THE UNIVERSITY OF MICHIGAN

INDUSTRY PROGRAM OF THE COLLEGE OF ENGINEERING

SOLUTION THERMODYNAMICS FROM GAS LIQUID CHROMATOGRAPHY

Raymond E. Pecsar

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Science in the
University of Michigan
Department of Chemical and Metallurgical Engineering
1964

December, 1964

IP-690

Doctoral Committee:

Professor Joseph J. Martin, Chairman
Associate Professor Richard E. Balzhiser
Professor Edward E. Hucke
Professor Edgar F. Westrum
Professor G. Brymer Williams

ACKNOWLEDGEMENTS

The author would like to express his appreciation to the following persons and organizations for their assistance and support in this work.

Dr. J. J. Martin -- for his interest and encouragement in all phases of the work.

The members of the doctoral committee: Dr. R. E. Balzhiser, Dr. E. E. Hucke, Dr. E. F. Westrum, and Dr. G. B. Williams -- for their cooperation and contributions.

Mr. F. B. Drogosz -- for many helpful discussions concerning the experimental work.

The Industry Program staff -- for their aid in the publishing of this dissertation.

The Allied Chemical Corporation -- for their support during part of this work.

The California Research Corporation -- for their support and encouragement during part of this work.

The Horace H. Rackham School of Graduate Studies -- for a predoctoral fellowship during part of this work.

My parents -- for their encouragement and support to continue in my educational pursuits.

Above all my wife -- for her patient helpfulness, understanding, and encouragement through my undergraduate and graduate studies, for her invaluable assistance in the preparation of this manuscript, and most of all just for being my wife.

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NOMENCLATURE

Upper Case Letters

A	Helmholtz free energy
B_{ij}	Second virial coefficient
C_j	Arbitrary constant
D	Hydrocarbon radical
E	Intermolecular potential energy
F	Carrier gas flow rate
$\mathfrak{F}$	Total partition function
ΔG^E	Partial molar excess Gibbs free energy
ΔH^E	Partial molar excess enthalpy
ΔH_{vap}	Enthalpy of vaporization
I	Ionization potential
J	Martire's specific interaction factor
K	Henry's law constant
L	Column length
M	Molecular weight of solvent
N_G	Molar density of gas
N_L	Molar density of liquid
$\mathcal{N}$	Number of molecules
$\mathcal{N}_o$	Avogadro's number
P	Total pressure
$\bar{P}$	Mean column pressure
Q	Configurational partition function

R	Gas constant
ΔS^E	Partial molar excess entropy
T	Temperature
U	Configurational potential energy
V_G	Gas phase volume
V_L	Liquid phase volume
V_R	Retention volume
$\bar{V}_R$	Specific retention volume
X	Generalized physical property
Y	Functional group
Z	Generalized molecular force

Lower Case Letters

d	Cluster product term
e	Mathematical constant
f	Fugacity
f^o	Vapor fugacity
$\bar{f}$	Fraction of time solute is in gas phase
g	Combinatorial partition function
h	Planck's constant
j	Martin's pressure correction factor
k	Partition coefficient
$\bar{k}$	Boltzmann's constant
ℓ	Number of methylenic groups
m	Mass of solvent in column

n	Total number of moles
p	Partial pressure
p^o	Vapor pressure
q_{int}	Partition function for internal degrees of freedom
r	Ratio of molar volumes, $r > 1$
s	Cell theory parameter
t_R	Retention time
u	Linear velocity
v	Partial molar volume
v^o	Molar volume
w	Interaction energy
x	Liquid mole fraction
y	Gas mole fraction
z	Number of nearest neighbors

Greek Letters

α	Polarizability
β	Cubical coefficient of expansion
γ	Activity coefficient
γ^∞	Infinitely dilute activity coefficient
γ^{ath}	Athermal contribution to γ
γ^{th}	Thermal contribution to γ
δ	Solubility parameter
ϵ	Dielectric constant
μ	Dipole moment

ν	Characteristic vibration frequency
π	Mathematical constant
ρ	Solvent density
σ_{ij}	Intermolecular distance
τ	Generalized coordinate
Υ	Generalized coordinate
ϕ	Volume fraction
ψ	Relative volatility
ω	Dipole interaction parameter

Subscripts

A,B,C...	Components
E	Energetic contribution
G	Geometric contribution
f	Final condition
i	Inlet condition
o	Outlet condition
s	Initial condition
u	Unretained component
1	Solvent
2	Solute

Superscripts

E	Excess
G	Gas
L	Liquid
M	Mixing
∞	Infinite dilution

ABSTRACT

The purpose of this study is the determination and prediction of thermodynamic properties of two component volatile nonelectrolyte solutions essentially at infinite dilution by gas-liquid chromatography. This technique is to be preferred to static equilibrium techniques as no analysis of the liquid phase is needed and a very rapid equilibration is established.

The components to be studied were chosen on the basis of hydrogen bonding and intermolecular forces so as to encompass all types of solution behavior. The solvents utilized in this work were water, 2 pentanone and 2,3,4 trimethylpentane. In each of these solvents homologous series of alkanes, chlorinated methanes, alkyl formates, aldehydes, amines and alcohols were studied at 20°, 30° and 40°C. At these temperatures from experimental measurements the values of the activity coefficient, the partial molar excess free energy, the partial molar excess enthalpy and the partial molar excess entropy were determined. The overall average accuracy of the results was ± 5% based on repetitive measurements. These results show excellent agreement both with data available in the literature and anticipated properties deduced from possible solute-solvent interactions.

The prediction of the experimental results took one of two forms depending on whether hydrogen bonding was the primary solution interaction. For water solutions, as hydrogen bonding was the predominant solution force, no theoretical method of representing

the experimental data quantitatively could be formulated. Rather an empirical correlation providing a linear relation between the partial molar excess free energy and the number of methylenic groups in the solute was employed which fit the data very well. This technique can be justified based on a semi-theoretical group interaction scheme.

For the other binary systems studied the nonelectrolyte solution theories based on Van der Waals forces and molecular geometry can be used to predict deviations from ideality. The cell theory of liquids may be employed to ascertain the athermal contribution to the activity coefficient while a modification of Hildebrand's work is used to obtain the thermal contribution. The product of these two contributions represents the experimental data of the 2,3,4 trimethylpentane solutions within 18% and the results for the 2 pentanone systems within 39%. This agreement is quite remarkable considering the fact that the predictive method utilizes only the physical properties of the pure components.

A development is also presented based on the lattice theories of statistical mechanics. The relations evolved allow an evaluation of the geometric and energetic terms of the partial molar excess entropy. A number of qualitative conclusions are reached concerning nonelectrolyte solution behavior. Thus the technique of gas liquid chromatography has been proven to be a valid method of obtaining infinitely dilute equilibrium properties of two component volatile systems and methods have been developed for predicting and correlating these properties.

I. INTRODUCTION

As this thesis is concerned with the determination of thermodynamic properties of solutions utilizing gas-liquid chromatography, it would seem advisable to define the general concepts of chromatography to a slight extent so as the thermodynamic implications can be more fully appreciated.

Chromatography has been defined as a physical method of separation in which the components to be separated are distributed between two phases, one of these phases being stationary with large surface area, the other being a fluid that percolates through or moves along the stationary phase. The phase equilibria for different components will differ due to the varying intensity of the force by which the stationary phase retains each component, whether the nature of this force be absorption, solubility, chemical bonding, or related phenomena. Because of the phase equilibrium differences, the sample components will tend to separate by repeated equilibration between the stationary and mobile phases as they move through the stationary phase. This operation is analogous to that of an equilibrium still and this analogy has been carried over through such factors as Height Equivalent to a Theoretical Plate, Relative Volatility, and other common expressions.

While the above definition speaks in terms of a multicomponent mixture and its resolution, the principle can be equally well applied to a single pure component. The repeated equilibrium distribution of the component between the stationary and the mobile phase provides a method of determining the vapor-liquid equilibrium of binary solutions consisting of the pure component, hereafter referred to as the solute, and the immobile solvent phase.

A. Objective of Thesis

The purpose of this work is primarily two-fold. Initially it is desired to determine the thermodynamic properties of binary solutions by means of gas-liquid chromatography (GLC). These binary solutions, in contrast to those normally studied by this technique, are two component volatile systems. By investigating such volatile binary systems, the range and versatility of GLC has been extended and also a comparison with other established equilibrium techniques can be made. Although other recent work has established GLC as a method for studying vapor-liquid equilibrium at any desired solute concentration, this work is confined to solutions essentially at infinite dilution of the solute. While such solutions are not of immediate practical value, their properties have much theoretical significance in enabling one to establish a so called "end point" value to which properties of more concentrated solutions can be extrapolated. In actuality, it is in this extremely dilute region that the greatest discrepancies exist, and therefore data in this region is definitely needed.

The second objective of this thesis is the investigation of the behavior of nonelectrolyte solutions, and the establishment of methods for predicting their behavior based on sound principles.

Rather than merely characterizing solution behavior on a macroscopic level phenomenologically, it is desired to describe the solute-solvent interactions on a molecular level and thus gain a clearer understanding of the predominant forces responsible for solution behavior, primarily deviations from ideality. To this end the binary systems will be chosen with care so as to adequately represent the various types of anticipated behavior. When studying solutions near infinite dilution the interactions and resulting behavior often deviate considerably from that displayed in more concentrated solutions due to different forces being predominant. This effect will be pointed up in the analysis and discussion of the results.

B. Present Methods

The principal techniques for experimentally determining vapor liquid equilibria presently consist of:

1. Dew Point-Bubble Point methods in which a gas mixture is introduced to a visual cell in a controlled temperature environment and the pressure is varied. The point at which condensation begins and ends is determined by visual observation.

2. Static methods where a gas mixture is placed within an equilibrium cell and subjected to suitable temperatures and pressures. After adequate mixing and contact is assured, it is assumed that equilibrium exists within the cell and samples of each phase are withdrawn and analyzed.

3. Flow systems wherein a vapor phase is passed through an equilibrium vessel in which a portion of the vapor is condensed, forming two phases within the vessel. The two phases are continually removed for analysis.

4. Vapor-Recycle techniques which combine the best features of the static and flow systems. The vapor phase is drawn off from the vessel and recirculated through the liquid until equilibrium is reached. This assures a much better approach to equilibrium. Again vapor and liquid samples must be very carefully removed for analysis.

5. Optical methods in which a condensed mixture of known composition is charged to an optically transparent cell. After vaporizing a portion of the mixture and establishing equilibrium, light is passed through the cell and the decrease in incident intensity at a suitable frequency is determined.

6. Electrochemical techniques where the potential of a half cell reaction of a solution of known concentration is determined. As this reaction is generally reversible, equilibrium is established and the desired properties can be obtained.

Of the above techniques, the first four represent the standard methods for determining equilibrium in such systems as hydrocarbons, organic liquids and other relatively low boiling liquids. The latter two methods are more applicable to high boiling binary mixtures and electrolytes. The technique of GLC, however, can be employed to study solutions in any of these classifications.

C. Advantages of GLC

In the present research, the scope of GLC has been considerably curtailed, as this study is concerned solely with nonelectrolyte solutions at infinite dilution. However, in the following discussion, the full range of applicability will be considered. The bubble point-dew point method is dependent on the vision of the observer and is best suited for close boiling binary mixtures. Although GLC is normally utilized with large solute and solvent volatility differences, the present work studies close boiling binaries and the method is suited for the entire range of relative volatilities. In the static methods great care must be taken not to disturb equilibrium when removing the samples for analysis. In GLC no direction measurement of the liquid phase is needed and the mobile effluent phase is easily analyzed. The flow systems require large samples of the vapor phase and equilibrium is difficult to achieve, in contrast to GLC where minimal samples are needed and equilibrium is nearly instantaneous. The vapor-recycle technique, while quite flexible, requires fairly elaborate equipment. GLC is noted for the rather elementary apparatus required. In the optical method, suitable absorption frequencies must be available in the vapor state and the computational procedure for processing the data is rather complex. The computational requirements for GLC, as will be shown, are fairly elementary. The electrochemical techniques are only applicable to conductive solutions while GLC in principle can be used for either type of solutions.

