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THE ENTHALPY OF INTERACTION OF NONELECTROLYTE PAIRS IN DILUTE A--ETC(U)
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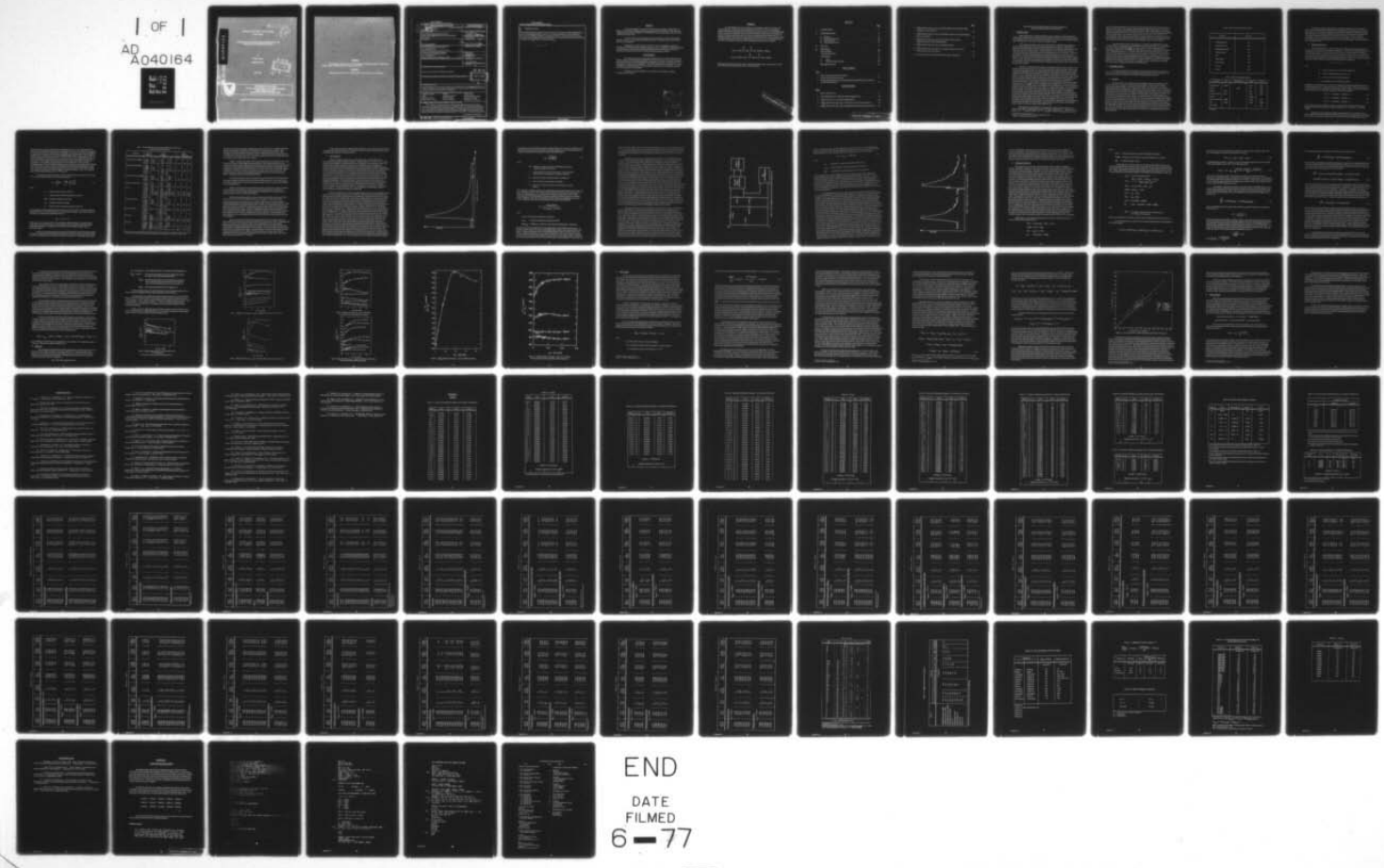

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SPECIAL PUBLICATION ARCSL-SP-77003

(EC-SP-77004)

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THE ENTHALPY OF INTERACTION OF NONELECTROLYTE PAIRS IN DILUTE AQUEOUS SOLUTIONS

by

James J. Savage

Research Division

April 1977

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1. REPORT NUMBER ARCSL-SP-77003	2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) THE ENTHALPY OF INTERACTION OF NONELECTROLYTE PAIRS IN DILUTE AQUEOUS SOLUTIONS.	5. TYPE OF REPORT & PERIOD COVERED Special Publication July 1973 — January 1975
	6. PERFORMING ORG. REPORT NUMBER EC-SP-77004
7. AUTHOR(s) James J. Savage, Ph.D.	8. CONTRACT OR GRANT NUMBER(s) DAAA15-71-A-0074-005
9. PERFORMING ORGANIZATION NAME AND ADDRESS Director, Chemical Systems Laboratory Attn: DRDAR-CLB-C Aberdeen Proving Ground, Maryland 21010	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Director, Chemical Systems Laboratory Attn: DRDAR-CLJ-I Aberdeen Proving Ground, Maryland 21010	12. REPORT DATE April 1977
	13. NUMBER OF PAGES 89 p.
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report) UNCLASSIFIED
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE NA

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

This Special Publication consists of material submitted as a doctoral dissertation to the Chemistry Department of the University of Delaware as a result of a research study program under the sponsorship of the Department of the Army and Edgewood Arsenal (Contract DAAA15-71-A-0074-005).

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Additivity principle	Density	Hydrocarbons
Amides	Enthalpy of dilution	Nonelectrolyte
Aqueous solutions	Excess enthalpy	Partial molal expansibility
Binary-solute mixtures	Heat of interaction	Partial molal volume
		Polyhydroxy compounds

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The enthalpy of dilution of single- and binary-solute aqueous mixtures of a series of compounds were measured from about 0.2 to 2 mol/kg^{-1} at 25°C. The compounds included in the study were N-methylformamide, N-methylacetamide, N-methylpropionamide, N-butylacetamide, urea, ethylene glycol, pentaerythritol, glucose and sucrose. The apparent molal volumes of each solute in dilute aqueous solutions were measured at 0°, 25°, and 45°C. A statistical analysis of the

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20. ABSTRACT (Contd)

excess enthalpy data showed that solute-pair heats of interaction could be roughly represented by a sum of several independent group interactions. The sign and magnitude of the six interactions between a CH_2, CONH and CHOH functional group are reported. These group interaction values were used to calculate the pairwise heats of interaction for several previously reported nonelectrolytes to within 45 cal kg/mol of prior experimental values.

PREFACE

The work described in this report was a research study program conducted by the author at the University of Delaware under the sponsorship of the Department of the Army and Edgewood Arsenal (Contract DAAA15-71-A-0074-005). This work was started in July 1973 and completed in January 1975.

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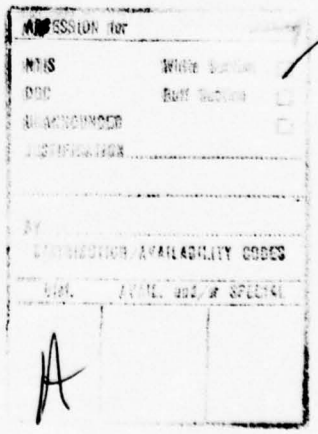
Acknowledgment

The author wishes to express his sincere appreciation to Dr. Robert H. Wood for his patience, guidance and encourgement throughout the course of this study. The author is indebted to Dr. Peter Thompson for his willing guidance and suggestions and to Mr. David Schneck for his administrative expertise and encouragement. The author would also like to thank the U. S. Army, and Edgewood Arsenal in particular for providing their support of this work through a formally authorized long-range training program.

I dedicate a very special thanks to my wife, Rita, for her patience, constant encouragement and support.



SUMMARY

An LKB 10700-2 batch microcalorimeter was modified to improve its accuracy and reproducibility and to shorten the time required for each experiment. The excess enthalpies, partial molal volumes and partial molal expansibilities of aqueous solutions of N-methylformamide, N-methylacetamide, N-methylpropionamide, N-butylacetamide, ethylene glycol, pentaerythritol, glucose, sucrose, urea and binary mixtures of these compounds have been measured at 25°C. A statistical analysis of the pairwise heats of interaction calculated from the excess enthalpies showed that these interaction heats could be roughly represented by a sum of several independent group interactions. The sign and magnitude of the following group interactions are reported:

$$(CH_2)-(CH_2),\ (C(=O)-NH)-(C(=O)-NH),\ (CHOH)-(CHOH),$$

$$(CH_2)-(CHOH),\ (CH_2)-(C(=O)-NH) \text{ and } (C(=O)-NH)-(CHOH).$$

These group interaction values were used to calculate the pairwise heats of interaction for several previously reported nonelectrolytes with a σ of 45 cal kg/mol^2.

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I. INTRODUCTION.

Many theories exist to explain the behavior of ions in aqueous as well as nonaqueous solutions; yet the development of such theories to explain the behavior of nonelectrolyte solutions is just beginning. This is in spite of the fact that the behavior of nonelectrolyte solutions should be easier to interpret since long-range forces due to charges are absent.

The overall goal of this research was to understand how individual functional groups affect the interactions between pairs of nonelectrolytes in aqueous solutions. Around each nonelectrolyte molecule there will be one or more layers of water molecules which differ from the bulk water; this is the cosphere model.[1] When the cosphere on one nonelectrolyte molecule overlaps the cosphere on another molecule, the resulting interaction forces, attractive or repulsive, were expected to depend on dipole-dipole effects, van der Waal forces, the effect due to the replacement of water hydrogen bonds with intermolecular hydrogen bonds and cosphere overlap forces.[1] In this work the heats of interaction resulting from a dilution of a nonelectrolyte solution were measured. The heats were measured since very little is known about the interactions between nonelectrolytes in aqueous solutions and because enthalpy measurements are easily performed with the equipment available.

Kauzmann demonstrated[2] the tendency of nonpolar groups in proteins to adhere to one another in aqueous environments. This is termed hydrophobic bonding. Qualitative results found in the work of Scheraga[3] and the free energy data for the large tetraalkylammonium salt systems[4] suggests that hydrophobic bonds are attractive. Based on the hydrogen bonding found in amide solutions[5-9] one would expect an attractive interaction between these groups. In this study we are trying to measure quantitative values for the heats of these interactions. Quantitative values for the heats of interactions between different molecular groups should provide accurate predictions for the thermodynamic behavior of large molecules that are composed of pieces for which the interactions are known. A large variety of molecules could conceivably be predicted with a small amount of data. For example, once the interaction between a hydrocarbon with a hydrocarbon, a hydrocarbon with a (CHOH) group and a (CHOH) with a (CHOH) group are known it should be possible to predict the properties of a wide variety of alcohols, hydrocarbons and carbohydrate mixtures simply on the basis of these three parameters. When the interaction parameters for a wide variety of functional groups are measured, it should be possible to understand how various nonelectrolytes interact with proteins to alter their relative stability in aqueous solutions. It may even be possible to predict for example the ability of an enzyme to bind to a substrate and perhaps predict small changes in the known enzyme structures for this process. This research will not achieve such far-ranging goals, but these objectives are possible and as a start, the present research has collected data on a wide variety of nonelectrolytes to determine if accurate predictions of the heats of interaction on nonelectrolytes can be made from a knowledge of the individual group interactions involved by using a simple additivity rule.

Thermodynamic investigations of nonelectrolyte systems have been reported by several authors, Kozak, Knight and Kauzmann,[10] Friedman and Krishnan,[11] Lilley and Scott,* Lange *et al.*,[12,13] Franks,** Wood *et al.*,[14,15] and others. Much of the earlier data are not

* Lilley, T. H., and Scott, R. H. Private communication, 1974.
** Franks, F. Private communication, 1975.

useful in investigating the heats of interaction between nonelectrolyte pairs and their mixtures in dilute solutions. Some of the data have not been measured with enough accuracy or have been obtained with equipment not suitable for heats of dilution. Most of the enthalpy data consists of dilutions of single nonelectrolytes. The aim of this research was to measure the effect that different functional groups have on the observed pairwise heats of interaction. This could only be accomplished by testing calorimetrically dilutions of binary nonelectrolyte mixtures for which the data is extremely scarce. Also it is only by a large systematic study such as performed here that the formulation of overall trends in the data and quantitative results could be expected.

The compounds chosen for this study were: N-methylformamide (NMF), N-methylacetamide (NMA), N-methylpropionamide (NMP), N-butylacetamide (NBA), urea (U), ethylene glycol (EG), pentaerythritol (P), glucose (G), and sucrose (S). Aqueous solutions of these compounds as well as their I-I mixtures were diluted from 2 molal to approximately 0.2 molal or lower. McMillan-Mayer theory [16] was used to show that measurements performed in this way resulted in the heats of interactions for pairs of solute molecules. These heats of interaction were then analyzed by a general least squares program to determine the quantitative values for the pairwise heats of interaction between hydrocarbon groups, amide groups, (CHOH) groups and the unlike group interactions. With these data we were able to obtain for the first time a quantitative prediction of the enthalpies of interactions for a number of simple nonelectrolytes containing different amounts of hydrocarbons, amide and (CHOH) groups.

II. EXPERIMENTATION.

The experimental procedure and results of the density measurements are presented in this section as well as a description of the equipment used to measure the heats of dilution. The procedure and method of calculation of the heats of dilution are also presented.

A. Solutions.

Nine compounds were tested for the heat of dilution and density experiments. These were the following: four amides - N-methylformamide (NMF), N-methylacetamide (NMA), N-methylpropionamide (NMP), and N-butylacetamide (NBA); four polyhydroxy compounds - ethylene glycol (EG), pentaerythritol (P), glucose (G), and sucrose (S); and urea (U). The NMP and NBA were Eastman Kodak high-purity compounds and the NMF was "Baker" grade material; these compounds were used as received. The NMA was Aldrich analytical grade which was recrystallized three times in a dry box and then zone-melted for five days before use. Ethylene glycol was Fischer-certified and used as received. Glucose, sucrose and urea were Fischer-certified and dried in a vacuum oven for three days at 60°C before use. The pentaerythritol was Baker analytical grade which was recrystallized from water three times and dried in a vacuum oven for three days at 90°C before use. Table 1 lists the water content of all the compounds, as determined by Karl Fischer analysis, and table 2 the impurities of the Fischer certified compounds as listed on the bottle labels. The NMF, NMP and NBA were analyzed (gas-chromatography) and found to be greater than 99.3% pure. The only impurity found was water which was corrected for in making up these solutions. The pentaerythritol which had a melting range of 252-258°C before purification melted at 260°C after purification.

Table 1. Water Content by Karl Fischer Analysis

Compound	Wt % H_2O
N-Methylformamide	0.50
N-methylacetamide	<0.03
N-Methylpropionamide	0.60
N-Butylacetamide	0.19
Urea	0.03
Ethylene glycol	0.06
Pentaerythritol	0.06
Glucose	0.08
Sucrose	<0.03

Table 2. Fischer-Certified Label Impurities

Compound	Urea	Ethylene glycol	Glucose	Sucrose
Insoluble matter	0.009*		0.002	0.003
Acidity		0.009	0.01	0.002
Chloride	0.003		0.003	0.003
Sulfate and sulfite	0.001		0.002	0.001
Arsenic			0.00001	
Heavy metals (Pb)	0.0003		0.0002	0.002
Iron	0.0002		0.0001	0.0001
Invert sugar				0.05

* % Impurity.

All solutions of these compounds were prepared by weight to ±0.01% with distilled water which was trickled through a Barnstead ion exchange column. Bouyancy corrections were made in all work. In all cases the solutions were made up and used within a 36-hr period during which time they were stored in polyethylene screw cap bottles. This treatment of the solutions was thought advisable to forestall any decomposition which might occur due to bacterial contamination. This is especially important in the case of the sugars. In three experiments, a solution of sucrose was measured approximately 52 hours after preparation. The heat of dilution was an average of 2% low.

B. Density Measurements.

The solution densities of 1 and 0.3 molal, of the compounds used in this study, were measured at 0, 25 and 45°C using a single-stem dilatometer. The density of pentaerythritol (P) was measured at 0, 25 and 45°C for only one concentration (0.3 m) because of its low solubility in water. The dilatometer was constructed from a 25-cc volumetric flask to which a 21-cm-long stem of precision bore tubing (approximately 1-mm inside diameter) was attached. The dilatometer was loaded with degassed material by a syringe equipped with Teflon tubing. The experiment measures volumes of a known weight of solution using the following general equation:

$$V = V^\circ - A \times L \qquad (1)$$

where

V = volume of material in cc of a known weight in gm

V° = volume of dilatometer to top of stem in cc

A = stem area in cm^2 not filled with material

L = stem length in cm not filled with material.

Calibrations were performed at 0, 25 and 45°C on degassed, ion-exchanged, distilled water by use of published density data.[17] Bath temperatures were monitored within ±0.02°C with a platinum resistance thermometer. The calibrations provided the capillary reading L as a linear function of the total volume shown in the following equations for the three temperatures:

$$0^\circ C \quad V = 25.3956(3) - 0.01833 \times L \qquad (2)$$

$$25^\circ C \quad V = 25.4016(5) - 0.01828 \times L \qquad (3)$$

$$45^\circ C \quad V = 25.4079(5) - 0.01826 \times L \qquad (4)$$

where V and L have been described in equation 1 and the numbers in the parentheses are the standard deviations of the last digit for a single measurement, *i.e.*, 25.3956(3) = 25.3959 to 25.3953.

The solutions were prepared by weight using deaerated water. The dilatometer was rinsed several times with water followed by Fischer-certified acetone and dried inside with a stream of dry nitrogen. The outside of the dilatometer was then wiped with a slightly damp towel and

placed in the balance case to equilibrate for approximately one hour. The empty weight of the dilatometer was recorded when two successive weighings, five minutes apart, agreed. The apparatus was then filled with solution, again allowed to equilibrated in the balance case and the full weight of the dilatometer recorded when two successive weighings agreed. Measurements of stem length not filled with solution (L) were then made at 0, 25 and 45° ±0.01°C with a caliper gauge to ±0.01 cm. Thermal equilibrium of the dilatometer and its contents with each bath temperature was achieved when three successive height measurements performed five minutes apart agreed. Because the expansibility of the solutions exceeded the capacity of the dilatometer over the measured temperature range, all the 45°C height measurements were made after some solution had overflowed from the dilatometer. The outside of the dilatometer was then rinsed with distilled water, wiped with a damp towel, allowed to equilibrate in the balance case and weighed. The solution densities were calculated by dividing the solution weight by the measured solution volume. The estimated precision of the density measured was 1×10^{-4} gm/cm^3.

The apparent molal volume of the 1 and 0.3 molal solutions were calculated at 0, 25 and 45°C from the solution densities using the following equation:

$$\phi_V = \frac{1}{d}\left[MW - \frac{1000}{\underline{m}}\left(\frac{d - d^\circ}{d^\circ}\right)\right] \qquad (5)$$

where

ϕ_V = apparent molal volume in cm^3/mol

d = solution density at desired temperature in gm/cm^3

MW = molecular weight of solute in gm

$\underline{m}$ = molality of solution in mol/kg

d° = density of water at desired temperature in gm/cm^3.

An extrapolation to infinite dilution of ϕ_V versus $\underline{m}$ plots at 0, 25 and 45°C was used to obtain the partial molal volumes at infinite dilution ϕ_V° for the compounds measured. These values of ϕ_V° were then fitted to a second order polynomial of the form:

$$\phi_V^\circ = a + bt + ct^2$$

where a, b and c are constants and t is the temperature in degrees centigrade. The partial molal expansibility at infinite dilution ϕ_E°, was then calculated for each solute by differentiating these polynomials with respect to temperature. The results as well as available literature data are presented in table 3.

Of the nine compounds studied, N-methylformamide (NMF) and N-butylacetamide (NBA) were the only compounds for which literature density data could not be found. The data are shown in table 3 are ±0.02 based on the precision of the density measurement. Comparison of the present

Table 3. The Partial Molal Volume (ϕ_V) and Partial Molal Expansibility (ϕ_E) of Aqueous Nonelectrolyte Solutions

Compound	m / mol/kg	ϕ_V / cm^3/mol			ϕ_E / cm^3/mol K		
		0°C	25°C	45°C	0°C	25°C	45°C
N-Methylformamide (NMF)	0.9989	54.8	56.6	57.8			
	0.2987	54.9	56.6	57.9			
	0 expt.	54.9 (3)*	56.6 (3)	57.9 (3)	.070	.066	.064
N-Methylacetamide (NMA)	1.0003		73.3	74.5			
	1.0000	71.9					
	0.3000	72.5	73.5	74.7			
	0 expt.	72.7 (3)	73.6 (3)	74.8 (3)	.023	.049	.070
	0 lit.[18]		73.9 (1)				
	0 lit.[19]		72.9 (4)				
N-Methylpropionamide (NMP)	0.9977	86.8	88.7	90.3			
	0.2981	86.0	89.3	90.8			
	0 expt.	88.4 (3)	89.5 (3)	90.9	.030	.058	.082
	0 lit.[20]		90.4 (1)				
N-Butylacetamide (NBA)	1.0001	117.4	120.9	123.9			
	0.2987	119.1	121.6	124.2			
	0 expt.	119.8 (3)	121.9 (3)	124.3 (3)	.064	.104	.136
Urea (U)	1.0000	42.1	44.3	45.4			
	0.3001	41.6	43.9	45.1			
	0 expt	41.4 (3)	43.8 (3)	44.9 (3)	.119	.073	.037
	0 lit.[21]	41.75 (10)	44.20 (10)	45.10 (10)	.116	.073	.039
	0 lit.[22]	41.9 (3)	44.2 (3)	45.3 (3)	.113	.072	.039
	0 lit.[18]		43.8 (1)				
	0 lit.[23,24]		43.7 (3)				
Ethylene glycol (EG)	1.0111	53.3	54.5	55.4			
	0.9993	53.4	54.5				
	0.3003	53.4	54.6	55.5			
	0 expt.	53.4 (3)	54.6 (3)	55.6 (3)	.047	.049	.051
	0 lit.[25]		54.2 (2)				
	0 lit.[26]		54.3 (3)				
Pentaerythritol (P)	0.3000	99.7 (3)	102.0 (3)	103.6 (3)	.099	.085	.075
	0 lit.[27]		101.3 (5)				
	0 lit.[28]		101.9 (1)				
	0 lit.[29]		101.9 (1)				
Glucose (G)	0.9869	109.4	112.3	113.9			
	0.3005	109.0	112.2	114.0			
	0 expt.	108.8 (3)	112.2 (3)	114.0 (3)	.162	.110	.070
	0 lit.[22]	108.8 (1)	112.1 (1)	113.7 (1)	.161	.103	.057
Sucrose (S)	1.0002	208.1	212.6	215.2			
	0.3000	206.7	211.5	214.5			
	0 expt.	206.3 (3)	211.0 (3)	214.2 (3)	.204	.173	.148
	0 lit[30]	206.4 (1)	211.5 (1)				
	0 lit.[22]	206.3 (1)	211.0 (1)	213.6 (1)	.220	.156	.104

* The number in the parenthesis represents the estimated error of the last digit, *e.g.*, 54.9 (3) = 54.6 to 55.2.

