taking successive readings after the system had reached equilibrium. The readings were taken periodically every ten minutes until four or more readings agreed to within ± .20 mm Hg. The solvent vapor pressure was then taken as the average of these readings.

After the solvent vapor pressure had been determined, an electrolytic solution of concentration of about .30 molal was made up by dissolving a weighed amount of a previously dried salt. The drying time for each salt varied from one to three days at a temperature of about 120°C. The volume of a typical batch was 300 ml.

The electrolytic solution was then poured through a funnel into the boiling chamber of the still, while being extremely careful to avoid mixing any of the salt solution with the pure solvent contained in the condensed vapor phase reservoir (See Figure I).

Once the solution was in the still, the heat exchanger was loaded with dry ice and the coolant pump was turned on. Next the vacuum pump evacuating one side of the manometer was started up. When the coolant had reached a temperature of -35°C., the system vacuum pumps were started and the system was slowly evacuated. The rate of evacuation was controlled by a separate bleed valve in the system. During this process, it was necessary to make sure that the solution did not flash causing unwanted mixing of the salt solution with the pure solvent in the reservoir.

Before each run the manostat was preset to operate in the pressure range of the boiling solution so that the only adjustment which had to be made was by the use of the two bleed valves and the micro-set regulator . Once the system was under the control of the manostat, the heaters were turned on and the system was allowed to continually reflux for about forty-five minutes. After this period, pressure readings were taken successively every ten minutes until four or more readings agreed to within ± .20 mm Hg. The system pressure was then taken to be the average of these readings.

At this point air was let into the system and all pumps, heaters and motors were turned off. The solution in the boiling chamber was then emptied into a 400 ml beaker until all but about 50 ml was drained out of the still. An appropriate amount was pipetted into a beaker and then titrated with standard solution. The analyses were performed in duplicate until two readings agreed to within ± .1 ml of titrant. Following quantitative analysis, a pycnometer determination of the density of the solution was made in order to convert from molarity to molality.

THEORY - PART I: THERMODYNAMIC CONCEPTS

A. Ideal Solution

An ideal solution is one for which the thermodynamic properties of the pure components may be combined to give the solution properties by the same equations derived for an ideal gas. i.e.,

$\Delta V = 0$ (Volume change of Mixing = 0)

$\Delta E = 0$ (Internal Energy change of Mixing = 0)

$\Delta H = 0$ (Heat of Mixing = 0)

$\Delta S = R \sum x_i \ln 1/x_i$ (Entropy change of Mixing)

B. Chemical Potential

The chemical potential is a quantity first defined by Gibbs. He showed that at equilibrium between phases, the chemical potential of a given component must have the same value in each phase. The chemical potential of a component, i, in a solution may be thought of as the driving force for transfer of that material between phases. It is equivalent to the partial molal free energy of component i when the pressure, temperature, and moles of other components are held constant. The classical thermodynamic formula for the chemical potential, μ_i, of a nonelectrolyte solute in an ideal solution is:

$$\mu_i = \mu_i^\circ + RT \ln x_i \qquad (1)$$

In this expression x_i is the concentration of solute in mole fraction units and μ_i° is the chemical potential in a standard state. (See Appendix F for a discussion of the standard state.)

C. Non-Ideal Electrolytic Solutions

Whereas solute interactions are negligible in dilute solutions of non-electrolytes, ion-ion interactions are significant even in the most dilute solutions, thus Equation (1) does not apply to solutions of electrolytes and:

$$\mu_i \neq \mu_i^o + RT \ln x_i \text{ (for electrolytes)}$$

D. Activity and Activity Coefficient

In order to use an expression of the form of Equation (1) to treat non-ideal electrolytic solutions, an empirical correction factor was introduced by Lewis(2) to represent the effective concentration, i.e.,

$$\mu_i = \mu_i^o + RT \ln f_i x_i \qquad (2\text{-A})$$

or

$$\mu_i = \mu_i^o + RT \ln a_i \qquad (2\text{-B})$$

This effective concentration is called the activity, a_i, of species i:

$$a_i = x_i f_i$$

and f_i is called the activity coefficient.

Comparing Equation (2-A) with Equation (1), it is obvious that

$$\mu_i(\text{ideal}) = \mu_i^o + RT \ln x_i$$

and $$\mu_i(\text{real}) = \mu_i^o + RT \ln x_i + RT \ln f_i$$

thus $$\mu_i(\text{real}) - \mu_i(\text{ideal}) = \Delta\mu_{i-I}$$

where $\Delta\mu_{i-I}$ is the change in chemical potential arising from interactions between solute particles, therefore:

$$\Delta\mu_{i-I} = RT \ln f_i \qquad (2\text{-C})$$

and the activity coefficient is a measure of the chemical potential change arising from ion-ion interactions.

E. Mean Ionic Activity Coefficient

Since neither the positive nor the negative ions can be added separately to a solution, the individual contributions of each ionic species to the activity coefficient of the system cannot be determined. One can only measure the activity coefficient of the net electrolyte. Therefore, it is necessary to establish a conceptual link between the activity coefficient of an electrolyte in solution and that of only one of its ionic species.

The following conventions are noted. Consider a general electrolyte, X, which dissociates into ν ($\nu = \nu^+ + \nu^-$) ions according to the equation, $X = \nu^+X^+ + \nu^-X^-$ and let a_2 denote the activity of the solute; a_+ and a_- denote the cation and anion activities, respectively. The activity of the solute is then:

$$a_2 = (a_+)^{\nu^+}(a_-)^{\nu^-}$$

The mean ionic activity, $a_\pm$, is defined as the geometric mean of the ion activities:

$$a_\pm = (a_2)^{1/\nu} = ((a_+^{\nu^+})(a_-^{\nu^-}))^{1/\nu} \qquad (3)$$

The mean ionic activity coefficient, is defined as the geometric mean of the ion activity coefficients:

$$\gamma_\pm = ((\gamma_+^{\nu^+})(\gamma_-^{\nu^-}))^{1/\nu} \qquad (4)$$

Since $\gamma_+ = a_+/m_+$ and $\gamma_- = a_-/m_-$, Equation (4) becomes:

$$\gamma_\pm = ((a_+/m_+)^{\nu^+}(a_-/m_-)^{\nu^-})^{1/\nu} = a_\pm/m_\pm \qquad (5)$$

If a single salt is added to a solvent, $m_+ = \nu^+m$ and $m_- = \nu^-m$. Here, m_+ and m_- are the molality of the cation and anion.

Substitution of these relations into Equation (5) yields:

$$\gamma_{\pm} = (a_{\pm})/(m\ ((\nu^{+})^{\nu^{+}}\ (\nu^{-})^{\nu^{-}}\ )^{1/\nu}) \qquad (6)$$

F. The Gibbs-Duhem Equation

The Gibbs-Duhem Equation relates the activities of each component in a solution, with the composition of the liquid phase. It may be derived by considering the free energy, F, of a solution. The total differential of this quantity may be written as:

$$dF = -Sdt + VdP + \mu_1 dn_1 + \mu_2 dn_2 + \ldots + \mu_c dn_c \qquad (7)$$

where $\mu_1 = (\partial F/\partial n_1)_{P,T,n_2,\ .\ .\ .\ n_c}$

At constant temperature and pressure,

$$dF = \mu_1 dn_1 + \mu_2 dn_2 + \ .\ .\ .\ \mu_c dn_c = \sum \mu_i dn_i \qquad (8)$$

Integrating* at constant $\mu_1, \mu_2,\ .\ .\ .\ \mu_c$ yields:

$$F = \mu_1 n_1 + \mu_2 n_2 + \ .\ .\ .\ + \mu_c n_c \qquad (9)$$

In deriving Equation (9) no values of $\mu_1, \mu_2,\ .\ .\ .\ \mu_c$ were specified. The Equation, being entirely general, can be differentiated with respect to any change in composition:

$$dF = \mu_1 dn_1 + n_1 d\mu_1 + \ .\ .\ .\ + \mu_c dn_c + n_c d\mu_c$$

or

$$dF = \sum \mu_i dn_i + \sum n_i d\mu_i \qquad (10)$$

Comparison of Equations (8) and (10) yields:

$$\sum_{i=1}^{c} n_i d\mu_i = 0 \qquad (11)$$

---

*See Appendix G for the details of this integration.

Dividing Equation (11) by the total number of moles yields the general form of the Gibbs-Duhem Equation:

$$\left[\sum x_i d\mu_i\right]_{T,P} = 0 \qquad (12)$$

Differentiation of Equation (2-B) and substitution into Equation (12) results in:

$$x_i\, d(\ln a_i) = 0$$

For a binary system this becomes

$$d(\ln a_1) = (-x_2/x_1)\, d(\ln a_2) \qquad (13)$$

The practical osmotic coefficient, ϕ,(16) is defined by

$$\ln a_1 = (-\, mM_1/1000)\, \phi \qquad (14)$$

Converting Equation (13) to units of molality by substituting

$$x_2/x_1 = m/(1000/M_1)$$

and combining it with Equations (3) and (6) gives:

$$(1000/M_1)\, d(\ln a_1) = -m\, d(\ln a_2) = -\nu m\, d(\ln a_\pm)$$

$$\text{and} \qquad -\nu m\, d(\ln a_\pm) = m\, d(\ln \gamma_\pm m_\pm) \qquad (15)$$

Combining Equations (3) and (6) defines $m_\pm$:

$$m_\pm = m((\nu^+)^{\nu^+}(\nu^-)^{\nu^-})^{1/\nu} \qquad (16)$$

Taking logarithms of both sides of Equation (16) results in:

$$\ln m_\pm = \ln m + \ln ((\nu^+)^{\nu^+}(\nu^-)^{\nu^-})^{1/\nu} \qquad (17)$$

Substitution of Equation (17) into Equation (15) after differentiation of Equation (17) yields:

$$1000/M_1\, d(\ln a_1) + \nu m\, d(\ln \gamma_\pm m_\pm) = 0$$

which leads to the important relation first derived by Bjerrum(16) for the relation between the practical osmotic coefficient and the activity coefficient, namely

$$d(m(1-\phi)) + m\, d(\ln \gamma_{\pm} m) = 0 \qquad (18)$$

Integration of Equation (18) yields the following expression for the mean ionic activity coefficient of the solute in a binary system:

$$\ln \gamma_{\pm} = -(1-\phi) - 2\int ((1-\phi)/m^{1/2})\, dm^{1/2} \qquad (19)$$

THEORY PART II: ELECTROSTATIC INTERACTIONS

A. The System

The system to be considered is a strong electrolyte dissociated completely into ions, and the problem to be solved is to quantitatively evaluate the ion-ion interactions. One approach is to consider an initial state in which the ion-ion interactions are "switched off." In order to achieve this hypothetical state of noninteracting ions in solution, the ions would have to be initially uncharged. Thus the problem of going from an initial state of noninteracting ions to a final state of ion-ion interactions becomes one of taking an assembly of discharged ions, charging them up, and setting this electrostatic charging work equal to the free energy, ΔF_{i-I}, of ion-ion interactions.

It is desirable to isolate the contributions of one ionic species to the total free energy change. This partial free energy change is, by definition, the chemical potential change, $\Delta \mu_{i-I}$, arising from interactions of one ionic species with the ionic assembly. To compute $\Delta \mu_{i-I}$ imagine one reference ion alone is in an uncharged state. Let W be the work of charging this reference ion up to its normal charge. Then the chemical potential of ion-ion interactions is equal to the charging work per ion times Avogadro's number of ions, Na,

$$\Delta \mu_{i-I} = Na\ W \tag{20}$$

Assuming that an ion can be represented by a charged sphere of radius R_0 and charge $z_i e_0$, the expression for the work of charging a sphere from a state of zero charge to charge $z_i e_o$ will represent the work of charging an ion in a medium of dielectric constant, ϵ :

$$W = (z_i e_o)^2/2\epsilon R_o = (z_i e_o/2)\ (z_i e_o/\epsilon R_o) \qquad (21)$$

But $z_i e_o/\epsilon R_o$ is the electrostatic potential, ψ_r, at the surface of the ion, therefore,

$$\Delta\mu_{i-I} = (Naz_i e_o/2)\,\psi_r \qquad (22)$$

The problem of determining $\Delta\mu_{i-I}$ now becomes one of the calculation of the electrostatic potential produced at the surface of a reference ion by the rest of the ions in the solution.

B. The Debye Huckel Model(17)

The essentials of the Debye Huckel model comprise three basic assumptions. First, one ion is selected as a reference or central ion. Only the reference ion is given the individuality of discrete charge. The rest of the ions in solution are viewed as being smeared out into a continuous net charge density, ρ_r. The total charge in the atmosphere of the ion is of opposite sign and exactly equal to the charge on the reference ion. The final assumption involves looking at the solvent molecules as a continuous dielectric medium of dielectric constant, ϵ.

C. Derivation of the Debye Huckel Limiting Law

Assuming spherical symmetry, the relation between charge density and electrostatic potential may be represented by Poisson's Equation.

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{d\psi}{dr}\right] = \frac{-4\pi}{\epsilon}\rho_r \qquad (23)$$

The charge density may also be represented by a linearized Boltzman Equation.

$$\rho_r = \sum n_i z_i e_o - \sum(n_i z_i^2\, e_o^2\, \psi_r/kT) \qquad (24)$$

From the principle of electroneutrality,

$$\sum n_i z_i e_o = 0 \qquad (25)$$

Combining Equations (24) and (25) yields

$$\rho_r = -\sum(n_i z_i^2 e_o^2 \psi_r/kT) \qquad (26)$$

and substitution of Equation (26) into Equation (23) results in the linearized Poisson Boltzman Equation.