The standard techniques also possess the disadvantage that vapor-liquid equilibria for a fixed composition in either phase can only be established by a trial and error approach to the desired composition. In GLC a fixed composition in the vapor phase can be determined directly. A primary advantage lies in the fact that a dynamic equilibrium exists between the solute in the mobile and stationary phases. Thus vapor liquid equilibrium can be established in a much shorter time using fairly simple equipment and uncomplicated procedure, by GLC. The technique also provides a very convenient method for measuring equilibrium in very dilute solutions without necessitating analysis of the liquid phase or extrapolation from finite concentrations to infinite dilution.

II. REVIEW OF LITERATURE

A. Gas Liquid Chromatography

Although the technique of chromatography had been known and utilized since the turn of the century, the first suggestion of using a liquid as a stationary phase and a gas as the mobile phase was made by Martin and Synge(70) in 1941, along with their now famous derivation of the plate theory. However, it was not until 1952 that James and Martin(47) heeded their own suggestion and utilized the technique of GLC to separate volatile fatty acids. Also in this paper the assumption of a constant pressure across a column, made in the plate theory, was theoretically removed. The importance of Martin's basic work was fully recognized when in 1952 he received the Nobel Prize. Following 1952 the number of published works in GLC has increased almost exponentially, indicating the high degree of interest and the utility of this simple inexpensive technique.

The majority of work done utilizing GLC has been in purely analytical applications. However, again following suggestions made by Martin, other applications began to be investigated. In 1955, Littlewood and coworkers(65) published the first paper relating GLC to thermodynamics of solutions. Until this time much difficulty existed in attempting to reproduce a given set of results in another laboratory. Littlewood defined the specific retention volume which is the retention volume of the solute in the solvent divided by the amount of solvent in the column under consideration. This parameter when further corrected to a standard temperature, as also done by Littlewood et al., provided a means for comparing work which was independent of many GLC operating variables. These workers also investigated the effect of many other experimentally variable factors such as size of the solid support, void volume in the column, percentage coating of solvent on the solid support and the effect of repacking a column with only a portion of the original contents. The specific retention volume was independent of all these parameters at a given temperature and pressure thus validating its utilization as a thermodynamic quantity. Littlewood, Phillips and Price also demonstrated the essentially linear relation between the specific retention volume and the reciprocal temperature of the column for a given solute in a given solvent. From this relation they were able to determine the heat of solution at infinite dilution.

Subsequent to the initial paper of Littlewood, a number of papers appeared relating GLC and the thermodynamic properties of solutions, verifying that true vapor liquid equilibrium existed in the chromatographic column, and investigating the behavior of nonelectrolyte solutions by this rather novel technique. However, essentially all of these works pertained directly to GLC systems. Now in GLC, as it is desired to have the solvent as a stationary phase, high boiling non-volatile liquids are normally utilized as solvents. In this manner the solvent remains intact on the solid support and the characteristics of the column remain invariant with time. However, this led to studies of binary solutions such as butanol in carbowax and octane in transformer oil. Generally this type of binary mixture is not easily amenable to verification of solution theories, as the exact composition of the solvent is unkown. A few early works were done, however, utilizing fairly volatile solvents and thus yielding solutions of more general interest.

A basic desire of this thesis was to study water as the solvent or stationary phase. This was prompted by the early works of Purnell and Spencer(95) and Pollard and Hardy.(86) Purnell in 1955 conducted a rather preliminary investigation on the separation of chlorinated methanes utilizing water as the solvent. He concluded that essentially a boiling point separation resulted. Later, in 1956, Pollard and Hardy in a more thorough study determined that as the quantity of water involved increased, i.e., the solute concentration decreased, the elution order changed from that dependent on boiling points to that based on the solubilities of the chloromethanes in water. The present investigation confirms the results of Pollard and Hardy. Later work by Hardy included a further investigation of chlorinated methanes in water and also included the methanol-water system. These early workers were bothered by the nonstationary nature of the stationary phase and attempted to correct for this by calculating the rate of solvent depletion due to volatilization into the mobile gas phase. To partially reduce this problem of solvent depletion or "bleeding", Kwantes and Rijnders(58) first utilized a forecolumn or presaturator. In this presaturator the solid support is coated with the same solvent as that employed in the primary column. The mobile carrier gas passes through this column prior to introduction of the solute and is saturated with solvent at the presaturator temperature and pressure. While this reduces bleeding in the primary column to a large extent, the problem can never be fully alleviated due to the expansion of the gas phase during its movement through the column. In addition to the works of Purnell and Pollard and Hardy previously mentioned, the study by

Kwantes and Rijnders represents the only other recorded usage of a volatile solvent in GLC. They studied normal paraffins, butane through heptane, in the next higher homolog, octane. The results concur very well with other theoretical and experimental studies by other techniques, thus verifying the feasibility of investigating two component volatile systems by GLC.

Although this work is confined to infinitely dilute solutions, recently GLC has been applied to the study of solutions at finite concentrations by Kobayashi and his coworkers.(56,110,111) In this work, a rather different experimental technique is utilized. To study a mixture of fixed composition, special carrier gas blends are prepared containing the desired solute concentrations. Once equilibrium has been established within the column a radioactive isotope of the solute is injected and tracer techniques are used to detect its retention volume. This retention volume is actually that of the solute at the predetermined concentration in the solvent. A rather extensive theory has been developed concurrently justifying this technique and the equilibrium properties have been verified by separate solubility studies and existing data in the literature. The work had been entirely confined to n-paraffin systems but included an extremely wide range of temperatures and pressures. This same technique has been applied by Chueh(19) to the study of benzene in diethylene glycol and n-hexane in 1,2,4 trichlorobenzene. The results again concur with literature values obtained by alternate methods.

The validity of GLC data has been challenged by some investigators who question the role of the solid support.(71,72,79) Many of the early supports used such as firebrick, Chromosorb P or R and similar materials undoubtedly exerted a considerable adsorption force on the solute. In fact in the above cited works the magnitude of the noted effect decreases most substantially when Chromosorb W is utilized as the support. Perhaps utilization of some of the more recently developed inert supports would alleviate the effect entirely. In any case one method of circumventing the solid support effects is to remove the solid support. To this end investigations of the thermodynamic properties of solutions utilizing capillary columns have been undertaken by Adlard, Kahn and Withham.(3) This type of column has the stationary phase deposited directly on the column surface and so is unsuited for use with volatile solvents. The results obtained for benzene in dinonyl phthalate using capillary columns show excellent agreement with the data taken previously on a packed column by these investigators.(2) Thus the role of the solid support in a properly packed column with sufficient solvent seems to be only that of an inert carrier for the solvent as deduced from the above results. Indeed, however, for nonvolatile solvents the capillary column provides an even simpler method of measuring thermodynamic properties of solutions.

B. Thermodynamics and Gas Liquid Chromatography

As mentioned in the above discussion, the first work in which thermodynamics was related to GLC was the investigation of Littlewood, Phillips and Price(65) in 1955. However, during the same time the workers at Shell were actively pursuing a similar course. Pierotti *et al.*(81) initiated work on a structural correlation which was developed using data obtained by means other than GLC. However, the relation to equilibrium properties obtained by GLC and to the partition coefficient was well established. More will be said concerning this correlation in the analysis of the data. Porter and coworkers(87) conducted an extensive investigation into the verification of GLC data as representing true vapor-liquid equilibrium, and also undertook to assess the effect of all the GLC operating variables on the partition coefficient. Even today this work constitutes one of the most thorough investigations in the field. They delve extensively into the manner of sample charging, the quantity charged and the effect on the shape of the elution curve. They conclude that the average chromatogram more closely resembles the case of complete mixing than the case of plug flow. However, the size of samples studied was quite large in comparison to today's standard. More significant is the effect of operating variables. For a six-fold variation in column length and a ten-fold variation in carrier gas velocity the partition coefficient only exhibited a 5% deviation between the extremes. They also varied the amount of solvent per unit of solid support and the size of the support particles with no apparent effect. The work involves n-paraffins and substituted alcohols in diisodecyl phthalate. The verification of vapor liquid equilibrium was made by comparison with data for the same systems using both supported and bulk liquid solvent in static experiments. This not only verifies vapor liquid equilibrium but also the nonexistence of solid support effects for properly packed columns. From the thermal variation of the partition coefficient, the excess molar enthalpies were also calculated and found to be in suitable accord with data obtained by other workers using static techniques.

In addition to Porter's work in 1956, the First International Symposium on GLC held in London brought forth many other papers applying thermodynamics to GLC. The introductory paper by Herington(41) discussed the role of thermodynamics in GLC and pointed up its importance. The theoretical development, however, was based heavily on utilization of carbon number correlations and, as was pointed out in the discussion, these relations can only be expected to be rigidly valid for water as the solvent. Relations were also derived to handle multicomponent mixtures provided that sufficient resolution existed between the peaks. Bosanquet and Morgan(15) have calculated the heat of solution of propane and of propene in triisobutene from GLC data and compared these values with the heats of vaporization. As the difference is quite small, they conclude that the effect of temperature on the deviation from ideality is negligible. For most GLC systems this conclusion is valid as the deviation arises mainly in the excess molar entropy due to the large difference in molecular size between the solute and solvent. However, as a general statement, the conclusion is erroneous, and often led early investigators to believe they were determining the heat of vaporization irrespective of the solute-solvent pair studied.

In a series of publications, Purnell and coworkers(45,96) developed a theory relating the GLC variables to thermodynamic properties. These workers investigated paraffins, chlorinated paraffins and oxygenated hydrocarbons in "liquid paraffin". From the GLC data heats of solution were calculated. They also computed the ratio of the heat of solution to the heat of vaporization and deduced that for negative deviations from Raoult's law the ratio was greater than one, while for positive deviations the ratio was less than unity. Both the ratio and the heat of solution are determined graphically from the data. Adlard(1) conducted an extensive study utilizing polyglycols for the stationary phase. For less than 100°C, polyethylene glycol 200 is recommended while for temperatures greater than 100°C polythylene glycol 400 must be used. For alkanes, aromatics, ketones, and esters, the solutions exhibit positive deviations from Raoult's law while alcohols have negative deviations, as would be anticipated. The determination of thermodynamic properties of halogenated hydrocarbons on a large variety of stationary phases has been investigated by Pollard and Hardy,(40,85,86) utilizing GLC. Both volatile and nonvolatile solvents were studied. No effect was noted on varying the sample introduction time from 3 to 20 seconds provided a column of sufficient length was used. With volatile solvents the specific retention volumes were corrected for the loss of solvent to the carrier gas, assuming a linear rate of solvent depletion. For nonpolar solvents, i.e., "liquid paraffin" and silicone oil 702, a boiling point separation was achieved, while for polar solvents, i.e., dinonyl phthalate, glycerol and water, the separation was determined by relative solubilities and hydrogen bonding. Static equilibrium experiments were also conducted using CH_2Cl_2, $CHCl_3$ and CCl_4 as solutes in silicone oil 702 and dinonyl phthalate and the partition coefficients thus obtained agreed quite well with the GLC data. Purnell's hypothesis concerning the ratio of the heat of solution to the heat of vaporization and the deviation from ideality was tested and verified for the chlorinated hydrocarbons in silicone oil 702, dinonyl phthalate and glycerol.