ϕ_E° data for urea, sucrose, and glucose with literature data at 0°C and 25°C demonstrates that this accuracy was achieved. The ϕ_E data at 45°C appear to be conisderably less accurate. This is probably a result of the experimental procedure used to measure the density at 45°C. The expansibility of all the solutions exceeded the capacity of the dilatometer at this temperature and its contents after a measurement at 45°C. The errors involved in this procedure would account for the reduced accuracy noted in ϕ_E° for the 45°data.

Hepler[31] and Neal and Goring[22] have reported that the ϕ_E° of a substance in water could be used as an index of its structural interaction with water. They considered water to be an equilibrium mixture of bulky icelike species with a relatively low density and a denser species formed by breaking or deforming the hydrogen bond network of the bulky species. Hydrophobic solutes are believed to cause an increase in water structure around the solute molecules; when the solution temperature is increased, the change in ϕ_V° would be less than expected for an ideal solute. The opposite behavior is expected for hydrophilic solutes which break water structure around the solute. This produces larger than expected values in ϕ_E°.

Neal and Goring believe that the magnitude of ϕ_{E_2} (the apparent specific expansibility), shows good correlations with the ability of a solute to alter water structure. Large values of ϕ_{E_2} were used to identify solutes as water structure breakers while smaller or negative values indicated structure-making solutes.

Hepler[31] used the results of several literature studies on the density of aqueous solutions to show that the sign of $(\delta\phi_E^\circ/\delta T)_p$ is positive for structure-making solutes and negative for structure breakers. He also considered the magnitude of this slope term to be indicative of the ability of a solute to make or break water structure.

Based on these theories, glucose, sucrose and urea were classified as structure breakers because each of these solutes had large values for ϕ_{E_2} and exhibited a fairly large negative change in ϕ_E° with respect to temperature. The values of $(\delta\phi_E^\circ/\delta T)_p$ for N-methylacetamide, N-methylpropionamide and N-butylacetamide, shown in table 3, are fairly large and positive. These solutes can therefore be classified as structure makers. The results of other workers using nuclear magnetic resonance spectroscopy[32] and dielectric constant measurements[33] have also shown that these amides appear to make water structure. N-Methylformamide and ethylene glycol do not show a sufficient ϕ_E° slope change to classify these solutes as structure makers or breakers whereas pentaerythritol may be a structure breaker due to its positive ϕ_E° slope. The magnitude of this slope change however is much smaller than that found for other structure-breaking solutes such as urea and glucose.

The structure theories of Neal and Goring and Hepler encounter problems when the results obtained for ethylene glycol and pentaerythritol are examined more closely. Hydrophilic OH groups in a molecule were considered to have a structure-breaking effect by these authors. Pentaerythritol and ethylene glycol should therefore exhibit structure-breaking behavior because of the number of hydrophilic OH groups in these molecules. Yet based on Neal's and Goring's and Hepler's theory, ethylene glycol is neither a structure breaker or maker and pentaerythritol is only a marginal structure breaker. The validity of classifying amides as structure makers is also questionable since other experimental techniques have been used to classify these compounds as either water structure makers[32] or breakers.[34]

Finally, even the validity of using ϕ_E° data to determine a solutes effect on water structure is uncertain since Holtzer and Emerson[34] have questioned the usefulness of water structure itself in rationalizing the properties of aqueous solutions.

C. The Calorimeter.

All heat of dilution experiments were performed using an LKB 10700-2 batch microcalorimeter previously described by Wadso,[36] LKB Instruments[37] and Levin.[38] It is of the heat flow design utilizing a rotatable calorimeter unit suspended in a thermostated air bath. The rotatable unit consists of an aluminum block serving as a heat sink. Block temperature is continuously monitored with a thermistor bridge. Two 18-carat-gold reaction cells are located in the aluminum block with each cell divided into two compartments whose volumes are approximately 3 and 5 cc respectively. During an experiment, the rotation of the calorimeter unit allows the contents of the cell compartments to mix. Heaters located within each cell are used to calibrate the calorimeter. Each reaction cell is sandwiched between two semiconductor thermopiles. The difference in temperature produced between the sample and reference cells during an experiment causes a voltage difference which is proportional to the difference in heat flow between the cells through the thermopiles to the aluminum block. The heat of reaction is proportional to the integral of the heat flow. The thermopiles sense this temperature difference as a voltage which is then amplified by a Keithley instruments model 150B microvoltmeter and fed into a Sargent recorder, equipped with a ball-and-disk integrator. An example of a typical heat of dilution curve is given in figure 1. The area under this curve, when multiplied by the calorimeter constant is a direct measurement of the heat produced in an experiment.

Since the calorimeter was not used for approximately one year, it was thoroughly checked for proper operation before the start of any experiments. The thermostated air bath, which was inoperative due to a broken heater,and cooler, was modified by using a drinking fountain to supply the calorimeter with 15°C cooling water. This change was made because no cost was involved for the cooler and any repairs needed could be easily made by the maintenance staff of the University. The 85-ohm nichrome heater for the air bath was found to be shorted out and was modified in design to prevent possible future electrical shorts. A voltmeter was inserted into the air bath heater circuit to allow continuous monitoring of the amount of power supplied to the air bath heater. Previously a panel light was used to indicate whether the heater was full on or off. An adjustable resistor (R_{max} = 100 ohms, R_{exp} = 10 ohms) was mounted externally and wired in series with the 85-ohm air-bath heater. As a result of this change it is now possible to adjust the 85-ohm air-bath heater to half power using the external resistor and continuously monitor the power level with the added voltmeter. Coolant water temperature was set to provide an exit water temperature of 15°C with a flow rate of about 0.2 liters per minute for 25°C bath operation (860 on thermistor dial). The air bath and block temperatures were measured at the above setting with a thermocouple, using an ice bath reference junction, checked against a platinum resistance thermometer in a 25.00- ± -0.01°-C water bath. The thermocouple voltage read with the Keithley microvoltmeter indicated the calorimeter's air bath and block temperature was 25.00 ±0.02°C. Another check of this temperature was provided with a microvoltmeter null reading when the thermocouple reference junction was placed in the air bath while the primary junction was mounted in the block. The resistance of the calibration heater located in the sample and reference cells was measured with an ESI voltohmmeter and found to be 50.060 ohms and 49.827 ohms respectively. These measured values compared favorably with the previously measured values of 50.06 ohms and 49.835 ohms by Dr. R. Wood on 20 September 1971. The calorimeter has a power supply which provides constant

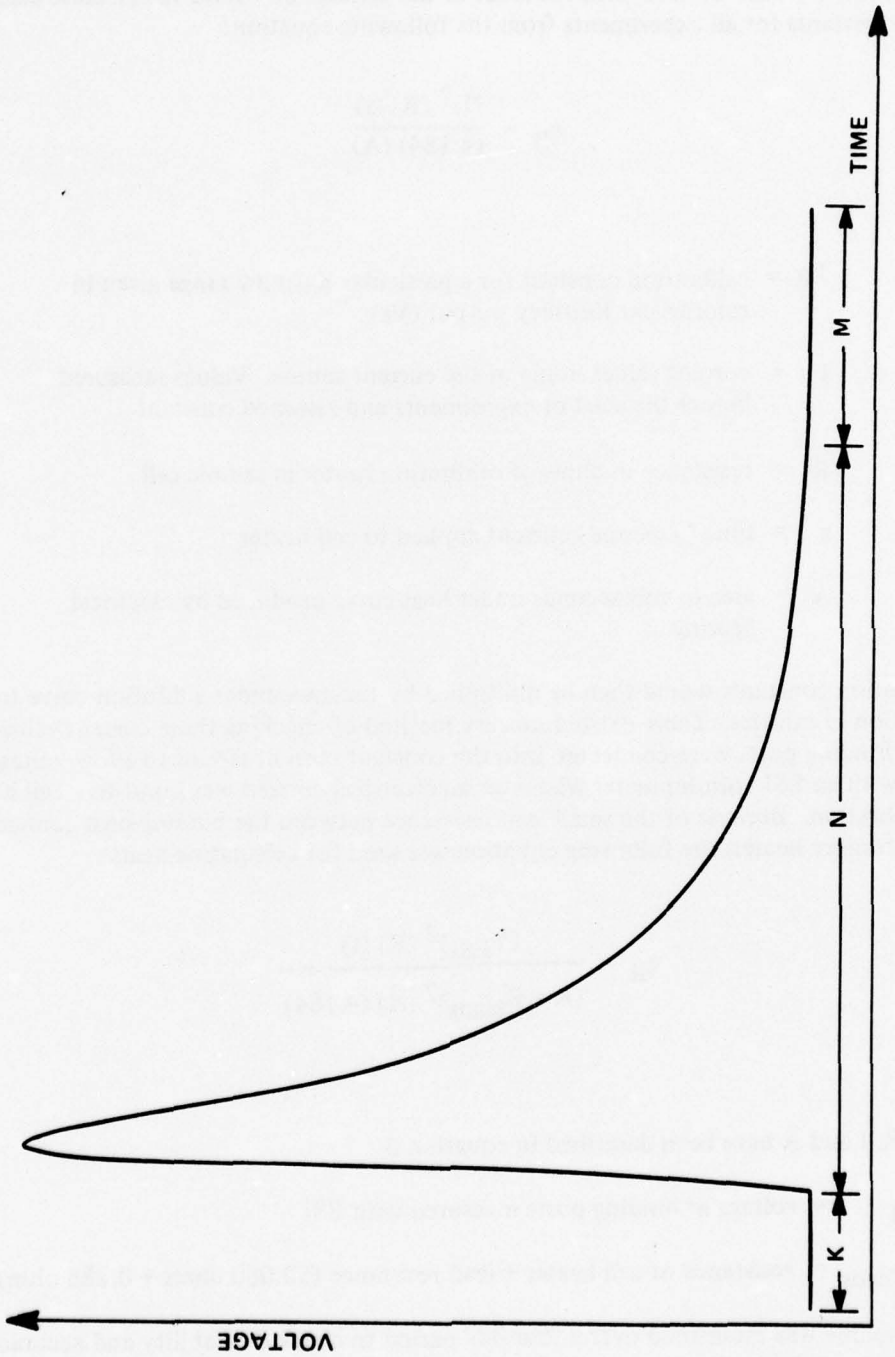

Figure 1. Heat of Dilution Curve

current inputs to the cell calibration heaters. In the past these current values and resistances of the calibration heaters would be used with the areas of the calibration curves to calculate calorimeter calibration constants for all experiments from the following equation:

$$\epsilon_R = \frac{(I)^2 (R) (t)}{(4.184) (A)} \tag{6}$$

where

ϵ_R = calibration constant for a particular Keithley range given in calories per Keithley output (Vs)

I = current values in ma of the current source. Values measured before the start of experiments and assumed constant

R = resistance in ohms of calibration heater in sample cell

t = time in seconds current applied to cell heater

A = area in volt seconds under heat curve produced by electrical heating

These calibration constants would then be multiplied by the area under a dilution curve to give the heat of dilution in calories. There existed no easy method of checking these current values on a daily basis. Binding posts were connected into the constant current circuit to allow voltage monitoring with an ESI voltohmmeter whenever an electrical current was input to a cell heater during a calibration. Because of the small lead resistance between the binding-post connection and the calorimeter heater, the following equation was used for calculating heats:

$$\epsilon_R = \frac{(V_{ESI})^2 (R) (t)}{(R + R_{leads})^2 (A) (4.184)} \tag{7}$$

where

ϵ_R, R, t and A have been described in equation 6

V_{ESI} = voltage at binding posts measured with ESI

$R+R_{leads}$ = resistance of cell heater + lead resistance (50.060 ohms + 0.286 ohm).

The current source was monitored over a four-day period to check its stability and accuracy. A 40-ohm precision resistance box and a 10-ohm NBS standard resistor were substituted for the cell heaters. Voltage measurements off the 10-ohm NBS standard resistor were made with the ESI whenever current was supplied from the constant current source. The current output was found to be 0.8% low on the 3 ma range, ±0.025% to ±0.29% for the 10 ma range, ±0.02% to ±0.05% for the 60 ma range and ±0.02% to ±0.05% for the 90 ma range. Current stability for the four-day test

period was ±0.33% for the 3 ma range, ±0.5% for the 10 ma range, ±0.3% for the 60 ma range and ±0.3% for the 90 ma range. The accuracy and current stability from day to day during these tests was not within the manufacturer's specification of ±0.1% and ±0.05% respectively. This presented no problems since the changes made to the calorimeter allowed current measurements for each experiment.

The data retrieval system was augmented with the addition of a high-frequency filter (τ = 2s) on the output of the Keithley, a Digitek digital voltmeter, interface, teletypewriter and computer. The signal from the digtal voltmeter is fed through an interface, designed by Mr. Richard Breen, to a computer teletype equipped with a paper tape punch system. The paper tape records the amplified voltages in digitized form as a function of time. These voltages are processed with a computer program on a Data-General-Nova-1200 minicomputer to yield the area of the heat curve. This method of data retrieval was tried because occasional errors, in the heats measured, as much as ±2% were found using the recorder's ball-and-disk integrator. The program which processes the voltage data of an experiment can be found in appendix A. The software was tested using the calibration heater system of the calorimeter to provide simulated heats of dilution. Experiments were performed to determine the data collection rate and the number of points necessary for an accurate heat determination. A data collection rate of one voltage point every 6 seconds was chosen since an error of only 0.04% of the experimental heat was found at this setting when compared with a one-second-date-collection rate for a 0.6-calorie heat effect. The heat curve shown in figure 1 was divided into three sections. The points in the first and third section, K and M respectively were used to calculate a least squares baseline. The points in section N were then integrated using Simpson's rule to provide the curve area under section N. The area between the curve and baseline is then calculated as the area under the curve minus the area under the baseline. The number of voltage points used for each curve section was, 20 points (2 min) for K, 150 points (15 min) for N and 50 points (5 min) for M. These values were chosen since they allowed measurement of greater than 99.9% of the experimental heat and provided a long-term precision, based on calibration experiments with mixing shown in tables A-1 to A-7, appendix A of: ±1.8% for the 0.01-mv scale, ±1.3% for the 0.03-mv scale, ±0.6% for the 0.1-mv scale, ±0.5% for the 0.3-mv scale, ±0.2% for the 1-mv scale, ±0.1% for the 3-mv scale and ±0.08% for the 10-mv scale. Thus the software retrieval system represents an order of magnitude improvement in the precision of the data collected with the ball-and-disk integrator of the recorder.

The results of tables A-1 to A-7, appendix A indicate that the precision of calibration constants determined for several months was excellent and was greater on high-heat ranges. Because of these results, experiments were performed to determine range factors which would allow calculation of calibration constants for any heat range from a single calibration measurement on the 10-mv range each day. The range factors are ratios of the Keithley output voltage to the input voltage. These were measured with an ESI voltohmmeter off an NBS standard resistor when the Keithley microvoltmeter was driven full-scale. A typical circuit diagram for these experiments is shown in figure 2. The results of two ratio experiments performed two weeks apart were averaged and are shown in table A-8 (appendix A) as range factors. Assuming the 10-mv range of the Keithley to be correct (range factor = 1), the following adjusted-Keithley ranges (KR) were obtained by dividing the respective Keithley range by its range factor: the 3-mv range is then 2.9904 mv, the 1-mv range is 0.9962 mv, the 0.3-mv range is 0.3000 mv, the 0.1-mv range is 0.1000 mv and the 0.03-mv range is 0.0301 mv. Electrical noise problems prevented the accurate measurement of the 0.01-mv range factor, and consequently this range factor was set at unity, making the 0.01-mv Keithley range exactly 0.01 mv. Based on the other range measurements, setting this range factor at unity could lead to calibration constant errors for this range of ±0.4%

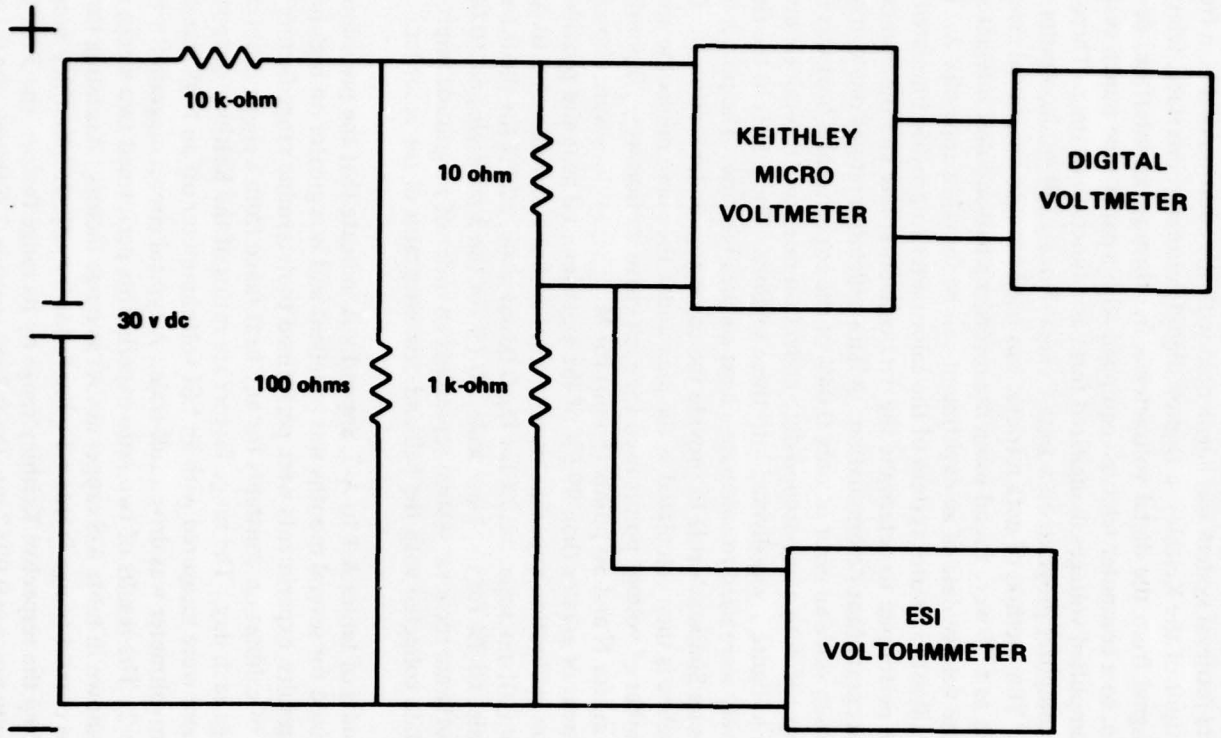

Figure 2. Circuit Diagram Used to Determine Keithley Range Factors

which is acceptable since the long-term calibration constant precision was ±1.8%. The following equation indicates how these adjusted-Keithley ranges and a single 10-mv electrical calibration with mixing each day were used to calculate calibration constants for all the other heat ranges:

$$\epsilon_R = (\epsilon_{10\ mv} \times KR)/10\ mv \tag{8}$$

where ϵ

ϵ_R = calibration constant for the desired Keithley range

ϵ_{10mv} = 10-mv calibration constant calculated from equation 7

KR = actual Keithley range obtained by using the range factors.

Table A-8 presents a comparison between the average calibration constants for various heat ranges obtained from long-term calibration experiments listed in tables A-1 through A-7, and calibration constants for these ranges calculated using the average 10-mv calibration constants is good since the largest difference noted is only 0.35% for the 1-mv range. This procedure was justified by the fact that the Keithley range resistors are rated at ±0.025% and the stability of the digital voltmeter and ESI are ±0.01% and ±0.02 respectively. Thus only one calibration per day on the 10-mv range provides calibration constants for all the heat ranges of the calorimeter. This procedure represents a savings in time of as much as five hours per day depending on the number of experiments performed.