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{d\psi}{dr}\right] = \left[\frac{4\pi}{\epsilon kT}\sum n_i z_i^2 e_o^2\right]\psi r \qquad (27)$$

Letting $\kappa^2 = \frac{4\pi}{\epsilon kT}\sum n_i z_i^2 e_o^2$ and substituting this relation into Equation (27) simplifies the form to

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{d\psi}{dr}\right] = \kappa^2\psi_r \qquad (28)$$

Equation (28) must satisfy the boundary conditions

$$\text{as } r \rightarrow \infty,\ \psi_r \longrightarrow 0 \qquad (29)$$

and $$\text{as } \kappa \rightarrow 0,\ \psi_r \rightarrow (z_i e_o)/\epsilon \qquad (30)$$

Solving Equation (28) with boundary conditions (29) and (30) gives the expression for the electrostatic potential as a function of the distance r from the point charge

$$\psi_r = \left[(z_i e_o)/\epsilon\right]\left[(e^{-\kappa r})/r\right] \qquad (31)$$

Using the principle of superposition allows the potential at a distance r from the central ion to be broken up into its two contributions:

$$\psi_r = \psi_{ion} + \psi_{cloud} \qquad (32)$$

But ψ_{ion} is the potential due to the ion alone.

$$\psi_{ion} = (z_i e_o)/\epsilon r \qquad (33)$$

Combining Equations (31), (32), and (33) and solving for ψ_{cloud} results in:

$$\psi_{cloud} = \left[(z_i e_o)/\epsilon r\right](e^{-\kappa r} - 1) \qquad (34)$$

In sufficiently dilute solutions, $r \lll 1$ and

$$e^{-\kappa r} - 1 = (1 - \kappa r + (\kappa r)^2 + \ldots) - 1 = \kappa r \qquad (35)$$

Based on this approximation,

$$\psi_{cloud} = (z_i e_o)/\epsilon \kappa^{-1} \qquad (36)$$

where the term κ^{-1} is termed the effective radius of the ion atmosphere surrounding the central ion. Substituting Equation (36) into Equation (22) results in the following expression describing the chemical potential change due to ion-ion interactions:

$$\Delta \mu_{i-I} = -(Na/2)\ (z_i e_o)^2/\epsilon \kappa^{-1} \qquad (37)$$

Combining Equations (37) and (2-C) results in an equation for the activity coefficient.

$$RT \ln \gamma_i = -(Na(z_i e_o)^2)/2\epsilon \kappa^{-1} \qquad (38)$$

Taking logarithms of both sides of Equation (<u>6</u>) results in:

$$\ln \gamma_\pm = \frac{1}{\nu}(\nu^+ \ln \gamma_+ + \nu^- \ln \gamma_-) \qquad (39)$$

Combining this result with Equation (38) yields

$$\ln \gamma_{\pm} = -\frac{1}{\nu} \quad (Nae_0^2 \kappa / 2\epsilon RT) \; (\nu^+ z_+^2 + \nu^- z_-^2) \qquad (40)$$

Since $\nu^+ z_+^2 + \nu^- z_-^2 = z_+ z_- \nu$, Equation (40) becomes

$$\ln \gamma_{\pm} = -(Nae_0^2 \kappa |z_+ z_-|)/2\epsilon RT \qquad (40\text{-B})$$

Recalling the definition of κ, the value of $\sum n_i z_i^2 e_0^2$ may be expressed in macroscopic terms. Here, d_1 is the solvent density.

$$\kappa = (4\pi/\epsilon kT) \sum n_i^2 z_i^2 e_0^2 \qquad (41)$$

and $$\sum n_i^2 z_i^2 = (Nad_1/1000) \sum m_i z_i^2 \qquad (42)$$

At this time it becomes convenient to define the ionic strength as proposed by Lewis and Randall(20)

$$I = (1/2) \sum m_i z_i^2 \qquad (43)$$

Substituting Equations (42) and (43) into Equation (41) results in

$$\kappa^2 = (8\pi e_0^2 \; Nad_1/1000\epsilon kT) \; I \qquad (44)$$

Combining Equations (44) and (40-B) results in the limiting law of Debye and Huckel:

$$\log \gamma_{\pm} = -A_\gamma |z_+ z_-| \; I^{1/2} \qquad (45)$$

where the constant $\overset{*}{A_\gamma}$ is defined as

$$A_\gamma^2 = (2 \; Na \; d_1)/1000(2.303)^2 \; (e^2/\epsilon kT)^3 \qquad (46)$$

D. Range of Validity of the Limiting Law

Due to the assumptions inherent in the derivation of the Debye Huckel law, the range of validity of Equation (45) extends only to the most dilute solutions (i.e. about .01N). By refining this model it becomes possible to extend this

*See Appendix A for calculation of A_γ in methanol.

range. By removing the assumptions that the ions are point charges and repeating the derivation of Equation (45) it may be shown that the expression for the activity coefficient takes the form of

$$\log \gamma_\pm = -(A_\gamma |z_+ z_-| I^{1/2})/(1 + \kappa a) \qquad (47)$$

It will be recalled, however, that the thickness of the ionic cloud can be written as

$$\kappa = CI^{1/2} \qquad (48)$$

where C is defined in Equation (44). Combining Equations (47) and (48) results in

$$\log \gamma_\pm = (-A_\gamma |z_+ z_-| I^{1/2})/(1 + CaI^{1/2}) \qquad (49)$$

In this expression a is referred to as the ion size parameter. By picking a reasonable value of a, Equation (49) has been shown to give a fairly good fit with experimental data up to an ionic strength of .1.

By combining the first order effects of specific ion interactions with the limiting law, Bronsted(18) suggested equations of the form

$$1 - \phi = \alpha z^2 I^{1/2} - \beta_{mx} m \qquad (50)$$

and

$$2.303 \log \gamma_\pm = -3\alpha z^2 I^{1/2} + 2\beta_{mx} m \qquad (51)$$

In 1935 Guggenheim(19) improved the Bronsted type equations; by picking a standard value of a of 3 A°, the value of Ca in Equation (49) becomes equal to one. Each of the Guggenheim Equations contained a single adjustable parameter B:

$$\log \gamma_\pm = (-A_\gamma |z_+ z_-| I^{1/2})/(1 + I^{1/2}) + (2\nu^+ \nu^- / \nu)Bm \qquad (52)$$

and $$1 - \phi = (2.303/3)\, A_{\gamma}\, z_{+} z_{-}\, I^{1/2} \sigma(I^{1/2}) - 2.303 B m \frac{\nu^{+}\nu^{-}}{\nu} \quad (53)$$

The function $\sigma(I^{1/2})$ is a function of the ionic strength defined by

$$\sigma(I^{1/2}) = (3/I^{3/2}) \left[1 + I^{1/2} \left(1/(1 + I^{1/2})\right) - 2 \ln (1 + I^{1/2}) \right] \quad (54)$$

E. Ion-Solvent Interactions

Although the ion-ion interactions have been mentioned extensively, the role of the solvent molecules in solution has not been explicitly stated. All equations have been derived using the assumptions of Debye-Huckle theory in which the solvent is viewed as one continuous media of dielectric constant, ϵ. The solvent molecules are not really looked upon as having discrete identities. This assumption, although valid at the low concentrations (around .001 molal), becomes quite invalid at the higher concentrations (especially around 1 molal or greater). Even the inclusion of the ion size parameter, a, of Equation 49 does not really correlate the experimental results much beyond .1 molal.

The reason for this becomes easier to visualize by looking past the Debye Huckel assumptions toward what is actually happening in the solution. In actuality each ion is surrounded by solvent molecules and wanders through the solution in this solvated state. For very dilute solutions the number of solvent molecules that are 'removed' from the solvent is insignificant. However, as the concentration increases, more and more of these solvent molecules become bound up with the individual ions and are forced to travel through the solution with the ion. As a result, less and less solvent molecules are actually available for solvating additional ions. Thus, the effective concentration of the dissolved electrolyte is increased. This is reflected in the activity coefficient.

Since the activity coefficient is actually a factor which multiplies the simple apparent ionic concentration to make it the effective concentration, it is easy to see why $\gamma_{\pm}$ actually rises to much above unity as the concentration is increased. Experiments have shown that sometimes these increases can more than compensate for the decrease brought about by the increased interionic forces. To get an idea of this effective concentration, a 1 normal solution of sodium chloride in water causes the concentration of moles of water in the solution to change from 55.5 moles/l. in an infinitely dilute solution to 48.5 moles/l. A 5 normal solution of NaCl has more than half of the water in the solution associated with the individual ions.

RESULTS AND DISCUSSION

A. Experimental Results

In order to determine the accuracy of the experimental apparatus the vapor pressure for several known systems was compared with the available literature values. The systems used for comparison were pure water, pure methanol, and a sodium chloride solution in water. The results for these systems are shown in Tables I, II, and III.

Table I compares the literature and experimental values for pure water at two temperatures. The relative percent errors are .0064 percent and .91 percent. This corresponds to an error in the measurement of the pressure of .02 mm and -2.55 mm Hg, respectively. As can be seen from Table II, the errors between literature and experimental values range from .21 to 2.27%. This corresponds to errors in the pressure ranging from -.26 mm to - 2.86 mm. Table III-B compares the vapor pressure of aqueous solutions of sodium hydroxide with the literature values for this system. The errors in the pressure measurement are 3.32 mm Hg and 3.97 mm Hg. at temperatures 99.0°C and 100°C respectively. The literature value at 99.0°C was obtained by correcting a value at 100°C to the desired temperature. This procedure is described in Appendix C.

Thus, it can be seen that the experimental apparatus can determine vapor pressures to within .21 mm Hg of the literature value for some systems, while in some cases the difference between literature and experimental values gets as high as 3.97 mm. In all cases the apparatus reproduces its own readings to within ±.20 mm Hg. as described in the experimental procedure.

The results of this study for five methanol-salt systems are shown in Tables IV through VIII. The actual vapor pressure lowering as a function of concentration is shown in these tables, along with the relevant functions computed from the data. The points listed as 'old data' and 'new data' correspond to different runs using starting solvent with different vapor pressures.

The vapor pressure lowering should be a smooth function of the concentration of dissolved solute, therefore, a plot of ΔP against molality should show up experimental errors in the data. These plots for the five systems considered are shown in Figures III-VII. The data appears fairly smooth (except for lithium chloride) in these plots.

In order to compute the activity coefficient of each salt in methanol, a plot of $(1 - \phi)/m^{1/2}$ vs $m^{1/2}$ is needed to evaluate the integral of Equation 19. These plots are shown in Figures VIII to XII. The data points are numbered in Figures VIII and IX for later reference to certain points in this text. From these plots the true scattering of the data points may be readily observed. A plot of $(1 - \phi)/m^{1/2}$ vs $m^{1/2}$ should show a continuous curve that is a smooth function of molality. The scattering appears most obvious in the system lithium chloride and methanol (Figure VIII). In order to use plots of this type to determine $\gamma_{\pm}$, it is necessary to extrapolate the function

$(1 - \phi)/m^{1/2}$ to infinite dilution. Conventional methods rely on an empirical one parameter correlation that works well up to about m = .1. Therefore, it is necessary to have accurate data at this concentration. In an attempt to determine the reliability of the data in the low concentration range several points were run in this range. These points (numbered 1-5 on Figure VIII) when worked up according to conventional methods, seem to establish three different families of curves - none of which seem to form a continuous curve with the rest of the data points! In order to determine the sensitivity of the osmotic coefficient in this range, the effect of a difference of one mm of mercury in the measurement of the pressure at a low concentration has been determined (See Appendix B). This effect can produce as much as a 67% difference in the function $(1 - \phi)/m^{1/2}$.

The system sodium iodide in methanol was tested in a similar manner. The 'old data' was obtained using Fisher methanol (vapor pressure: 124.64 mm, purity 99.9 mol%), and the 'new data' was obtained using the 'Baker Analyzed' Reagent methanol (vapor pressure: 123.88 mm, purity 99.8 mol %). The points marked 'old data' and 'new data' seem to diverge at first, and then converge at higher concentrations. The differences in these groupings of points may or may not be attributable to the fact that different solvent batches were used in the determinations.

In any case the scatter in this system seems to be somewhat less than in the system lithium chloride and methanol. An interesting test was run on this system to determine a lower limit for the reproducibility of the osmotic coefficient. A one liter batch of .77 molal sodium iodide solution in methanol was made up. Two separate runs were made using 300 mol of this solution for each run. The points obtained from these runs are designated numbers 14 and 15 and are shown in Figure IX. From Figure IX it can be seen that the points coincide nicely thus establishing reproducibility at this concentration.

Since the experimental data obtained was inaccurate at the low concentrations (m = .1), it became obvious that a new extrapolation procedure would have to be devised in order to evaluate $\gamma_{\underline{+}}$. It was necessary that this method use results at as high a concentration as possible so as to have a reliable value (or values) for extrapolation to infinite dilution. An empirical correlation of the form:*

$$(1-\phi)/m^{1/2} = 2.303\, A_{\gamma}\sigma(m^{1/2}) + X(1)m^{X(2)} \qquad (55)$$

was tried for ten uni-univalent salts in water at 25°C. The data was regressed by a non-linear regression program written in Basic called 'Nonlin.' In attempting to correlate literature data for 1-1 salts to a molality of six, Equation 55 showed errors greater than tolerable for some of the salts. As a result, the correlation was limited to m = 1. The results of regressing the literature data up to m = 1 on to Equation (55) are shown in Table

*See Appendix D

IX. Even with this limitation the maximum error in $\gamma_{\pm}$ for the systems $RbNO_3$ and NaCNS was about 20 %. Another fault of this correlation was that only a limited number of data points could be used for the extrapolation procedure. This would tend to make the graphical integration somewhat cumbersome to perform on the computer since there would be a discontinuity between the range of Equation (55) and the range over which the experimental data had to be integrated. For these reasons work was discontinued on this method of correlation.

The next method of correlation tried was a graphical procedure which consisted of two steps:

1. From the available experimental data, the constant B is evaluated in the following equation.

   $$1 - \phi = (2.303/3)A_{\gamma} m^{1/2} \sigma(m^{1/2}) - (2.303/2)B\, m \qquad (56)$$

   The method of evaluating B consists of making a plot of $1 - \phi - (2.303/3)A_{\gamma} m^{1/2} \sigma(m^{1/2})$ vs m. The slope of the straight line obtained is then $-(2.303/2)$ B.