The work utilizing polyethylene glycol cresyl ether as the stationary phase is of interest as it offers not only a comparison between GLC and static data, but also a comparison between GLC data derived from two independent laboratories. Anderson and Napier(5,6) studied benzene and cyclohexane in the above named solvent and determined partition coefficients and heats and entropies of solution. The agreement between static measurements and GLC data was quite satisfactory. The validity of Henry's law in the dilute concentration region was also verified. Then Pyke and Swinbourne(98) independently remeasured the same systems, verifying the results, and extended the work to include cyclopentene and cyclohexene solutes. Benzene and cyclohexene systems behave essentially ideally while cyclohexane and cyclopentene systems exhibit positive deviations from Raoult's law.

In addition to binary organic solutions, the thermodynamics of other types of systems have been studied by GLC. Barber *et al.*(9) have studied systems in which transition metal stearates and oleates were used as solvents. The transition metal ions form complexes of varying stability with many compounds giving rise to specific interactions of a type other than hydrogen bonding. Organic solutes in these solvents all have activity coefficients considerably less than unity depending on the strength of the complex formed with the solvent. The solutions formed are endothermic in nature. Conversely metal salts may be utilized as solutes. Keller and Freiser(51) studied tin, tantalum, titanium and niobium chlorides in squalane and octadecane. They determined the specific retention volumes and the heats of solution. Many other metals possessing volatile halides may be studied thermodynamically in this manner.

Interest has also existed in the thermodynamics of GLC as applied to the area of distillation. Warren and coworkers(118) have considered the analogy to extractive distillation. They obtained data by GLC and from a reflux still operated at equilibrium. As the solute concentration in the still was reduced toward infinite dilution the relative volatility obtained by the two methods converged. Thus GLC is a simple method of obtaining limiting relative volatilities. Vapor liquid equilibrium constants may also be obtained from GLC data. The partition coefficient of GLC is actually an equilibrium constant but it is commonly expressed in other units. However, the two are very simply related. Preston(92) considered the relationship between GLC and hydrocarbon vapor liquid equilibrium and introduced the compressibility factor into the relations to account for the gas phase nonideality. Kobayashi and coworkers in a continuing project have extensively determined hydrocarbon vapor equilibrium constants. In their initial work(55) the system butane-dodecane was studied near atmospheric pressure, the results showing excellent agreement with the N.G.A.A. tabulations. The heats of solution of the C_4 hydrocarbons in furfural were also determined in this study, again showing good agreement with static data of other investigations. Following this initial study more sophisticated investigations were made by Stalkup and Kobayashi.(110,111) The theoretical relations between vapor liquid equilibrium and GLC have been derived both from a plate concept and from a rate theory approach considering longitudinal mixing and radial diffusion effects. The mathematics have been formulated for considering a two component solute mixture at any desired concentration, not solely infinite dilution. Interestingly enough, for conditions normally existent in a chromatographic column, the results of the more rigorous rate theory approach reduce to that obtained from the very elementary plate theory, thus justifying its usage under normal conditions. The solutes ethane, propane and butane were studied in the methane-decane system from 20 to 2000 psia and from 160 to -20°F. Propane was also studied at finite concentrations in the methane-decane system at 40°F from 20-460 psia. The GLC data was also used to develop the phase diagram for the methane-decane system in the gas-solid region. Subsequently Koonce and Kobayashi(56) modified the previous theory to include an "n" component solute mixture. This study verified the earlier work and extended the technique to the methane-propane-heptane system, but only from -40 to -20°F. Equally important, however, static equilibrium measurements were taken for the same systems and found to substantiate the GLC data completely thus further verifying GLC data as representing true vapor liquid equilibrium. Excellent agreement was also shown between this work and other data established in the literature.

When determining accurate thermodynamic data from GLC, as was mentioned above, care must be taken to insure that the solid support does not contribute to the solute retention. Prior to the newer organic and inorganic supports now available this presented a formidable problem when studying polar solutes in nonpolar solvents. Following a suggestion made by Swedish workers,(109) investigators replaced conventional firebrick with metal helices. Evered and Pollard(26) used this device when determining the activity coefficient of alkanes, alkyl nitrates, nitroalkanes and alcohols in squalane. However, when studying the same solutes in dinonyl phthalate and diglycerol, standard supports were used. From the temperature dependence of the activity coefficients the heats of solution of the alkyl nitrates and the nitroalkanes in squalane and dinonyl phthalate are determined. The dinonyl phthalate systems have a much smaller excess molar enthalpy than do the squalane systems. Kwantes and Rijnders,(58) in addition to studying a volatile solvent, also studied all possible combinations of solute and solvent based on polarity. They too used metal helices as a support for nonpolar solvents. For nonpolar solutes in nonpolar solvents, aliphatic and aromatic hydrocarbons were studied in hexadecane, tetracosane, pentatriacontane and squalane. The results agreed with those calculated from theoretical methods. Water in diethylene glycol representing the polar solute in polar solvent and n-paraffins in 1,2,4 trichlorobenzene representing nonpolar solutes in a polar solvent also checked existing literature data. Alcohols, aldehydes, ketones and esters were studied in hexadecane for the final class of polar solutes in nonpolar solvents, again concurring with existing results. In addition to the above studies butane, pentane, hexane and heptane were studied in octane using the presaturator technique described earlier, this being the only accurate work reported using a volatile solvent.

Desty and Swanton(24) in a study primarily designed to determine selective stationary phases for hydrocarbon separations utilized thermodynamics as a basis for evaluating solvent selectivity. In doing so, however, they compiled a vast quantity of thermodynamic data from GLC. The authors also show why it is preferable to use the temperature variation of the activity coefficient rather than the retention volume or the partition coefficient to determine the excess molar enthalpy. In all the polar solvents studied the activity coefficients of aliphatic and aromatic hydrocarbons are greater than unity. The excess molar enthalpies and entropies of the various solutes in the solvents studied are also determined. Langer and Purnell,(61) in a solution study, measure the same systems as those of the above work. By carefully controlling all the parameters such as column temperature, carrier gas flow rate and column pressure drop they were able to reproduce the data of Desty and Swanton to better than ± 1%, showing the value of data by independent workers.

To further verify the validity of GLC data as representative of true vapor liquid equilibrium a few more checks between the two methods will be cited. Ashworth and Everett(8) studied benzene, cyclohexane, pentane, hexane, heptane, octane and 2,2 dimethylbutane in dinonyl phthalate and squalane by static equilibrium. Spreading the solvent on the solid support did not affect the equilibrium state achieved in the bulk solvent but merely enhanced the rate of attainment of equilibrium. Only when the solvent constituted less than 10% of the stationary phase did the solid support affect the equilibrium. In dinonyl phthalate the aliphatic solutes exhibit positive deviations from ideality, while in squalane the converse is true. Then in a follow up study Everett and Stoddart(27) studied the same solutes in dinonyl phthalate by means of GLC. Again variation in sample charging time had no effect on the retention volume. The results obtained in this study agreed very well with the earlier static measurements. The author's hypothesis concerning the use of the initial retention time, while satisfactorily representing data on overloaded columns, cannot be seen to have any actual basis in theory. In order to obtain sharp narrow peaks in the present study, very small samples were used along with low carrier gas flow rates. This prevented overloading and allowed equilibrium to be established in the column. Freeguard and Stock(32) also studied the two solvents dinonyl phthalate and squalane by static equilibrium measurements. The solutes examined were the chlorinated methanes. The dinonyl phthalate systems show very satisfactory agreement with the GLC data of Hardy.(40)

A few other applications of GLC to determine some of the less common thermodynamic properties will now be presented. Takamiya and coworkers,(115) utilizing the solution theory of Hildebrand and Scott,(42) derived the relation between the specific retention volume and the solubility parameter of the solute and the solvent. The relation is used to calculate solubility parameters for many solvents of interest in GLC using alcohol solutes. Then the relation's validity is confirmed using n-paraffins by checking the measured retention volumes with the calculated values. Good agreement is obtained. Following the technique pioneered by Kobayashi and coworkers, Chueh(19) studied benzene in diethylene glycol and hexane in 1,2,4 trichlorobenzene for a wide range of solute concentrations and temperatures. The activity coefficients thus obtained agree well with data in the literature obtained by other means. Desty, Goldup, Luckhurst and Swanton(23) in an extremely thorough investigation removed the gas phase nonideality contribution to the activity coefficient. They derive the correct relation representing the true activity coefficient of the solute in the solution alone. Utilizing this relation along with very careful experimental measurements the authors are able to determine the interaction second virial coefficient from GLC data. This work represents a great stride forward in our ability to understand solution behavior from relatively simple experiments. Adlard, Khan and Whitham(2) in an earlier very careful work also were able to assess the effect of the gas phse nonideality on the activity coefficient. However some deficiencies existed in their theoretical development and so the absolute values of the results are slightly in error. The authors place the magnitude of the correction factor at 4-5%. Again the results obtained for the GLC measurements agree quite well with the static values obtained by Ashworth and Everett.(8) In a later paper(3) the same authors also reproduce the data using a capillary column and thus eliminate all possibility of solid support effects.

In addition to all of the above cited works relating GLC to thermodynamics and verifying the equilibrium nature of the process, the subject matter has been adequately treated in a number of very excellent texts.(21,54,66,97) It is thus felt that the technique has been very adequately verified and substantiated in the literature and sufficient justification exists for extension of GLC into adjacent areas without further proof of its basic validity.

C. Solution Studies

Coincidently in 1955, along with Littlewood's initial work relating thermodynamics to GLC, Keulemans, Kwantes and Zaal(53) conducted the pioneering investigation of solution behavior by GLC. The authors considered deviations from ideal behavior in two parts, a geometric effect and an energetic effect. The geometric effect was due to unequal solute and solvent molecular dimensions while the energetic effect was attributed to Van der Waals forces. In the region of low solute concentrations encountered in GLC, Henry's law was considered a valid relationship. The Van der Waals forces in turn were broken up into Keesom, Debye and London forces. The Keesom or orientation forces represent the interaction between permanent dipoles of the solute and the solvent. The Debye or induction forces represent the interaction between the permanent dipole of the solute or solvent and the induced dipole of the other component. The London or dispersion forces represent the interaction between instantaneous dipoles in the solute and instantaneous dipoles in the solvent, neither possessing permanent dipoles. Generally speaking the induction forces are negligible when compared to the other two. However, in some instances, i.e., cyclohexane and benzene in dinonyl phthalate, the higher polarizability of benzene causes a larger induction force for the benzene and accounts for the separation of the two solutes, benzene being selectively retained. Keulemans _et_ _al_. made extensive studies for separating polar and nonpolar solutes on many classes of solvents. They investigates systems in which orientation forces predominated and systems in which hydrogen bonding was a major factor. However, generally the dispersion forces represented the main contribution to the deviation from ideality.

A second approach to analyzing the deviation from Raoult's law consists in considering the activity coefficient to be made up of two terms, an athermal term essentially temperature independent and a thermal term varying with temperature. The former corresponds roughly to the excess molar entropy while the latter is related to the excess molar enthalpy. Ashworth and Everett(8) analyzed their static data by this technique. The athermal contribution arises from statistical effects due to molecular size differences between the solute and the solvent. To calculate this effect the technique developed by Guggenheim(37) is used which assumes a cell model of the liquid, each molecule having a given number of interacting neighbors. The thermal term is postulated to be proportional to the mole fraction of the solvent squared, which for most GLC systems is unity. The constant of proportionality is the interaction energy divided by the Boltzmann thermal term. Generally this interaction energy is temperature dependent.