On a high-sensitivity range (1 μv), electrical noise, errors due to the heat of friction of the sample liquid against the cell walls and baseline drift are at a maximum. An attempt was made to improve the accuracy of the heats under these conditions by reducing the number of points measured. Less baseline drift would be recorded and any loss in the experimental heat measured could be corrected with a calibration run under the same conditions. Ten electrical calibrations with mixing were performed on the 1-μv range by inputing 1 ma through the sample cell heater for 45 seconds. The areas under these curves were calculated using several different curve-section times. The results are listed in table A-9. The heat curves were found to fall into two classes due to different heat curve profiles. Six of the electrical calibrations produced normal heat curves like the one shown in figure 3,A while four of the calibrations had a large negative peak followed by a positive peak at the beginning of the heat curve like that shown in figure 3, B. This anomalous peak in four of the ten experiments appears to be a result of mechanical stress on the semiconductor thermopiles, and the area averages shown for these curves are equivalent to the effect of a loss of approximately 30% of the experimental heat and show a 15% increase in the standard deviation of a measurement. It should be pointed out that the lowest heat range used in the later experimental work was 10 μv so that the effect is one-tenth as large. Whenever it occured the experiment was rerun. Based on the average curve areas for the six calibrations with normal heat profiles listed in table A-9, the optimal curve section time which should be used to compute curve areas on the 1-μv scale is 2-10-4. This setting detects 96% of the experimental heat with a standard deviation for an individual measurement of 2 volt seconds or 7 μ calories. Since these calibration experiments were performed before optimal control of the calorimeter air bath was achieved and without the high-frequency filter on the output of the Keithley microvoltmeter, another series of calibrations were performed on the 1-μv scale with mixing after all the calorimeter modificationshad been finalized in order to measure the calorimeter's sensitivity. The areas for these experiments were computed using a curve section time of 2-15-5 in order to measure 100% of the heat. The areas

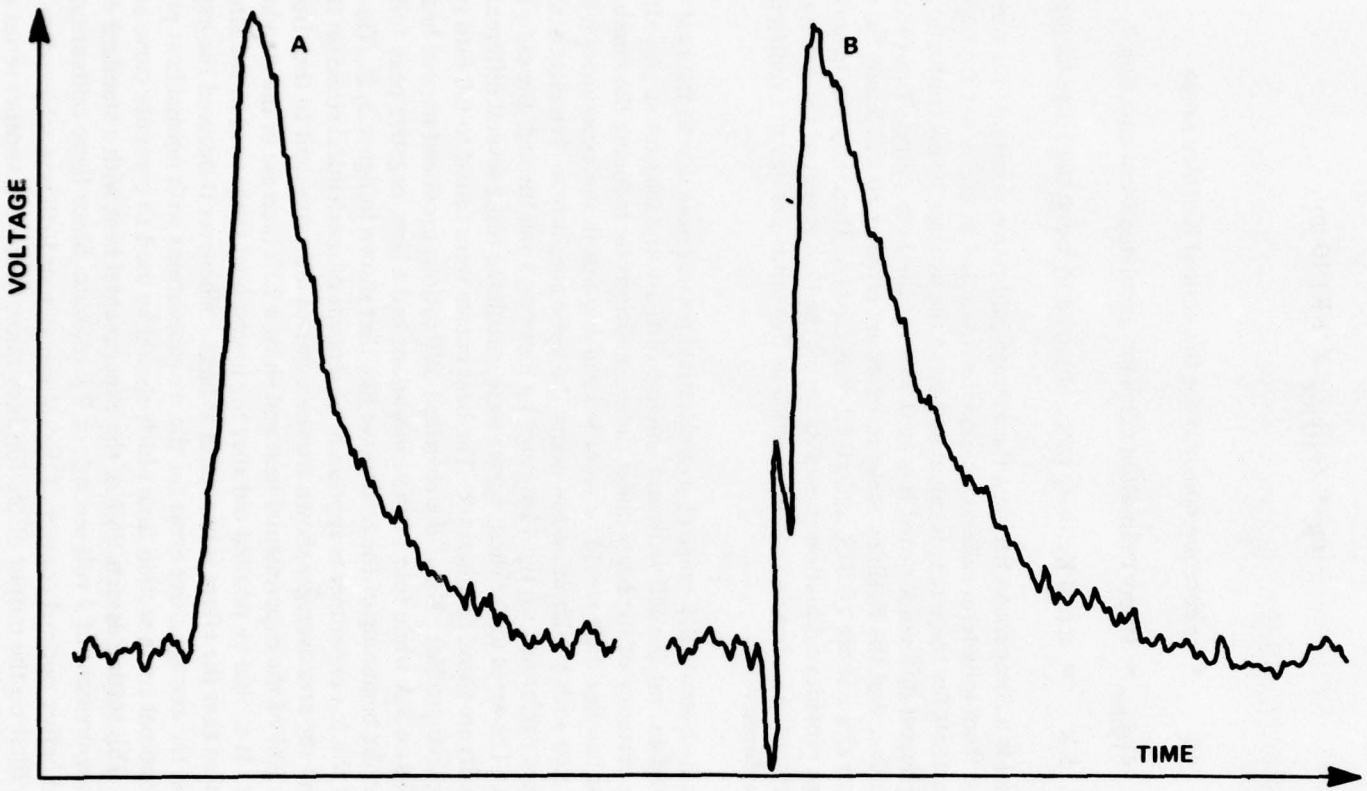

Figure 3. Calibration Curves on 1-μv Range (with Rotation)

were then multiplied by a calibration constant calculated from the average 10-mv calibration constant and equation 8. The results, presented in table A-10, indicate that the sensitivity of the calorimeter, given by the standard deviation of a single heat measurement is ±21 μcalories. This value agrees exactly with that obtained when the standard deviation of the class A area for a curve section time of 2-15-5 in table A-9 is multiplied by the same calibration constant used in table A-10. This value also agrees favorably with the value of ±20 μcalories, reported by Falcone.[39]

D. Calorimetric Procedure.

The solutions were made up on a single-pan Mettler balance capable of weighing to ±0.1 mg. The sample cell was rinsed with water, followed by a rinse with Fischer-certified methanol and dried with a stream of nitrogen. W(2) grams of solution containing N(2) moles of solute at concentration $\underline{m}_i$ (2), and W(4) grams of solvent water were loaded by weight into the 2- and 4-cc cell compartments with 5-cc plastic syringes equipped with lengths of Teflon tubing. When a mixture was measured, N(2) is the moles of solute a, (N_a), plus the moles of solute b, (N_b). The materials were allowed to equilibrate at the calorimeter temperature until a stable baseline was achieved on a heat range one-hundred times more sensitive than the experimental range (1-2 hr). The first dilution was begun by rotating the calorimeter unit through at least one rotation cycle, resulting in q calories of heat being released and a final solution concentration of $\underline{m}_f$. A series of rotations were performed after the first dilution of each solute until there was no detectable heat effect. The number of rotations for each solute series was then used in subsequent dilutions of these solutes to assure complete mixing. After the initial baseline was reestablished, a calibration (with mixing) was performed on the 10-mv range. Keithley range factors were then used to calculate calibration constants for all the experimental heat ranges from the 10-mv calibration. Previously, calibrations were performed after every dilution. The 4-cc compartment was then emptied by weight. $W(4)_{out}$ grams was withdrawn, with a 10-cc plastic syringe leaving 16.5 ± 2 mg of solution on the walls of the 4-cc cell or 8.4 ± 2 mg if the 2-cc compartment was emptied. Pure solvent $W(4)_{in}$ grams was then loaded into the 4-cc compartment producing a dilute solution containing N(4) moles of solute at concentration $\underline{m}_i$ (4). This dilute solution concentration was calculated from the number of moles of solute left on the walls N(4) and the total weight of solvent added to the 4-cc compartment. Thus the ensuing dilutions involve N(4) moles of solute at concentration m_i (4) mixing with N(2) moles of solute at concentration $\underline{m}_i$ (2) to give N(2) + N(4) moles of solute at concentration m_f'. The concentration of the solution in either cell is easily calculated, since the weights of solution and solvent added and withdrawn and the amount of solution retained on the walls is known at any point in a series of dilutions. The following equations indicate the computer procedure used to calculate the solute concentration in either cell for a series of dilutions.

Initially the 2-cc cell is loaded with W(2) grams of solution at molality $\underline{m}_i$ (2) and the 4-cc cell is filled with W(4) grams of water.

$$WTA = W(2)/[1000. + MW \times m_i(2)]$$

$$WTBB = W(4) \times 0.001$$

$$N(2) = \underline{m}_i(2) \times WTA$$

$$\underline{m}_f = N(2)/(WTA + WTBB)$$

where

WTA = the number of grams of solvent in W(2) grams of solution

WTBB = the number of kg of solvent used to dilute W(2) grams of solution

MW = molecular weight of solute.

At this stage, the contents of solution in cell 2 are mixed with the solvent in cell 4, creating a uniform solution concentration m_f in each of the two cells. The 4-cc compartment is then emptied [$W(4)_{out}$ grams being removed] leaving 16.5 ± 2 mg of solution of $\underline{m}_f$ on the cell walls. $W(4)_{in}$ grams of solvent are then added, creating a dilute solution $\underline{m}_i(4)$ in the 4-cc cell. Another rotation is then performed resulting in a new solution concentration $\underline{m}_f'$ in both cells.

$$\underline{m}_i(2) = \underline{m}_f \text{ (from previous dilution)}$$

$$\text{WTA} = \frac{[W(2) + W(4)] - [W(4)_{out} + 0.0165]}{1000 + MW \times \underline{m}_f}$$

$$\text{WTB} = 0.0165/(1.000. + MW \times \underline{m}_f)$$

$$\text{WTBB} = [W(4)_{in}] \times 0.001$$

$$N(2) = \underline{m}_f \times \text{WTA}$$

$$N(4) = \underline{m}_f \times \text{WTB}$$

$$\underline{m}_i(4) = N(4)/(\text{WTB} + \text{WTBB})$$

$$\underline{m}_f' = [N(2) + N(4)/\text{WTA} + \text{WTB} + \text{WTBB})$$

where

WTB = the number of grams of solvent remaining in the 4-cc cell after it was emptied.

Dilutions were performed in this manner until the final concentration $\underline{m}_f$ was 0.1 molal or less.

The experimental heat, q, is related to the initial and final solution excess enthalpies by the following equation:

$$-q = [N(2) + N(4)]H^{ex}[\underline{m}_f] - N(4)H^{ex}[\underline{m}_i(4)] - N(2)H^{ex}[\underline{m}_i(2)] \qquad (9)$$

where H^{ex} (m) is the excess enthalpy of the solution per mole of solute at molality m($\phi_L = H^{ex}$). The excess enthalpy of the solute represented by the equation:

$$H^{ex} = \phi_L = B_1\underline{m} + B_2\underline{m}^2 + B_3\underline{m}^3 + \ldots \tag{10}$$

was substituted into equation 9 in order to fit the experimentally measured values for the change in the excess enthalpy per mole ΔH^{ex} to the following equation:

$$-q/N(2) = H^{ex} = \sum_{j=1,n} B_j\left[\frac{N(F)\underline{m}_f^j - N(2)\underline{m}_i(2)^j - N(4)\underline{m}_i(4)^j}{N(2)}\right] \tag{11}$$

where N(F) = total moles of solute. This equation was used in a least squares procedure to determine the coefficients B_j of the polynomial and to extrapolate the heat data to infinite dilution. The right hand side of the equation is the heat per mole of solute. Statistical tests were performed to assure using the minimum number of coefficients to represent the data. Only coefficients which were not zero with 95% confidence were used.

At this point a brief derivation based on the solution theory of McMillan-Mayer is shown to indicate how these B_j coefficients were used to calculate the pairwise heats of interaction $\{\}_h$ between nonelectrolyte solutes. Wood[14] has shown that for a system containing solutes and 1 kg of solvent, the excess free energy G^{ex} may be expressed as a polynomial in the molalities of the solute species:

$$\frac{G_W^{ex}}{RT} = A_n\{N_iN_j\}_g\underline{m}_i\underline{m}_j + A_n\{N_iN_jN_k\}_g\underline{m}_i\underline{m}_j\underline{m}_k + \ldots \tag{12}$$

where the coefficient A for an n particle term involving n_1 particles of species N_1, n_2 particles of species N_2 etc. is:

$$A_n = \frac{n!}{(n_1!n_2!n_3!\ldots)}.$$

These A_n coefficients permit $\{N_iN_i\} = \{N_iN_j\} = \{N_jN_j\}$ for the three cases in which species i and j are the same except for some type of label which does not affect the intermolecular forces between these molecules. The species within the brackets $\{N_iN_j\}_g$ correspond to the McMillan-Mayer[16] cluster integrals and indicates that the cluster integrals are functions of the excess free energy. The equation for the excess heat content is obtained by taking the partial derivative of the excess free energy with respect to the reciprocal absolute temperature as follows:

$$\frac{\delta\,(G_W^{ex}/T)}{\delta\,1/T} = H^{ex}$$

so that $\left[N_iN_j\right]_h = \dfrac{\delta\,([N_iN_j]_g/T)}{\delta\,1/T}$

By applying this derivative to equation (12) a power series in molality results:

$$\frac{H^{ex}}{W} = A_n \{N_i N_j\}_h \underline{m}_i \underline{m}_j + A_n \{N_i N_j N_k\}_h \underline{m}_i \underline{m}_j \underline{m}_k + \cdots \quad (13)$$

where the subscript h indicates an enthalpy of interaction. Since all of the work performed in this study involved the enthalpy of dilution of single and binary nonelectrolyte solutions, equation 13 was used to express the change in excess enthalpy per mole for a dilution of a solution containing $\chi_s \underline{m}_i$ molal sucrose (S) and $\chi_u \underline{m}_i$ molal urea (U) as follows:

$$\frac{-\Delta H^{ex}}{n} = (\underline{m}_i - \underline{m}_f)[2\chi_s\chi_u\{US\}_h + \chi_u^2\{UU\}_h + \chi_s^2\{SS\}_h] + \chi_s^2\chi_u(\underline{m}_i^2 - \underline{m}_f^2)[3\{USS\}_h]$$

$$+ \chi_s\chi_u^2(\underline{m}_i^2 - \underline{m}_f^2)[3\{UUS\}_h] + \chi_s^3(\underline{m}_i^2 - \underline{m}_f^2)[\{SSS\}_h] + \chi_u^3(\underline{m}_i^2 - \underline{m}_f^2)[\{UUU\}_h] + \ldots \quad (14)$$

where n is the total moles of solute of all types, $\underline{m}_i$ the initial molality, $\underline{m}_f$ the final molality after a dilution and χ the mole fraction of the respective solute. Substitution of the experimental heat data data for this dilution into the least squares equation (11), results in a B_1 coefficient which is equal to the first term of equation (14): $2\chi_s\chi_u\{US\}_h + \chi_u^2\{UU\}_h + \chi_s^2\{SS\}_h$. Thus this B_1 coefficient contains all of the pairwise heats of interaction which result when a binary urea-sucrose solution is diluted. The dilution of a single nonelectrolyte solution results in a B_1 coefficient which directly gives the heat of interaction between the two like solute molecules since in this case, using the dilution of a urea solution as an example, the change in excess enthalpy per mole is given by:

$$\frac{-H^{ex}}{n} = \{UU\}_h(\underline{m}_i - \underline{m}_f) + \{UUU\}_h(\underline{m}_i^2 - \underline{m}_f^2) + \cdots \quad (15)$$

Thus the heat of interaction between to unlike nonelectrolyte solute molecules was calculated from the knowledge of the like pairwise heats of interaction obtained by diluting single nonelectrolyte solutions and combining these values with the interaction expression obtained for the dilution of a binary mixture of these solutes. Table A-11, Appendix A gives heats of dilution values in cal/mol for many single and binary nonelectroltye solutes. Table A-12, Appendix A lists the sum of the heats of interaction for an equal mole fraction, binary solution of urea (U) and pentaerythritol (P), *i.e.*, $1/4(2\{UP\}_h + \{UU\}_h + \{PP\}_h)$ as -10.5 cal kg/mol^2. The heats of interaction for the single nonelectrolyte solutions are also reported in table 3 as $\{UU\}_h$ = -83.7 and $\{PP\}_h$ = 94.4 cal kg/mol^2. Substituting these values into the expression for the 1-1 urea pentaerythritol dilution gives $-10.5 = 1/4[2\{UP\}_h + \{-83.7\} + \{94.4\}]$ and solving for $\{UP\}_h$ yields the pairwise heat of interaction between a urea and pentaerythritol molecule $\{UP\}_h$ = -26.4 cal kg/mol^2 as shown in table A-13, Appendix A.

An approximately equal number of dilutions were performed with the roles of the 2- and 4-cc compartments being reversed. The experimental dilutions were usually continued until the heat of dilution was approximately 100 calories; at which time, the sample cells were emptied, rinsed, dried and loaded for another series of dilutions.

A correction for the wet wall heat of friction of approximately 0 ± 20 μcal, produced by the motion of the liquid sample against the cell walls during mixing, was made whenever the experimental heat of dilution was 60 mcal or less. The method used for this correction was to subtract from the heat of dilution, the heat of friction observed upon rotation of the homogeneous solution produced by the previous dilution. The estimated error for this procedure on the reported heat values, was ±20 μ calories.

Since the heat of friction of an initial dilution (cell walls dry) has been reported to be as much as ± 200 μcalories by Levine,[38] a slightly different procedure was used for a few dilution runs which gave initial heats of dilution of only 100 mcalories or less. For these runs, the 4-cc cell was initially filled with approximately 5 mg of solution by weight. The cells were then rotated and any solution found in the 2-cc cell was withdrawn by weight leaving 8.4 ± 2 mg of solution on the walls. The 2-cc cell was then filled with a weighed amount of solvent and the normal procedure for the dilutions was used from this point. The dilution runs performed by this procedure are labelled wet wall in table A-11 of the results section and are indicated by (C).

All of the single and binary nonelectrolyte dilutions performed in this work were plotted as $-\Delta H^{ex}/(\underline{m}_i-\underline{m}_f)n$ versus $(\underline{m}_i+\underline{m}_f)$ in figures 4-10 of the results section. The intercepts of these plots gives B, of equation 11 directly as the sum of all the pairwise heats of interaction, and the slope of these curves yields a sum containing all the triplet heats of interaction. Since we were interested in only the interaction heats of molecular pairs, it was important to measure the enthalpy of dilution at low concentrations. At concentrations below 0.2 molal, the probability of molecules having more than pair-type interactions becomes quite small. Therefore the extrapolation of $-\Delta H^{ex}/(\underline{m}_i-\underline{m}_f)n$ to infinite dilution provides the pairwise heats of interaction with good accuracy.

In order to plot the data in the form $-\Delta H^{ex}/(\underline{m}_i-\underline{m}_f)n$ versus $(\underline{m}_i+\underline{m}_f)$, it was necessary to correct it for the fact that the solvent compartment (4-cc) periodically contained small amounts of solute in addition to the diluent solvent. Since the number of moles of solute in the 4-cc compartment was quite small, the calculation of the heat that would have been observed if the 4-cc compartment had been filled with pure solvent involved only a small correction. These corrected ΔH^{ex}_{corr} values shown in table A-11 of the results section for the nonelectrolyte mixtures, were obtained by using the experimental concentration data for the 2- and 4-cc compartments, together with the experimental heats of dilution q, in the following equation:

$$\Delta H^{ex}_{corr} = \phi_{L_{corr}} = H^{ex}(\underline{m}_f) - H^{ex}[\underline{m}_i(2)] = -q/N(2) + N(4)/N(2)\{H^{ex}[\underline{m}_i(4)] - H^{ex}(\underline{m}_f)\} \quad (16)$$

where $H^{ex}[\underline{m}_i(4)]$ and $H^{ex}(\underline{m}_f)$ were evaluated from the coefficients of the final least squares fit of the data. This correction never exceeded 2% of q.

III. RESULTS.

The experimental dilution data for all the single and binary nonelectrolyte mixtures were fitted to the least squares equation (11) previously described. A computer program used equation (11) to express the change in excess enthalpy per mole as a function of the initial and final molalities of the solutions being diluted. The following information from the computer outputs is presented in table A-11, appendix A:

$\underline{m}_i(2)$, N(2), N(4), $\underline{m}_f$ defined earlier

$\chi_a = N_a/(N_a+N_b)$ = mole fraction of solute a in a mixture (a+b) excluding solvent.

$H^{ex}_{exp} = -q/N(2)$ = the experimental change in the excess enthalpy per mole of the solute in the more concentrated solution.

H^{ex}_{corr} = the experimental change in excess enthalpy per mole of the solute in the more concentrated solution equal to -q/N(2) corrected for setting N(4) equal to zero (see equation 16).

H^{ex}_{calc} = the calculated least squares value for H^{ex}_{corr} above.

The B_j coefficients required to fit the heat data to the least squares equation (11) are shown in table A-12 together with the standard deviations for the coefficients.

As shown earlier, for a dilution of a single nonelectrolyte solute A, the first coefficient obtained from a least squares analysis of the heat data is simply the heat of interaction between two A molecules, *i.e.*, $B_1 = \{AA\}_h$; while the dilution of an equimolal mixture of A and C yields a coefficient $B_1 = 1/4\,[2\{AC\}_h + \{AA\}_h + \{CC\}_h]$. These B_1 coefficients were subsequently used to calculate (table A-13) pairwise heats of interaction $\{AB\}_h$ for all the nonelectrolytes studied.

Finally, a series of $-H^{ex}_{corr}/(\underline{m}_i - \underline{m}_f)n$ versus $(\underline{m}_i + \underline{m}_f)$ plots are shown in figures 4-10 are both the single and binary nonelectrolyte dilutions. The corrected experimental excess-enthalpy points are shown in relation to the least square calculated curves.

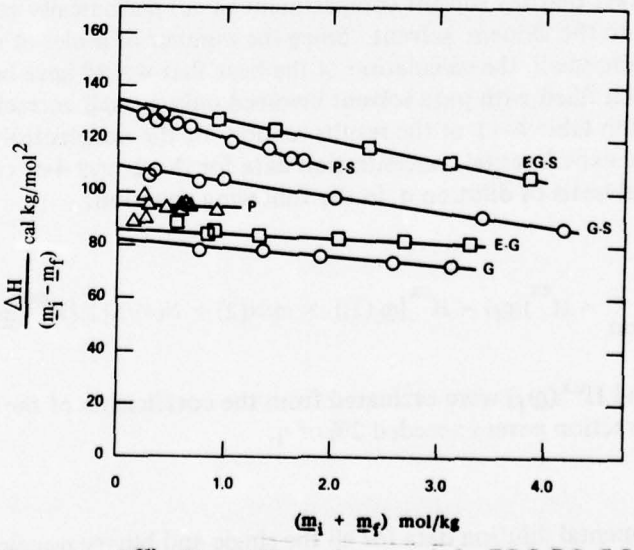

Figure 4. ΔH^{ex}_{corr} Plotted Versus $(\underline{m}_i + \underline{m}_f)$, for EG-S, P-S, G-S, P, E-G and G Solutes

The line gives values calculated by the least squares fit.