2. The activity coefficient, $\gamma_{\pm}$, is then calculated from the equation

   $$\log_{10} \gamma_{\pm} = - A_{\gamma} m^{1/2}/(1 + m^{1/2}) + B\, m \qquad (57)$$

The above equations are for 1-1 electrolytes. For 1-2 or 2-1 electrolytes, Equations (56) and (57) become:

$$1 - \phi = \left[2(2.303)\sqrt{3}/3\right] A_{\gamma} m^{1/2} \sigma(3 m^{1/2}) - 2(2.303)/3 \; B \, m \qquad (58)$$

and

$$\log_{10} \gamma_{\pm} = (-2\sqrt{3} A_{\gamma} m^{1/2})/(1 + \sqrt{3} m^{1/2}) + 4/3 \; B \, m \qquad (59)$$

This approach was tested on ten 1-1 and nine 1-2 electrolytic systems using data from the literature. Sample plots for a typical 1-1 and 1-2 electrolyte are shown in Figures XIII and XIV. In Figure XIII the quantity δ for 1-1 systems is defined by

$$\delta = 1 - \phi - (2.303/3) A_{\gamma} \sigma(m^{1/2}) m^{1/2} \qquad (60)$$

In Figure XIV the corresponding quantity δ' for 1-2 electrolytes is defined by

$$\delta' = 1 - \phi - (2(2.303)\sqrt{3}/3) A_{\gamma} m^{1/2} \sigma(\sqrt{3} m^{1/2}) \qquad (61)$$

Instead of determining the slope graphically, a computer program was used which determined the best slope by the method of least squares. The value of B was then calculated for each electrolyte and was used in Equations (57) and (59) to determine $\gamma_{\pm}$. The average maximum percent error in $\gamma_{\pm}$ was determined for all systems by comparing the $\gamma_{\pm}$ obtained by this method with the $\gamma_{\pm}$ listed in the literature. The results of these calculations are shown in Tables X and XI. As can be seen the 1-1 systems gave significantly better results with an average maximum percent error in $\gamma_{\pm}$ of less than 5%, while the 1-2 systems had an average maximum percent error of about 18.3%.

Noting the curvature in Figure XIV, especially for the last few points at the higher concentrations, it became feasible to try and 'weight' these higher concentration points a little heavier. Since the constant B in Equations (56) and (58), is not a true constant but rather varies with concentration, individual values of B were obtained from each value of at a given concentration. To get an average 'weighted' value of B from the individual B values, each individual B value was weighted according to the molality at which it was obtained. Thus, a new set of values B' were obtaind using this weighted method. Mathematically, B' is expressed in Equation (62) as:

$$B' = \sum B_j m_j / \sum m_j \qquad (62)$$

where the summation is taken over all the experimental points for a given system. In essence this method simply gives greater weight to the points at the higher end of the concentration range and reduces the error in this range.

The results of this method of correlation for 1-1 and 1-2 salts in water are shown in Tables XII and XIII. As can be seen, the average maximum percent error in $\gamma_{\pm}$ was slightly reduced for both the 1-1 and the 1-2 systems. In order to see if limiting the concentration range would have any effect on this correlation, this same method was applied to the 1-2 salts but only up to an ionic strength of six. Imposing this limitation cut the error down in these systems by about one and one half percent. The results are shown in Table XIV.

B. Correlation of Experimental Results

The experimental results were correlated by use of the method of 'weighted' B values previously described. The correlation was not limited to an ionic strength of six, since in some cases the experimental data went beyond this concentration. The parameter B' was found for each of the five methanol-salt systems. It was assumed that the accuracy of the correlation used was independent of the solvent. This being the case, the activity coefficients found by application of these B' values should be accurate to within a maximum error of 4.16 % for the 1-1 salts and 17.50 % for the 1-2 salts. The individual B' values for each system along with the computed values of the activity coefficient of the salt as a function of concentration are shown in Tables XV through XIX.

Referring back to Figures VIII, IX and X, there are some points that lie far from the curve and appear to be experimentally 'bad' points. In order to reject some of these points, a method was used to estimate the precision of the data and systematically eliminate certaine values based on their average deviations. The average deviation(21) is defined by:

$$\bar{Z} = \sum |y_j| / \zeta \qquad (63)$$

Here, y_j represents the absolute value of an individual deviation. Each deviation was expressed as a deviation from the value B':

$$|y_j| = |B_j - B'| \qquad (64)$$

ζ represents the number of experimental points used to find $\bar{Z}$.

This method assumes that unusually large deviations are unlikely to result from indeterminate (random) errors and are probably the results of some determinate error overlooked by the experimentalist. Two rules are used to define these limits:

1. The 2.5 $\bar{Z}$ rule causes a value to be rejected if its deviation from the trial mean, calculated by ignoring the doubtful value, is greater than 2.5 times the average deviation.
2. The 4.0 $\bar{Z}$ rule is analogous but uses 4.0 times the average deviation as the limit of acceptability.

The way in which this method was applied to the experimental data was by means of a trial and error procedure. First, the individual B values of Equation (56) were found. The weighted B value, B', was then found from all data points except the doubtful values. The average deviation of all points was then calculated and checked to make sure that all points which were used in the calculation of B' had an average deviation of less than 2.5 $\bar{Z}$ and that all the points left out had a deviation of greater than 2.5 $\bar{Z}$.

This procedure was used for the points in Figures VIII and IX. Because there were fewer data points to deal with in Figure X, the 4.0 $\bar{Z}$ rule was used instead of the 2.5 $\bar{Z}$ rule. As a result of this procedure, several points were eliminated from Figures VIII and IX and none were eliminated from Figure X. The points which have been eliminated in

Figures VIII and IX are shown in large triangles.

C. Conclusions

The only literature source of data which was available for comparison with the experimental results was that of Skabacheevski.$^{(13)}$ The activity coefficients of the salt for the system Lithium Chloride in Methanol at 25°C are compared in Table XX. The error between the two sources, exprimental and literature, seems to vary from about 9 percent to 235 percent at the highest concentrations. There are two main reasons for this. The first one is that the activity of the solvent at the highest concentrations was different in each of the sources. However, this could not bring about a 235 percent difference in $\gamma_{\pm}$. That difference seems to be a result of the graphical integration and especially the method used for extrapolation to infinite dilution. Skabacheevski's method of extrapolation is based on a correlation that works up to about .1 molal. Since his data start at .328 molal, the correlation does not rigorously apply and probably accounts for a large portion of the error.

In order to make a comparison in which this factor does not enter into the calculations, a comparison of $_{solvent}$ for both sets of data was made. Tables XXI and XXII show $\gamma_{solvent}$ together with the calculated mole fractions of methanol in the solutions. $\gamma_{solvent}$ was found by application of the following equation:

$$\gamma_{solvent} = \text{(Activity of the Solvent)/(Mole fraction Methanol)}$$

In this equation the mole fraction methanol was based on moles of undissociated solute plus moles of solvent as the total moles. The results of this comparison are shown in Table XXIII. The largest error occurs at the highest salt concentrations where there is a considerable difference between the experimental and literature values for the activity coefficient of the solvent.

The experimental method as presented here seems to be adequate and accurate to a degree, but there is still obviously some error in the operation of the equipment which gives rise to some of the 'bad' points as well as some of the discrepancies in Table II (values of the pure component vapor pressure of methanol.). One source of error noticed was an air leak that periodically appeared at the stem of the teflon valve and also along the glass sleeve of the condensed vapor phase reservoir. The effect of the presence of air mixed in with the vapor phase is unknown.

The methods presented here for determining the activity coefficient of an electrolyte in solution seem to be adequate for the 1-1 electrolytes but leave a maximum error of about 17.5 % for the 1-2 systems. The uncertainty lies in the extrapolation procedure since this seems to be the limiting factor in this situation.

As for the uncertainty about $\gamma_{solvent}$ for Lithium Chloride in Methanol, it seems worthwhile to make some new determinations of the activty coefficient near saturation so as to resolve this discrepancy.

TABLE I

Vapor Pressure of Pure Water

RUN	TEMP.	EXPER. VALUE	LITER.(14) VALUE	% ERROR
1.	43.6°C	278.65mm	281.20mm	.91
2.	77.0°C	314.20mm	314.18mm	.64

TABLE II

Vapor Pressure of Pure Methanol

RUN	TEMP.	EXPER. VALUE	LITER.(12) VALUE	% ERROR
1.	24.88°C	123.20mm	126.06mm	2.27
2.	"	123.90mm	"	1.71
3.	"	124.10mm	"	1.55
4.	"	124.62mm	"	1.14
5.	"	125.80mm	"	.21

TABLE III-A

Literature Data for Sodium Chloride and Water at 100°C (4)

MOLARITY	ΔP
.5	12.3
1.00	25.2
2.00	52.1
3.00	80.0
4.00	111.0
5.00	143.0
6.00	176.5

TABLE III-B

Experimental Data for Sodium Chloride and Water

MOLARITY	T	ΔP_{lit}^{*}	ΔP_{exp}	$\frac{\Delta P_{exp} - \Delta P_{lit}}{\Delta P_{lit}}$
3.169	99°C	86.5	89.7	.03699
4.397	100°C	123.0	126.85	.03130

[*] See Appendix C

TABLE IV-A

Old Data for Sodium Iodide and Methanol (P solvent =123.88)

Molality	Activity	Osmotic Coeffic.	ΔP	$\frac{1-\phi}{m^{1/2}}$	$m^{1/2}$
.2299	.9921	.5384	.98	.9627	.4795
.7413	.9753	.5265	3.055	.5499	.8610
1.157	.9394	.8432	7.51	.1458	1.0756
1.5755	.8970	1.0767	12.76	-.0626	1.2252
2.3222	.8195	1.3377	22.36	-.2216	1.5239
2.7593	.7711	1.4701	28.36	-.2830	1.6611
3.7048	.6696	1.6894	40.93	-.3582	1.9248
4.520	.5875	1.8363	51.1	-.3934	2.1260
5.7710	.5144	1.7976	60.26	-.3320	2.4023

TABLE IV-B

New Data for Sodium Iodide and Methanol (P solvent = 124.62)

Pt. No.	Molality	Activity	Osmotic Coeffic	ΔP	$\frac{1-\phi}{m^{1/2}}$	$m^{1/2}$
1.	.2308	.9890	.7482	1.37	.5227	.4804
2.	.3659	.9831	.7232	2.10	.4457	.6212
3.	.5305	.9709	.8684	3.63	.1806	.7283
4.	.6767	.9571	1.0100	5.34	-.0121	.8226
5.	.9629	.9432	.9483	7.08	.0527	.9812
6.	1.1256	.9082	1.3347	11.44	-.3155	1.0609
7.	1.3870	.8995	1.1920	12.53	-.1630	1.1777
8.	1.6237	.8801	1.2273	14.94	-.1784	1.2474
9.	1.7031	.8579	1.4045	17.71	-.3100	1.3050
10.	2.1796	.8228	1.3963	22.08	-.2684	1.4763
11.	2.4523	.7861	1.5318	26.66	-.3396	1.5659
12.	2.7648	.7628	1.5283	29.56	-.3177	1.6628
13.	3.2387	.7145	1.6199	35.58	-.3444	1.7996
14.	.7601	.9585	.8692	5.21	.1500	.8719
15.	.7837	.9553	.9101	5.62	.1016	.8853

TABLE V-A

Old Data for Lithium Chloride and Methanol (P solvent = 123.60)

Pt. No.	Molality	Activity	Osmotic Coeffic	Δ P	$\frac{1-\phi}{m^{1/2}}$	$m^{1/2}$
1.	.2925	.9776	1.2086	2.77	-.3857	.5408
2.	.6632	.9561	1.0564	5.42	-.0693	.8144
3.	.8996	.9351	1.1640	8.02	-.1730	.9485
4.	1.1540	.9033	1.3753	11.95	-.3494	1.0742
5.	1.6288	.8765	1.2630	15.27	-.2061	1.2762
6.	2.0301	.8204	1.5218	22.20	-.3662	1.4248
7.	2.6508	.7447	1.7354	31.55	-.4517	1.6281
8.	3.2300	.6946	1.7607	37.75	-.4233	1.7972
9.	4.0436	.5388	2.3866	57.00	-.6895	2.0109
10.	4.6901	.4697	2.5143	65.55	-.6992	2.1657
11.	5.5300	.4364	2.3399	69.65	-.5678	2.3516
12.	6.526	.2658	3.1684	90.75	-.8488	2.5546
13.	7.3120	.1930	3.5109	99.75	-.9286	2.7041

TABLE V-B

New Data for Lithium Chloride and Methanol (P solvent = 123.78)

Pt. No.	Molality	Activity	Osmotic Coeffic.	ΔP	$\frac{1-\phi}{m^{1/2}}$	$m^{1/2}$
14.	.1157	.9946	.7264	.67	.8045	.3401
15.	.2220	.9919	.5717	1.00	.9090	.4712
16.	.2908	.9879	.6561	1.50	.6377	.5392
17.	.2806	.9904	.8734	1.19	.2390	.5297
18.	.2830	.9917	.4586	1.03	1.0177	.5319
19.	.5030	.9710	.9124	3.59	.1235	.7093
20.	.6911	.9604	.9131	4.91	.1045	.8313
21.	1.2880	.9251	.9430	9.23	.0502	1.1349
22.	1.5969	.9057	.9682	11.67	.0252	1.2637
23.	1.9611	.8806	1.0116	14.78	-.0082	1.4003
24.	2.3994	.8080	1.3859	23.78	-.2491	1.5490
25.	2.5768	.8067	1.3008	23.92	-.1874	1.6000

TABLE VI

Data for Sodium Hydroxide and Methanol (P solvent = 123.34)

Pt. No.	Molality	Activity	Osmotic Coeffic.	ΔP	$\frac{1-\phi}{m^{1/2}}$	$m^{1/2}$
1.	.3400	.9792	.9648	2.55	.0604	.5831
2.	.8504	.9260	1.4108	9.13	-.4451	.9222
3.	1.1232	.8967	1.5118	12.73	-.4829	1.0598
4.	1.4099	.8847	1.3560	14.23	-.2998	1.1874
5.	2.2787	.7056	1.7740	28.23	-.6116	1.5095
6.	3.1721	.5485	2.0397	41.88	-.6177	1.7810
7.	2.7113	.6606	2.0070	36.33	-.5837	1.6466
8.	4.1500	.4756	2.2584	55.60	-.6153	2.0372
9.	4.9077	.3936	2.3632	64.70	-.5983	2.2153
10.	5.9413	.7712	2.4583	74.70	-.5127	2.4375

TABLE VII

Data for Calcium Chloride and Methanol (P solvent = 122.85)