An alternate approach is that proposed by Hildebrand and Scott.(43) They define a regular solution as one in which the excess molar entropy is zero. Then to calculate the excess molar enthalpy, which is directly related to the activity coefficient, they assume that dispersion forces are the predominant solution interaction and express this in terms of Hildebrand's solubility parameters. This method while neglecting orientation and induction forces at least allows a quantitative estimate of the deviation from ideality to be made. The next step in the modification of Hildebrand's theory was developed by Van Arkel.(116) As the orientation forces can represent as large a contribution as the dispersion forces, Van Arkel added a term to Hildebrand's solubility parameters which expresses the permanent dipole-dipole interaction between solute and solvent.

In both of the above formulations the concept of a negative excess free energy was impossible to attain due to the nature of the restrictions imposed during the development. Martire,(73) in a very thorough work investigating the theoretical selection of a solvent for a given GLC separation, introduced an empirical constant which represented the specific interactions in a solution, such as hydrogen bonding. As Martire's technique is an extension of Hildebrand's work this empirical constant was expressed in terms of the solubility parameters of the solute and the solvent. In order to apply this development at least one experimental point was needed to establish this constant for each solvent, independent of the solute. Using this technique Martire predicted naphthylamine as the solvent for separating 2,4 dimethylpentane and 2,2,3 trimethylbutane, and the predicted values of the specific retention volumes agree closely with the experimentally determined values. In a later study Martire(74) utilized the development separating the activity coefficient into athermal and thermal contributions. Hildebrand's theory was used to estimate the thermal term while the athermal term was determined from Guggenheim's development. The GLC values of the activity coefficients for hydrocarbons in aniline, isoquinoline, quinoline, 2 methyl quinoline and methyl naphthalene agree quite well with those predicted from the theoretical formulation.

Hardy and Pollard(39) in a very comprehensive review have utilized the three types of Van der Waals forces along with specific interactions to classify solutes and solvents into five categories to be described in greater detail under the experimental program. They have then utilized these categories to predict selective solvents for separating various solutes by GLC. Solutes are more strongly retained by solvents which are in a category adjacent to that of the solute. Bergeron(14) in a rather exhaustive study investigated solutions of ketones, alcohols, and aromatic, aliphatic and cyclic hydrocarbons in tetradecane, hexadecane, eicosane and tetracosane from 30° to 125°C by GLC. He attempted to correlate all the resulting binary mixtures using a single relationship but deduced that this task was impossible. Instead for each homologous series of solutes in each solvent he evolved a correlating equation which expressed the activity coefficient as a polynomial in the temperature. The constants for these correlating equations were determined from a regression analysis of the data. Littlewood in a pair of publications(67,68) investigated the factors affecting solution behavior by means of GLC. He attempts to relate the behavior of solutes in various solvents relative to two parameters, one being the specific retention volume ratio of an alkane in a nonpolar and polar solvent, the second being the specific retention volume ratio of a polar solute in a polar and nonpolar solvent, the solvents being the same in both instances. He notes the inability to describe the various solution behaviors in terms of a single parameter and chooses instead to correlate the behavior in terms of the above two parameters, the dipole moment and the polarizability. The GLC systems studied and correlated include paraffins, olefins, alcohols, esters, aldehydes, organic cyanides and halogenated hydrocarbons in monofunctional hexadecyl derivatives, i.e., chloro, bromo, cyano and hydroxy hexadecane. As can be seen this represents a very extensive study.

In addition to the above quoted studies of solution behavior utilizing GLC techniques, the generally available literature describes countless other studies by different methods as discussed in the introduction. Barker,(10) Guggenheim,(37) Hildebrand and Scott, (42,43) Hirschfelder et al.,(44) Ketelaar,(52) Prigogine and Defay,(93) Prigogine(94) and Rowlinson(102) have all written excellent texts, of which the major portions are devoted to solution studies. The theoretical development and analysis of the results to follow owe much to all of these works. However, some of the above developments while theoretically sound are as yet in a highly unapplicable state. Also certain of these theories are amenable to verification if thermodynamic data are available over a range of concentrations, but for the present work with data at only one concentration, i.e., infinite dilution, no substantiation is possible.

III. THEORETICAL DEVELOPMENT

A. Derivation of Plate Equation

The theoretical origin of GLC can be traced back to the initial work of Martin and Synge.(70) In addition to describing the basic process in which a liquid stationary phase and a mobile gas phase are used, they developed the basic mathematics describing the equilibrium process within the column. As the surface area is high with respect to the volume of the solvent, the attainment of equilibrium is very rapid and thus the assumption of equilibrium existing throughout the column was made. To aid in understanding this equilibrium process the authors invoked the theoretical plate analogous to other separation processes. Corresponding to this is the Height Equivalent to a Theoretical Plate, the thickness of the layer such that solute emerging from the layer is in equilibrium with the mean concentration of solute in the stationary phase throughout the layer. By developing the distribution of the solute in the column for infinitesimal volumes of the mobile phase, the resultant expression is a binomial expansion. Considering the relation for a large number of plates results in the plate equation of Martin and Synge

$$V_R = V_G + k V_L \tag{1}$$

The above assumes a small sample size so the solute is initially charged to a single plate, a constant partition coefficient k throughout the column, negligible mixing and diffusion effects, a linear distribution isotherm, i.e., validity of Henry's law, and no pressure drop across the column.

This relation has been rederived countless times utilizing different approaches. Keulemans(54) develops the above relation from a consideration of statistical distributions of solutes in a theoretical plate. Although not the first to apply the concept, Stalkup(110) approaches the problem from a chemical engineering standpoint. A material balance is written for each plate in the column assuming equilibrium to be existent. The differential equations resulting are solved by Laplace transforms to yield the concentration on the "n-th" plate. The integrand of this expression is the Poisson distribution. To obtain the maximum in the solute concentration on plate "n" the derivative of the expression is equated to zero. After suitable mathematical manipulations Equation (1) is obtained.

Rather than proceeding to reestablish this derivation in its formal entirety again, after having been treated exhaustively by previous workers, a slightly different approach will be developed. In this development the plate equation will be derived without recourse to the theoretical plate concept. While not completely rigorous in its development, relying on one's intuitive ability, it does provide a different insight into the problem. The general concept is due to Sternberg.(113) Consider the definition of the partition coefficient, k . It is the ratio of the concentration of solute in the stationary phase to the concentration of solute in the mobile phase. Mathematically,

$$k \equiv \frac{n_2^L / V_L}{n_2^G / V_G} = \frac{n_2^L}{n_2^G} \cdot \frac{V_G}{V_L} \qquad (2)$$

Now the total moles of solute is

$$n_2 = n_2^G + n_2^L \tag{3}$$

The velocity of solute movement in the column is given by

$$U_2 = U_U \cdot \bar{f} \tag{4}$$

As the fraction of the solute in the gas phase is n_2^G/n_2 (4) becomes

$$U_2 = U_U \cdot \frac{n_2^G}{n_2} \tag{5}$$

but from (2) and (3)

$$\frac{n_2^G}{n_2} = \frac{n_2^G}{n_2^G + n_2^L} = \frac{n_2^G}{n_2^G + n_2^G k \frac{V_L}{V_G}} = \frac{V_G}{V_G + kV_L} \tag{6}$$

Also the velocity of an unretained component may be expressed as

$$U_U = \frac{F}{(V_G/L)} \tag{7}$$

Therefore substituting (6) and (7) into (5) yields

$$U_2 = \frac{F}{(V_G/L)} \cdot \frac{V_G}{V_G + kV_L} = \frac{F}{[(V_G + kV_L)/L]} \tag{8}$$

However, the velocity of solute movement may also be expressed as

$$U_2 = \frac{F}{(V_R/L)} \tag{9}$$

analogous to Equation (7). Now by equating (8) and (9), Equation (1) results

$$V_R = V_G + k\, V_L \tag{1}$$

Thus with no recourse to theoretical plates, plate heights, or plate equilibrium the equation of Martin and Synge may be developed. Inherent in this development, however, is the concept of equilibrium involved by definition in the partition coefficient. While the plate concept is therefore no longer actually necessary, it still serves a useful purpose from an illustrative point of view.

B. Thermodynamic Considerations

In a chromatographic column the volatile solute molecules are for the greater part of the time dissolved in the stationary phase and are not transported during that time. For a small fraction of their total residence time in the column the solute molecules are in the mobile phase where they are transported by the moving carrier gas. As the rate of movement of the solute through the column is dependent on the distribution of the solute between the mobile and stationary phases, one must deal with the theory of vapor liquid equilibrium in binary mixtures.

In the ideal case for a binary liquid the partial pressure of the vapor above the solution is given by the familiar expression

$$p = x p^{\circ} \tag{10}$$

or for both components

$$p_1 = (1 - x_2) p_1^{\circ} \qquad p_2 = x_2 p_2^{\circ} \tag{11}$$

A binary liquid mixture will form an ideal solution only if the solute molecules interact in the same way with the solvent molecules as they would with the surrounding solute molecules in the pure state. However, due to differences in molecular dimensions, polarities, or interactions the assumption of an ideal solution is generally unjustified. The deviation from Raoult's law may be either positive or negative and will be discussed in greater detail in the analysis of the results.

Fortunately, however, as the solute molecules commonly occur in very low concentrations and are not close enough to exert a mutual interaction, the environment of a solute molecule can be considered as a medium consisting of solvent molecules only. Thus these solutions may be referred to as "infinitely dilute". In such solutions the escaping tendency is mainly determined by the intermolecular forces between solute and solvent molecules alone. Therefore Henry's law will apply

$$p_2 = K x_2 \qquad (12)$$

and a linear distribution isotherm will result. This relation will fail for higher solute concentrations so care must be exercised to use small solute charges. For low concentrations Henry's law approximates true solution behavior for either positive or negative deviations from Raoult's law. In this region the elution curves should be symmetric and this represents a valid test of the data.

In order to evaluate K, Henry's law constant, one needs to compare Equations (11) and (12). For an ideal solution K is equivalent to the solute vapor pressure. To complete the evaluation it will be necessary to introduce a factor to correct for the nonideality of the solution behavior. Therefore

$$p_2 = \gamma_2 x_2 p_2^{\circ} \qquad (13)$$

For ideal solutions γ_2, the activity coefficient, is unity. Throughout this work the activity coefficient will be defined with reference to the pure solute standard state at the temperature and pressure of the solution under consideration. The activity coefficient, which is a measure of the deviation of the solution from ideality, is a function of the nature of the solute and the environment in which the solute exists. Although not limiting the scope of γ_2 to the nonideality of the liquid phase, it will be assumed that the gas phase behaves ideally. Later this limiting assumption will be removed. By definition p_2 may also be expressed as

$$p_2 = y_2 P \tag{14}$$

which leads to

$$y_2 P = \gamma_2 x_2 p_2^\circ \tag{15}$$

For dilute solutions, the partition coefficient k may be related to the mole fractions in the two phases.

$$k = \frac{x_2}{y_2} \cdot \frac{N_L}{N_G} \tag{16}$$

From (15) and (16)

$$k = \frac{P}{\gamma_2 p_2^\circ} \cdot \frac{N_L}{N_G} \tag{17}$$

Using Boyle's law for the gas phase

$$P/N_G = RT \tag{18}$$

one obtains from (17) and (18)

$$k = \frac{N_L R T}{\gamma_2 P_2^\circ} \tag{19}$$

The retention volume, defined as the volume of carrier gas required to elute the solute component from the column, may be related to the partition coefficient by Equation (1). The specific retention volume may also be expressed in terms of the parameters already established.

$$\overline{V}_R = \frac{V_R - V_G}{m} \tag{20}$$

In addition the expression for $\overline{V}_R$ is usually corrected for the finite pressure gradient across the column by multiplying Equation (20) by

$$j \equiv \frac{3}{2}\left[\frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1}\right] \tag{21}$$

This is the correction factor theoretically derived by James and Martin(47) to account for the inequality of the inlet and outlet pressures of the column. In the present study the magnitude of j was always quite close to unity due to the low pressure drop across the column. By comparing Equations (1) and (20) one may express $\overline{V}_R$ in terms of k

$$\overline{V}_R = \frac{k}{e} \tag{22}$$

Now realizing that

$$N_L = e/M \tag{23}$$

Equations (19), (22) and (23) may be combined to give

$$\gamma_2^{\infty} = \frac{RT}{\bar{V}_R M p_2^{o}} \tag{24}$$

This expression is the actual relation which links the normally obtained thermodynamic property, the activity coefficient, with the chromatographically determined variable, the specific retention volume.