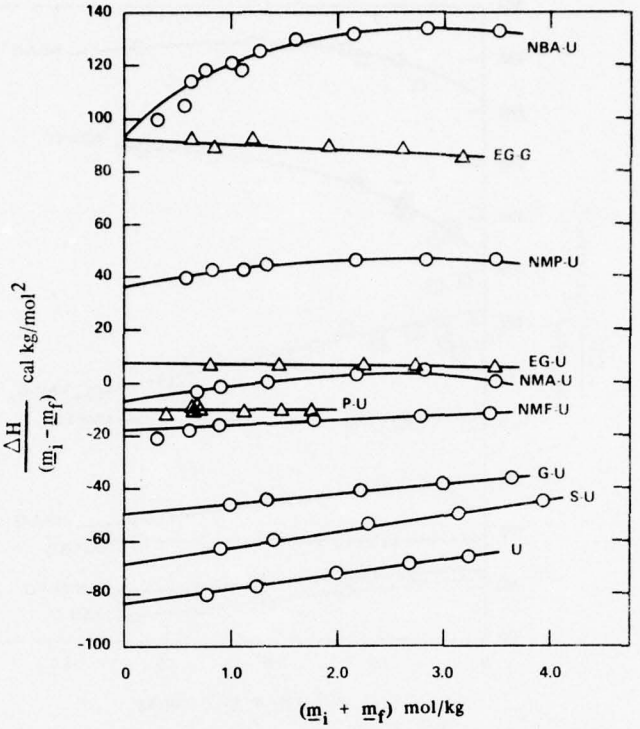

Figure 5. ΔH^{ex}_{corr} Plotted Versus $(\underline{m}_i + \underline{m}_f)$, for Eight Binary Nonelectrolytes and for Urea

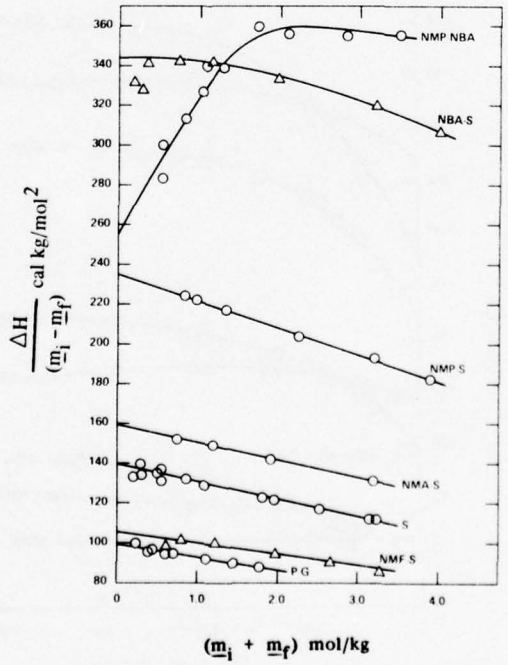

Figure 6. ΔH^{ex}_{corr} Plotted Versus $(\underline{m}_i + \underline{m}_f)$, for Six More Binary Nonelectrolytes and Sucrose

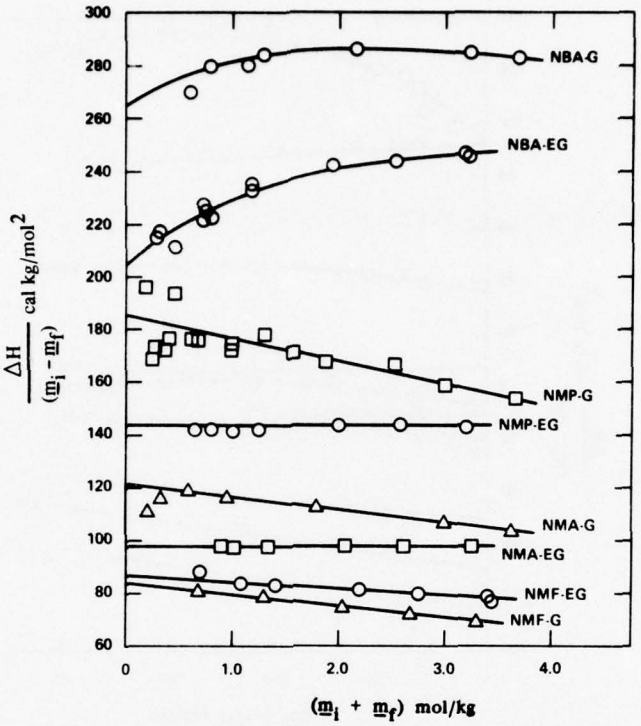

Figure 7. ΔH^{ex}_{corr} Plotted Versus $(\underline{m}_i + \underline{m}_f)$, for Eight Binary Nonelectrolytes, Most Having Glucose as a Member

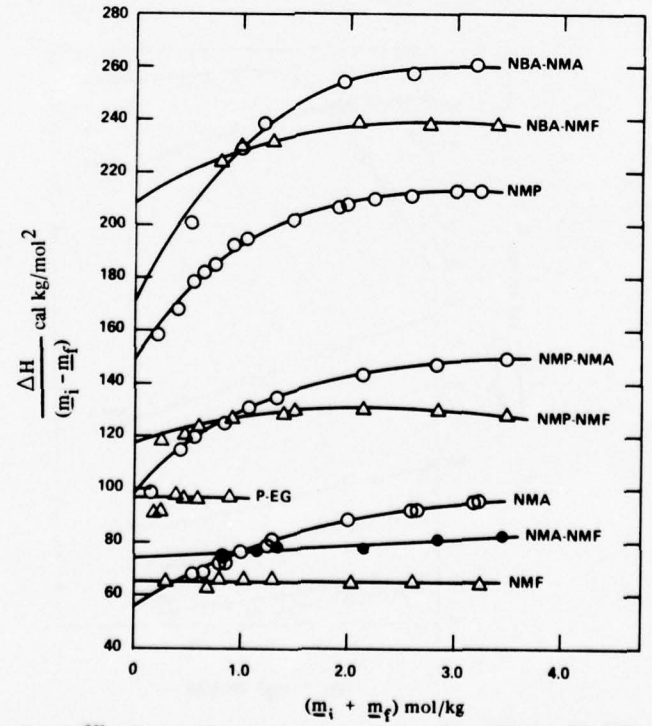

Figure 8. ΔH^{ex}_{corr} Plotted Versus $(\underline{m}_i + \underline{m}_f)$, for Seven Binary Nonelectrolytes, N-Methylformamide and N-Methylacetamide

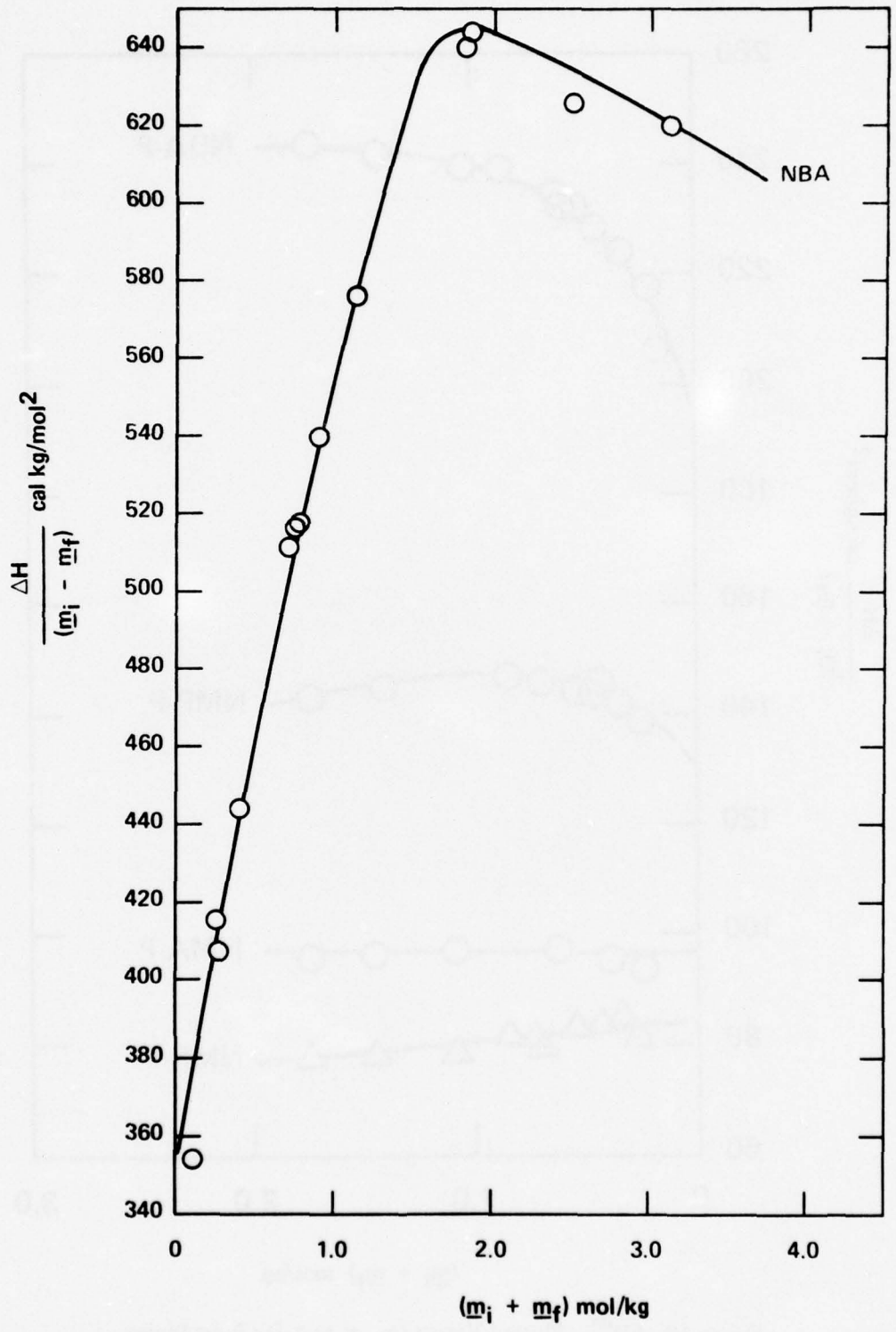

Figure 9. ΔH^{ex}_{corr} Plotted Versus $(\underline{m}_i + \underline{m}_f)$, for N-Butylacetamide

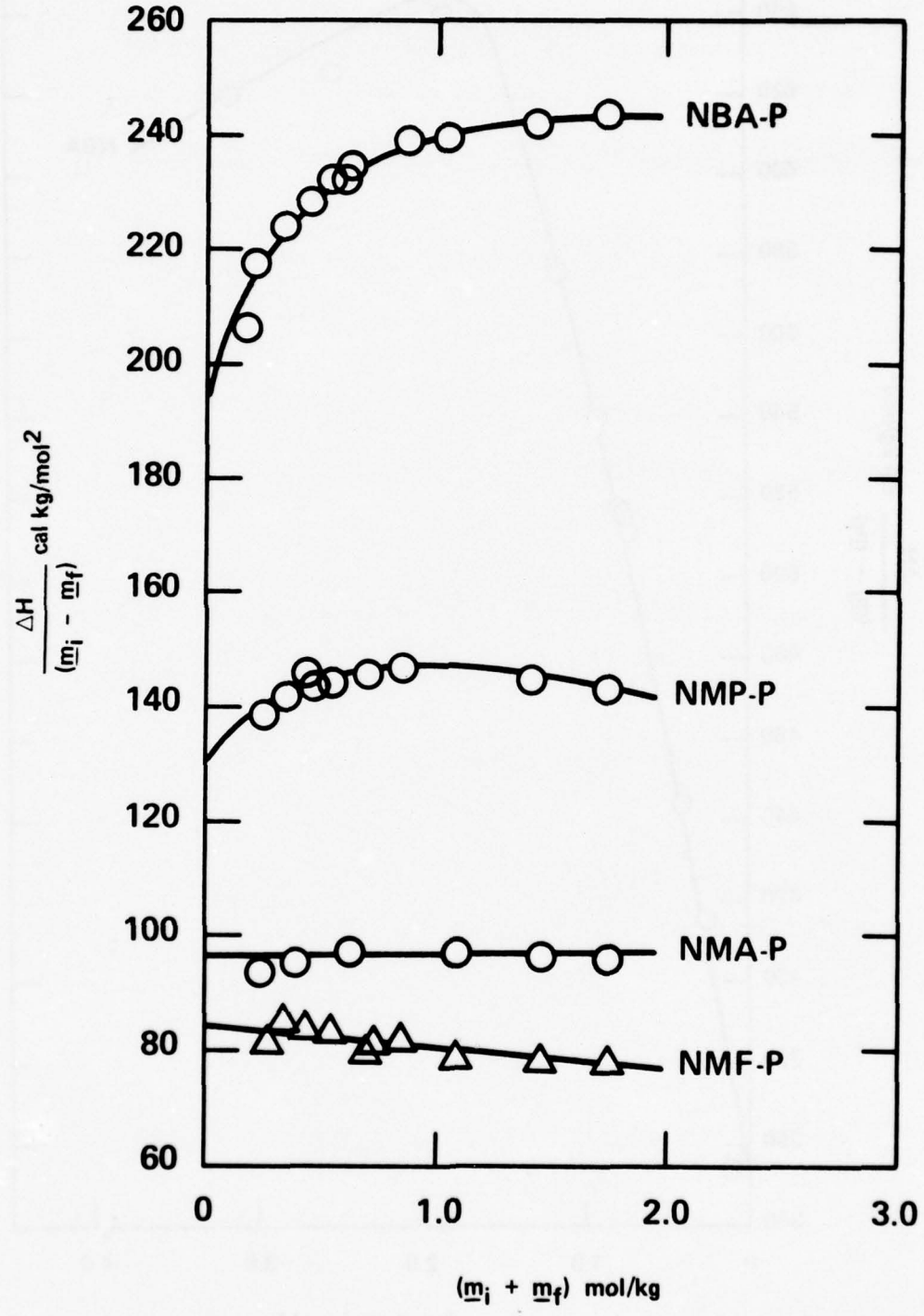

Figure 10. ΔH^{ex}_{corr} Plotted Versus $(\underline{m}_i + \underline{m}_f)$, for Four Binary Nonelectrolytes with Pentaerythritol as One Component

IV. DISCUSSION.

A comparison of the present work with the literature indicates that very little work has been done in measuring the thermodynamic properties of aqueous nonelectrolyte mixtures. The available data on single nonelectrolyte solutions has been reviewed by Kozak, Knight and Kauzmann.[10] The pairwise heat of interaction for sucrose 137.9 ± (1.4) cal kg/mol^2 measured here agrees within experimental error with the values reported by Lange[40] of 133.6 and Gucker and Pickard[41] of 134.6 cal kg/mol^2. The most recent and most accurate literature data for the heat of interaction for urea was reported by Hamilton and Stokes.[42] Their data was fit by the same computer program used in treating the present data and resulted in a value of -83.2 ± (1.2) cal kg/mol^2 which is in excellent agreement with the present result of -83.7 ± (2.7) cal kg/mol^2. Values for urea of -84.4 ± (2.9) by Cassel and Wood[14] and -85.9 by Gucker and Pickard[43] also agree well with our results. Lange[40] reported a heat of interaction for glucose of 82.1 cal kg/mol^2 which essentially is in exact agreement with the value of 82.0 ± (2.3) found in this study. A heat of interaction for ethylene glycol of 92.5 cal kg/mol^2 reported by Lange[12] is somewhat outside the estimated experimental error with the value of 86.5 ± (1.0) found in this study.

Friedman and Krishnan[11] have measured the enthalpies of dilution for a series of alcohols and binary alcohol mixtures. Unfortunately, the accuracy of this data is poor because these authors did not have a calorimeter designed for dilution experiments. Another contributing factor to the poor accuracy obtained by Friedman and Krishnan was the lack of an accurate extrapolation of $-\Delta H^{ex}/(\underline{m}_i - \underline{m}_f)n$ versus $(\underline{m}_i + \underline{m}_f)$ for their data. The value of $(\underline{m}_i + \underline{m}_f)$ was approximately equal to one, which is too large to obtain an accurate extrapolation. Thus the pairwise interaction heats obtained from this extrapolation probably contain contributions from triplet terms. The more accurate enthalpy of dilution data for a series of alcohols reported by Lange[12,40] and Franks* are listed in table A-14 of this section.

It must be emphasized that the heats of interaction, $\{\ \}_h$, reported here are not equal to the second virial coefficient in the McMillian-Mayer theory of solutions. Friedman[11] has given an equation from which one can show that the free energy interaction parameter, $\{\ \}_g$, is related to the McMillan-Mayer second virial coefficient B* as follows:

$$B^*_{AA} = \{AA\}_g V^\circ_w + RT\phi_v(A) - 1/2 j V^\circ_w \qquad (17)$$

where

V°_w is the volume of water in liters per kilogram,

ϕ_v is the apparent molal volume of the solute A at infinite dilution

j is a constant for water at 25°C equal to 1.1×10^{-3}

* Franks, F. Private communication, 1975.

The heat of interaction parameter then follows from equation (17), if one neglects the last term

$$\frac{\delta B^{*}_{AA}/T}{\delta 1/T} = \{AA\}_h V^{\circ}_w - \frac{\alpha RT^2 \{AA\}_g V^{\circ}_w}{RT} - RT^2 \phi_E(A) \qquad (18)$$

Thus the heat term shown in equation (18) is directly proportional to the temperature variation of the solute-solute intermolecular interaction. By analyzing the respective terms in equation (18) for urea, sucrose and a urea-sucrose mixture, an estimation of the magnitudes of these terms can be obtained. The free energy interaction parameters reported by Ellerton and Dunlop[44] and the interaction heats and partial molal expansibilities measured here for urea and sucrose were substituted into equation (18). The magnitude of each term is shown in table A-15 for the different solutes. The values listed in table A-15 show that the heat of interaction terms are the most important in determining the value of the temperature variation of the solute-solute intermolecular interaction $\frac{\delta B^{*}/T}{\delta 1/T}$. It is also observed that the partial molal expansibility term may represent as much as 40% of the total, whereas the free energy term is much smaller than either the heat or expansibility terms and has the same sign as the heat term. It should therefore be possible to use the pairwise heats of interaction to look for trends in nonelectrolyte group interactions, develop sign rules for these interactions and determine whether or not these group effects are additive. Friedman[11] has already reported a similar study for monofunctional alcohols in which he reported a correlation between the values of the heats of interaction for the alcohols and the length of their alkyl chains. Ratcliff *et al.*,[45-47] have also published a number of papers in which a group solution model was used to predict the heats of mixing alcohols and hydrocarbons.

The compounds used in our experiments were chosen to study group interactions between amides, hydrocarbons and polyhydroxy compounds. As seen from table A-13, appendix A the amides form a series of increasing-hydrocarbon-chain length while keeping the amide contribution constant; *i.e.*, N-methylformamide (NMF) has one CH_3 group, N-methylacetamide (NMA) has two CH_3 groups, N-methylpropionamide (NMP) has a methylene group and two methyl groups and N-butylacetamide (NBA) has three methylene groups and two methyl groups. In this analysis no distinction was made between a methylene and a methyl group. The polyhydroxy compounds were selected for an increase in the number of hydroxy groups per molecule. Thus ethylene glycol (EG) has two OH groups, pentaerythritol (P) has four OH groups, and glucose (G) and sucrose (S) each have five and eight OH groups respectively. Urea was also included to represent a pure amide group and has arbitrarily been equated to one and one half amide groups in this work. Using these three different classes of molecules, the pairwise group interactions between hydrocarbons, polyhydroxy compounds and amides with themselves as well as the combinations between these groups have been determined.

The pairwise heats of interaction for the series of amides NMF-NMF, NMA-NMA, NMP-NMP and NBA-NBA, was used to determine the hydrocarbon-hydrocarbon group interaction. In this amide series, the amide portion of the molecule remains constant as the length of the hydrocarbon chain increases. The heats of interaction for this series increases in value thereby indicating that a hydrocarbon-hydrocarbon group interaction is positive. This result agrees with

the work of Friedman and Krishnan[11] and Franks* on aqueous alcohols where they found the unlike pairwise enthalpies of interaction to be positive and show an increasing trend as a function of the length of the alkyl chain on an alcohol. A positive heat of interaction and dependence on the length of the alkyl chain is also expected for hydrocarbon groups in an aqueous solution, based on the free energy experiments of proteins by Nemethy and Scheraga.[3] These authors maintain that nonpolar groups preferentially interact with each other rather than water in an aqueous environment by hydrophobic bonding, resulting in an entropy-dominated process which can be used to explain the large positive free energies of solution for hydrocarbons and related compounds in water.

Based on the pairwise heat of interaction for urea with itself, amide-amide group interactions are negative. This is consistent with the results reported by Hamilton and Stokes,[42] and Schellman[5] for urea in which they also measured an endothermic enthalpy of dilution. The series formed by urea interacting with N-methylformamide (NMF), N-methylacetamide (NMA), N-methylpropionamide (NMP) and N-butylacetamide (NBA) provides a measure of the amide-hydrocarbon group interactions. The amide-amide contribution should remain constant for this series, and since the hydrocarbon chains are being increased on one of the solute pair molecules, an amide hydrocarbon interaction which is positive is observed. Another indication that the sign of the amide-hydrocarbon interaction is positive is provided by the series NMF interacting with NMA, NMP and NBA. Again the amide-amide contribution is expected to remain constant for this series while the hydrocarbon chain length on one solute is increasing. If the contribution due to the hydrocarbon-hydrocarbon interaction is small relative to the amide-hydrocarbon interaction then the trend in the interaction heats observed for this series suggests that the sign of the amide-hydrocarbon interaction is positive.

Focusing attention on the polyhydroxy compounds shown in table A-13, appendix A, specifically the series of pairs ethylene glycol (EG), pentaerythritol (P), glucose (G) and sucrose (S), shows that the interaction heats are approximately constant for EG, P and G, whereas sucrose (S) shows a moderate increase. This indicates that the heats of interaction for hydroxy groups are small and probably positive. The fact that the pairwise interaction heat for sucrose is larger than the rest of this series could be a result of steric effects or the availability of the hydroxy groups to interact. The similarity between the heats of interaction for ethylene glycol (EG), pentaerythritol (P) and glucose (G) pairs is maintained when these molecules interact with each other. The values for EG-P, EG-G and P-G are approximately the same. Sucrose again remains unique for the polyhydroxy compounds when it interacts with the other compounds in this series. Sucrose (S) interacting with ethylene glycol (EG), pentaerythritol (P) and glucose (G) forms a fairly regular trend in the heats, with S-EG having the largest pairwise interaction heat, (larger than S-S pairs), and S-G the smallest value. Thus it appears that the OH-OH interaction is positive and probably small because of the equality of the interaction heats between molecules with two, four and five hydroxy groups. The fact that a fairly regular trend exists for the interaction of the polyhydroxy compounds with sucrose and that EG-S is the largest pairwise interaction heat, suggests a steric mechanism controlling the ability of the hydroxy groups to interact with each other.

The sign of the hydrocarbon-hydroxy group interaction heat is positive based on the heats of interaction for the series of amides with each polyhydroxy compound. As the length of the amide chain is increased, the heats of interaction for the amide-polyhydroxy pair increase. This series also shows much more of a regular increase in the interaction heats than the polyhydroxy

* Franks, F. Private communication, 1975.

compounds with themselves. As one increases either the hydrocarbon chain or the number of hydroxy groups available for interaction, the pairwise heats of interaction increase, although pentaerythritol seems to give lower values than expected.

The final group interaction obtained from the data in table A-13, appendix A is an amide group with a hydroxy group. The series, urea interacting with the polyhydroxy compounds, indicates that this group interaction is negative since urea-ethylene glycol is slightly positive and urea interacting with progressively higher hydroxy substituted molecules becomes increasingly more negative. It is disturbing to note that N-methylformamide (NMF) has a pairwise heat of interaction of 65 cal kg/mol^2 while N-methylacetamide (NMA) pairs give 56 cal kg/mol^2, yet $\{\text{NMF-NMA}\}_h$ = 88 cal kg/mol^2. Based on simple group additivity, $\{\text{NMF-NMA}\}_h$ is expected to be an average of the like pair interactions, and this is clearly not the case. Also, the interaction value of NMA with N-methylpropionamide (NMP) or N-butylacetamide (NBA) is consistently smaller than the interaction values of NMF with these compounds. This is in spite of the fact that the NMA has one more methyl group than NMF with which to interact.