Molality	Activity	Osmotic Coeffic.	ΔP	$\frac{1-\phi}{M^{1/2}}$	$M^{1/2}$
.3186	.9909	.2985	1.125	1.2429	.5644
.8831	.9489	.6179	6.275	.4066	.9397
1.2405	.9101	.7900	11.05	.1885	1.1138
1.3944	.9064	.7332	11.50	.2259	1.1808
1.8799	.8380	.9781	19.90	.0160	1.3711
2.4254	.7670	1.1380	28.80	-.0886	1.5573
2.6345	.7289	1.2487	33.30	-.1532	1.6231

TABLE VIII

Data for Copper Chloride and Methanol (P solvent = 123.75)

Molality	Activity	Osmotic Coeffic.	ΔP	$\frac{1-\phi}{M^{1/2}}$	$M^{1/2}$
.3868	.9907	.2513	1.15	1.2040	.6220
.7294	.9752	.3582	3.07	.7515	.8540
1.0334	.9612	.3984	4.80	.5915	1.0166
1.6263	.9352	.4286	8.03	.4475	1.2753
2.1463	.9133	.4396	10.73	.3825	1.4650
2.4751	.9022	.4326	12.10	.3609	1.5732
2.7342	.8742	.5116	15.57	.3049	1.6535
3.3957	.8313	.5661	20.88	.2355	1.8427
3.9739	.7899	.6175	26.00	.1917	1.9934

TABLE IX

Parameters of Equation 55 for ten 1-1 salts in water

SALT	X(1)	X(2)	Maximum % Error in $(1-\phi)/m^{1/2}$
RbCl	-.0175769	.272243	1.28 %
RbI	-.0127031	.365285	1.06 %
RbBr	-.0146993	.314133	2.12 %
CsBr	+.0184680	.822782	1.14 %
CsI	+.0214858	.713388	1.15 %
$RbNO_3$	+.0665265	.281805	21.50 %
NaCNS	-.1091290	.557832	19.40 %
KCNS	-.0381413	.568564	8.08 %
KCl	-.0396430	.546362	6.38 %
NaCl	-.0748903	.512211	5.25 %

TABLE X

Values of B in Equations 56 and 57 for ten 1-1 salts in Water

SALT	B	Maximum % Error in $\gamma_{\pm}$
KCl	.0231557	3.27 %
HI	.20140	9.60 %
RbBr	.01244	1.27 %
$RbNO_3$	-.0749556	11.60 %
RbI	.0132393	.80 %
RbCl	.0177719	.63 %
CsBr	.0041455	5.80 %
NaCNS	.0685637	8.70 %
KCNS	.0127402	4.70 %
$CsNO_3$	-.1092444	3.60 %

Average Maximum % Error in $\gamma_{\pm}$ = 4.99 %

TABLE XI

Values of B for 1-2 salts in Water

SALT	B	Maximum % Error in $\gamma_{\pm}$
$CaCl_2$	.2241	18.0 %
$Ca(NO_3)_2$	.0760042	15.0 %
$BaCl_2$	.1347	13.8 %
$MgCl_2$	.2607	19.2 %
$MgBr_2$	.3270	22.0 %
MgI_2	.3880	22.0 %
$SrCl_2$	.1751	15.8 %
$CuCl_2$	.1114	22.9 %
$NiCl_2$	.2366	15.8 %

Average Maximum % Error in $\gamma_{\pm}$ = 18.30 %

TABLE XII

Values of B' in Equation 58 for 1-1 salts in Water

SALT	B'	Maximum % Error in $\gamma_{\pm}$
KCl	.0248912	3.50 %
HI	.20660	7.50 %
RbBr	.0127282	1.27 %
$RbNO_3$	-.0807605	8.79 %
RbI	.0130304	.79 %
RbCl	.0172348	.73 %
CsBr	.0014169	4.78 %
NaCNS	.0741785	7.44 %
KCNS	.014892	4.17 %
$CsNO_3$	-.1148203	2.67 %

Average Maximum % Error in $\gamma_{\pm}$ = 4.16 %

TABLE XIII

Values of B' for 1-2 Salts in Water

SALT	B'	Maximum % Error in $\gamma_{\pm}$
$CaCl_2$	.2186342	24.96 %
$Ca(NO_3)_2$	.0861798	13.33 %
$BaCl_2$	.1597748	9.79 %
$MgCl_2$	.268703	19.60 %
$MgBr_2$	.337365	20.70 %
MgI_2	.3998681	20.56 %
$SrCl_2$	.1825795	14.80 %
$CuCl_2$	.1269439	19.22 %
$NiCl_2$	.2465565	14.53 %

Average Maximum % Error in $\gamma_{\pm}$ = 17.50 %

TABLE XIV

Values of B' for 1-2 Salts in Water to I = 6

SALT	B'	Maximum % Error in $\gamma_{\pm}$
$CaCl_2$	.2350789	12.3 %
$Ca(NO_3)_2$	.106577	10.6 %
$BaCl_2$	.1347	13.1 %
$MgCl_2$	.26703	19.6 %
$MgBr_2$	.337365	20.7 %
MgI_2	.3998681	20.6 %
$SrCl_2$	.1825795	14.8 %
$NiCl_2$	.2465564	14.5 %
$CuCl_2$	.13838	16.3 %

Average Maximum % Error in $\gamma_{\pm}$ = 15.8 %

TABLE XV

Activity Coefficients of Lithium Chloride in Methanol at 24.88°C

B' = .3503

MOLALITY	LOG $\gamma_{\pm}$	$\gamma_{\pm}$
.1	−.3929	.4046
.2	−.4803	.3308
.3	−.5252	.2984
.5	−.5626	.2737
.7	−.5661	.2715
1.0	−.5402	.2882
1.5	−.4549	.3507
2.0	−.3427	.4542
3.0	−.05837	.8742
3.5	+.06544	1.163
4.0	.2139	1.636
4.5	.3659	2.322
5.0	.5209	3.319
5.5	.6781	4.766
6.0	.8371	6.875
6.5	.9977	9.951
7.0	1.160	14.45

TABLE XVI

Activity Coefficients of Sodium Iodide in Methanol at 24.88°C

$B' = .3224$

MOLALITY	LOG $\gamma_{\pm}$	$\gamma_{\pm}$
.1	-.3957	.4020
.2	-.4859	.3266
.3	-.5335	.2927
.5	-.5765	.2651
.7	-.5856	.2596
1.0	-.5681	.2703
1.5	-.4968	.3185
2.0	-.3985	.3994
2.5	-.2850	.5188
3.0	-.1420	.7210
3.5	-.03221	.9285
4.0	+.1023	1.266
4.5	+.2404	1.740
5.0	+.3814	2.407

TABLE XVII

Activity Coefficients of Sodium Hydroxide in Methanol at 24.88°C

B' = .4115

MOLALITY	LOG $\gamma_{\pm}$	$\gamma_{\pm}$
.1	-.3867	.4104
.2	-.4680	.3403
.3	-.5068	.3112
.5	-.5320	.2937
.7	-.5233	.2997
1.0	-.4790	.3318
1.5	-.3632	.4333
2.0	-.2203	.6021
2.5	-.06223	.8665
3.0	+.1252	1.334
3.5	.2796	1.904
4.0	.4587	2.876
4.5	.6413	4.380
5.0	.8269	6.715
5.5	1.015	10.35
6.0	1.204	16.02

TABLE XVIII

Activity Coefficients of Calcium Chloride in Methanol at 24.88°C

B' = .3261

MOLALITY	Log $\gamma_{\pm}$	$\gamma_{\pm}$
.1	-1.217	.06064
.2	-1.46783	.03403
.3	-1.6037	.02489
.5	-1.74359	.018034
.7	-1.80323	.015719
1.0	-1.8233	.015006
1.5	-1.768592	.017025
2.0	-1.65979	.021873
2.5	-1.52218	.03002

TABLE XIX

Activity Coefficients of Copper Chloride and Methanol at 24.88°C

B' = .1163

MOLALITY	LOG $\gamma_\pm$	$\gamma_\pm$
.1	-1.2449	.0568571
.2	-1.523781	.029918
.3	-1.68757	.020517
.5	-1.8835	.013067
.7	-1.999	.010014
1.0	-2.10310	.007879
1.5	-2.18816	.006478
2.0	-2.21921	.006030
2.5	-2.22146	.005999
3.0	-2.20622	.0066135
3.5	-2.17917	.0066135
4.0	-2.1437	.007176

TABLE XX

Comparison of Literature and Experimental Values for $\gamma_{\pm}$ of Lithium Chloride in Methanol

MOLALITY	$\gamma_{\pm}$ (lit.)	$\gamma_{\pm}$ (exp.)	% DIFFERENCE
.3	.361	.4046	12.1 %
.5	.331	.2737	17.3 %
1.0	.336	.2882	14.2 %
2.0	.458	.4542	8.30 %
3.0	.695	.8742	25.8 %
4.0	1.180	1.636	38.6 %
5.0	2.03	3.319	63.5 %
6.0	3.30	6.875	108 %
7.0	4.31	14.45	235 %

TABLE XXI

Experimental Values of $\gamma_{solvent}$ for Lithium Chloride in Methanol

MOLALITY	MOLE FRACTION METHANOL	ACTIVITY	$\gamma_{solvent}$
.6632	.9792	.9561	.9764
.8896	.9723	.9351	.9617
1.6288	.9519	.8765	.9208
2.0301	.9389	.8204	.8738
2.6508	.9217	.7447	.8080
3.2300	.9062	.6946	.7665
4.0436	.8853	.5388	.6086
4.6901	.8694	.4697	.5403
6.526	.8271	.2658	.3214
7.3120	.8102	.1930	.2382
.1157	.9963	.9946	.9983
.2908	.9908	.9879	.9971
.2806	.9911	.9904	.9993
.5030	.9841	.9710	.9867
.6911	.9783	.9604	.9817
1.2880	.9604	.9251	.9632
2.3994	.9286	.8080	.8701

TABLE XXII

Literature Values of $\gamma_{solvent}$ for Lithium Chloride in Methanol

MOLALITY	MOLE FRACTION METHANOL	ACTIVITY	$\gamma_{solvent}$
.328	.9896	.9830	.9933
1.340	.9588	.9150	.9543
1.953	.9411	.861	.9149
2.560	.9242	.801	.8667
2.971	.9131	.756	.8279
3.667	.8949	.671	.7498
4.259	.8793	.590	.6710
4.502	.8739	.561	.6419
5.669	.8463	.432	.5105
8.877	.7786	.218	.2800

TABLE XXIII

Comparison of Literature and Experimental Values of $\gamma_{solvent}$ of Lithium Chloride in Methanol

Mole Fraction Methanol	$\gamma_{solvent}$ (lit*)	$\gamma_{solvent}$ (exp)	% Difference
.98	.985	.975	1.02 %
.96	.955	.938	1.83 %
.94	.910	.885	2.75 %
.92	.850	.815	4.12 %
.90	.775	.745	3.87 %
.88	.680	.650	4.41 %
.86	.580	.538	7.33 %
.84	.495	.400	19.19 %
.82	.410	.270	34.15 %