From the above formulae k has been expressed as a function dependent on the characteristics of the solvent, N_L , of the solute, p_2^o , and of a factor which depends on both, γ_2 . Also k and γ_2 have been related to the measureable parameters of a GLC experiment. Since k has been assumed constant throughout the column in the plate theory, this also places a restriction on γ_2 . Neither of these conditions is entirely fulfilled in GLC, but the solute concentrations are generally so low that they can be considered to approach infinite dilution. In this case the activity coefficient will be referred to as γ_2^{∞} , the activity coefficient at infinite dilution, which is a constant. It should be realized, however, that in a band of solute in the actual chromatographic column a concentration gradient exists, and that particularly near the column inlet the assumption of constant γ_2^{∞} or k is not rigorously valid. Nevertheless for a column of sufficient length the value of k is determined by γ_2^{∞} and p_2^o and is a true equilibrium value. This means that the experimentally determined values of γ_2^{∞} are independent of all the GLC operating variables as elaborated in the literature review.

The analogy between GLC and distillation referred to earlier can be pointed up clearly by a consideration of the above derived relations. Considering a pair of solutes in a given solvent, the partition coefficient can be obtained for each solute as

$$k_A = \frac{N_L R T}{\gamma_A P_A^o} \quad \text{and} \quad k_B = \frac{N_L R T}{\gamma_B P_B^o} \tag{25}$$

Now the relative volatility is defined as

$$\Psi_{AB} \equiv k_B / k_A = \frac{\gamma_A P_A^o}{\gamma_B P_B^o} \tag{26}$$

Thus it can be seen that although N_L affects k, it does not affect the relative volatility. Also, so long as the heats of vaporization of the two solutes do not differ greatly, the vapor pressure ratio will not vary rapidly. It is only when large temperature changes are involved that the ratio varies appreciably. Thus the concept of relative volatility has the same meaning essentially in GLC as in distillation, namely a factor which defines the ease of separation.

Having established the relationships between the activity coefficient at infinite dilution and the GLC parameters, by further consideration of these relationships the partial molar properties of the solution will be determined. Consider the basic equation for the partial molar excess free energy

$$\Delta G_2^E = \Delta H_2^E - T \Delta S_2^E \tag{27}$$

The activity coefficient is related to ΔG_2^E by

$$\Delta G_2^E / T = R \ln \gamma_2 \tag{28}$$

and

$$\Delta G_2^E / T = \Delta H_2^E / T - \Delta S_2^E \tag{29}$$

Now assuming ΔS_2^E and ΔH_2^E constant for a small change in temperature, the derivatives with respect to temperature of (28) and (29) are

$$\frac{d(\Delta G_2^E / T)}{dT} = - \frac{\Delta H_2^E}{T^2} = R \frac{d \ln \gamma_2}{dT} \tag{30}$$

Therefore

$$\frac{d \ln \gamma_2}{dT} = - \frac{\Delta H_2^E}{R T^2} \tag{31}$$

or alternately

$$\frac{d \ln \gamma_2}{d(1/T)} = \frac{\Delta H_2^E}{R} \tag{32}$$

Also, combining (28) and (29)

$$\ln \gamma_2 = \frac{\Delta H_2^E}{RT} - \frac{\Delta S_2^E}{R} \tag{33}$$

Now from (32) it can be seen that a plot of $\ln\gamma_2$ as a function of reciprocal temperature for a small range should yield a straight line, the slope of which is related to the partial molar excess enthalpy.

All of the above equations involve relationships between thermodynamic properties. These properties will now be related to the appropriate GLC parameters. Taking the logarithm of (24)

$$\ln \gamma_2 = \ln \frac{RT}{M} - \ln \bar{V}_R - \ln p_2^{o} \qquad (34)$$

and differentiating with respect to T yields

$$\frac{d \ln \gamma_2}{dT} = \frac{1}{T} - \frac{d \ln \bar{V}_R}{dT} - \frac{d \ln p_2^{o}}{dT} \qquad (35)$$

For most studies of interest the 1/T term is negligible and it will be considered so here. Now the Clapeyron equation is

$$\frac{d \ln p_2^{o}}{dT} = \frac{\Delta H_{vap}}{RT^2} \qquad (36)$$

Substituting (31) and (36) into (35) and rearranging gives

$$\frac{d \ln \bar{V}_K}{dT} = \frac{\Delta H_2^E - \Delta H_{vap}}{RT^2} \qquad (37)$$

or

$$\frac{d \ln \bar{V}_R}{d(1/T)} = \frac{\Delta H_{vap} - \Delta H_2^E}{R} \qquad (38)$$

Therefore the slope of a plot of $\ln \bar{V}_R$ as a function of reciprocal temperature, for a small range, will determine the partial molar excess enthalpy. In many of the works cited in the literature review this method is the one actually used. An alternate procedure to the one delineated above consists in substituting (23) into (19)

$$k = \frac{eRT}{M \gamma_2 p_2^o} \tag{39}$$

Taking the logarithm of (39)

$$\ln k = \ln e + \ln \frac{RT}{M} - \ln \gamma_2 - \ln p_2^o \tag{40}$$

and differentiating with respect to T yields

$$\frac{d \ln k}{dT} = \frac{d \ln e}{dT} + \frac{1}{T} - \frac{d \ln \gamma_2}{dT} - \frac{d \ln p_2^o}{dT} \tag{41}$$

Now again substituting (31) and (36) into (41) and neglecting the 1/T term

$$\frac{d \ln k}{dT} = \frac{d \ln e}{dT} + \frac{\Delta H_2^E}{RT^2} - \frac{\Delta H_{vap}}{RT^2} \tag{42}$$

or

$$\frac{d \ln k}{d(1/T)} = \frac{\Delta H_{vap} - \Delta H_2^E - RT^2 \, d \ln e/dT}{R} \tag{43}$$

A plot of ln k as a function of 1/T will generate a curve due to the added term $RT^2 d \ln \rho/dT$. This is the relation postulated by Littlewood et al.(65) in their original work. From the above equations, utilizing parameters obtained from GLC data, values of γ_2^∞ , ΔG_2^E , ΔH_2^E and ΔS_2^E can be obtained.

As mentioned earlier, the activity coefficient in the above relations is actually a hybird value representing the nonideality of the vapor and the liquid phases. This is due to the inclusion of the ideal gas law in the above derivations. This implies that no change occurs in the volume of an element of gas as it passes through the column. This condition does not hold rigorously as the gas density fluctuates throughout the column. A partial means of correcting this discrepancy lies in replacing the solute vapor pressure by its fugacity. In this manner Equation (24) is modified to

$$\gamma_2 = \frac{RT}{\overline{V}_R M f_2^\circ} \tag{44}$$

The activity coefficient calculated from (44) has a smaller temperature dependence than that determined from (24). However, the improvement is only slight and the problem of ascertaining fugacities for many compounds hardly justifies the added accuracy in the activity coefficient.

An alternate approach to removing the gas phase nonideality, which has been more fruitful, involves the utilization of the virial equation of state, in particular the second virial coefficient. Although some early attempts to evaluate this gas phase nonideality in GLC were attempted by Adlard et al.(2) and Everett and Stoddart,(27) the mathematical representation of the problem was only recently correctly formulated by Desty, Goldup, Luckhurst and Swanton.(23,35) The following development is due in large measure to their work. The activity coefficient of a solute in a solution is given by Equation (13). More correctly, the solute partial pressure as well as the solute vapor pressure should be replaced by the corresponding fugacities

$$f_2 = \gamma_2 x_2 f_2^\circ \tag{45}$$

Now Guggenheim(37) relates the fugacities to the corresponding pressures by means of the second virial coefficients as follows

$$\ln f_2^\circ = \ln p_2^\circ + \frac{B_{22}\, p_2^\circ}{RT} \tag{46}$$

and

$$\ln f_2 = \ln p_2 + \frac{\bar{P}}{RT}\left[B_{22} - (1-y_2)^2 (B_{11} - 2B_{12} + B_{22})\right] \tag{47}$$

where

$$\bar{P} \equiv P_o / j \tag{48}$$

The second virial coefficient B_{12} characterizes the interactions between unlike molecules and is an important parameter in studying solution behavior. Now Equation (16) may be expressed as

$$k = \frac{x_2}{y_2} \cdot \frac{N_L}{N_G} = \frac{x_2}{y_2} \cdot \frac{n_1^L + n_2^L}{V_L} \cdot \frac{V_G}{n_1^G + n_2^G} \tag{49}$$

In the gas phase the solvent is the carrier gas, while in the liquid phase the solvent is the stationary liquid. Solving (45) for γ_2 and taking the logarithm of the resulting expression gives

$$\ln \gamma_2 = \ln f_2 - \ln x_2 - \ln f_2^{\circ} \tag{50}$$

Equation (49) may then be solved for x_2 and the logarithm taken of this relation

$$\ln x_2 = \ln\left[\frac{k V_L}{n_1^L + n_2^L} \cdot \frac{n_1^G + n_2^G}{V_G}\right] + \ln y_2 \tag{51}$$

Now (46), (47) and (51) may be substituted into (50) to yield

$$\ln \gamma_2 = \ln p_2 + \frac{\overline{P}}{RT}\left[B_{22} - (1-y_2)^2(B_{11} - 2B_{12} + B_{22})\right] + \ln\left[\frac{n_1^L + n_2^L}{k V_L} \cdot \frac{V_G}{n_1^G + n_2^G}\right] - \ln y_2 - \ln p_2^{\circ} - \frac{B_{22} p_2^{\circ}}{RT} \tag{52}$$

Now utilizing the logarithm of (14) in (52)

$$\ln \gamma_2 = \ln\left[\frac{n_1^L + n_2^L}{k V_L} \cdot \frac{V_G}{n_1^G + n_2^G}\right] + \ln \overline{P} - \ln p_2^{\circ} - \frac{B_{22} p_2^{\circ}}{RT} + \frac{\overline{P}}{RT}\left[B_{22} - (1-y_2)^2(B_{11} - 2B_{12} + B_{22})\right] \tag{53}$$

However

$$\frac{V_G}{n_1^G + n_2^G} = \frac{RT}{\overline{P}} + y_2^2 B_{22} + 2 y_2(1-y_2) B_{12} + (1-y_2)^2 B_{11} \tag{54}$$

therefore

$$\ln \gamma_2 = \ln\left\{ \frac{n_1^L + n_2^L}{k V_L} \left[\frac{RT}{\overline{P}} + y_2^2 B_{22} + 2 y_2 (1-y_2) B_{12} + (1-y_2)^2 B_{11} \right] \right\}$$

$$+ \ln \overline{P} + \frac{\overline{P}}{RT}\left[B_{22} - (1-y_2)^2 (B_{11} - 2B_{12} + B_{22}) \right]$$

$$- \ln p_2^\circ - \frac{B_{22} P_2^\circ}{RT} \tag{55}$$

Since in GLC the solute is essentially at infinite dilution, y_2 and n_2^L approach zero and $\gamma_2 \to \gamma_2^\infty$. Thus

$$\ln \gamma_2^\infty = \ln \frac{n_1^L RT}{k V_L \overline{P}} + \ln\left(1 + \frac{B_{11}\overline{P}}{RT}\right) + \ln \overline{P}$$

$$+ \frac{\overline{P}}{RT}\left(2 B_{12} - B_{11}\right) - \ln p_2^\circ - \frac{B_{22} P_2^\circ}{RT} \tag{56}$$