Although the data listed in table A-13, appendix A contain nonadditivities, it appears that at least the signs of the various group interactions have been obtained. These sign rules are shown in table A-16, appendix A. It had been hoped that group additivity in the heats of interaction of nonelectrolytes would be found in this work since the work of other authors suggests this to be the case. Friedman and Krishnan[11] and Franks,* for example, have shown a correlation between the length of the alkyl chain for simple alcohols and their heats of interaction. Schrier[48] has also shown a group additivity for amide groups, methyl groups, and methylene groups interacting with ions from the salting-out behavior of various amides. In light of their results, the heats of interaction shown in table A-13, appendix A, were fitted to a linear least square equation to determine if a simple additivity existed in the pairwise heats of interaction and whether a knowledge of the additive interactions could be used to predict the heats of interaction of nonelectrolytes which have not been measured. We assumed that every group on a solute molecule could freely interact without steric hindrance with every group on another solute molecule, and that the interaction between groups was independent of nearest neighbor effects. The following general equation was used:

$$\{ab\}_h = C_O + \left(n_{CH_{2a}} \times n_{CH_{2b}}\right)E_{CH_2-CH_2} + \left(n_{A_a} \times n_{A_b}\right)E_{A-A} +$$

$$\left(n_{CHOH_a} \times n_{CHOH_b}\right)E_{CHOH-CHOH} + \left(n_{CH_{2a}} \times n_{A_b} + n_{CH_{2b}} \times n_{A_a}\right)E_{CH_2\text{-}A}$$

$$+ \left(n_{CH_{2a}} \times n_{CHOH_b} + n_{CH_{2b}} \times n_{CHOH_a}\right)E_{CH_2\text{-}CHOH} +$$

$$\left(n_{CHOH_a} \times n_{A_b} + n_{CHOH_b} \times n_{A_a}\right)E_{CHOH\text{-}A} \qquad (19)$$

where $n_{CH_{2a}}$ is the number of hydrocarbon groups on a molecule a, n_{A_b} is the number of amide groups on molecule b, n_{CHOH_a} is the number of polyhydroxy groups on molecule a and $E_{CH_2\text{-}CH_2}$,

* Franks, F. Private communication. 1975.

$E_{A\text{-}A}$, etc. are the interaction energies between each group given in cal kg/mol^2. The term C_O represents the interaction between a terminal hydrogen atom (group) on a particular solute molecule with the available hydrocarbon, amide and polyhydroxy groups on another solute molecule. If each of these interactions were included in equation 19, C_O would have been expressed as follows:

$$C_O = \left(n_{H_a} \times n_{H_b}\right)E_{H-H} + \left(n_{H_a} \times n_{CH_{2b}} + n_{H_b} \times n_{CH_{2a}}\right)E_{H-CH_2} +$$

$$\left(n_{H_a} \times n_{A_b} + n_{H_b} \times n_{A_a}\right)E_{H-A} + \left(n_{H_a} \times n_{CHOH_b} + n_{H_b} \times n_{CHOH_a}\right)E_{H-CHOH}$$

The interaction of a H atom with the other available groups was not expected to be as important as the interactions between the groups previously defined because of the size disparity between a H atom and these groups. The inclusion of these terms would also have resulted in more variables than were warranted by the data. These interactions were consequently summed in the form of a constant C_O. It should also be observed that the hydroxy group previously used in determining the sign of group interactions has been expanded to include the methylene carbon and hdyrogen as part of this group. This is done for convenience in treating the heats of interaction of the sugars.

As a result of this analysis, the following group interaction values (E) in cal kg/mol^2 were determined:

$$E_{CH_2\text{-}CH_2} = 7.6 \pm 5,\ E_{A\text{-}A} = -88 \pm 32,\ E_{CHOH\text{-}CHOH} = 0.3 \pm 0.5,\ E_{CH_2\text{-}CHOH} = 9 \pm 1,$$

$$E_{CH_2\text{-}A} = 14 \pm 11 \text{ and } E_{CHOH\text{-}A} = -12 \pm 4.$$

The plus or minus limits shown for each group interaction value represents the 95% confidence limits for these results. The signs of the interaction heats obtained with equation 19 agree with our earlier observations shown in table A-16, appendix A. Even the magnitude of the CHOH-CHOH interaction agrees with our earlier estimates. The pairwise heats of interaction calculated by using these group interaction parameters are compared with the experimentally determined interaction heats for all the compounds studied in this work in table A-17, appendix A. An indication that these analytical interaction values could only be obtained by a comprehensive study, such as that done here, is seen from the inability to obtain statistically significant values when the amide series or the polyhydroxy series alone was analyzed by the least-squares equation.

Although the standard deviation of the predicted pairwise interaction heats for the compounds shown in table A-17 was approximately ± 45 cal kg/mol^2, the range of the heats of interaction measured extends from -100 to over +400 cal kg/mol^2 as illustrated in figure 11. This figure illustrates the pairwise interaction heats, calculated using the group interaction parameters as points, versus the experimentally determined heats of interaction, shown as a line for all the nonelectrolytes used in this work, as well as several other compounds reported in the literature. These results provide the first group interaction values for aqueous binary nonelectrolytes at low concentrations.

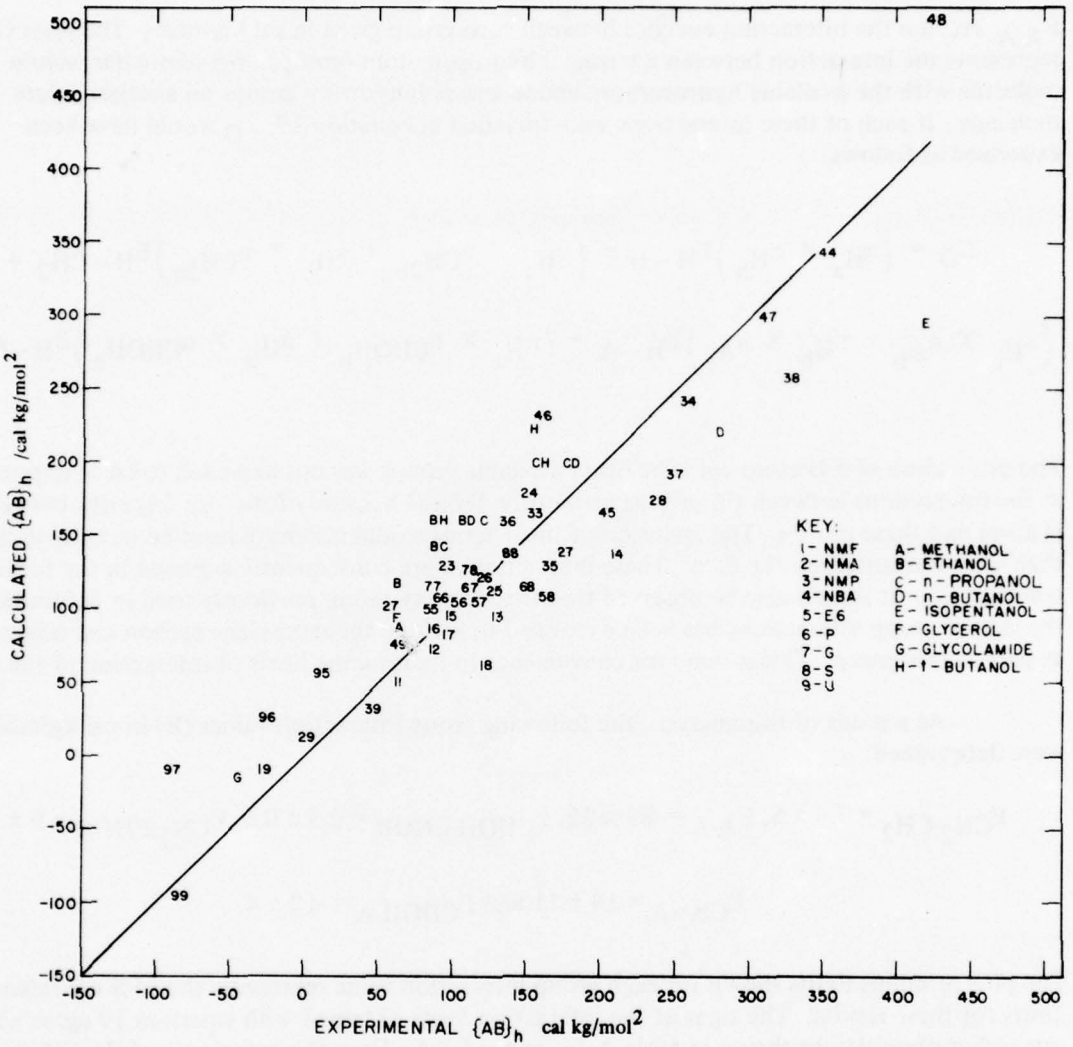

Figure 11. The Experimental Versus Calculated Pairwise Heats of Interaction

To determine if the group interaction values could be used to calculate the pairwise heats of interaction of other molecules containing amide groups, alkyl groups and polyhydroxy groups, the enthalpies of interaction for the alcohols, reported by Franks* and Lange[1,2] and several other nonelectrolytes, were compared to those calculated by using the group interaction parameters. The results are shown in table A-14. The agreement between the calculated and literature values is as good as the least-squares fit of our data. This is remarkable in light of the number of simplifying assumptions which had to be made to obtain the group interaction parameters. The effect of structure in the form of steric effects was not accounted for by the simple group additivity postulated. Each functional group on one solute molecule was assumed to interact with every other group on another solute molecule no matter how inaccessible certain groups were to each other. Because of the inability to account for structural effects in determining various group interaction parameters, we would expect discrepancies between the calculated and experimental heats of interaction to increase as the amount of steric hindrance present in the molecule increases.

* Franks, F. Private communication. 1975.

This accounts for the identical calculated heats of interaction obtained for n-butyl alcohol and t-butyl alcohol even though Franks* has reported that the heat of interaction of t-butyl alcohol is lower than n-butyl alcohol because of steric hindrance.

In the case of sugars, both glucose and sucrose were assumed to consist of six and twelve polyhydroxy groups respectively. One would expect the contribution to the heat of interaction due to the hemiacetal and hemiketal oxygens to be different than the contribution of the CHOH groups on the molecules, since the oxygen atoms are totally ring-bound, whereas the CHOH groups are more available to interact. In view of these simplifying assumptions, the calculated results presented in table A-14 are quite encouraging. Except for isopentanol, the pairwise heats of interaction of the remaining compounds have been calculated to within 45 cal kg/mol^2.

V. CONCLUSIONS.

This work was originally performed to determine if structure rules could be formulated and used to predict the sign of ΔH when nonelectrolytes and their mixtures were diluted with water. The enthalpies of dilution of four amides (N-methylformamide, N-methylacetamide, N-methylpropionamide and N-butylacetamide), four polyhydroxy compounds (ethylene glycol, pentaerythritol, glucose and sucrose), and of urea were measured in this work. These nonelectrolytes and their binary mixtures were investigated at 25°C using a modified LKB batch microcalorimeter. The enthalpy data for these solutes was used to study the pairwise heats of interaction between hydrocarbon, amide and CHOH groups. Trends found in the pairwise heats of interaction data for these nonelectrolyte solutions resulted in the following sign rules for the group heats of interaction:

hydrocarbon-hydrocarbon = +, amide-amide = -, CHOH-CHOH = +

hydrocarbon-amide = +, hydrocarbon-CHOH = +, and amide-CHOH = -.

The concept of group additivity in the heats of interaction of nonelectrolytes was employed to fit the pairwise heats of interaction measured in this work to the following linear least-squares equation:

$$\{ab\}_h = C_O + \sum_{i,j} n_i^A n_j^B E_{ij}.$$

It was assumed that every group on a solute molecule could freely interact without steric hindrance with every group on another solute molecule and also that the interaction between groups was independent of nearest neighbor effects. For the first time, as a result of this work, quantitative values have been obtained for the heats of interaction between hydrocarbon, amide and CHOH groups. The standard deviation of the pairwise interaction heats calculated using these group interaction parameters was approximately 45 cal kg/mol^2. The validity of these results was demonstrated by using the group interaction parameters to successfully calculate the pairwise heats of interaction of the following previously measured aqueous solutions: methanol, ethanol, n-propanol, n-butanol, t-butanol, isopentanol, glycerol, glycolamide, ethanol-n-propanol, ethanol-n-butanol, ethanol-t-butanol, n-propanol-n-butanol, and n-propanol-t-butanol.

* Franks, F. Private communication. 1975.

The magnitude of the group heats of interaction obtained were larger than the magnitude of the hydrocarbon-hydrocarbon heats, except for the CHOH-CHOH interaction. This result is significant, since the hydrophobic effect has been used to explain the structure of protein in aqueous solutions.[2,3] Yet in terms of the group heats of interaction, amide-amide, amide-hydrocarbon, amide-CHOH and hydrocarbon-CHOH interactions have been shown to be more important than hydrocarbon-hydrocarbon interactions.

These group interaction parameters should be used to evaluate the pairwise heats of interaction of nonelectrolyte systems which have already been measured and predict those for which there are no data. Work should also be performed to evaluate the assumption that interactions between groups are independent of nearest neighbor effects. A good compound to study would be N-methylbutyramide since the enthalpy of dilution of N-butylacetamide has already been measured in this work. A comparison of the results for these solutes should determine the importance of the position of the alkyl groups in an amide molecule (carbonyl or nitrogen substituted) on the hydrocarbon-amide interaction. Additional work is also needed to more accurately assign the magnitude of the amide-amide group interaction. The enthalpy of dilution of formamide should provide this information.

In order to investigate the thermodynamics of biological systems, the heats of interaction for amine and carboxylic acid groups should be studied in acidic, neutral and basic pH solutions. If additivity in the heats of interaction for these groups can be established, it should be possible to predict the pairwise heats of interaction of complex biological molecules that are composed of pieces for which the interactions are known.

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APPENDIX A

TABLES

Table A-1. Long-Term Calibration Constants, 10 mv Range (with Rotation)

Date	I/ma	A/vs*	ϵ/mcal/vs
3/28	89.7966	156.84	36.908
3/28	89.7986	156.67	36.949
4/2	89.8125	156.77	36.938
4/2	89.8085	156.75	36.938
4/4	89.8502	156.89	36.940
4/8	89.8721	157.07	36.915
4/8	89.8741	156.78	36.985
4/10	89.8761	156.95	36.947
4/10	89.8780	157.06	36.923
4/11	89.8761	156.89	36.961
4/11	89.8800	156.75	- 36.998
5/22	89.9595	157.06	36.990
5/22	89.9992	157.39	36.945
5/23	90.0032	157.16	37.001
5/24	90.0131	157.28	36.981
5/30	90.0091	157.40	36.951
5/30	90.0032	157.39	36.948
5/30	90.0052	157.35	36.960
5/30	90.0072	157.38	36.952
5/30	90.0091	157.39	36.953
5/31	89.9923	157.31	36.958
6/3	90.0131	157.03	37.042
6/4	90.0111	157.32	36.970
6/6	90.0191	157.46	36.946
6/7	90.0210	157.16	37.017
6/12	90.0290	157.46	36.951
6/14	90.0330	157.36	36.980
6/19	90.0330	157.60	36.924
6/21	90.0290	157.44	36.958
6/24	90.0389	157.40	36.975

Table A-1. (Contd)

Date	I/ma	A/vs*	ϵ/mcal/vs
6/28	90.0350	157.40	36.972
7/1	90.0389	157.25	37.011
7/2	90.0350	157.59	36.928
7/3	90.0310	157.39	36.971
7/10	90.0369	157.29	36.999
7/10	90.0369	157.53	36.942
7/10	90.0369	157.39	36.976
7/10	90.0369	157.23	37.013
7/10	90.0369	157.31	36.994
7/10	90.0369	157.19	37.023
7/15	90.0369	157.26	37.005
7/16	90.0429	157.36	36.988
7/18	90.0429	157.33	36.995
7/19	90.0389	157.39	36.977
7/22	90.0449	157.49	36.959
7/23	90.0429	157.39	36.980
7/26	90.0429	157.24	37.017
7/31	90.0429	157.51	36.953
8/1	90.0449	157.35	36.992
8/2	90.0409	157.43	36.970
8/5	90.0429	157.40	36.979
8/6	90.0449	157.52	36.951
8/7	90.0469	157.43	36.975
8/8	90.0449	157.44	36.970
8/12	90.0429	157.47	36.962
8/13	90.0449	157.39	36.983
8/14	90.0449	157.25	37.015
8/30	90.0072	157.21	36.994
9/3	90.0270	157.25	37.000
9/4	90.0330	157.47	36.954
9/6	90.0330	157.27	37.001
		Average ϵ = 36.971 mcal/vs	
		σ (Single measurement) = 0.029 = 0.08%	

* In each experiment the current was passed for exactly 60 seconds.

Table A-2. Long-Term Calibration Constants, 3 mv Range (with Rotation)

Date	t/s	I/ma	A/vs	ϵ/mcal/vs
10/25	11	88.7062	93.70	11.097
10/26	13	89.2325	111.79	11.079
10/29	14	88.7678	119.07	11.085
12/14	22	89.5702	190.64	11.077
12/14	14	89.5741	121.26	11.084
12/15	18	89.6059	156.13	11.075
12/15	18	88.8571	153.26	11.095
12/19	18	89.5165	155.68	11.085
12/20	18	88.5671	152.45	11.081
12/28	18	89.3080	154.98	11.083
2/20	18	89.8483	156.78	11.090
2/20	20	89.8105	173.99	11.094
2/20	20	89.8522	174.19	11.091
2/21	18	89.8681	156.86	11.088
2/22	18	89.9297	157.17	11.082
2/29	18	89.8721	156.44	11.119

Average ϵ = 11.088 mcal/vs

σ (Single measurement) = 0.010 = 0.1%

Table A-3. Long-Term Calibration Constants, 1 mv Range (with Rotation)

Date	t/s	I/ma	A/vs	ϵ/mcal/vs
10/11	20	49.6008	159.99	3.680
10/11	20	49.6008	159.37	3.694
10/11	20	49.5948	159.81	3.683
10/17	18	49.7021	144.43	3.683
10/18	17	49.4220	134.13	3.704
10/21	20	49.1340	156.72	3.686
10/22	20	49.3584	158.14	3.687
10/25	15	49.4578	118.81	3.695
10/29	15	49.3684	118.62	3.688
10/31	18	49.4160	142.42	3.693
11/1	18	49.0188	140.09	3.694
11/19	20	49.1002	155.86	3.702
11/20	17	49.1459	132.97	3.694
11/21	18	49.0903	140.01	3.707
11/26	20	49.4875	158.74	3.692
11/29	20	49.5948	159.29	3.695
12/3	20	49.4081	158.34	3.689
12/5	20	49.4617	158.14	3.702
12/6	20	49.7160	160.35	3.688
12/7	19	49.7219	152.33	3.690
12/7	18	49.7299	144.28	3.692
12/14	20	49.7756	160.63	3.691
12/15	20	49.3843	157.01	3.717
12/18	20	49.7934	160.65	3.693
12/19	20	49.2015	157.04	3.689
12/21	22	49.3684	173.82	3.691
12/27	25	49.5034	198.53	3.692
12/28	20	49.6206	159.66	3.690
1/2	20	49.7219	160.20	3.693
1/2	20	49.7219	160.16	3.694
1/2	20	49.7100	159.99	3.696
1/2	20	49.7100	160.16	3.692

Table A-3. (Contd)

Date	t/s	I/ma	A/vs	ϵ/mcal/vs
1/2	20	49.7080	160.13	3.692
1/2	20	49.7080	160.12	3.692
1/2	20	49.7100	160.31	3.689
1/2	20	49.7100	160.31	3.688
1/2	20	49.7100	160.44	3.686
1/17	24	49.7398	191.67	3.707
1/17	26	49.7398	208.45	3.692
1/17	20	49.7398	160.34	3.692
1/21	25	49.7477	200.66	3.689
1/21	20	49.7497	160.45	3.691
1/21	24	49.7616	192.68	3.690
1/30	20	49.7001	160.06	3.693
1/30	20	49.0883	155.40	3.710
1/31	20	49.1876	156.66	3.696
1/31	20	49.0605	155.96	3.693
2/5	20	49.9364	161.77	3.689
2/5	20	49.9364	161.60	3.692
2/7	20	49.9206	160.66	3.712
2/7	23	49.9265	184.89	3.710
2/8	20	49.8530	160.26	3.711
2/12	20	49.9345	160.83	3.710
2/13	20	49.9285	160.55	3.716
2/13	20	49.9285	160.96	3.706
2/14	20	49.9145	160.45	3.716
2/14	20	49.9225	161.26	3.698
2/14	20	49.9265	161.36	3.697
2/15	20	49.9305	161.24	3.700
2/15	20	49.9305	161.33	3.698
2/19	20	49.9305	161.52	3.694
2/21	20	49.9682	161.60	3.697
2/21	20	49.9742	161.33	3.704
2/22	20	49.9702	161.40	3.702
2/22	20	49.9642	161.55	3.698
2/25	20	49.9881	162.20	3.686
2/25	20	49.9881	161.82	3.695
2/26	20	49.9901	161.96	3.692
2/26	20	49.9901	161.75	3.697
2/28	20	49.9901	162.05	3.690

Average ϵ = 3.696 mcal/vs

σ (Single measurement = 8×10^{-3} = 0.2%

Table A-4. Long-Term Calibration Constants, 0.3 mv Range (with Rotation)

Date	t/s	I/ma	A/vs	ϵ/mcal/vs
10/5	17	29.9587	165.9	1.101
10/5	20	29.9586	194.6	1.104
10/18	17	29.6727	162.3	1.103
10/26	12	29.7879	115.1	1.106
10/29	15	29.6449	141.6	1.114
11/1	16	29.4403	148.9	1.114
11/20	21	29.5158	195.0	1.123
11/26	19	29.7025	180.5	1.111
12/3	20	29.2079	183.6	1.112
12/6	22	29.8395	210.6	1.113
12/6	13	29.8395	124.7	1.111
12/7	21	29.8415	201.0	1.113
12/14	17	29.8730	163.3	1.111
12/14	21	29.8772	202.0	1.110
12/15	17	29.8812	163.0	1.114
12/15	17	29.6270	159.6	1.118
12/19	18	29.5158	168.4	1.114
12/20	17	29.5714	159.9	1.112
12/27	20	29.7183	189.8	1.113
1/21	17	29.8593	163.3	1.111
1/30	17	29.4423	161.2	1.094
1/31	17	29.5078	159.2	1.112
1/31	20	29.5256	188.2	1.108
2/7	17	29.9587	163.4	1.118
2/7	17	29.9130	163.1	1.116
2/8	17	29.9388	163.7	1.114
2/13	19	29.9627	182.4	1.119
2/13	17	29.9567	163.8	1.114
2/14	18	29.9607	173.5	1.114
2/15	19	29.9646	183.7	1.112
2/19	19	29.9627	184.1	1.108
2/20	17	29.9587	163.4	1.118
2/20	19	29.9527	183.0	1.114
2/20	17	29.9646	164.0	1.113
2/21	20	29.9646	193.7	1.109
2/21	17	29.9906	164.1	1.115
2/21	17	29.9924	163.9	1.116
2/22	17	29.9880	164.4	1.112
2/22	17	29.9905	164.3	1.113
2/25	17	30.0004	165.3	1.108
2/26	17	30.0004	164.5	1.112
2/28	17	30.0004	164.7	1.111