Average Percent Difference = 8.74 %

---

* Read from Figure XV

FIGURE III

Lithium Chloride and Methanol

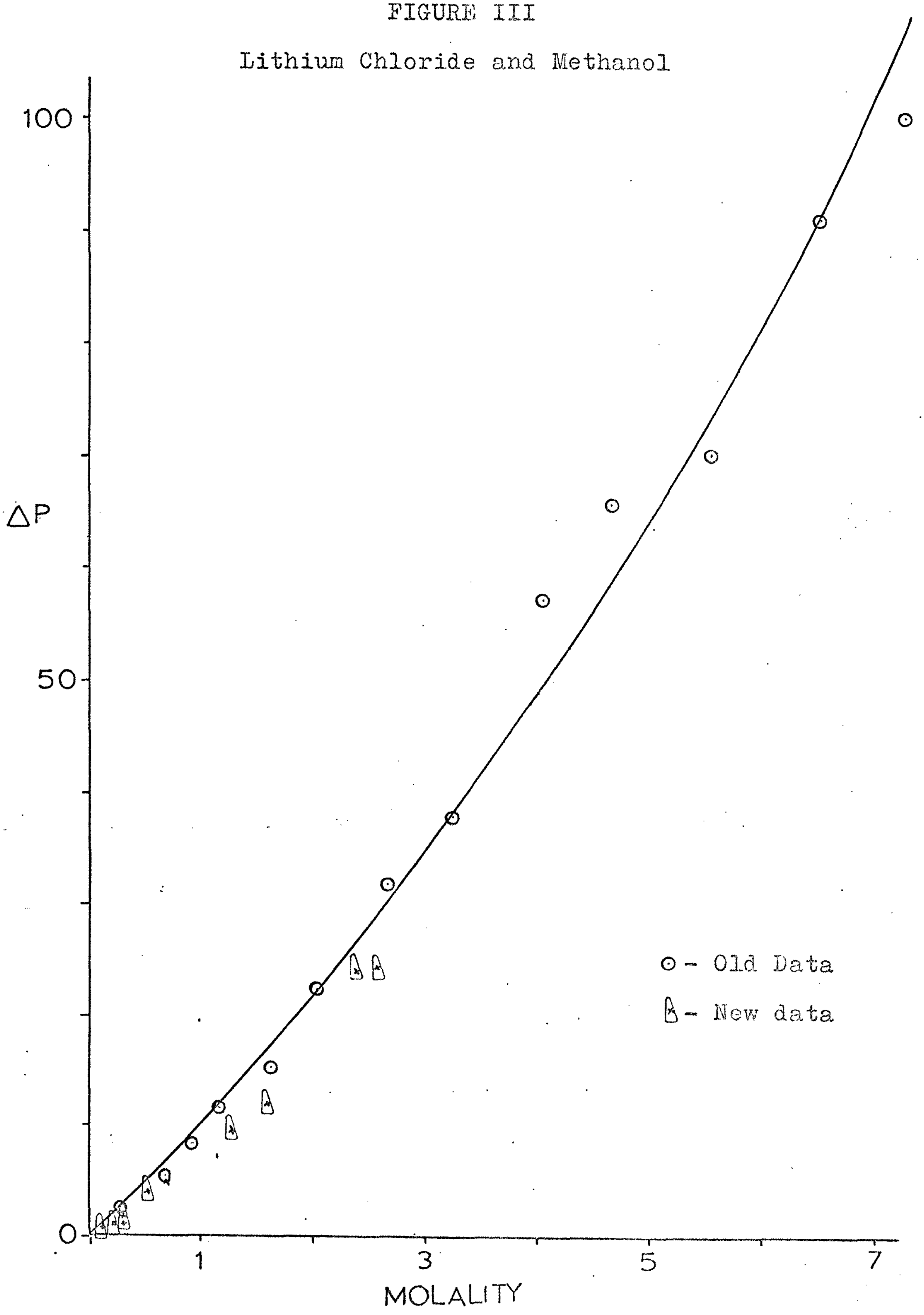


FIGURE IV

Sodium Iodide and Methanol

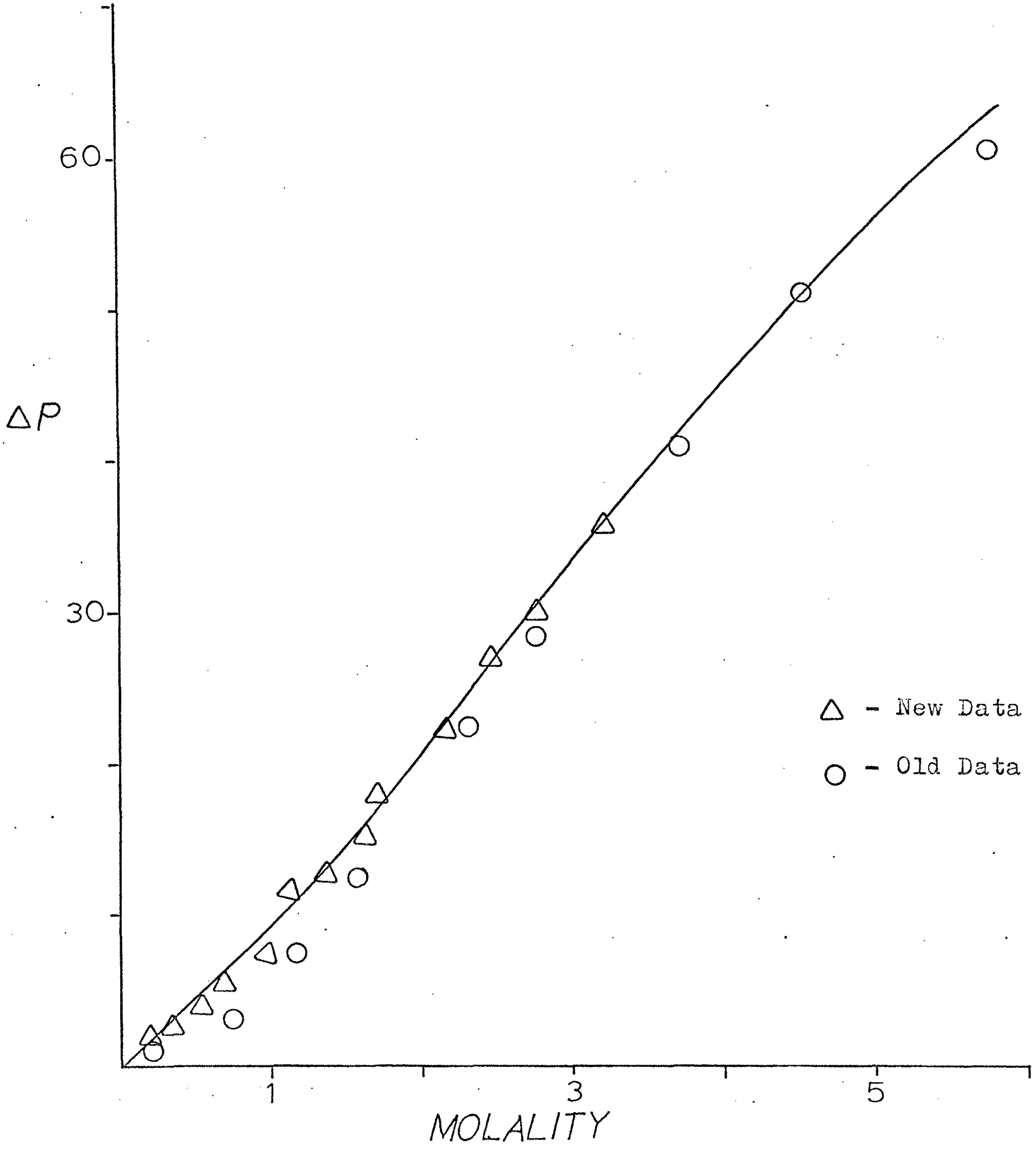


FIGURE V

Sodium Hydroxide and Methanol

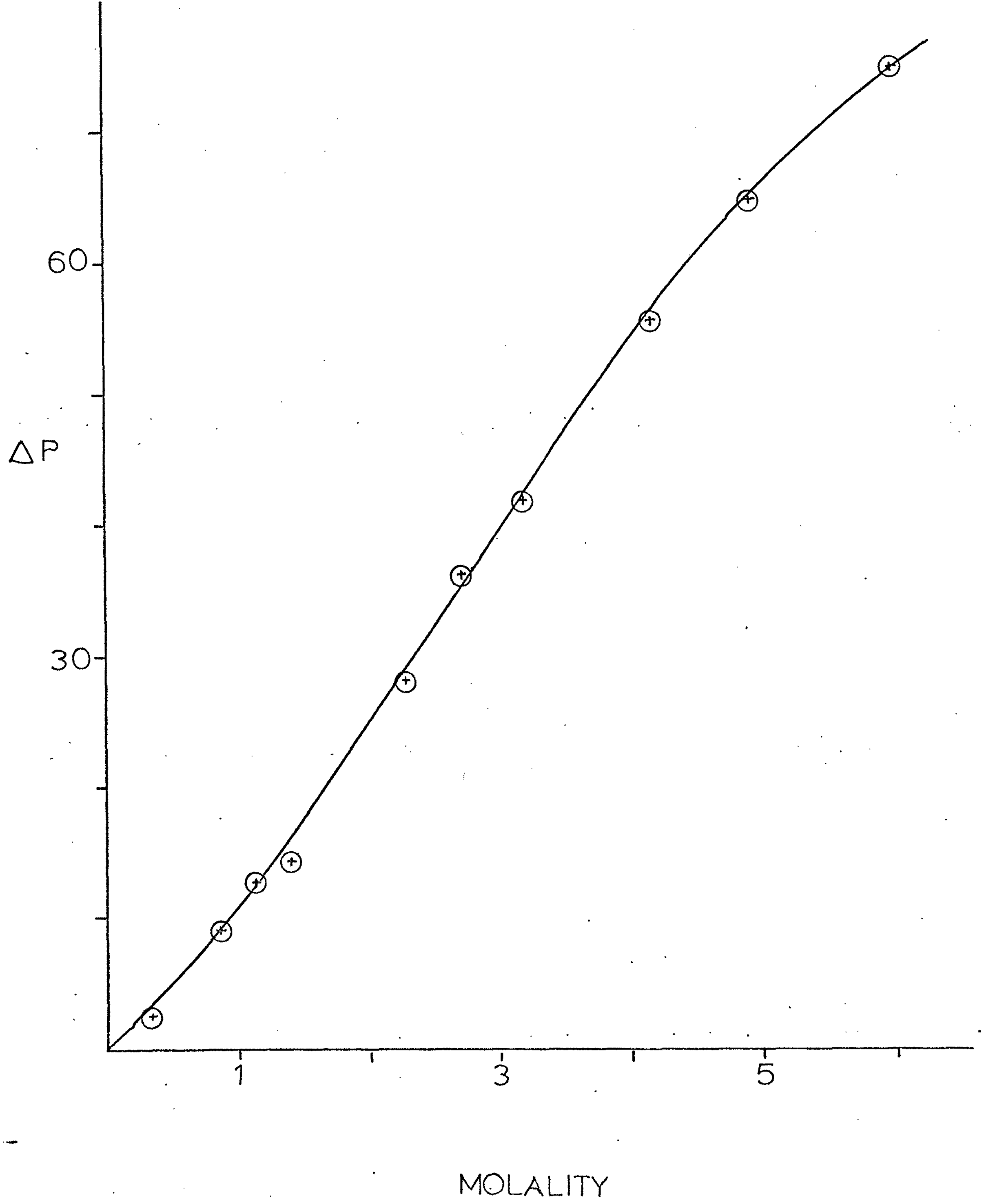
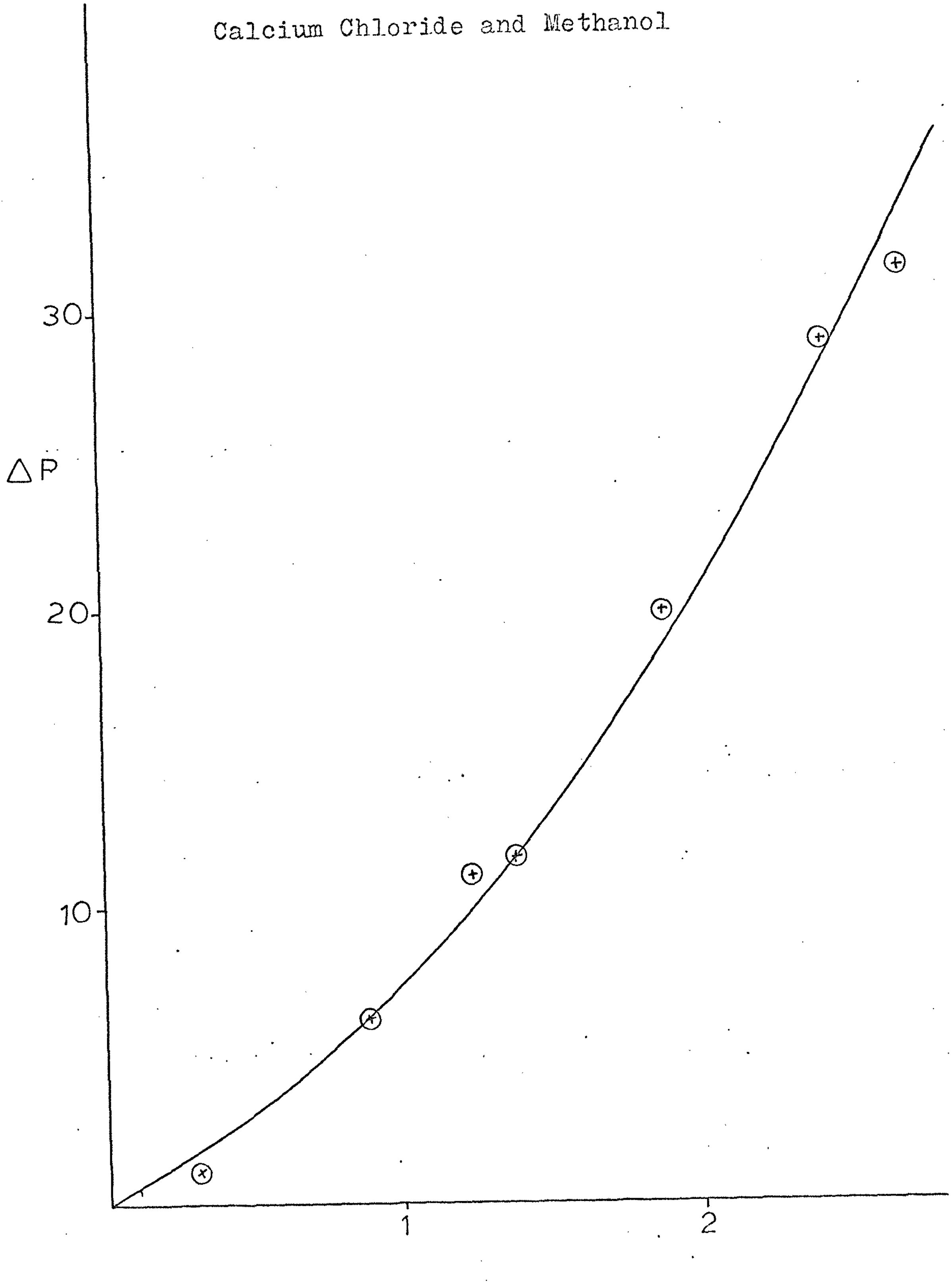