Now as a first approximation

$$\ln\left(1 + \frac{B_{11}\overline{P}}{RT}\right) = \frac{B_{11}\overline{P}}{RT} \tag{57}$$

so substituting (57) in (56) and cancelling terms yields

$$\ln \gamma_2^\infty = \ln \frac{n_1^L RT}{k V_L p_2^\circ} + \frac{2 \overline{P} B_{12}}{RT} - \frac{B_{22} P_2^\circ}{RT} \tag{58}$$

The fugacity varies with pressure according to the relation

$$\frac{\partial \ln f}{\partial P} = \frac{v}{RT} \tag{59}$$

Integrating (59)

$$\ln f(P) = \frac{Pv}{RT} + \ln f(0) \tag{60}$$

Applying (60) for the pure solute vapor

$$\ln f_2^\circ(p_2^\circ) = \ln f_2^\circ(0) + \frac{p_2^\circ v_2^\circ}{RT} \tag{61}$$

while for the solute at pressure $\overline{P}$

$$\ln f_2(\overline{P}) = \ln f_2(0) + \frac{\overline{P} v_2}{RT} \tag{62}$$

Since the solutions are very dilute $v_2^o = v_2$. Correcting the fugacities in (46) and (47) to a standard reference state would alter (58) as follows

$$\ln \gamma_2^\infty = \ln \frac{n_1^L RT}{k V_L p_2^\circ} + \frac{\overline{P}}{RT}(2B_{12} - v_2^\circ) - \frac{p_2^\circ}{RT}(B_{22} - v_2^\circ) \tag{63}$$

Now as $n_1^L/V_L = N_L$, the first term in (63) is seen to be the logarithm of the hybrid activity coefficient as given by Equation (19). Utilizing (22) and (23) in (63) results in

$$\ln \gamma_2^\infty = \ln \frac{RT}{\overline{V}_R M p_2^\circ} + \frac{\overline{P}}{RT}(2B_{12} - v_2^\circ) - \frac{p_2^\circ}{RT}(B_{22} - v_2^\circ) \tag{64}$$

A comparison of (24) and (64) will show that the second and third terms of (64), involving the second virial coefficients, account for the gas phase nonideality and thus γ_2^∞ as determined from (64) is a true activity coefficient representing the deviation from ideality of the solute in the liquid phase. If instead of utilizing (54) for the gas phase molar volume, one neglects the second virial coefficient of the gas mixture then

$$\frac{V_G}{n_1^G + n_2^G} \approx \frac{RT}{\bar{P}} \tag{65}$$

and (64) becomes

$$\ln \gamma_2^\infty \approx \ln \frac{RT}{\bar{V}_R M p_2^0} + \frac{\bar{P}}{RT}\left(2B_{12} - B_{11} - v_2^0\right) - \frac{p_2^0}{RT}\left(B_{22} - v_2^0\right) \tag{66}$$

which is the equation derived by Everett and Stoddart.(27) Further if one utilizes the Lewis-Randall postulate

$$2B_{12} \approx B_{11} + B_{22} \tag{67}$$

then (66) becomes

$$\ln \gamma_2^\infty \approx \ln \frac{RT}{\bar{V}_R M p_2^0} + \frac{\bar{P}}{RT}\left(B_{22} - v_2^0\right) - \frac{p_2^0}{RT}\left(B_{22} - v_2^0\right) \tag{68}$$

which is the equation derived by Adlard, Kahn and Whitham.(2) Desty and coworkers studied helium, hydrogen, nitrogen, carbon monoxide, argon, oxygen and carbon dioxide to illustrate the effect of carrier gas on the true activity coefficient. They conclude that the magnitude of the correction factor is a minimum when using helium as a carrier gas. When exceptionally accurate values of $\bar{V}_R$ are obtained the above relationships can be used to determine B_{12} from GLC data. Rearranging Equation (64) yields

$$\frac{P_2^\circ}{RT}(B_{22}-V_2^\circ)-\ln\frac{RT}{\bar{V}_R M P_2^\circ}=\frac{\bar{P}}{RT}(2B_{12}-V_2^\circ)-\ln\gamma_2^\infty \tag{69}$$

By plotting the left hand side of Equation (69) as a function of $\bar{P}$, the slope is $(2B_{12} - v_2^o)$ and the intercept is $-\ln\gamma_2^\infty$. By assuming B_{ij}, v_2^o, P_2^o and γ_2^∞ independent of pressure for small changes in pressure, the variation in $\bar{V}_R$ with $\bar{P}$ is determined experimentally by GLC and a plot of Equation (69) is used to evaluate B_{12} and γ_2^∞.

C. Nonelectrolyte Solution Theory

As can be surmized from the literature review, three basic approaches to the theory of nonelectrolyte solutions will be attempted. In actuality one general procedure will be outlined with two variants to one part to follow later. From an inspection of Equation (33)

$$\ln\gamma_2=\frac{\Delta H_2^E}{RT}-\frac{\Delta S_2^E}{R} \tag{33}$$

it can be seen that for small ranges of temperature the activity coefficient is composed of two terms, one thermally dependent and one essentially independent of temperature. This may be expressed as

$$\ln\gamma_2=\ln\gamma_2^{th}+\ln\gamma_2^{ath} \tag{70}$$

A direct relation, however, may not be drawn from (33) and (70) as γ_2^{th} is not related solely to ΔH_2^E but also to ΔS_2^E. The γ_2^{ath} term arises from statistical effects due to molecular size differences between the solute and the solvent. On the other hand γ_2^{th} is associated with the interaction energies between the solute and the solvent and therefore is temperature dependent. The dependence of γ_2^{th} on ΔS_2^E also, arises from the nonconfigurational terms in the partition function to be described in the statistical mechanics of solutions. The two terms in Equation (70) may be treated separately as they are independent.

Since γ_2^{ath} is dependent on molecular configurations and geometry, the best approach for a theoretical formulation can be based on the cell theory of liquids and mixtures. A basic work in this area is the fine text of Guggenheim.(37) In the cell theory each molecule is considered imposed in a semi-rigid cell surrounded by neighboring molecules. Of these surrounding molecules a certain number immediately adjacent to the molecule under consideration are deemed nearest neighbors and only these are considered to have primary interactions with the molecule of interest. Other interactions are of a second order and considered negligible.

The mathematical treatment of these interactions need be considered in two cases depending on the molar volumes or sizes of the solute and the solvent. Consider the case where $V_1^o > V_2^o$, i.e., the solvent is larger than the solute. According to Guggenheim the resultant relation is

$$\frac{P_2}{P_2^o} = \frac{1-\phi_1}{\left[1-\frac{r-s}{r}\phi_1\right]^{z/2}} \tag{71}$$

where s is a parameter defined by

$$\left(\tfrac{1}{2}z-1\right)r \equiv \tfrac{1}{2}zs-1 \tag{72}$$

For an infinitely dilute solution, $\phi_1 \approx 1$ and x_2 approaches zero. Then

$$p_2 = p_2^\circ x_2 \gamma_2^{ath} \tag{13}$$

and

$$\phi_1 = \frac{r n_1}{n_2 + r n_1} \approx 1 \tag{73}$$

so

$$1 - \phi_1 = 1 - \frac{r n_1}{n_2 + r n_1} \approx \frac{x_2}{r} \tag{74}$$

and utilizing (72)

$$1 - \frac{(r-s)}{r}\phi_1 \approx \frac{s}{r} = 1 - \frac{2}{z} + \frac{2}{zr} \tag{75}$$

Substitution (13), (74) and (75) into (71) yields

$$x_2 \gamma_2^{ath} = \frac{x_2/r}{\left[1 - 2/z + 2/zr\right]^{z/2}} \tag{76}$$

and taking the logarithm of (76) gives

$$\ln \gamma_2^{ath} = \ln \frac{1}{r} - \frac{1}{2} z \ln\left(1 - \frac{2}{z} + \frac{2}{zr}\right) \tag{77}$$

No accurate method is available of estimating z correctly. However, z will be chosen as 12 in view of the fact that most common lattices have coordination numbers near this value. In actuality Guggenheim has shown that for z greater than ten, the difference in results between choosing $z = 10$ and $z = \infty$ is very small. Therefore setting $z = 12$ in Equation (77) results in

$$\ln \gamma_2^{ath} = \ln \frac{1}{r} + 6 \ln \frac{6r}{5r+1} \tag{78}$$

On the other hand when the solute is larger than the solvent, i.e., $v_2^o > v_1^o$ the resultant relation is

$$\frac{p_2}{p_2^o} = \frac{\phi_2}{\left[\frac{r}{s}(1 - \frac{r-s}{r}\phi_2\right]^{zs/2}} \tag{79}$$

with only the definition of "r" inverted. Again considering an infinitely dilute solution, ϕ_2 and x_2 approach zero and

$$\phi_2 = \frac{r n_2}{n_1 + r n_2} \approx r x_2 \tag{80}$$

also

$$1 - \frac{(r-s)}{r}\phi_2 \approx 1 \tag{81}$$

Substituting (72), (13), (80) and (81) into (79) yields

$$x_2 \gamma_2^{ath} = \frac{r x_2}{\left[\frac{1}{1 - 2/z + 2/zr}\right]^{zs/2}} \tag{82}$$

Taking the logarithm of (82) gives

$$\ln \gamma_2^{ath} = \ln r + \left(\tfrac{1}{2}zr - r + 1\right) \ln\left(1 - \frac{2}{z} + \frac{2}{zr}\right) \tag{83}$$

or with $z = 12$

$$\ln \gamma_2^{ath} = \ln r + (5r+1) \ln \frac{5r+1}{6r} \tag{84}$$

Therefore for either of the above cases it can be seen that γ_2^{ath} is a function only of r, the molar volume ratio which is always greater than unity. For the case where $r = 1$ both Equations (78) and (84) give $\gamma_2^{ath} = 1$. It should also be noted that $\ln \gamma_2^{ath}$ is always negative, this result being in agreement with the fact that the size contribution to the excess entropy term will always be positive. From either Equation (78) or (84) then, the athermal contribution to the activity coefficient may be calculated.

While the above treatment appears to be the only theoretical development for determining γ_2^{ath} which has been refined to a point of practical application, the same situation does not hold for γ_2^{th}. A number of methods have been proposed for computing the thermal contribution to the activity coefficient. In addition to the above determined relations, Guggenheim also formulated an expression for γ_2^{th}

$$\ln \gamma_2^{th} = \frac{z \Delta W}{2kT} \phi_1^2 \tag{85}$$

where

$$\Delta W = W_{11} + W_{22} - 2W_{12} \tag{86}$$

and w_{ij} represents the energy associated with each interaction of an "i" molecule with a neighboring "j" molecule. However, the above relation is difficult to apply as the determination of the w_{ij} terms is not readily accomplished.