Average ϵ = 1.112 mcal/vs

σ (Single measurement) = 5×10^{-3} = 0.5%

Table A-5. Long-Term Calibration Constants, 0.1 mv Range (with Rotation)

Date	t/s	I/ma	A/vs	ϵ/mcal/vs
10/5	16	19.9817	211	0.362
10/5	9	19.9817	117	0.366
10/5	12	19.9797	166	0.371
10/18	16	19.7910	204	0.367
10/29	14	19.7732	117	0.370
10/31	11	19.4300	135	0.369
10/31	11	19.7811	139	0.371
11/19	14	19.6540	175	0.370
11/21	18	19.6361	226	0.368
11/26	18	19.8070	228	0.370
11/26	12	19.8030	152	0.371
12/3	17	19.5150	209	0.371
12/5	11	19.8308	140	0.369
12/6	11	19.8983	141	0.370
12/7	18	19.9003	232	0.368
12/7	10	19.9003	128	0.369
12/7	12	19.9023	154	0.368
12/15	17	19.7632	211	0.376
12/20	14	19.6262	175	0.370
12/27	15	19.8228	190	0.370
12/28	17	19.8665	217	0.370
1/17	18	19.9062	230	0.370
1/21	14	19.9122	179	0.371
1/21	17	19.9142	218	0.370
1/21	13	19.9102	166	0.372
1/30	13	19.8904	166	0.371
1/31	17	19.6897	213	0.370
1/31	13	19.6898	163	0.369
1/31	14	19.6262	174	0.370
2/5	15	19.9837	194	0.369
2/5	17	19.9837	218	0.372
2/8	13	19.9678	166	0.373
2/12	13	19.9837	168	0.371
2/14	13	19.9817	167	0.372
2/14	16	19.9797	206	0.371
2/14	13	19.9797	169	0.368
2/15	17	19.9817	219	0.370
2/15	13	19.9817	167	0.371
2/19	17	19.9678	218	0.372
2/20	13	19.9778	166	0.375
2/20	15	19.9758	193	0.371
2/21	15	19.9837	192	0.373
2/21	13	19.9996	168	0.370
2/22	15	19.9936	192	0.373

Average ϵ = 0.370 mcal/vs

σ (Single measurement) = 2×10^{-3} = 0.61%

Table A-6. Long-Term Calibration Constants, 0.03 mv Range (with Rotation)

Date	t/s	I/ma	A/vs	ϵ/mcal/vs
10/18	13	9.8995	135	0.113
10/22	17	9.8856	178	0.112
10/26	11	9.9420	119	0.110
10/29	11	9.8898	115	0.112
11/19	17	9.8266	176	0.112
11/19	17	9.8210	176	0.112
11/29	17	9.9364	182	0.111
12/3	20	9.7795	207	0.109
12/3	22	9.7801	225	0.111
12/3	25	9.7825	257	0.111
12/4	13	9.8216	137	0.109
12/5	14	9.9319	153	0.108
12/14	20	9.9684	213	0.112
2/8	19	9.9909	205	0.111
2/21	20	10.0048	214	0.112
2/28	16	10.0068	171	0.112
3/1	15	10.0068	162	0.111

Average ϵ = 0.111 mcal/vs

σ (Single measurement) = 1.4×10^{-3} = 1.3%

Table A-7. Long-Term Calibration Constants, 0.01 mv Range (with Rotation)

Date	t/s	I/ma	A/vs	ϵ/mcal/vs
10/18	13	5.9957	152	0.0367
11/1	12	5.9764	137	0.0375
11/26	14	5.9959	165	0.0366
11/29	18	5.9933	208	0.0372
1/30	14	5.9949	156	0.0387
3/1	15	5.9826	172	0.0373
3/1	15	5.9727	171	0.0373

Average ϵ = 0.0373 mcal/vs

σ (Single measurement) = 7×10^{-4} = 1.8%

Table A-8. Keithley Range Calibration Constants

Range	ϵ_{expt} [a]	Range factor [b]	Range [c]	ϵ_{calc} [d]
mv	mcal/vs		mv	mcal/vs
10	36.971 (30) [e]	1.0	10	36.971
3	11.088 (11)	1.0032 (1) [f]	2.990	11.056
1	3.697 (7)	1.0038 (2)	0.996	3.683
0.3	1.112 (6)	0.9999 (2)	0.300	1.109
0.1	0.370 (2)	0.999 (3)	0.100	0.370
0.03	0.111 (1)	0.997 (1)	0.301	0.111
0.01	0.0373 (7)	1.0	0.01	0.0370

[a] Average calibration constants from long-term calibration experiments shown in tables 4-10.

[b] Ratio of indicated calorimeter full-scale voltage output to actual ESI-measured voltage – average or two experiments.

[c] Adjusted-Keithley ranges obtained by dividing the original Keithley ranges by range factors.

[d] Calculated calibration constant obtained by using the average 10 mv experimentally determined calibration constant in equation 8.

[e] The numbers in the parentheses are the standard deviations of the last digit for a single measurement, *i.e.*, 36.971 (30) = 36.941 to 37.001.

[f] The numbers in the parentheses are the experimental spread in the last digit for two measurements, *i.e.*. 1.0032 (1) = 1.0031 to 1.0033.

Table A-9. Area Averages for Calibration Curves, 1-μv Range (with Rotation)

Curve section time [a]	Average curve areas [b]	
	Class A [c]	Class B [d]
min	vs	
2-15-5	144 (6) [e]	114 (14)
2-10-4	138 (2)	105 (5)
2-8-4	133 (1)	103 (6)
2-6-4	121 (2)	93 (9)
2-10-2	137 (2)	106 (9)
2-8-2	131 (1)	101 (6)
2-6-2	116 (1)	91 (5)
0-10-2	110 (11)	102 (31)
0-8-2	106 (17)	61 (34)
0-6-2	64 (15)	46 (7)

[a] The areas listed for each curve section time were computed from the same experimental curves.

[b] Based on the average 10-mv calibration constant, the area that should be observed if there is no heat of friction or electrical noise is 146 volt seconds.

[c] Area averages of six heat curves characterized by figure 3,A.

[d] Area averages of four heat curves characterized by figure 3,B.

[e] The numbers in the parentheses are the standard deviations of a single area measurement, *i.e.*, 144 (6) = 138 to 150.

Table A-10. Calorimeter Sensitivity, 1-μv Range (with Rotation)

Experiment No.	I/ma	t/s	A [a]/vs	q_{obs} [b]	$q_{obs}-q_{avg}$
				μcal	μcal
1	0.9999	35	102	377	20
2	0.9999	35	102	377	20
3	0.9999	35	95	352	-5
4	0.9999	35	94	348	-9
5	0.9999	35	89	329	-28

Average q = 357 μcal

Sensitivity = σ (Single measurement in q) = ±21 μcal

[a] 2-15-5 Curve section time; ϵ_R = 3.697 μcal.

[b] Electrical heat added was 419 μcal.

Table A-11. Experimental Heats of Dilution

m_i (2) mol/kg	N (2) mmol	N (4) μmol	m_i (4) mmol/kg	m_f mol/kg	$-\Delta H^{ex}_{exp}$ cal/mol	$-\Delta H^{ex}_{calc}$ cal/mol	$-\Delta H^{ex}_{corr}$ cal/mol
N-Methylformamide (NMF)							
1.9958	7.396	0	0	1.2501	48.06	48.54	48.07
1.2500	4.950	9.8	4.3	0.7962	29.42	29.54	29.52
0.7962	3.215	6.4	2.8	0.5105	18.90	18.59	18.97
0.5106	1.120	8.2	1.9	0.1749	21.25	21.85	21.33
2.0015	3.922	0	0	0.6313	89.14	89.18	89.14
0.6312	2.587	5.1	2.2	0.4070	14.85	14.59	14.91
0.5960	1.426	0	0	0.2115	25.48	25.02	25.48
0.2115	0.547	3.5	7.8	0.0788	8.70	8.64	8.73
0.5960	1.518	0	0	0.2220	24.95	24.34	24.95
N-Methylacetamide (NMA)							
1.9990	3.994	0	0	0.6509	124.71	124.76	124.71
1.9990	6.926	0	0	1.2376	73.25	73.31	73.25
1.2376	4.743	9.5	4.3	0.7868	39.90	40.24	40.01
0.7868	3.130	6.3	2.8	0.5068	22.77	22.52	22.84
0.5068	2.051	4.1	1.9	0.3298	13.25	12.94	13.29
0.3298	1.363	2.7	1.2	0.2162	7.70	7.71	7.73
1.9990	3.623	0	0	0.6135	128.18	127.76	128.18
0.6135	2.439	4.9	2.3	0.3966	16.57	16.50	16.62
0.3966	1.620	3.2	1.5	0.2581	9.57	9.67	9.60
1.9682	7.189	0	0	1.2291	70.83	71.11	70.83
1.2291	4.667	9.5	4.1	0.7687	40.64	40.97	40.75
0.7687	3.048	6.1	2.7	0.4929	21.73	22.05	21.80
0.4929	1.992	4.0	1.7	0.3136	12.96	13.02	13.00
1.9682	3.915	0	0	0.6407	122.57	122.60	122.57
0.6407	1.374	10.1	2.4	0.2180	30.67	31.01	30.76

Table A-11. (Contd)

$\underline{m_i(2)}$ mol/kg	N (2) mmol	N (4) μmol	$\underline{m_i(4)}$ mmol/kg	$\underline{m_f}$ mol/kg	$-\Delta H^{ex}_{exp}$ cal/mol	$-\Delta H^{ex}_{calc}$ cal/mol	$-\Delta H^{ex}_{corr}$ cal/mol
N-Methylpropionamide (NMP)							
1.6814	3.459	0	0	0.5605	235.33	234.89	235.33
0.5605	2.166	4.5	2.1	0.3642	37.73	37.47	37.85
1.6814	6.698	0	0	1.0907	126.07	125.94	126.07
1.0907	2.580	16.5	4.0	0.4014	138.95	139.50	139.38
1.4487	3.006	0	0	0.4796	200.75	200.88	200.75
2.0088	4.000	0	0	0.6446	288.21	288.25	288.21
0.6446	2.534	5.1	2.3	0.4119	45.28	45.25	45.42
0.4119	0.876	6.6	1.5	0.1377	48.73	48.77	48.89
2.0088	7.215	0	0	1.2329	165.69	165.81	165.69
1.2328	4.612	9.4	4.1	0.7679	96.53	97.50	96.82
0.5456	1.458	0	0	0.2084	62.46	62.43	62.46
0.3975	1.625	0	0	0.2492	27.08	26.96	27.08
0.2492	1.021	2.1	0.8	0.1540	15.97	16.38	16.02
0.1540	0.386	2.5	0.6	0.0583	15.12	15.63	15.17
N-Butylacetamide (NBA)							
1.9765	6.467	0	0	1.1803	493.29	494.56	493.29
1.1803	4.113	8.7	3.8	0.7132	300.05	300.94	300.80
0.7132	2.618	5.5	2.4	0.4396	157.28	157.90	157.70
0.4396	1.676	3.5	1.6	0.2763	83.27	83.10	83.51
1.9765	3.306	0	0	0.5672	882.25	882.27	882.25
0.5672	1.184	8.8	2.1	0.1900	194.37	194.07	194.93
0.1900	0.428	3.1	0.7	0.0660	51.37	51.47	51.54
1.9985	3.365	0	0	0.5776	*	887.93	

* Experimental error.

Table A-11. (Contd)

$m_i(2)$ mol/kg	N (2) mmol	N (4) μmol	$m_i(4)$ mmol/kg	m_f mol/kg	$-\Delta H^{ex}_{exp}$ cal/mol	$-\Delta H^{ex}_{calc}$ cal/mol	$-\Delta H^{ex}_{corr}$ cal/mol
N-Butylacetamide (NBA) (Contd)							
0.5776	1.215	8.9	2.2	0.1994	195.14	195.89	195.73
0.1994	0.429	3.2	0.8	0.0695	52.78	54.32	52.97
0.0695	0.287	0.6	0.3	0.0460	8.30	8.98	8.33
1.9985	6.651	0	0	1.1738	511.82	510.56	511.82
1.1738	4.036	8.7	3.3	0.6699	322.09	322.87	322.80
0.6699	1.592	10.3	2.4	0.2420	230.36	230.96	231.00
0.2420	0.958	2.0	0.8	0.1479	41.68	41.87	41.80
Urea (U)							
1.9955	7.898	0	0	1.2447	-49.78	-49.77	-49.78
1.2448	4.993	9.7	3.8	0.7609	-34.86	-35.28	-34.98
0.7609	3.112	6.1	2.6	0.4807	-21.56	-21.59	-21.63
0.4807	1.994	3.9	1.5	0.2958	-14.90	-14.71	-14.95
1.9955	4.503	0	0	0.6921	-90.35	-90.28	-90.35
Ethylene glycol (EG)							
2.0301	4.190	0	0	0.6635	112.45	112.46	112.45
0.6635	1.516	10.5	2.5	0.2333	36.40	36.59	36.53
2.0301	7.574	0	0	1.2595	62.70	62.70	62.70
1.2595	4.945	9.8	4.3	0.7983	38.33	38.41	38.47
0.7983	3.223	6.4	2.8	0.5141	23.94	23.99	24.03
0.5141	2.107	4.2	1.8	0.3305	15.39	15.63	15.45
0.3305	1.360	2.7	1.2	0.2134	10.28	10.03	10.32
0.2134	0.476	3.5	0.8	0.0739		11.91	

Table A-11. (Contd)

$\underline{m_i}$ (2) mol/kg	N (2) mmol	N (4) μmol	$\underline{m_i}$ (4) mmol/kg	$\underline{m_f}$ mol/kg	$-\Delta H^{ex}_{exp}$ cal/mol	$-\Delta H^{ex}_{calc}$ cal/mol	$-\Delta H^{ex}_{corr}$ cal/mol
Pentaerythritol (P)							
0.5000	1.102	0	0	0.1717	31.29	30.99	31.29
0.1717	0.709	1.4	0.6	0.1115	5.72	5.68	5.74
0.1115	0.247	1.8	0.4	0.0382	*	6.92	
0.5000	2.097	0	0	0.3460	14.63	14.54	14.63
0.3460	0.696	5.5	1.2	0.1090	22.21	22.37	22.29
0.1090	0.246	1.8	0.4	0.0383	6.30	6.67	6.32
0.5000	1.279	0	0	0.1906	29.02	29.21	29.01
0.1906	0.492	3.1	1.0	0.0863	9.34	9.84	9.39
0.5362	2.360	0	0	0.4001	12.78	12.85	12.78
0.4001	1.622	3.2	1.5	0.2642	12.96	12.83	13.01
0.2642	0.540	4.2	1.2	0.1000	*	15.50	
0.1696	0.436	0	0	0.1690	**		
0.1690	0.436	0	0	0.0651	10.29	9.81	10.29
0.1696	0.760	0	0	0.1690	**		
0.1690	0.760	0	0	0.1149	†	5.10	
0.1149	0.279	1.9	0.4	0.0414	6.52	6.94	6.54
Glucose (G)							
1.9992	3.398	0	0	0.5830	104.94	104.91	104.94
0.5830	1.102	8.7	2.1	0.1834	31.38	31.82	31.49
1.9644	6.546	0	0	1.1793	57.25	56.81	57.25
1.1793	4.389	8.2	3.5	0.7282	34.44	34.35	34.54
1.0413	1.975	0	0	0.3235	56.56	55.84	56.56
1.9995	3.368	0	0	0.5764	104.94	105.45	104.94
0.5764	1.125	8.6	2.0	0.1795	31.16	31.62	31.27

*Data point outside 2 σ in least squares fit.

**Wet wall experiment.

† Experimental error.

Table A-11. (Contd)

$m_i(2)$ mol/kg	N (2) mmol	N (4) μmol	$m_i(4)$ mmol/kg	m_f mol/kg	$-\Delta H^{ex}_{exp}$ cal/mol	$-\Delta H^{ex}_{calc}$ cal/mol	$-\Delta H^{ex}_{corr}$ cal/mol
Sucrose (S)							
2.0048	3.022	0	0	0.5299	173.26	173.25	173.26
0.5299	2.000	3.8	1.7	0.3340	25.83	25.65	25.92
0.3340	1.309	2.5	1.1	0.2119	16.71	16.30	16.76
0.2119	0.457	3.3	0.8	0.0719	19.49	18.99	19.56
2.0048	6.171	0	0	1.2165	88.74	88.23	88.74
1.2165	4.056	7.2	3.4	0.7469	57.08	57.34	57.26
2.0152	5.727	0	0	1.1375	98.41	98.73	98.41
1.1375	3.832	6.9	3.0	0.6755	56.79	56.96	56.95
0.6755	2.508	4.6	2.0	0.4097	34.28	34.33	34.38
0.4097	0.920	5.9	1.4	0.1398	35.30	36.03	35.42
0.1398	0.352	2.2	0.5	0.0518	11.71	12.00	11.76
2.0117	5.760	0	0	1.1526	96.40	96.55	96.40
1.1526	1.880	13.6	3.0	0.3080	*	106.53	
0.3080	1.222	2.3	1.0	0.1913	15.76	15.63	15.81
0.1913	0.777	1.5	0.6	0.1183	9.76	9.89	9.79
N-Methylformamide-N-methylacetamide (NMF-NMA)							
(x_{NMF} = 0.5026)							
2.1289	7.966	0	0	1.3325	65.42	65.85	65.42
1.3325	5.128	10.3	4.3	0.8217	39.78	40.64	39.90
0.8217	3.262	6.6	3.2	0.5420	21.97	21.72	22.05
0.5420	2.206	4.4	1.8	0.3412	15.06	15.37	15.11
2.1289	4.458	0	0	0.7191	114.97	114.50	114.97
0.7191	2.883	5.8	2.4	0.4476	20.94	20.96	21.01

* Experimental error.

Table A-11. (Contd)

$\underline{m_i(2)}$ mol/kg	N(2) mmol	N(4) μmol	$\underline{m_i(4)}$ mmol/kg	$\underline{m_f}$ mol/kg	$-\Delta H^{ex}_{exp}$ cal/mol	$-\Delta H^{ex}_{calc}$ cal/mol	$-\Delta H^{ex}_{corr}$ cal/mol
N-Methylformamide-N-methylpropionamide (NMF-NMP)							
(x_{NMF} = 0.5062)							
2.1545	7.816	0	0	1.3280	107.51	107.76	107.51
1.3280	5.047	10.2	4.9	0.8599	*	62.39	
0.8599	3.361	6.8	3.0	0.5458	40.89	41.04	41.03
0.5458	2.206	4.4	2.0	0.3533	24.55	24.53	24.63
2.1545	4.258	0	0	0.6800	194.05	193.79	194.05
1.3051	2.938	0	0	0.4391	113.95	114.03	113.95
0.4391	1.160	7.0	1.7	0.1709	33.48	33.47	33.60
0.1709	0.455	2.8	0.7	0.0670	12.47	12.57	12.51
1.3051	5.610	0	0	0.8332	62.59	62.84	62.59
0.8332	2.325	13.0	3.1	0.3367	*	64.12	
0.3367	0.946	5.4	1.3	0.1357	24.56	24.82	24.65
N-Methylformamide-N-butylacetamide (NMF-NBA)							
(x_{NMF} = 0.5077)							
2.1309	7.482	0	0	1.2947	199.44	199.52	199.44
1.2947	4.692	9.8	4.3	0.7947	119.25	119.73	119.61
0.7947	3.016	6.3	2.8	0.4983	68.55	68.82	68.78
0.4983	1.959	4.0	1.9	0.3229	39.19	39.50	39.33
2.1309	4.026	0	0	0.6564	351.74	351.66	351.74
0.6564	2.518	5.2	2.2	0.4096	56.51	56.52	56.69

* Data point outside 2 σ in least squares fit.