FIGURE VI

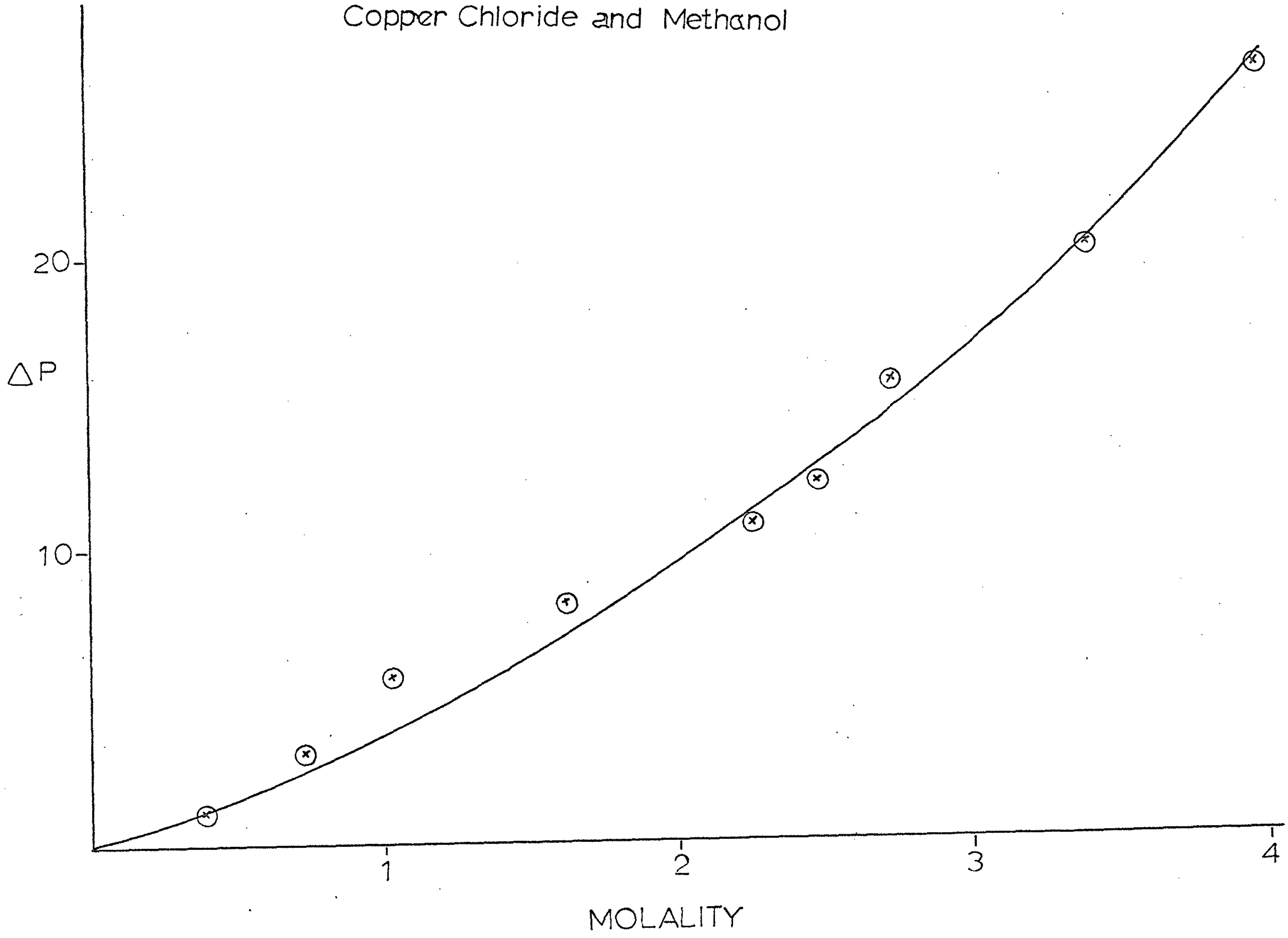
Calcium Chloride and Methanol



MOLALITY

FIGURE VII

Copper Chloride and Methanol



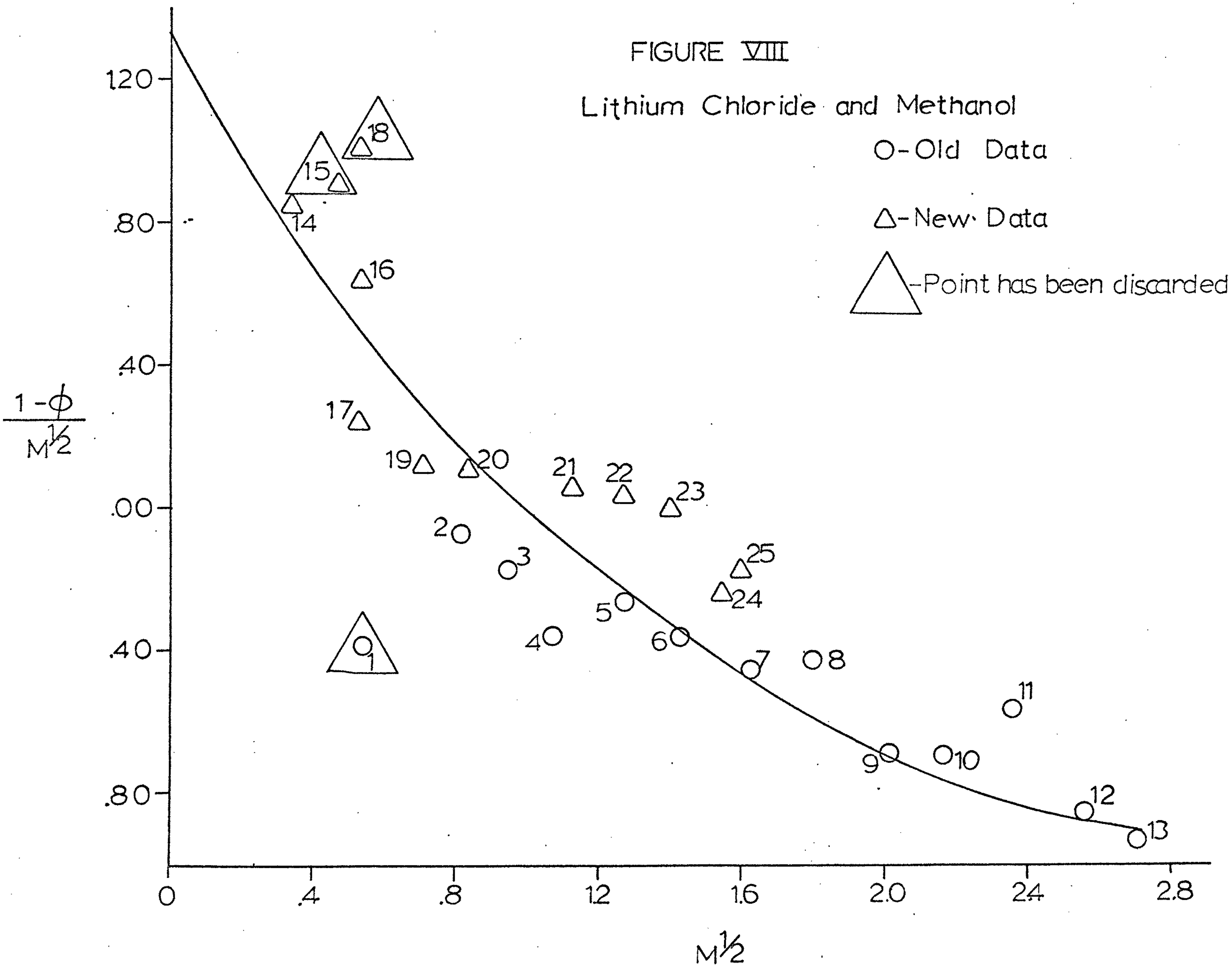
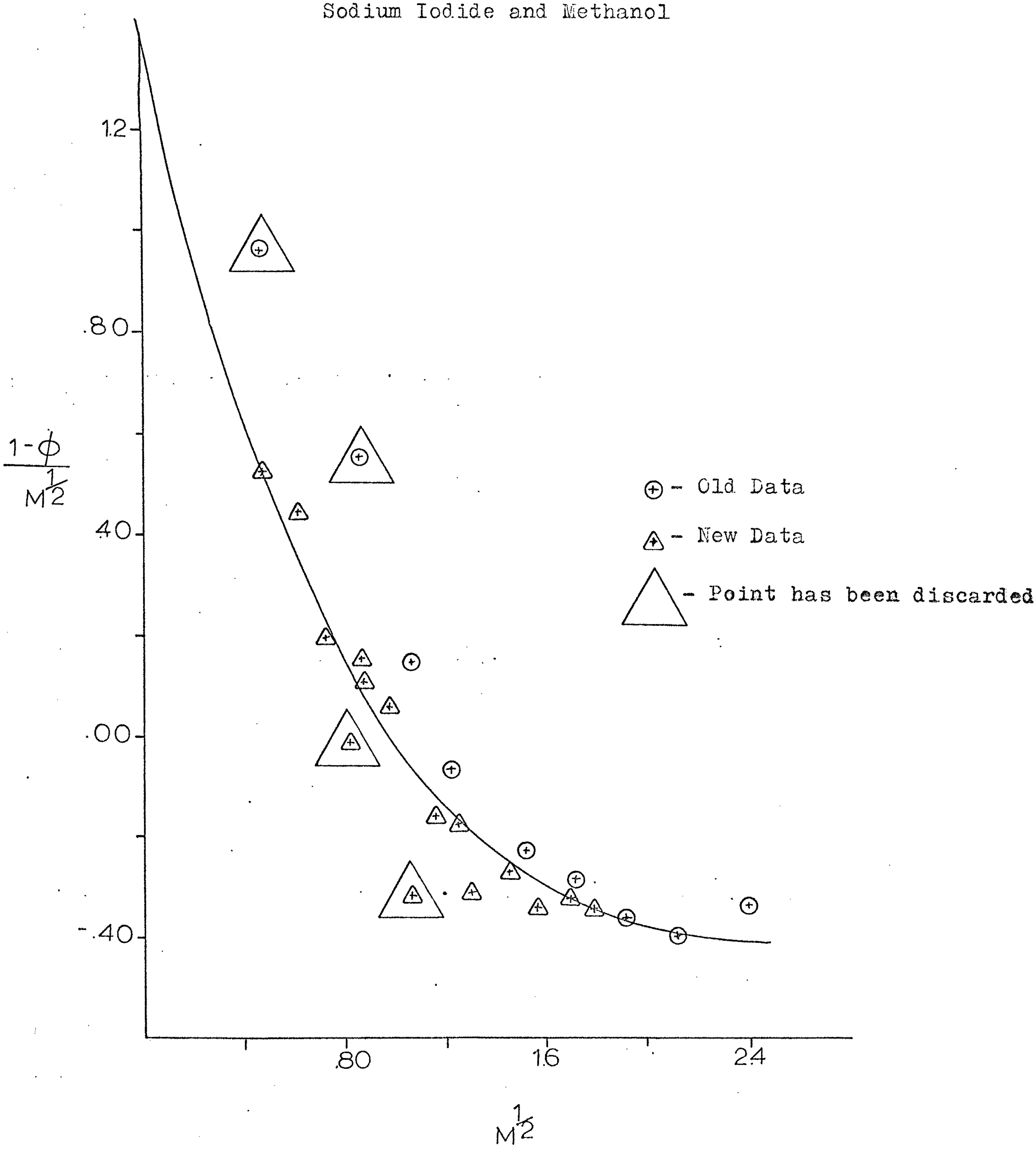