The most generally applicable relation for determining γ_2^{th} is that derived from the solution theory of Hildebrand and Scott.$^{(42)}$ These authors consider regular solutions for which by definition ΔS_2^E is zero. The basic relation of Hildebrand's theory is

$$\Delta H^E = \frac{n_2^L n_1^L v_1 v_2}{n_1^L v_1 + n_2^L v_2} (\delta_1 - \delta_2)^2 \tag{87}$$

which is formulated by analogy to the early work of Van Laar. Utilizing the definition of volume fractions, (87) may be written as

$$\Delta H^E = (n_1^L v_1 + n_2^L v_2)[\delta_1 - \delta_2]^2 \Phi_1 \Phi_2 \tag{88}$$

Taking the derivative of (87) with respect to n_2^L yields

$$\Delta H_2^E \equiv \left(\frac{\partial \Delta H^E}{\partial n_2^L}\right) = \frac{(n_1^L v_1)^2 v_2}{(n_1^L v_1 + n_2^L v_2)^2} (\delta_1 - \delta_2)^2 \tag{89}$$

or

$$\Delta H_2^E = v_2 (\delta_1 - \delta_2)^2 \Phi_1^2 \tag{90}$$

Now from (33), (70) and (90) one obtains

$$\ln \gamma_2^{th} = \frac{v_2}{RT} (\delta_1 - \delta_2)^2 \Phi_1^2 \tag{91}$$

Equation (91) is the most useful equation for calculating the thermal contribution to the deviation from ideality. However, Hildebrand's solubility parameter is based solely on dispersion forces and therefore cannot possibly describe the behavior of polar solutes and solvents or solutions in which there are specific interactions. It does represent a large number of nonelectrolyte solutions, however, in which the solute and solvent are electrically neutral or only slightly polar. This field encompasses the bulk of the petroleum industry as well as many other solutions of interest.

Many variants of Hildebrand's theory have since appeared which attempt to remove the limitation of only being able to correctly explain dispersion forces. As can be judged from the above discussion, it would be highly desireable to treat solutions in which one or both components were polar in nature. Van Arkel(116) seems to have been the first to propose such a relation. Proceeding heavily on the basis formulated by Hildebrand, he added a second term to Equation (91) of the same form as the solubility parameters which was to account for dipole-dipole interactions, namely

$$\ln \gamma_2^{th} = \frac{v_2}{RT}\left[(\delta_1 - \delta_2)^2 + (\omega_1 - \omega_2)^2\right] \phi_1^2 \qquad (92)$$

The "ω" term was dependent on the dipole moment of the component being considered, but its exact form remained unspecified. The above relation still does not allow a negative deviation from Raoult's law, due to the assumption of a statistical distribution of molecules. However, when the pole of a dipole is near the surface of the molecule the distribution is no longer random and the theory fails to account for the resultant behavior. Therefore in all future considerations of this relation it is tacitly assumed that dipoles are imbedded at the center of the molecule. To obtain an exact relation for the dipole interaction parameter one must turn to the theory of intermolecular forces.

Before proceeding to such a discussion one further modification of Hildebrand's theory deserves comment. In an attempt to account for weak specific interactions such as only slight solute-solvent hydrogen bonding, Martire(73) has developed a modification of Equation (92) by again adding an additional term to those of the solubility parameters and the dipole interaction parameters. This term allows for negative deviations from ideality but is empirical in nature. The expression is

$$\ln \gamma_2^{th} = \frac{v_2}{RT}\left[(\delta_1 - \delta_2)^2 + (\omega_1 - \omega_2)^2 - J\right]\phi_1^2 \tag{93}$$

and J is defined by

$$J \equiv C_1 \left(\frac{V_2^\circ}{V_1^\circ}\right)\left(\frac{\delta_1}{\delta_2}\right) \tag{94}$$

where C_1 is a solvent dependent parameter given as

$$C_1 = C_2\left(\frac{V_1^\circ}{\delta_1}\right) \tag{95}$$

Therefore J may be expressed as

$$J = C_2\left(\frac{V_2^\circ}{\delta_2}\right) \tag{96}$$

Now C_2 must also be a solvent dependent parameter, so in order to determine its value at least one experimental value of γ_2^{th} must be known for each solvent under consideration, independent of the solute utilized. For systems of interest in GLC where no strong hydrogen bonding normally exists, Equation (93) predicts the specific retention volume very well.

An alternate method of determining the thermal component of the activity coefficient lies in the theory of intermolecular forces. Three types of physical forces exist between molecules: orientation forces, induction forces, and dispersion forces. The first two of these can be understood from the classical theory of electrostatics but the third type can only be properly understood through a quantum mechanical interpretation. London$^{(69)}$ was the first to consider these interactions in detail. The dispersion forces are due to the fluctuation or displacement of the electrons from their normal positions. These oscillations tend to induce dipoles in the surrounding molecules and cause interactions. Using the quantum mechanical treatment for the kinetic energy of the electrons, London evolved the following expression for the interaction energy due to oscillating electrons between the solute and the solvent

$$E_{dispersion} = -\frac{3}{2} \cdot \frac{\alpha_1 \alpha_2}{\sigma_{12}^6} \cdot \frac{h\nu_1 \, h\nu_2}{h\nu_1 + h\nu_2} \qquad (97)$$

while if it were an interaction between two molecules of the same component the expression would be

$$E_{dispersion} = -\frac{3}{4} \cdot \frac{\alpha_i^2}{\sigma_{ii}^6} \cdot h\nu_i \qquad (98)$$

The name dispersion forces arises from the similarity of the expressions with those evolved in optical dispersion studies. As it is often impossible to determine the characteristic vibration frequency associated with the electron motion a simplifying assumption has often been made that

$$I_i = h\nu_i \tag{99}$$

The ionization potential here referred to is that associated with the removal of the first electron from the molecule. This assumption, however, is not always a valid one and the disconcerting fact is that determining its validity is rather an extensive task. Pitzer,(84) investigating the quantum mechanics underlying this assumption, mathematically analyzed the determinantal wave function for the electrons. London's treatment was actually a second order perturbation treatment of the wavefunction. Now the utilization of Equation (99) can be shown to be valid only when the off-diagonal terms of the wavefunction are zero. However, generally certain of these terms are nonzero and thus the value of $h\nu_i$ may be two to three times the ionization potential. Nevertheless this relation is constantly used because of its simplicity.

An excellent discussion of Van der Waals forces is given by Hirschfelder <u>et al</u>.(44) and Dal Nogare and Juvet.(21) Considering two molecules at a distance σ_{ij} apart with their dipoles orientated in various manners, the mathematical relations for expressing the other two physical forces can be determined. By averaging over all possible orientations of the two dipoles, holding the intermolecular distance constant, and using the Boltzmann weighting factor, Hirschfelder derives the following relation for the orientation forces

$$E_{\text{orientation}} = -\frac{2}{3kT} \cdot \frac{\mu_1^2 \mu_2^2}{\sigma_{12}^6} \tag{100}$$

while for interactions between two molecules of the same component (100) becomes

$$E_{orientation} = -\frac{2}{3kT} \cdot \frac{\mu_i^4}{\sigma_{ii}^6} \tag{101}$$

To assess the induction forces consider two molecules a distance σ_{ij} apart with one molecule being charged, i.e., possessing a permanent dipole. From Coulomb's law one can deduce that

$$E_{induction} = -\frac{1}{\sigma_{12}^6}\left(\mu_1^2\alpha_2 + \mu_2^2\alpha_1\right) \tag{102}$$

while again for like component interactions this becomes

$$E_{induction} = -\frac{2\mu_i^2\alpha_i}{\sigma_{ii}^6} \tag{103}$$

As was pointed out in the literature review the magnitude of the induction forces is generally considerably less than that of the orientation or dispersion forces, the dispersion forces usually predominating. However, in some instances they can explain the differences in behavior between two components of similar nature but differing in electronic structure. The success of Hildebrand's basic theory is actually due to the predominance of the dispersion forces in most nonelectrolyte solutions.

Having formulated the expressions representing the molecular interactions due to physical forces, certain relations may now be drawn between the theory of intermolecular forces and Hildebrand's nonelectrolyte solution theory. First of all a relation may be derived for the dipole interaction parameter, ω . Considering Equations (92) and (101) it can be deduced that

$$\omega_i^2 = \frac{2\mu_i^4}{3kTv_{ii}\sigma_{ii}^6} \tag{104}$$

This is the form of the relation postulated by Martire based on Van Arkel's work and the theory of intermolecular forces. As will be seen below, this is also the result arrived at by Hildebrand and Scott.(42) Now in order to be able to combine the Van der Waals forces together into a workable expression for γ_2^{th} an analogy will be drawn with a more generalized from of Hildebrand's equation. One of the basic limitations of Hildebrand's method is the assumption of the geometric mean rule for expressing all the interaction properties between the solute and solvent molecules, namely

$$X_{12} = (X_{11}X_{22})^{1/2} \tag{105}$$

The most general form of Hildebrand's relation is

$$\ln \gamma_2^{th} = \frac{v_2}{RT}(Z_{11} + Z_{22} - 2Z_{12})\,\phi_1^2 \tag{106}$$

In this expression the assumption of the geometric mean has been avoided and thus negative deviations from ideality are possible. Comparing Equations (92) and (106), and invoking (105) it can be seen that in Hildebrand's normal expression, neglecting induction effects

$$Z_{11} = \delta_1^2 + \omega_1^2\,;\; Z_{12} = \delta_1\delta_2 + \omega_1\omega_2\,;\; Z_{22} = \delta_2^2 + \omega_2^2 \tag{107}$$

At this point the analogy already suggested by Equation (104) will be completed. Consider two solutes molecules interacting to form a 2-2 pair and likewise two solvent molecules interacting to form a 1-1 pair. Now for every solute-solvent interaction taking place when the binary solution is formed two 1-2 pairs are formed for each 1-1 and 2-2 pair interactions. Thus the bracketed group in Equation (106) could quite naturally represent the molecular interactions occurring in solution formation as postulated by the theory of intermolecular forces. Utilizing Equations (97) through (103) the following relations result

$$Z_{11} = \frac{3}{4} \cdot \frac{\alpha_1^2 I_1}{\sigma_{11}^6 V_{11}} + \frac{2\alpha_1 \mu_1^2}{\sigma_{11}^6 V_{11}} + \frac{2\mu_1^4}{3kT\sigma_{11}^6 V_{11}}$$

$$Z_{12} = \frac{3}{2} \cdot \frac{\alpha_1 \alpha_2 I_1 I_2}{(I_1+I_2)\sigma_{12}^6 V_{12}} + \frac{\alpha_1 \mu_1^2 + \alpha_2 \mu_2^2}{\sigma_{12}^6 V_{12}} + \frac{2\mu_1^2 \mu_2^2}{3kT\sigma_{12}^6 V_{12}} \tag{108}$$

$$Z_{22} = \frac{3}{4} \cdot \frac{\alpha_2^2 I_2}{\sigma_{22}^6 V_{22}} + \frac{2\alpha_2 \mu_2^2}{\sigma_{22}^6 V_{22}} + \frac{2\mu_2^4}{3kT\sigma_{22}^6 V_{22}}$$

Thus Equation (106) can be used in conjunction with (108) to determine γ_2^{th} using the theory of intermolecular forces. Conversely this analogy may be used to determine the relationship between Hildebrand's parameters andthe intermolecular force theory. Recalling that Hildebrand neglects induction effects, a comparison of (107) and (108) yields

$$\delta_i^2 = \frac{3}{4} \cdot \frac{\alpha_i^2 I_i}{\sigma_{ii}^6 V_{ii}} \tag{109}$$

and

$$\omega_i^2 = \frac{2}{3} \cdot \frac{\mu_i^4}{k T \sigma_{ii}^6 v_{ii}} \tag{104}$$

assuming that Equation (105) holds for all the interaction properties, and is approximately equivalent to the harmonic mean.