Table A-11. (Contd)

$\underline{m_i(2)}$ mol/kg	N (2) mmol	N (4) μmol	$\underline{m_i(4)}$ mmol/kg	$\underline{m_f}$ mol/kg	$-\Delta H^{ex}_{exp}$ cal/mol	$-\Delta H^{ex}_{calc}$ cal/mol	$-\Delta H^{ex}_{corr}$ cal/mol
N-Methylformamide–urea (NMF-U)							
(x_{NMF} = 0.4988)							
2.1225	8.228	0	0	1.3314	-9.46	-9.41	-9.46
1.3314	3.009	20.4	4.7	0.4613	-12.57	-12.94	-12.63
0.4613	1.111	7.4	1.7	0.1671	-5.32	-4.99	-5.34
2.1225	4.309	0	0	0.6786	-18.95	-18.87	-18.95
0.6786	1.556	10.8	2.5	0.2360	-7.07	-7.28	-7.09
0.2360	0.575	3.8	0.9	0.0838	-3.23	-2.66	-3.24
N-Methylformamide–ethylene glycol (NMF-EG)							
(x_{NMF} = 0.5050)							
2.0955	7.785	0	0	1.3119	62.08	61.53	62.08
2.0955	7.484	0	0	1.3236	60.17	60.59	60.17
1.3236	5.156	10.3	5.0	0.8655	37.10	37.37	37.25
0.8655	3.440	6.9	3.0	0.5500	26.22	26.34	26.31
2.0955	4.006	0	0	0.6585	115.14	115.19	115.14
0.6585	2.667	5.3	2.3	0.4224	19.77	19.92	19.84
0.4224	1.739	3.5	1.5	0.2723	13.19	12.80	13.23

Table A-11. (Contd)

m_i (2) mol/kg	N (2) mmol	N (4) μmol	m_i (4) mmol/kg	m_f mol/kg	$-\Delta H^{ex}_{exp}$ cal/mol	$-\Delta H^{ex}_{calc}$ cal/mol	$-\Delta H^{ex}_{corr}$ cal/mol
N-Methylformamide–pentaerythritol (NMP-P)							
(χ_{NMF} = 0.4989)							
0.5240	1.315	0	0	0.1983	26.56	26.45	26.56
0.1987	0.494	3.2	0.8	0.0739	10.13	10.36	10.17
0.5240	2.226	0	0	0.3409	15.04	14.79	15.03
0.3409	1.398	2.8	1.1	0.2102	10.80	10.71	10.83
0.2102	0.871	1.7	0.6	0.1280	6.97	6.81	7.00
1.0771	2.560	0	0	0.3829	54.33	54.46	54.33
0.3829	1.009	6.1	1.4	0.1466	19.25	19.39	19.32
1.0771	4.474	0	0	0.6708	31.61	31.42	31.61
0.6708	2.695	5.3	2.4	0.4345	18.60	18.86	18.67
0.4345	1.778	3.5	1.4	0.2720	13.03	13.22	13.07
0.2720	1.133	2.2	0.8	0.1657	8.90	8.76	8.92
N-Methylformamide-glucose (NMF-G)							
(χ_{NMF} = 0.5229)							
2.0604	7.198	0	0	1.2484	56.62	56.84	56.62
1.2484	4.744	9.2	4.1	0.7880	34.33	34.67	34.45
0.7880	3.111	6.1	2.7	0.5023	22.43	22.41	22.51
0.5023	1.100	7.8	1.8	0.1709	26.62	26.84	26.72
2.0604	3.820	0	0	0.6251	104.40	104.40	104.40

Table A-11. (Contd)

m_i (2) mol/kg	N (2) mmol	N (4) μmol	m_i (4) mmol/kg	m_f mol/kg	$-\Delta H^{ex}_{exp}$ cal/mol	$-\Delta H^{ex}_{calc}$ cal/mol	$-\Delta H^{ex}_{corr}$ cal/mol
N-Methylformamide-sucrose (NMF-S)							
(χ_{NMF} = 0.5723)							
2.0681	6.787	0	0	1.2216	72.98	73.44	72.98
1.2216	4.454	8.4	3.7	0.7516	44.43	44.35	44.58
0.7516	2.886	5.6	2.4	0.4716	28.03	27.63	28.13
0.4716	1.044	7.2	1.7	0.1621	30.30	31.59	30.41
2.0681	3.606	0	0	0.6012	132.78	132.51	132.78
0.6012	1.294	9.0	2.1	0.2010	40.62	40.46	40.77
N-Methylacetamide-N-methylpropionamide (NMA-NMP)							
(χ_{NMA} = 0.5038)							
2.1609	7.788	0	0	1.3219	125.78	126.12	125.78
1.3219	4.986	10.1	4.3	0.8186	72.03	72.56	72.23
0.8186	3.216	6.5	2.8	0.5137	41.13	41.46	41.25
0.5137	2.080	4.1	1.7	0.3237	23.83	24.03	23.90
2.1609	3.900	0	0	0.6634	220.50	220.15	220.50
0.6634	2.640	5.3	2.2	0.4147	32.53	32.72	32.63
0.4147	0.964	6.6	1.6	0.1508	31.54	31.41	31.65
0.3029	0.814	0	0	0.3020	*		
0.3020	0.814	0	0	0.1196	21.05	20.92	21.05
0.1196	0.317	2.0	0.5	0.0465	7.20	7.72	7.23

*Wet wall experiment.

Table A-11. (Contd)

$m_i(2)$ mol/kg	N (2) mmol	N (4) μmol	$m_i(4)$ mmol/kg	m_f mol/kg	$-\Delta H^{ex}_{exp}$ cal/mol	$-\Delta H^{ex}_{calc}$ cal/mol	$-\Delta H^{ex}_{corr}$ cal/mol
N-Methylacetamide-N-butylacetamide (NMA-NBA)							
(x_{NMA} = 0.5175)							
1.9880	6.870	0	0	1.2090	203.99	204.08	203.99
1.2090	4.350	9.1	4.0	0.7438	118.43	119.55	118.77
0.7438	2.807	5.8	2.6	0.4695	65.56	64.71	65.75
1.9880	3.747	0	0	0.6158	354.69	354.53	354.69
0.6158	2.357	4.9	2.2	0.3878	52.09	51.88	52.25
0.3878	0.832	6.2	1.5	0.1327	51.23	52.03	51.40
N-Methylacetamide-urea (NMA-U)							
(x_{NMA} ≈ 0.4996)							
2.1493	8.215	0	0	1.3525	*	5.27	
1.3525	5.247	10.4	4.4	0.8389	1.563	1.61	1.56
0.8389	3.409	6.7	2.8	0.5263	0.025	0.02	0.02
0.5263	1.266	8.4	1.8	0.1831	-1.221	-1.08	-1.23
2.1493	4.322	0	0	0.6899	6.984	6.98	6.98
0.6899	1.541	10.9	2.4	0.2309	-0.843	-0.97	-0.85
N-Methylacetamide-ethylene glycol (NMA-EG)							
(x_{NMA} ≈ 0.4976)							
1.9949	7.342	0	0	1.2569	72.09	72.43	72.09
1.2569	4.868	9.7	4.5	0.8050	44.29	44.35	44.45
0.8050	3.218	6.4	3.1	0.5289	26.93	27.10	27.03
0.5289	2.150	4.3	2.0	0.3447	17.97	18.07	18.04
1.9949	3.748	0	0	0.6202	135.11	134.92	135.11
0.6202	2.512	5.0	2.3	0.4060	20.81	21.01	20.89

*Experimental error.

Table A-11. (Contd)

m_i (2) mol/kg	N (2) mmol	N (4) μmol	m_i (4) mmol/kg	m_f mol/kg	$-\Delta H^{ex}_{exp}$ cal/mol	$-\Delta H^{ex}_{calc}$ cal/mol	$-\Delta H^{ex}_{corr}$ cal/mol
N-Methylacetamide-pentaerythritol (NMA-P)							
(x_{NMA} = 0.4995)							
1.0779	2.536	0	0	0.3818	67.13	67.31	67.13
0.3818	1.561	3.1	1.3	0.2390	13.90	13.81	13.95
0.2390	0.994	2.0	0.8	0.1511	8.39	8.51	8.42
0.1511	0.632	1.3	0.5	0.0957	5.16	5.35	5.18
1.0779	4.433	0	0	0.6786	38.54	38.61	38.54
0.6786	2.692	5.3	2.1	0.4136	25.81	25.62	25.89
0.4136	1.692	3.3	1.3	0.2547	15.51	15.37	15.56
0.2547	1.062	2.1	0.8	0.1584	9.39	9.31	9.42
0.1584	0.402	2.6	0.6	0.0581	9.42	9.70	9.46
1.0779	2.324	0	0	0.3624	69.26	69.19	69.26
0.3624	0.855	5.8	1.3	0.1280	22.66	22.67	22.74
N-Methylacetamide-glucose (NMP-G)							
(x_{NMA} = 0.5239)							
2.2847	7.725	0	0	1.3513	96.49	96.81	96.49
1.3513	2.725	19.1	4.4	0.4303	103.76	103.92	104.11
0.4303	1.012	6.7	1.6	0.1524	32.97	32.99	33.09
0.1524	0.379	2.5	0.6	0.0559	10.67	11.63	10.72
2.2847	4.343	0	0	0.7082	168.67	168.50	168.67
0.7082	1.567	10.8	2.5	0.2393	54.60	54.82	54.80
0.2393	0.585	3.8	0.9	0.0867	17.72	18.31	17.79

Table A-11. (Contd)

$\underline{m_i(2)}$ / mol/kg	N (2) / mmol	N (4) / μmol	$\underline{m_i(4)}$ / mmol/kg	$\underline{m_f}$ / mol/kg	$-\Delta H^{ex}_{exp}$ / cal/mol	$-\Delta H^{ex}_{calc}$ / cal/mol	$-\Delta H^{ex}_{corr}$ / cal/mol
N-Methylacetamide–sucrose (NMA-S)							
(x_{NMA} = 0.5717)							
1.9966	6.533	0	0	1.1902	106.02	106.01	106.02
1.1902	4.322	8.2	3.5	0.7278	65.72	65.98	65.92
0.7278	2.790	5.4	2.3	0.4529	41.03	41.02	41.16
0.4529	1.797	3.5	1.6	0.2899	24.74	24.95	24.83
N-Methylpropionamide-N-butylacetamide (NMP-NBA)							
(x_{NMP} = 0.5023)							
2.2015	3.895	0	0	0.6532	550.23	550.76	550.23
0.6532	2.488	5.2	2.4	0.4188	76.46	76.44	76.71
0.4188	0.847	6.6	1.6	0.1377	79.42	83.21	79.71
2.2015	7.226	0	0	1.3236	312.12	311.31	312.12
1.3236	4.671	9.8	4.3	0.8057	183.92	187.09	184.44
0.8057	3.025	6.3	3.0	0.5170	97.66	97.45	97.97
0.5170	2.009	4.1	1.8	0.3255	59.91	60.10	60.10
1.0738	4.134	0	0	0.6746	143.60	140.76	143.60
0.6746	2.548	5.3	2.4	0.4259	84.25	81.47	84.51
0.4259	0.898	6.7	1.5	0.1386	86.16	85.20	86.43

Table A-11. (Contd)

m_i (2) mol/kg	N (2) mmol	N (4) μmol	m_i (4) mmol/kg	m_f mol/kg	$-\Delta H^{ex}_{exp}$ cal/mol	$-\Delta H^{ex}_{calc}$ cal/mol	$-\Delta H^{ex}_{corr}$ cal/mol
N-Methylpropionamide-urea (NMP-U)							
(x_{NMP} = 0.4916)							
2.1580	8.110	0	0	1.3560	37.48	37.59	37.48
1.3560	5.198	10.4	4.2	0.8282	24.23	24.54	24.30
0.8282	3.294	6.6	2.8	0.5219	13.65	13.51	13.69
0.5219	2.122	4.2	1.7	0.3273	8.28	8.15	8.31
2.1580	4.368	0	0	0.6975	68.11	67.99	68.11
0.6975	2.796	5.6	2.4	0.4389	11.07	11.18	11.11
0.4389	1.024	7.0	1.6	0.1509	11.47	11.65	11.51
N-Methylpropionamide-ethylene glycol (NMP-EG)							
(x_{NMP} = 0.5054)							
1.9782	7.280	0	0	1.2295	107.11	107.63	107.11
1.2295	4.695	9.5	4.1	0.7676	66.27	66.40	66.49
0.7676	3.036	6.1	2.6	0.4845	40.15	40.70	40.29
0.4845	1.954	3.9	1.7	0.3115	24.50	24.86	24.59
1.9782	3.702	0	0	0.6086	197.35	196.88	197.35
0.6086	2.433	4.9	2.2	0.3899	30.86	31.44	30.97
0.3899	1.565	3.2	1.4	0.2506	19.74	20.03	19.81

Table A-11. (Contd)

$\underline{m_i}$ (2) mol/kg	N (2) mmol	N (4) μmol	$\underline{m_i}$ (4) mmol/kg	$\underline{m_f}$ mol/kg	$-\Delta H^{ex}_{exp}$ cal/mol	$-\Delta H^{ex}_{calc}$ cal/mol	$-\Delta H^{ex}_{corr}$ cal/mol
N-Methylpropionamide-pentaerythritol (NMP-P)							
(χ_{NMP} = 0.4980)							
0.5271	1.224	0	0	0.1885	49.44	49.41	49.44
0.1885	0.445	3.0	0.7	0.0671	16.79	16.94	16.85
0.5271	2.145	0	0	0.3369	27.92	27.90	27.92
0.3369	1.376	2.7	1.2	0.2138	17.71	17.89	17.76
0.2138	0.885	1.8	0.8	0.1404	10.40	10.43	10.44
1.0752	2.257	0	0	0.3497	105.05	105.04	105.05
0.3497	0.844	5.6	1.2	0.1237	32.46	32.52	32.57
1.0752	4.496	0	0	0.6802	56.73	56.75	56.73
0.6802	2.699	5.3	2.5	0.4466		34.05	
0.4466	1.811	3.6	1.5	0.2793	24.28	24.51	24.35
0.2793	1.160	2.3	0.9	0.1711	15.77	15.58	15.81
N-Methylpropionamide-glucose (NMP-G)							
(χ_{NMP} = 0.5186)							
2.2935	8.192	0	0	1.3834	140.24	140.31	140.24
1.3834	3.167	19.3	4.5	0.4855	150.23	152.14	150.76
0.4855	1.242	7.5	1.8	0.1837	52.99	54.20	53.19
0.1837	0.481	3.0	0.7	0.0685	19.42	21.09	19.50
2.2935	4.666	0	0	0.7170	251.24	251.93	251.24
0.7170	1.882	10.8	2.4	0.2669	77.47	79.62	77.75
0.2669	0.789	4.3	1.0	0.1076	27.38	28.99	27.49
1.5536	5.947	0	0	0.9759	96.44	94.66	96.44
0.9759	2.179	14.3	3.4	0.3406	112.98	110.61	113.38
0.3406	0.816	5.4	1.3	0.1236	42.02	39.35	42.17
0.1236	0.306	2.0	0.5	0.0459	15.20	14.27	15.26

Table A-11. (Contd)

m_i (2) mol/kg	N (2) mmol	N (4) μmol	m_i (4) mmol/kg	m_f mol/kg	$-\Delta H^{ex}_{exp}$ cal/mol	$-\Delta H^{ex}_{calc}$ cal/mol	$-\Delta H^{ex}_{corr}$ cal/mol
N-Methylpropionamide-glucose (NMP-G) (Contd)							
1.5536	5.683	0	0	0.9652	97.81	96.47	97.81
0.9652	3.642	7.2	3.2	0.6055	61.57	61.84	61.78
0.6055	2.377	4.7	2.1	0.3861	38.27	38.80	38.41
0.3861	1.562	3.1	1.4	0.2476	24.44	24.92	24.53
0.2476	1.025	2.0	0.9	0.1616	15.18	15.63	15.24
0.1616	0.677	1.3	0.6	0.1059	9.65	10.19	9.69
N-Methylpropionamide-sucrose (NMP-S)							
(χ_{NMP} = 0.5499)							
2.4865	7.600	0	0	1.4158	195.22	196.26	195.22
1.4158	4.896	9.3	3.9	0.8426	116.40	117.70	116.76
0.8426	3.125	6.1	2.5	0.5105	71.81	72.22	72.03
0.5105	1.994	3.9	1.6	0.3130	44.12	44.34	44.27
2.4865	4.392	0	0	0.7203	341.22	340.21	341.22
0.7203	1.687	10.4	2.4	0.2541	103.27	103.74	103.63
N-Butylacetamide-urea (NBA-U)							
(χ_{NBA} = 0.4855)							
2.1768	8.114	0	0	1.3698	107.68	108.29	107.68
1.3698	4.954	10.3	4.0	0.8054	74.30	75.88	74.49
0.8054	3.068	6.3	2.5	0.4881	39.80	39.29	39.90
0.4881	1.924	3.9	1.5	0.2955	22.78	21.91	22.84
2.1768	4.487	0	0	0.7042	197.77	197.06	197.77
0.7042	2.722	5.6	2.2	0.4232	33.24	33.97	33.33
0.4232	1.058	6.7	1.6	0.1585	27.77	28.81	27.87

Table A-11. (Contd)

$\underline{m}_i$ (2) mol/kg	N (2) mmol	N (4) μmol	m_i (4) mmol/kg	$\underline{m}_f$ mol/kg	$-\Delta H^{ex}_{exp}$ cal/mol	$-\Delta H^{ex}_{calc}$ cal/mol	$-\Delta H^{ex}_{corr}$ cal/mol
N-Butylacetamide-urea (NBA-U) (Contd)							
0.9987	4.183	0	0	0.6363	47.16	46.76	47.16
0.6363	2.452	5.1	2.1	0.3934	29.36	28.90	29.45
0.3934	1.555	3.2	1.3	0.2464	16.73	16.23	16.78
0.2464	0.570	4.0	0.9	0.0869	15.82	16.33	15.87
N-Butylacetamide-ethylene glycol (NBA-EG)							
(χ_{NBA} = 0.4743)							
2.0150	3.596	0	0	0.6058	*	344.43	
0.6058	1.279	9.5	2.3	0.2055	89.06	90.21	89.38
0.2055	0.460	3.3	0.8	0.0740	28.13	27.96	28.24
2.0150	7.078	0	0	1.2199	195.66	196.09	195.66
1.2199	4.408	9.3	3.9	0.7367	116.77	117.51	117.12
0.7367	2.803	5.8	2.4	0.4526	66.08	66.15	66.28
0.4526	1.770	3.7	1.5	0.2827	37.70	38.05	37.82
0.2827	1.113	2.3	1.0	0.1820	21.23	21.91	21.32
0.1820	0.740	1.5	0.6	0.1151	14.44	14.26	14.48
1.9835	3.357	0	0	0.5715	345.08	344.80	345.08
0.5715	1.146	9.0	2.1	0.1865	86.305	86.31	86.61
1.9835	7.051	0	0	1.2188	188.95	188.73	188.95
1.2188	4.403	9.3	3.9	0.7349	117.13	117.65	117.47
0.7349	2.797	5.8	2.4	0.4483	67.17	66.73	67.37
0.4483	1.760	3.6	1.5	0.2766	38.87	38.39	38.99

* Data point outside 2 σ in least squares fit.

Table A-11. (Contd)

m_i (2) mol/kg	N (2) mmol	N (4) μmol	m_i (4) mmol/kg	m_f mol/kg	$-\Delta H^{ex}_{exp}$ cal/mol	$-\Delta H^{ex}_{calc}$ cal/mol	$-\Delta H^{ex}_{corr}$ cal/mol
N-Butylacetamide-pentaerythritol (NBA-P)							
(χ_{NBA} = 0.4958)							
0.5326	2.250	0	0	0.3392	46.31	46.28	46.31
0.3392	1.341	2.7	1.1	0.2110	29.72	29.78	29.81
0.2110	0.849	1.7	0.7	0.1324	17.58	17.45	17.63
0.1324	0.542	1.1	0.5	0.0848	10.32	10.13	10.36
0.5326	2.244	0	0	0.3411	45.77	45.83	45.77
0.3411	0.899	5.4	1.2	0.1290	48.30	48.43	48.45
0.1290	0.373	2.1	0.5	0.0518	15.89	16.17	15.95
1.0701	2.431	0	0	0.3616	171.77	171.67	171.77
0.3616	1.433	2.9	1.2	0.2226	32.25	32.45	32.35
0.2226	0.891	1.8	0.7	0.1345		19.64	
1.0701	4.387	0	0	0.6678	98.13	98.22	98.13
0.6678	2.511	5.2	2.0	0.3958	65.06	65.31	65.24
0.3958	1.563	3.2	1.2	0.2406	36.32	36.47	36.42
N-Butylacetamide-glucose (NBA-G)							
(χ_{NBA} = 0.5100)							
2.3378	7.704	0	0	1.3706	273.77	273.89	273.77
1.3706	4.703	9.6	4.0	0.8057	161.30	162.44	161.75
0.8057	2.979	6.1	2.6	0.4932	88.62	88.36	88.89
0.4932	1.900	3.9	1.7	0.3078	51.81	51.45	51.97
2.3378	3.961	0	0	0.6717	474.61	474.43	474.61
0.6717	1.458	10.1	2.4	0.2308	123.24	122.82	123.66
0.4653	0.958	0	0	0.1512	85.00	86.39	85.00

Table A-11. (Contd)

m_i (2) mol/kg	N (2) mmol	N (4) μmol	m_i (4) mmol/kg	m_f mol/kg	$-\Delta H^{ex}_{exp}$ cal/mol	$-\Delta H^{ex}_{calc}$ cal/mol	$-\Delta H^{ex}_{corr}$ cal/mol
N-Butylacetamide-sucrose (NBA-S)							
(χ_{NBA} = 0.5457)							
2.5569	8.271	0	0	1.4723	332.80	360.27	332.80
1.4723	3.603	18.4	4.5	0.5508	306.33	311.29	307.28
0.5508	1.567	8.1	1.9	0.2199	112.93	112.94	113.31
0.2199	0.693	3.5	0.8	0.0923	41.71	43.74	41.86
2.5569	3.899	0	0	0.6722	602.72	630.27	602.72
0.6722	1.467	9.7	2.2	0.2272	151.47	151.75	151.98
0.2272	0.899	1.8	0.8	0.1454	27.83	27.99	27.93
0.1454	0.314	2.3	0.5	0.0476	32.34	33.54	32.46
Urea-ethylene glycol (U-EG)							
(χ_U = 0.4968)							
2.1236	8.209	0	0	1.3823	4.280	4.32	4.28
1.3823	5.468	10.7	4.9	0.8910	3.044	3.05	3.06
0.8910	3.609	7.1	3.3	0.5848	1.948	1.98	1.96
2.1236	4.364	0	0	0.6533	8.933	8.90	8.93
0.6533	2.666	5.3	2.3	0.4182	1.500	1.55	1.51

Table A-11. (Contd)

m_i (2) mol/kg	N (2) mmol	N (4) μmol	m_i (4) mmol/kg	m_f mol/kg	$-\Delta H^{ex}_{exp}$ cal/mol	$-\Delta H^{ex}_{calc}$ cal/mol	$-\Delta H^{ex}_{corr}$ cal/mol
Urea-pentaerythritol (U-P)							
(χ_U = 0.5000)							
0.5286	1.320	0	0	0.5268	*		
0.5268	1.320	0	0	0.1997	-3.500	-3.45	-3.50
0.5286	2.390	0	0	0.5267	*		
0.5267	2.390	0	0	0.3578	**	-1.78	
1.0790	2.685	0	0	1.0754	*		
1.0754	2.685	0	0	0.4051	-6.928	-7.07	-6.93
0.4051	1.660	3.3	1.3	0.2484	-1.524	-1.65	-1.53
0.2484	0.635	4.0	0.9	0.0925	**	-1.64	
1.0797	4.236	0	0	0.6991	-3.931	-4.01	-3.93
0.6991	2.793	5.5	2.3	0.4392	-2.865	-2.74	-2.87
0.4392	1.796	3.5	1.3	0.2633	**	-1.86	
1.0797	2.611	0	0	0.3908	-7.429	-7.27	-7.43
0.3908	1.601	3.2	1.4	0.2501	-1.642	-1.48	-1.65
0.2501	1.037	2.1	0.8	0.1571	-1.136	-0.98	-1.14
1.0796	4.506	0	0	0.6967	-3.889	-4.04	-3.89
Urea-glucose (U-G)							
(χ_U = 0.5267)							
2.2648	7.958	0	0	1.3886	-31.97	-31.88	-31.97
1.3886	5.277	10.0	4.0	0.8352	-22.66	-22.99	-22.73
0.8352	3.311	6.4	2.4	0.5030	-14.69	-14.86	-14.73
2.2648	4.896	0	0	0.7386	-59.10	-59.11	-59.10
0.7386	1.953	11.2	2.5	0.2739	-21.51	-21.34	-21.59

* Wet wall experiment.