FIGURE VIII

Lithium Chloride and Methanol

FIGURE IX

Sodium Iodide and Methanol



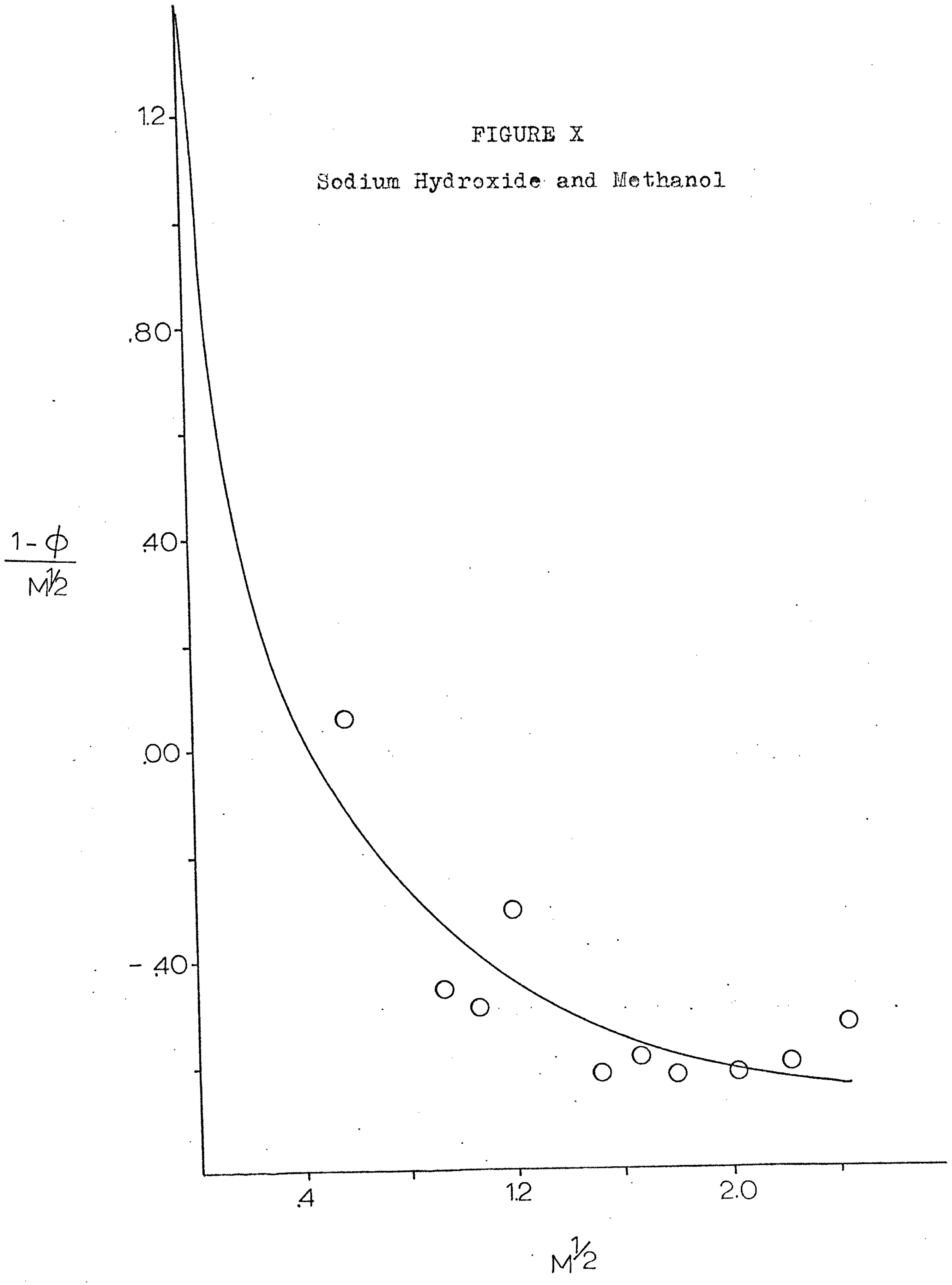


FIGURE X

Sodium Hydroxide and Methanol

FIGURE XI

Calcium Chloride and Methanol

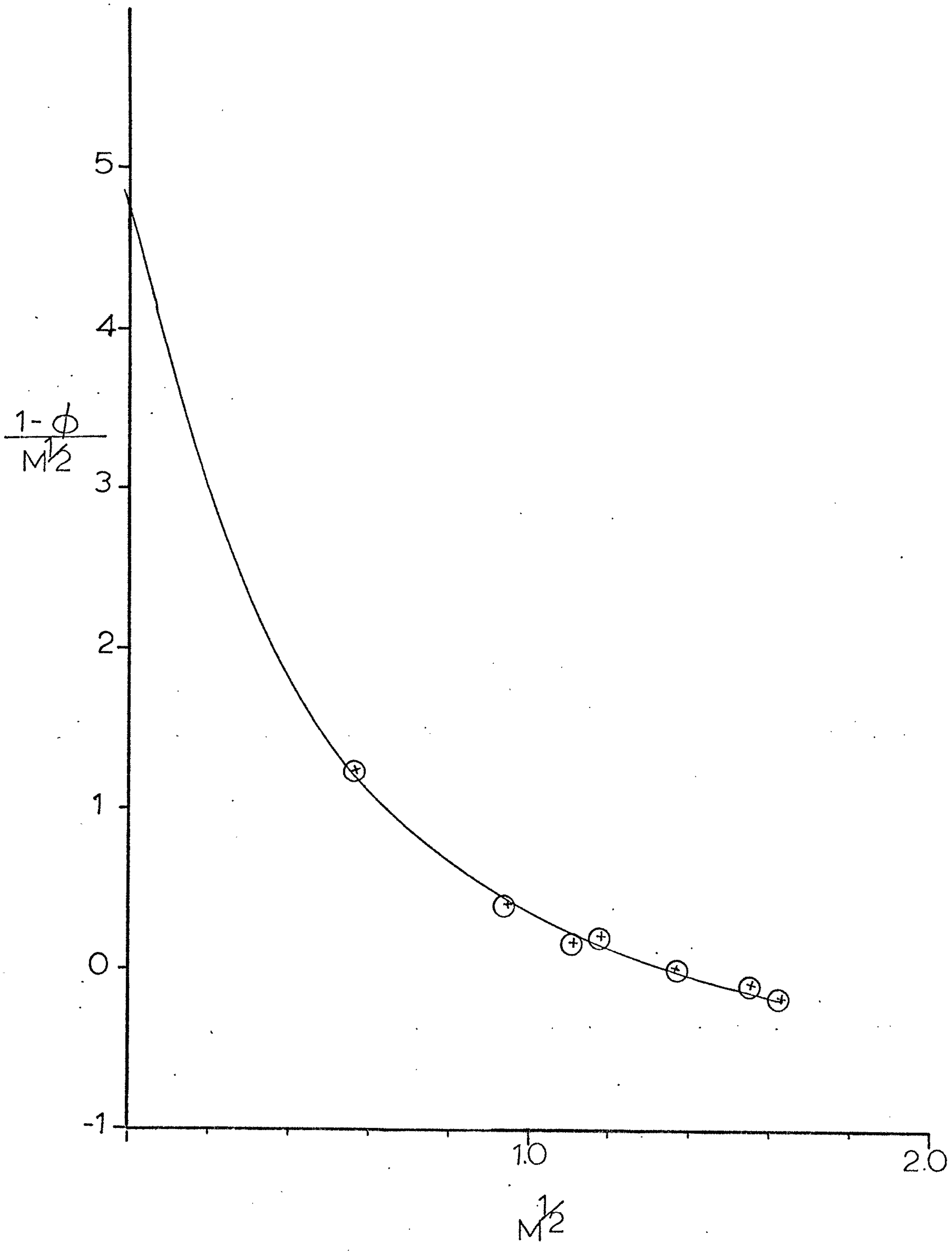


FIGURE XII

Copper Chloride and Methanol

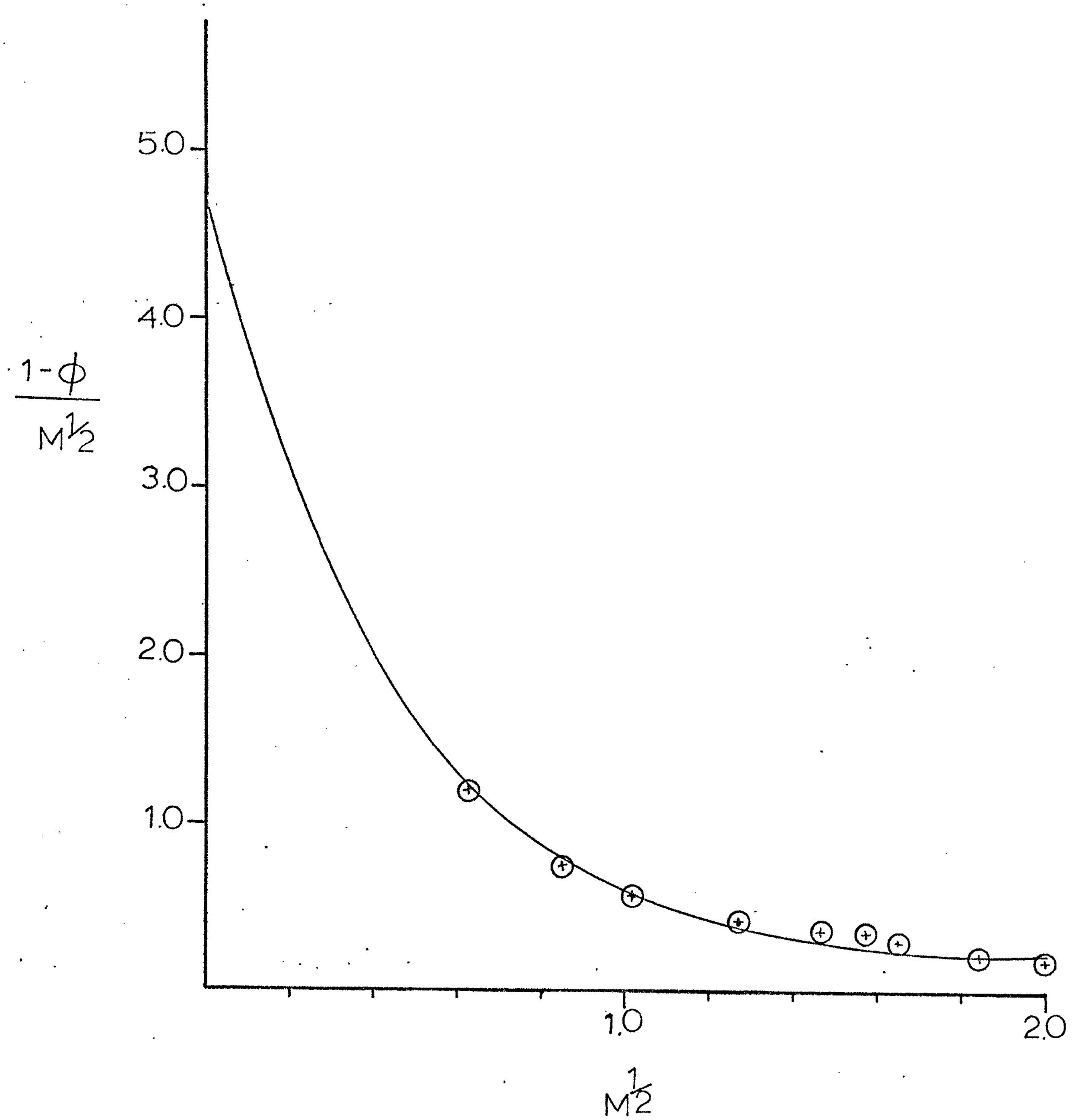


FIGURE XIII

Rubidium Chloride and Water

Illustration of Plotting Procedure Used to Determine

B in Equation 56

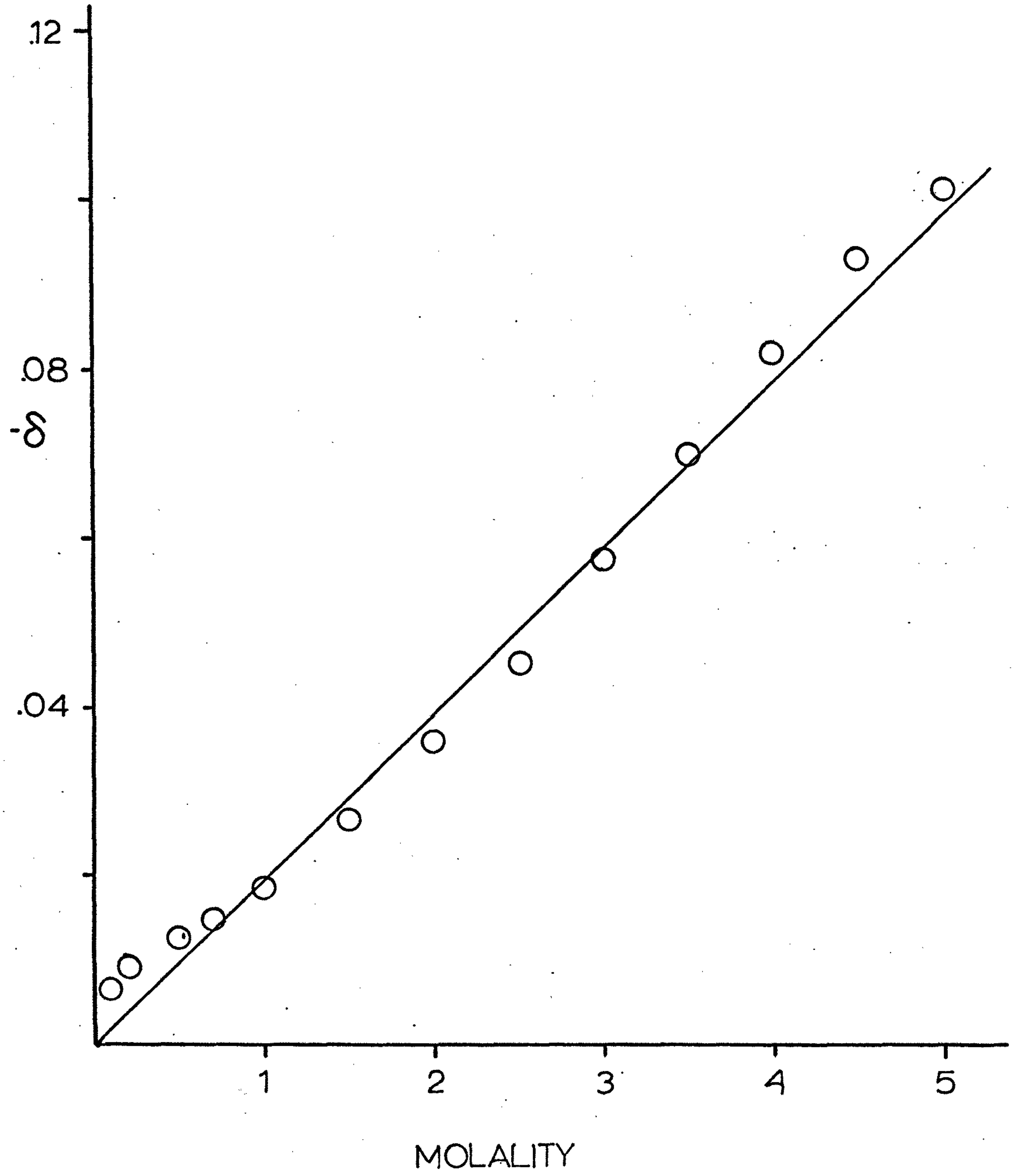
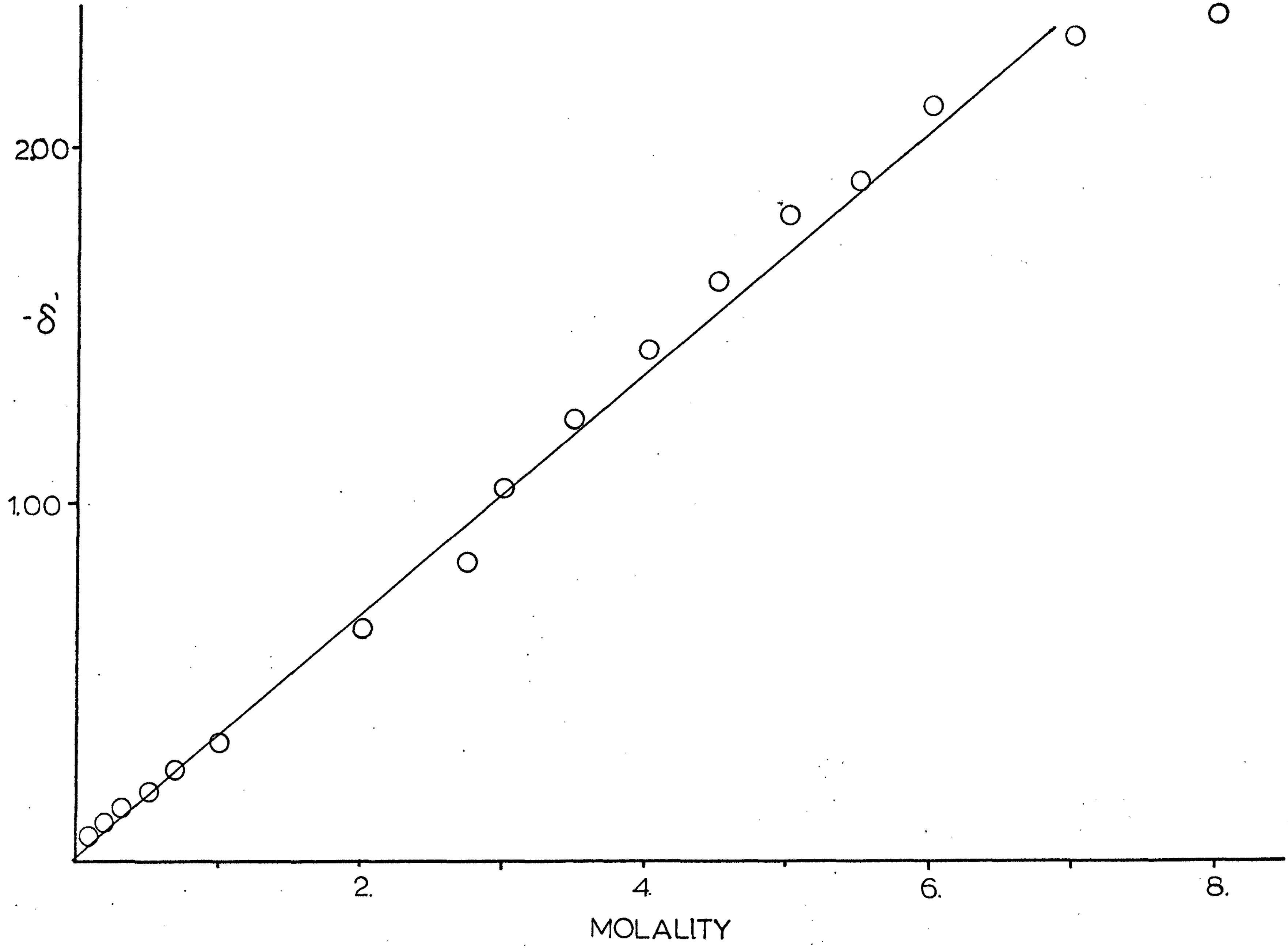


FIGURE XIV Calcium Chloride and Water

Illustration of Plotting Procedure Used to Determine B in Equation 58



Activity Coefficients of the Solvent for the System

Lithium Chloride and Methanol

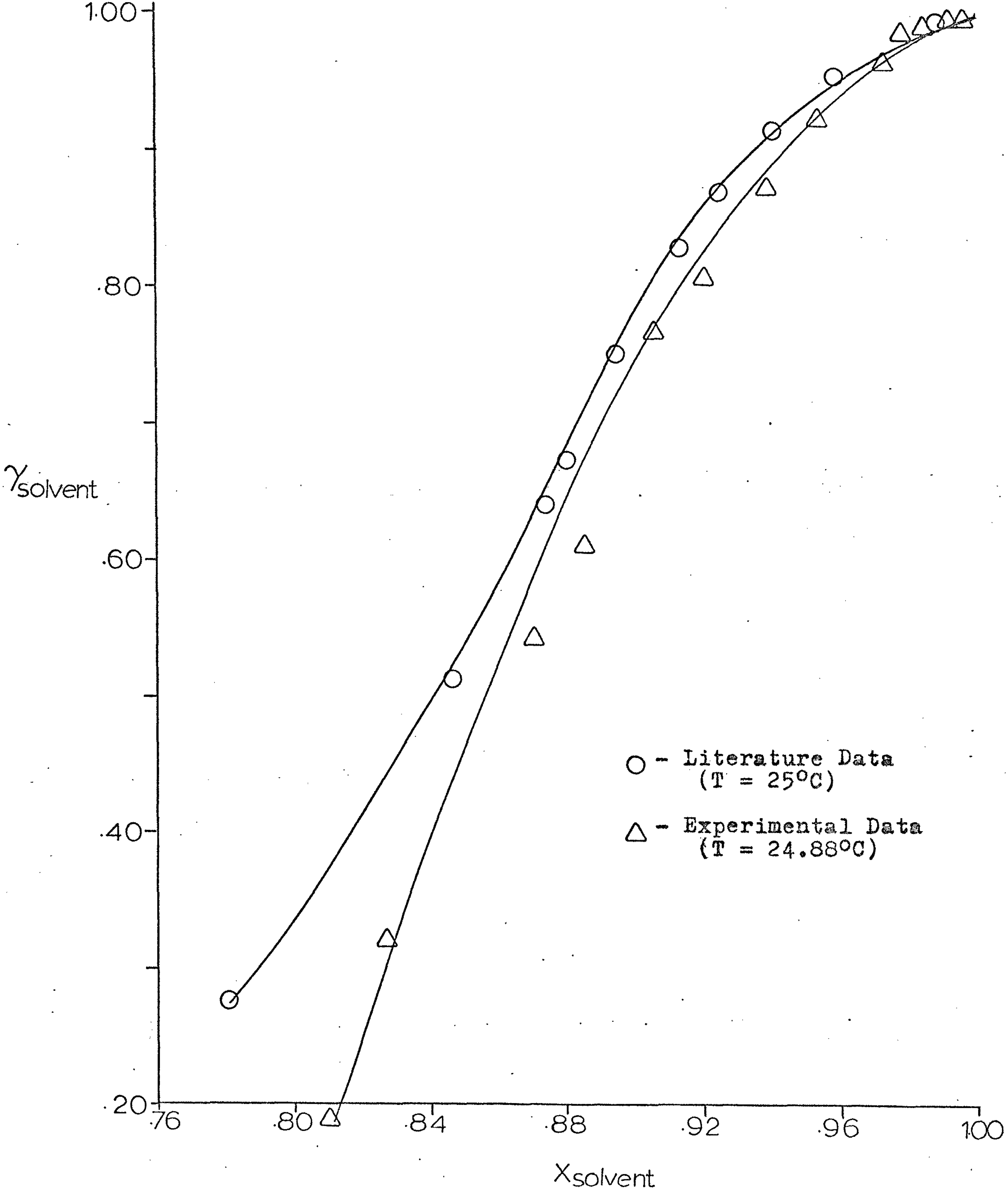


FIGURE XV

NOMENCLATURE

A_γ = constant defined in Equation (46)

a = activity

B = parameter of Equations (52), (56), (57), (58), (59).

B_j = individual B values of Equations (52) and (56) - (59) Each individual B value corresponds to an experimental value of the osmotic coefficient.

B' = $\sum B_j m_j / \sum m_j$, a 'weighted' B value used analagously to the B in Equation (52). B' is defined in Equation (62)

d_1 = density of the solvent

E = internal energy

e_o = charge on an electron

F = free energy

H = enthalpy

I = ionic strength, defined in Equation (43)

m = molality

n_i = moles of component i.

Na = Avogadro's number

P = pressure

R = gas constant

R_o = radius of an ion, if it is considered to be a charged sphere.

r = radial distance away from a point charge

S = entropy

W = work of charging an ion

X = $\nu^+ X^+ + \nu^- X^-$, where X is a general electrolyte and X^+ and X^- represent the cation and anion, respectively.

y = absolute value of an individual deviation, defined in Equation (64)

z = valence of an ion

$\bar{Z}$ = average deviation defined in Equation (63)

NOMENCLATURE (cont'd)

X(1) = parameter of Equation (55)

X(2) = parameter of Equation (55)

Greek Letters:

α = parameter of Equation (51)

β = parameter of Equation (51)

$\gamma_{\pm}$ = mean ionic activity coefficient

δ = quantity plotted in order to extrapolate data and evaluate B for 1-1 electrolytes. Defined in Equation (60).

δ' = analagous quantity for 1-2 electrolytes. Defined in Equation (61)

ϵ = dielectric constant

σ = function defined in Equation (54)

ϕ = osmotic coefficient

κ = thickness of the ionic cloud

ψ_r = electrostatic potential at a distance r from a point charge.

ψ_{ion} = electrostatic potential due to the ion alone

ψ_{cloud} = electrostatic potential due to the ionic atmosphere surrounding the central ion.

μ = chemical potential

ν = total number of ions an electrolyte dissociates into; ν^+ = number of cations, ν^- = number of anions.

ζ = total number of experimental points used in evaluating Z in Equation (63).

NOMENCLATURE (cont'd)

Subscripts:

1 = solvent

2 = solute

i = component in a solution

c = total number of components in a solution

+ = cation

− = anion

mx = electrolyte where m is the cation and x the anion

j = experimental data point having an osmotic coefficient and an individual B value (B_j) corresponding to it.

APPENDIX A

Calculation of A_γ

Data for Methanol at 25.0°C

N_o = Avogadro's Number = 6.02252×10^{23} mole^{-1}

d_1 = Density of Methanol = .7901

D = Dielectric Constant = 31.50

k = Boltzman Constant = 1.38054×10^{-16} erg-g^{-1}

e = Charge on an electron = 4.80298×10^{-10} cm$^{3/2}$-g$^{1/2}$-sec^{-1}

T = Temperature in °K = 298.16 °K

π = 3.14159

$$A_\gamma^2 = (2\pi N_o d_1/1000 \times 2.303^2)\ (e^2/DkT)^3$$

$$A_\gamma = 1.781$$

APPENDIX B

Sensitivity of $(1-\phi)/m^{1/2}$ to errors in Pressure

The following experimental values were determined for sodium iodide in methanol:

molality = .2299

$P_{solution}$ = 122.9 mm

$P_{solvent}$ = 123.88 mm

activity = 122.9/123.88 = .9921

ϕ = .5384

$(1-\phi)/m^{1/2}$ = .9627

Assume that the pressure of the solution was in error by 1 mm, then:

$P'_{solution}$ = (122.9 - 1) mm = 121.9 mm

activity' = 121.9/123.88 = .9840

ϕ' = .2336

$(1-\phi')/m^{1/2}$ = 1.598332

Percent Error in $(1-\phi)/m^{1/2}$ = (1.598 - .9627)/.9627 x 100 %

= 67 %

APPENDIX C

The literature value for $\triangle P$ of a 3.169 molar sodium chloride solution actually corresponds to a temperature of 100°C. The experimental data has been obtained at 99.0°C. The author assumes that the $\triangle P$ is not strongly affected by this difference in temperature.

APPENDIX D

Derivation of Equation 55

Equation (55) is derived from Equation (53) by assuming that the constant B in Equation (53) is really a function of concentration. The functional relationship chosen is then:

$$B = B_o\, m^{(X(2) - 1)}$$

Substitution of this relation into Equation (53) will then result in Equation (55). (In this equation X(2) is any number greater than zero.)

$$(1 - \phi)/m^{1/2} = 2.303\, A\gamma\sigma(m^{1/2}) + X(1)m^{X(2)} \qquad (55)$$

APPENDIX E

DATA SOURCES

AQUEOUS ELECTROLYTIC SYSTEMS	REF.
Sodium Chloride and water at 100°C.	4
Potassium Chloride and Water at 25°C	2
Hydrogen Iodide and Water at 25°C	5
Rubidium Bromide and Water at 25°C	6
Rubidium Nitrate and Water at 25°C	6
Rubidium Iodide and Water at 25°C	6
Rubidium Chloride and Water at 25°C	6
Cesium Bromide and Water at 25°C	6
Sodium Thiocyanate and Water at 25°C	7
Potassium Thiocyanate and Water at 25°C	7
Cesium Nitrate and Water at 25°C	6
Calcium Nitrate and Water at 25°C	8
Calcium Chloride and Water at 25°C	2
Barium Chloride and Water at 25°C	11
Magnesium Chloride and Water at 25°C	10
Magnesium Bromide and Water at 25°C	10
Magnesium Iodide and Water at 25°C	10
Strontium Chloride and Water at 25°C	11
Nickle Chloride and Water at 25°C	9
Copper Chloride and Water at 25°C	9
NONAQUEOUS ELECTROLYTIC SYSTEM	
Lithium Chloride and Methanol at 25°C	13

APPENDIX E (cont'd)

	REF.
PURE SOLVENTS	
Methanol at 25°C	12
Water at 43.6°C and 77.0°C	14

APPENDIX F

Discussion of the standard state for an electrolyte

Equation 1 defines the chemical potential of component i in solution in terms of its mole fraction and the chemical potential in the standard state. In this identity μ_i° is a function of temperature and pressure alone. The standard state is chosen on the basis of one of two conventions. These conventions assume that a component i of a real solution is normally found to approach ideal behavior both as $x_i \longrightarrow 1$ and as $x_i \longrightarrow 0$. For an electrolyte, which does not have a finite measurable partial pressure, it is conventient to choose the standard state as unit mole fraction. For this case μ_i° is simply the free energy per mole of the pure component at the same temperature and pressure as the solution under discussion.

APPENDIX G

Description of the Integration Involved in the Gibbs-Duhem Equation

Equation (9) was arrived at by a special type of integration performed at constant composition. It implies that composition of the solution remains unchanged while it is being formed. This may be achieved by simultaneously adding the components, 1, 2, 3, etc, in the ratio of their mole fractions in the final solution. Thus, the limits of the integration are from zero moles of component i to the final number of moles in the final solution. During this process, the mole fraction of component i remains constant at x_i.

An alternate more general method of deriving Equation (11) consists of using Euler's Theorem. Recognizing that for a binary system F is a function of two variables at constant temperature and composition:

$$F = f(n_1, n_2,) \qquad P, T \text{ are constant} \qquad \text{(G-1)}$$

Therefore, by the methods of calculus:

$$dF = \left[\partial F / \partial n_1\right]_{n_2} dn_1 + \left[\partial F / \partial n_2\right]_{n_1} dn_2 \qquad \text{(G-2)}$$

or,

$$dF = \mu_1 dn_1 + \mu_2 dn_2 \qquad \text{(G-3)}$$

For a binary system Equation (10) becomes:

$$dF = \mu_1 dn_1 + \mu_2 dn_2 + n_1 d\mu_1 + n_2 d\mu_2 \qquad \text{(G-4)}$$

Combining Equations (G-3) and (G-4) results in Equation (11) written for a binary system:

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \qquad \text{(G-5)}$$

LITERATURE CITED

1. H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolyte Solutions*, Reinhold Publishing Corporation, New York, 1950.
2. G. N. Lewis and M. Randall, *Thermodynamics*, McGraw-Hill Book Company, Inc. New York, 1961.
3. E. A. Guggenheim, *Thermodynamics*, North-Holland Publishing Company, Amsterdam, 1967.
4. Robert C. Weast, Editor in Chief, *C.R.C. Handbook of Chemistry and Physics*, 51st Edition, 1964.
5. H. S. Harned and R. A. Robinson, *Trans. Faraday Society*, *37*, 302 (1941).
6. R. A. Robinson, *J. Am. Chem. Soc.*, *59*, 84 (1937).
7. R. A. Robinson, *J. Am. Chem. Soc.*, *62*, 3131 (1940).
8. R. A. Robinson, *J. Am. Chem. Soc.*, *62*, 3130 (1940).
9. R. A. Robinson and R. A. Stokes, *Trans. Faraday Society*, *36*, 1137 (1940).
10. R. A. Robinson and R. H. Stokes, *Trans. Faraday Society*, *36*, 733 (1940).
11. R. A. Robinson, *Trans. Faraday Society*, *36*, 735 (1940).
12. V. N. Zubarev and P. G. Prusakov, and L. V. Sergeeva (USSR), *Tr. Mosk. Energ. Inst.*, *111*, 103-13 (Russ.), (1972)
13. P. A. Skabichevski, *Russian Journal of Physical Chemistry*, *43*, 1432 (1969).
14. American Society of Mechanical Engineers, *Steam Tables*, (1967).
15. J. O'M. Bockris and A. K. N. Reddy, *Modern Electrochemistry*, *1* (1973).

LITERATURE CITED (cont'd)

16. N. Bjerrum, Z. Elektrochem., 24, 259 (1907).

17. P. Debye and E. Huckel, Physik. Z., 24, 185, 334 (1923).

18. J. N. Bronsted, J. Am. Chem. Soc., 44, 932 (1922).

19. E. A. Guggenheim, Phil. Mag., 19, 588 (1935).

20. G. N. Lewis and M. Randall, J. Am Chem. Soc., 43, 1112 (1921).

21. W. L. Masterton and E. J. Slowinski, Elementary Mathematical Preparation for General Chemistry, 181 (1974).