** Data point outside 2 σ in least squares fit.

Table A-11. (Contd)

m_i (2) mol/kg	N (2) mmol	N (4) μmol	m_i (4) mmol/kg	m_f mol/kg	$-\Delta H^{ex}_{exp}$ cal/mol	$-\Delta H^{ex}_{calc}$ cal/mol	$-\Delta H^{ex}_{corr}$ cal/mol
Urea–sucrose (U-S)							
(χ_U = 0.5597)							
2.4594	7.564	0	0	1.4265	*	-46.86	
1.4265	5.104	9.5	4.2	0.8746	-29.58	-29.79	-29.68
0.8746	3.351	6.3	2.7	0.5405	-19.89	-19.93	-19.96
2.4594	4.072	0	0	0.6924	-87.41	-87.33	-87.41
0.6924	1.397	10.1	2.3	0.2209	-29.64	-29.77	-29.75
2.4594	8.671	0	0	1.4866	-43.75	-43.83	-43.75
Ethylene glycol-pentaerythritol (EG-P)							
(χ_{EG} = 0.5001)							
0.5257	2.358	0	0	0.3619	15.93	15.85	15.93
0.3619	1.486	2.9	1.3	0.2341	12.33	12.36	12.37
0.2341	0.971	1.9	0.9	0.1546	7.78	7.70	7.81
0.1546	0.645	1.3	0.6	0.1007	4.91	5.21	4.92
0.5257	2.260	0	0	0.3412	18.04	17.85	18.04
0.3412	0.861	5.5	1.3	0.1284	20.46	20.59	20.54
0.1284	0.329	2.1	0.5	0.0487	7.27	7.71	7.30
Ethylene glycol–glucose (EG-G)							
(χ_{EG} = 0.5176)							
2.0020	6.989	0	0	1.1977	68.87	69.64	68.87
1.1977	4.566	8.8	3.8	0.7435	40.55	40.54	40.68
0.7435	2.939	5.7	2.7	0.4815	24.23	23.80	24.32
0.4815	1.005	7.5	1.8	0.1587	29.83	29.71	29.94
2.0020	4.152	0	0	0.6347	120.58	120.02	120.58
0.6347	1.621	9.7	2.2	0.2330	35.62	36.79	35.75

*Experimental error.

Table A-11. (Contd)

m_i (2) mol/kg	N (2) mmol	N (4) μmol	m_i (4) mmol/kg	m_f mol/kg	$-\Delta H^{ex}_{exp}$ cal/mol	$-\Delta H^{ex}_{calc}$ cal/mol	$-\Delta H^{ex}_{corr}$ cal/mol
Ethylene glycol–sucrose (EG-S)							
(χ_{EG} = 0.5567)							
2.4221	7.496	0	0	1.4426	103.71	104.16	103.71
1.4426	5.109	9.6	4.4	0.8981	63.69	63.96	63.91
0.8981	3.394	6.5	2.9	0.5635	41.55	41.46	41.69
2.4221	4.114	0	0	0.7029	192.47	192.12	192.47
0.7029	1.407	10.3	2.4	0.2258	60.35	60.98	60.57
Pentaerythritol-glucose (P-G)							
(χ_P = 0.5000)							
1.0797	2.413	0	0	0.3643	64.32	64.38	64.32
0.3643	1.481	2.9	1.3	0.2330	12.41	12.50	12.45
0.2330	0.963	1.9	0.8	0.1456	8.35	8.45	8.38
0.1456	0.610	1.2	0.4	0.0893	5.61	5.49	5.62
1.0797	4.572	0	0	0.6924	34.15	34.07	34.15
0.6924	2.719	5.2	2.1	0.4231	24.76	24.78	24.84
0.4231	1.713	3.3	1.4	0.2661	14.84	14.87	14.89
0.2661	1.099	2.1	0.8	0.1648	9.77	9.76	9.80

Table A-11. (Contd)

m_i (2) mol/kg	N (2) mmol	N (4) μmol	m_i (4) mmol/kg	m_f mol/kg	$-\Delta H^{ex}_{exp}$ cal/mol	$-\Delta H^{ex}_{calc}$ cal/mol	$-\Delta H^{ex}_{corr}$ cal/mol
Pentaerythritol-sucrose (P-S)							
(χ_P = 0.5013)							
1.0772	2.129	0	0	0.3418	85.99	85.77	85.99
0.3418	1.366	2.7	1.1	0.2128	16.22	16.28	16.27
0.2128	0.872	1.7	0.8	0.1381	9.46	9.60	9.50
0.1381	0.574	1.1	0.4	0.0859	6.75	6.77	6.77
1.0772	4.171	0	0	0.6649	46.51	46.62	46.51
0.6649	2.550	4.8	2.0	0.4114	30.13	30.52	30.22
0.4114	1.635	3.1	1.3	0.2581	19.01	19.15	19.08
0.2581	1.052	2.0	0.8	0.1570	13.07	12.92	13.11
1.0772	3.721	0	0	0.6005	54.14	54.23	54.14
Glucose-sucrose (G-S)							
(χ_G = 0.5321)							
2.6869	8.586	0	0	1.5029	102.42	102.80	102.42
1.5029	3.512	17.9	4.3	0.5453	93.68	94.30	93.97
0.5453	1.410	7.9	1.8	0.2066	35.31	35.73	35.43
0.2066	0.566	3.2	0.8	0.0807	13.30	13.60	13.35
2.6869	4.427	0	0	0.7368	177.81	177.44	177.81
0.7368	1.682	10.2	2.3	0.2497	51.06	50.77	51.22
0.2497	0.676	3.9	0.9	0.0976	16.14	16.39	16.20

Table A-12.[a] B_j Coefficients

Solute[b] A-B	x_A[c]	B_1[d]	B_2	B_3	B_4	$\sigma\left(\Delta H^{ex}_{exp}\right)$[e]
		cal kg/mol^2	cal kg/mol^2	cal kg/mol^2	cal kg/mol^2	cal/mol
NMF	1	65.08 (0.5)[f]				0.41
NMA	1	56.3 (2.6)	22.80	-4.23		0.25
NMP	1	152.0 (5.7)	56.70	-23.09	3.525	0.36
NBA	1	353.1 (5.7)	256.85	71.116		0.73
U	1	-83.7 (2.7)	5.37			0.23
EG	1	86.5 (1.0)	-1.548			0.16
P	1	94.4 (0.9)				0.24
G	1	82.0 (2.3)	-3.06			0.49
S	1	137.9 (1.4)	-8.07			0.34
NMF-NMA	0.5026	74.4 (4.5)	2.38			0.53
NMF-NMP	0.5062	118.1 (1.9)	12.58	-3.405		0.18
NMF-NBA	0.5077	208.0 (4.9)	24.62	-5.984		0.17
NMF-U	0.4988	-18.07 (2.0)	1.79			0.39
NMF-EG	0.5050	87.1 (2.8)	-2.51			0.37
NMF-P	0.4989	84.1 (1.3)	-3.88			0.18
NMF-G	0.5229	83.8 (2.1)	-4.17			0.23
NMF-S	0.5723	105.7 (4.4)	-5.77			0.72
NMA-NMP	0.5038	98.7 (7.7)	43.60	-18.24	3.079	0.35
NMA-NBA	0.5175	172.4 (17.0)	67.20	-16.03		0.87
NMA-U	0.4996	-7.03 (1.9)	5.89	-0.748		0.12
NMA-EG	0.4976	98.1 (0.3)				0.19
NMA-P	0.4995	96.7 (0.3)				0.17
NMF-G	0.5239	121.6 (2.2)	-4.91			0.51
NMA-S	0.5717	159.6 (2.2)	-8.84			0.14
NMP-NBA	0.5023	255.1 (21.6)	82.70	-20.20		2.4
NMP-U	0.4916	36.7 (3.0)	7.11	-1.571		0.20
MNP-EG	0.5054	143.8 (0.6)				0.41
NMP-P	0.4980	130. (7)	48.20	-56.93	22.127	0.12
NMP-G	0.5186	185. (4)	-8.44			1.5
NMP-S	0.5499	235.5 (5.0)	-13.40			0.87
NBA-U	0.4855	92.6 (8.5)	31.30	-7.23		0.89
NBA-EG	0.4743	204.7 (3.8)	29.90	-6.86		0.47
NBA-P	0.4958	190.2 (6.1)	125.10	-136.25	54.470	0.13
NBA-G	0.5100	265.9 (10.9)	17.70	-4.56		0.97
NBA-S	0.5457	343.5 (3.6)	2.82			1.3
U-EG	0.4968	6.9 (0.5)[f]	-0.31			0.41
U-P	0.5000	-10.5 (0.2)				0.11
U-G	0.5267	-49.6 (1.7)	3.61			0.22
U-S	0.5597	-69.9 (1.5)	7.81	-0.498		0.91
EG-P	0.5001	96.8 (1.5)				0.23
EG-G	0.5176	93.4 (4.8)	-2.14			0.76
EG-S	0.5567	134.6 (3)	7.32			0.43
P-G	0.5000	98.9 (1.0)	-6.20			0.82
P-S	0.5013	132.4 (2.0)	-11.08			0.17
G-S	0.5321	109.6 (1.6)	-5.43			0.39

[a] This is a table of the coefficients B_j obtained by fitting the experimentally measured values for the change in the excess enthalpy per mole ΔH^{ex} to the following equation

$$\sqrt{N(2)} \cdot \Delta H^{ex}_{exp} = \sum_{j=1,m} B_j \left[\frac{N(F) \times \underline{m}(f)^j \cdot N(2) \times \underline{m}(2)^j \cdot N(4) \times \underline{m}(4)^j}{N(2)} \right]$$

[b] NMF = N-methylformamide, NMA = N-methylacetamide, NMP = N-methylpropionamide, NBA = N-butylacetamide, U = urea, EG = ethylene glycol, P = pentaerythritol, *G = glucose and S = sucrose.*

[c] x_A is the mole fraction of the first compound listed for a binary mixture.

[d] $B_1 = \{AA\}_h$ the heat of interaction between a pair of A molecules when $x_A = 1$, for a binary solution of solutes A and B, $B_1 = 2x_Ax_B\{AB\}_h + x_A^2\{AA\}_h + x_B^2\{BB\}_h$.

[e] The standard deviation between the computed changes in excess enthalpy per mole and the experimental changes in excess enthalpy per mole.

[f] The number in the parentheses represents the 95% confidence range of the coefficient, *i.e.*, 65.1 (0.5) = 65.6 to 64.6 with 95% confidence.

Table A-13. $\{AB\}_h$ Pairwise Heats of Interaction

Solute A	Solute B								
	Sucrose	Glucose	Pentaerythritol	Ethylene glycol	Urea	NBA	NMP	NMA	NMF
	cal kg/mol^2								
N-Methylformamide (NMF)	121*	95	88	99	-26	211	129	88	65
N-Methylacetamide (NMA)	237	176	118	125	0	150	94	56	
N-Methylpropionamide (NMP)	327	251	137	168	43	258	152		
N-Butylacetamide (NBA)	424	309	159	203	63	353			
Urea (U)	-143	-90	-26	11	-84				
Ethylene glycol (EG)	164	102	103	86					
Pentaerythritol (P)	149	110	94						
Glucose (G)	113	82							
Sucrose (S)	138								

* This is the heat of interaction for N-methylformamide and sucrose $\{NMF\text{-}S\}_h$.

Table A-14. Pairwise Enthalpies of Interaction $\{ab\}_h$

Compound		$\{ab\}_h$ calculated	$\{ab\}_h$ experimental
a	b		
		cal kg/mol^2	cal kg/mol^2
Methanol	Methanol	102	59[1]
Ethanol	Ethanol	128	59[1], 58[2]
n-Propanol	n-Propanol	169	121[1], 134[2]
n-Butanol	n-Butanol	225	280[3], 240[2]
t-Butanol	t-Butanol	225	157[2], 157[4], 145[5]
Ethanol	n-Propanol	144	89[2]
Ethanol	n-Butanol	161	111[2]
Ethanol	t-Butanol	161	88[2]
n-Propanol	n-Butanol	202	179[2]
n-Propanol	t-Butanol	202	158[2]
Isopentanol	Isopentanol	297	420[3]
Glycerol	Glycerol	104	60[3]
Glycolamide	Glycolamide	-10	-46[6]

[1] Reference 1.

[2] Franks, F. Private communication, 1975.

[3] Reference 2.

[4] Reference 3.

[5] Reference 4.

[6] Reference 5.

Table A-15. Magnitude of Terms in Equation 12

$$\frac{\delta B^{*}_{AA}/T}{\delta\ 1/T} = \{AA\}_h V^{\circ}_w - \frac{\alpha RT^2 \{AA\}_g V^{\circ}_w}{RT} - RT^2 \phi_E(A)$$

Compound	$\{AA\}_h V^{\circ}_w$	$\{AA\}_g$	$\frac{\alpha RT^2 \{AA\}_g V^{\circ}_w}{RT}$	$RT^2 \phi_E(A)$
	cal ℓ/mol^2	cal/mol^2	cal ℓ/mol^2	cal ℓ/mol^2
Urea	-83.9	-26	-2.1	18
Sucrose	138.1	42	3.3	36
Urea-sucrose	-143.4	-37	-3.0	27

Table A-16. Pairwise Enthalpies of Interaction

R – R	+	R – A	+
A – A	-	R – OH	+
OH – OH	+	A – OH	-

R = hydrocarbon group - methyl or methylene.
A = amide group.
OH = hydroxy group.

Table A-17. Experimental $\{ab\}_{h}$ exp Versus Calculated $\{ab\}_{h}$ calc Pairwise Heats of Interaction

Solute a-b	$\{ab\}_{h}^{*}$ calc	$\{ab\}_{h}$ exp
	cal kg/mol^2	cal kg/mol^2
NMF-NMF	50	65
NMF-NMA	72	88
NMF-NMP	94	129
NMF-NBA	137	211
NMA-NMA	101	56
NMA-NMP	131	94
NMA-NBA	189	150
NMP-NMP	168	152
NMP-NBA	242	258
NBA-NBA	346	353
U-U	-96	-84
NMF-U	-9	-26
NMA-U	13	0
NMP-U	34	43
NBA-U	77	63
EG-EG	103	86
EG-P	104	103
EG-G	105	102
EG-S	108	164
P-P	106	94
P-G	108	110
P-S	115	150
G-G	111	82
G-S	127	113
S-S	140	138
EG-U	64	11
P-U	27	-26
G-U	-10	-90
S-U	-122	-143
EG-NMF	95	99
EG-NMA	114	125
EG-NMP	132	168
EG-NBA	168	203

* These values were calculated by substituting the following least square parameters into equation (19): $C_O = 102$, $E_{CH_2\text{-}CH_2} = 7.6$, $E_{A\text{-}A} = -88$, $E_{CHOH\text{-}CHOH} = 0.3$,

$E_{CH_2\text{-}A} = 14$, $E_{CH_2\text{-}CHOH} = 9$, $E_{CHOH\text{-}A} = 12$.

NMF = N-methylformamide, NMA = N-methylacetamide, NMP = N-methylpropionamide, NBA = N-butylacetamide, U = urea.
EG = Ethylene glycol, P = Pentaerythritol, G = Glucose, S = Sucrose.

Table A-17. (Contd)

Solute a-b	$\{ab\}_h$ calc	$\{ab\}_h$ exp
	cal kg/mol^2	cal kg mol^2
P-NMF	89	88
P-NMA	125	118
P-NMP	162	137
P-NBA	234	159
G-NMF	82	95
G-NMA	137	176
G-NMP	191	251
G-NBA	301	309
S-NMF	62	121
S-NMA	172	237
S-NMP	281	327
S-NBA	500	424

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APPENDIX B

COMPUTER PROGRAM LISTING

The program listing contained in this appendix was used to obtain the areas in volt-seconds under the various heat of dilution curves. The computer used to run the program was a Data General Nova 1200. The calorimeter output for each dilution was stored on punched paper tape which was then read into the computer and stored as a data file on a magnetic disk. The program is set up to least-square the heat curve baseline and use Simpson's rule to calculate the area under the curve. These areas would then be multiplied by the appropriate calibration constant to obtain the heat of a dilution.

The data file consists of a set of voltage values listed in five columns, each column containing six digit numbers with a sign and decimal point. The last digit of each number serves to signal the computer that a dilution with mixing was initiated when this digit is unity. At all other times, the last digit is zero. An abbreviated example of a data file is shown below:

+0.00100	+0.00120	+0.00100	+0.00120	+0.00100
+0.00120	+0.00110	+0.00120	+0.00110	+0.00100
+0.00101	+0.00900	+0.01800	+0.02700	+0.00360

etc.

The program itself has been written in such a way as to require no further elaboration since descriptive comments have been included throughout.

Program Listing

```
LKB LINEAR LEAST SQUARE AND SIMPSONS RULE PROGRAM
THIS PROGRAM READS IN EXPERIMENTAL VOLTAGES, DOES
A LEAST SQUARES ON THE BASELINE, CALCULATES THE
AREA UNDER THE BASELINE PORTION OF THE CURVE AND
SUBTRACTS THIS AREA FROM THE AREA UNDER THE CURVE.
```

```
DIMENSION V(600),KM(600),IDATA(11)
DET(T1,T2,T3,T4)=T1*T4-T2*T3
ACCEPT " THE NUMBER OF POINTS BEFORE MIXING  K= ",K,
"THE NUMBER OF INTERVALS UNDER THE CURVE N(EVEN)=  ",N,
"THE NUMBER OF POINTS AFTER THE CURVE BEFORE LEAST<15>
SQUARING BEGINS NN=  ",NN,"THE NUMBER OF POINTS AFTER<15>
THE CURVE USED IN THE LEAST SQUARES IS M=  ",M,
"THE TIME INTERVAL BETWEEN EACH POINT ITIME=  ",ITIME,
"ITEST= ",ITEST
TYPE "INPUT DATA FILE NAME"
READ(11,100) IDATA(1)
FORMAT(S20)
CALL FOPEN (1,IDATA)
REWIND 1
L=1
N1=L+4
READ(1,101,END=20) (V(I),KM(I),I=L,N1)
FORMAT(F7.4,I1,4(F9.4,I1))
IF(ITEST.EQ.0) GO TO 7
WRITE(10,106) (V(I),KM(I),I=L,N1)
FORMAT(1X,5(F10.5,2X,I1))
L=L+5
GO TO 10

CALL FCLOS (1)
TEST FOR START OF EXPERIMENT

J=0
J=J+1
IF(J.GE.L) GO TO 200
IF(KM(J).EQ.0) GO TO 22
WRITE(10,102)  J
FORMAT(//1X,"THE START OF MIXING OCCURED AT POINT J =",I10)

SUMV=0.0
SUMT=0.0
SUMTT=0.0
SUMVT=0.0
SUMN=0.0

LEAST SQUARE THE BASELINE
```

```
      N2=J-K
      N3=J+M+N+1+NN
      DO 40 I=N2, N3, 1
      T=I
      N4=J+N+1+NN
      IF(I. GE. J. AND. I. LE. N4)  GO TO 40
      SUMV=SUMV + V(I)
      SUMT = SUMT + T
      SUMTT = SUMTT + T*T
      SUMVT = SUMVT + T*V(I)
      SUMN=SUMN+1. 0
 40   CONTINUE

      CRAMERS RULE PERFORMED ON

      A(K+M)    +    B(SUMT)    =    SUMV

      A(SUMT)        +    B(SUMTT)   =    SUMVT

      THE ABOVE DETERMINANT IS DERIVED FROM

      V(I) = A + B*T(I)

      A11 = SUMN
      A22 = SUMTT
      A12 = SUMT
      A21 = SUMT
      C1  = SUMV
      C2  = SUMVT

      DET1 = DET(A11, A12, A21, A22)

      DET2 = DET(C1, A12, C2, A22)

      DET3 = DET(A11, C1, A12, C2)

      A = DET2/DET1
      B = DET3/DET1
      WRITE(10, 103) A, B
103   FORMAT(//1X, "THE LEAST SQUARE CONSTANTS ARE: ",
     1//1X, "A =", F15. 9, //1X, "B =", F15. 9)

      FN=N
      FJ=J

      AREAB = A*FN +B*FJ*FN +(B/2)*(FN*FN)
      TIME=ITIME
      AREAB=AREAB*TIME
      IF(ITEST. EQ. 1) TYPE"AREAB", AREAB
```

```
      DO SIMPSONS RULE ON CURVE VOLTAGE

      SUM = V(J)
      N5=J+1
      N6=J+N-3
      DO 50 I = N5, N6, 2
 50   SUM = SUM+ 4*V(I)+2*V(I+1)
      SUM = SUM+4*V(J+N-1)+V(J+N)
      IF(ITEST. EQ. 1) TYPE"SUM", SUM

      AREAC = (TIME/3. 0)*SUM
      IF(ITEST. EQ. 1) TYPE"AREAC", AREAC

      AREA = AREAC-AREAB
      IF(ITEST. EQ. 1) TYPE"AREA", AREA

      WRITE(10, 104) AREA, AREAC, AREAB
104   FORMAT(//1X, "AREA = ", F15. 9, //1X, "AREAC = ", F15. 9,
     1//1X, "AREAB = ", F15. 9)
      IF(ITEST. EQ. 0) GO TO 70
      WRITE(10, 105) K, N, M, A11, A12, A21, A22, C1, C2
105   FORMAT(//1X, "K=", I4, /1X, "N=", I5, /1X, "M=", I5,
     2 /1X, "A11=", F10. 2, /1X, "A12=", F10. 1, /1X, "A21=", F10. 1,
     3 /1X, "A22=", F15. 2, /1X, "C1=", F15. 7, /1X, "C2=", F20. 7)
 70   CONTINUE

      SEARCH FOR NEXT START OF EXPERIMENT
      J=J+10
      GO TO 22
200   ACCEPT "NEW TIME INTERVAL NT, IF ZERO STOP, = ", NT
      IF (NT. EQ. 0) GO TO 300
      DO 210 I=NT, 3000, NT
      IN=I/NT
      V(IN)=V(I)
210   KM(IN)=KM(I)
      ITIME=NT*ITIME
      K=K/NT
      M=M/NT
      NN=NN/NT
      N=N/NT
      L=L/NT
      GO TO 20
300   STOP
      END
```

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