As has been mentioned a number of times, although the induction forces are usually negligible there are certain instances in which their effect is actually the determining factor in explaining solution behavior. For this reason a further refinement of Hildebrand's treatment is proposed here to account for this effect. As the solubility parameters term in Equation (92) represents the dispersion forces and likewise the dipole interaction parameters represents the orientation forces, a third term will be added to account for the induction forces. However, as can be seen from Equation (108) the approximation of (105) is in no way justifiable as a summation is involved for the Z_{12} term. Therefore the following relation by analogy is proposed

$$\ln \gamma_2^{th} = \frac{v_2}{RT}\left[(\delta_1 - \delta_2)^2 + (\omega_1 - \omega_2)^2 + I.T.\right]\phi_1^2 \tag{110}$$

where

$$I.T. \equiv \frac{2\alpha_1 \mu_1^2}{\sigma_{11}^6 v_{11}} + \frac{2\alpha_2 \mu_2^2}{\sigma_{22}^6 v_{22}} - \frac{2(\alpha_1 \mu_2^2 + \alpha_2 \mu_1^2)}{\sigma_{12}^6 v_{12}} \tag{111}$$

In this relation, provided the induction forces are the deciding factor in solution behavior, even negative deviations from ideality are possible.

It is thus felt that Equation (110) represents the most generalized variant of Hildebrand's basic theory and should prove most valuable in attempting to compute the thermal contribution to the activity coefficient.

D. Statistical Mechanics of Solutions

The application of statistical mechanics to the behavior of liquid mixtures on a molecular level has been widespread. In fact four excellent texts by Barker,(10) Guggenheim,(37) Prigogine(94) and Rowlinson(102) exist in the field. There appears to be two general approaches taken when treating liquids. Either one views a liquid as a disordered solid and applies a lattice theory to describe its behavior, or the liquid may be viewed as a dense gas and distribution function theory used to describe its properties. The lattice theory approach is championed by Barker and Guggenheim in the above cited works. Most lattice theories are still based on the works of Lennard-Jones and Devonshire. The theory of distribution functions is utilized by Hildebrand and Scott(43) through the radial distribution function. By proper modification of this theory the final relations can be expressed by the equations evolved in the previous section. The chief problem connected with these statistical mechanical theories is the intractability of the final results. The derived relations have been used to confirm very simple liquids such as argon, but as yet have not been applied successfully to more complex liquids or to liquid mixtures. Even the more advanced lattice theories utilizing the concept of free volumes or "holes" still predict thermodynamic properties more in accord with the solid than the liquid state. Some of the more advanced theories of Prigogine, while applied successfully to liquid mixtures of simple liquids, are sufficiently dependent on parameters which must be determined from other experimental data that they are of little value in a study such as this in which only one concentration is studied, i.e., infinite dilution.

Since the lattice theories of liquids based on statistical mechanics are in a higher state of development at the present time, an attempt will be made to apply this theory to the present work in order to gain a more fundamental insight into the molecular behavior of solutions. Much of the rigor, however, will be sacrificed in order to produce relations amenable to practical applications. In this respect certain rather plausible assumptions as proposed by Moelwyn-Hughes(76) and modified by Adlard, Kahn and Whitham(3) will be incorporated into the development.

Consider a binary solution of molecules, the solute and solvent having unequal molecular dimensions. In statistical mechanics the main goal is to express the thermodynamic properties of the system under study in terms of the partition function. As a general relation the total partition function for the binary solution may be expressed as

$$\mathcal{F}_i = (q_{int})_i^{n_i} \left(\frac{2\pi m_i \bar{k} T}{h^2}\right)^{3n_i/2} Q_i \qquad i=1,2 \tag{112}$$

Now the basic postulate of statistical mechanics is

$$A_i = -\bar{k} T \ln \mathcal{F}_i \qquad i=1,2 \tag{113}$$

By defining

$$g \equiv (q_{int}) \left(\frac{2\pi m \bar{k} T}{h^2}\right)^{3/2} \tag{114}$$

Equation (113) may be expressed as

$$A_1 + A_2 = -n_1 \bar{k} T \ln g_1 - n_2 \bar{k} T \ln g_2 - \bar{k} T \ln Q_1 - \bar{k} T \ln Q_2 \tag{115}$$

and

$$A^M = -n_1 \bar{k} T \ln g_1 - n_2 \bar{k} T \ln g_2 - \bar{k} T \ln Q^M \tag{116}$$

Now upon mixing the change in free energy is

$$\Delta A^M = A^M - (A_1 + A_2) = -\bar{k} T \ln \frac{Q^M}{Q_1 Q_2} \tag{117}$$

and the configurational partition functions are defined as

$$Q_i = \frac{1}{n_i!} \int \cdots \int e^{-(U_i/\bar{k}T)} (d\tau_i)^{n_i} \qquad i = 1, 2 \tag{118}$$

and

$$Q^M = \frac{1}{n_1!\, n_2!} \int \cdots \int e^{-(U^M/\bar{k}T)} (d\tau_1)^{n_1} (d\tau_2)^{n_2} \tag{119}$$

At this point the difficulty mentioned in the above discussion arises. No mathematically rigorous method exists for evaluating the configurational partition functions. The commonly accepted technique is to attempt an evaluation of Q by a cluster expansion. Expressing the exponential term within the integral as

$$\exp\left[-U(\tau)/\bar{k}T\right] = \prod_{i>j} (1 + d_{ij}) \tag{120}$$

where

$$d_{ij} = \exp\left[-U(\tau_{ij})/\bar{k}T\right] - 1 \tag{121}$$

and

$$U(\tau) = \sum_{i<j} U(\tau_{ij}) \tag{122}$$

Q is then represented as a sum of products of cluster integrals, each cluster representing a small subgroup of molecules comprising the whole of Q . In actuality the final state of affairs is only slightly improved mathematically as the cluster integrals cannot be rigorously evaluated either. Therefore it is at this point that the plausible assumptions discussed earlier will be drafted. As the problem lies with the evaluation of the integrals in Equations (118) and (119) it will be assumed that U is independent of coordinates. Then the relations can be integrated to

$$Q_i = \frac{(n_i v_i^\circ)^{n_i}}{n_i!} \exp\left(-U_i/\bar{k}T\right) \qquad i = 1, 2 \tag{123}$$

and

$$Q^M = \frac{(n_1 v_1 + n_2 v_2)^{n_1+n_2}}{n_1!\, n_2!} \exp\left(-U^M/\bar{k}T\right) \tag{124}$$

Now in order to formulate a practical solution for the thermodynamic properties of the binary solution in question some form must be assumed for U_i and U^M . According to Moelwyn-Hughes, these configurational potential energy terms may be related to the interaction energy of Guggenheim by

$$U_i = n_i w_i \qquad i = 1, 2 \tag{125}$$

and

$$U^M = n_1 w_1 + n_2 w_2 + \frac{n_1 n_2 (v_1 v_2)^{1/2}}{n_1 v_1 + n_2 v_2} \Delta W \tag{126}$$

Therefore with these relations, the expression for Q_i and Q^M are

$$Q_i = \frac{(n_i v_i^\circ)^{n_i}}{n_i !} \exp\left(- n_i w_i / \bar{k} T\right) \qquad i = 1, 2 \tag{127}$$

and

$$Q^M = \frac{(n_1 v_1 + n_2 v_2)^{n_1 + n_2}}{n_1 ! \, n_2 !} \exp\left[-\frac{1}{\bar{k} T}\left(n_1 w_1 + n_2 w_2 + \frac{n_1 n_2 \sqrt{v_1 v_2}}{n_1 v_1 + n_2 v_2} \Delta W\right)\right] \tag{128}$$

Assuming that the volume change on mixing is small, v_i will be replaced by v_i^o . Also based on this assumption ΔG^M is approximately equal to ΔA^M . With these changes in mind, substitution of (127) and (128) into (117) yields

$$\Delta G^M = n_1 \bar{k} T \ln \frac{n_1 v_1^\circ}{n_1 v_1^\circ + n_2 v_2^\circ} + n_2 \bar{k} T \ln \frac{n_2 v_2^\circ}{n_1 v_1^\circ + n_2 v_2^\circ} \tag{129}$$

$$+ \frac{n_1 n_2 \sqrt{v_1^\circ v_2^\circ}}{n_1 v_1^\circ + n_2 v_2^\circ} \Delta W$$

For an ideal solution, by definition $v_1^o = v_2^o$ and $\Delta w = 0$ so

$$\Delta G^M_{ideal} = n_1 \bar{k} T \ln \frac{n_1}{n_1 + n_2} + n_2 \bar{k} T \ln \frac{n_2}{n_1 + n_2} \tag{130}$$

Now

$$\Delta G^{E} = \Delta G^{M} - \Delta G^{M}_{ideal} \tag{131}$$

therefore

$$\Delta G^{E} = n_1 \bar{k} T \ln \frac{(n_1+n_2)v_1^{\circ}}{n_1 v_1^{\circ} + n_2 v_2^{\circ}} + n_2 \bar{k} T \ln \frac{(n_1+n_2)v_2^{\circ}}{n_1 v_1^{\circ} + n_2 v_2^{\circ}}$$

$$+ \frac{n_1 n_2 \sqrt{v_1^{\circ} v_2^{\circ}}}{n_1 v_1^{\circ} + n_2 v_2^{\circ}} \Delta W \tag{132}$$

Next dividing (132) by $\bar{k}T$ and differentiating with respect to n_2 yields

$$\frac{\Delta G_2^{E}}{\bar{k}T} = n_2 \frac{n_1 v_1^{\circ} + n_2 v_2^{\circ}}{(n_1+n_2)v_2^{\circ}} \left[\frac{(n_1 v_1^{\circ} + n_2 v_2^{\circ})v_2^{\circ} - (n_1+n_2)v_2^{\circ} v_2^{\circ}}{(n_1 v_1^{\circ} + n_2 v_2^{\circ})^2} \right]$$

$$+ n_1 \frac{n_1 v_1^{\circ} + n_2 v_2^{\circ}}{(n_1+n_2)v_1^{\circ}} \left[\frac{(n_1 v_1^{\circ} + n_2 v_2^{\circ})v_1^{\circ} - (n_1+n_2)v_1^{\circ} v_2^{\circ}}{(n_1 v_1^{\circ} + n_2 v_2^{\circ})^2} \right]$$

$$+ \ln \frac{(n_1+n_2)v_2^{\circ}}{n_1 v_1^{\circ} + n_2 v_2^{\circ}} + \frac{(n_1 v_1^{\circ} + n_2 v_2^{\circ}) n_1 \sqrt{v_1^{\circ} v_2^{\circ}} - (n_1 n_2 \sqrt{v_1^{\circ} v_2^{\circ}}) v_2^{\circ}}{\bar{k}T (n_1 v_1^{\circ} + n_2 v_2^{\circ})^2} \Delta W \tag{133}$$

At infinite dilution n_2/n_1 approaches zero. With this relation in the above derivative one obtains

$$\left(\frac{\Delta G_2^{E}}{\bar{k}T} \right)_{\frac{n_2}{n_1} \to 0} = \ln \frac{v_2^{\circ}}{v_1^{\circ}} + \left(1 - \frac{v_2^{\circ}}{v_1^{\circ}}\right) + \left(\frac{v_2^{\circ}}{v_1^{\circ}}\right)^{1/2} \frac{\Delta W}{\bar{k}T} \tag{134}$$

Expressing this relation in molar rather than molecular terms and substituting Equation (28) into (134) gives

$$\ln \gamma_2^\infty = \ln \frac{V_2^\circ}{V_1^\circ} + \left(1 - \frac{V_2^\circ}{V_1^\circ}\right) + \left(\frac{V_2^\circ}{V_1^\circ}\right)^{1/2} \frac{\Delta W}{RT} \qquad (135)$$

This relationship expresses the activity coefficient of the solute in terms of the solute and solvent molar volumes and the interaction energy. Differentiating Equation (135) with respect to the temperature yields

$$\begin{aligned} \frac{d \ln \gamma_2^\infty}{dT} = {} & \left(\frac{V_1^\circ}{V_2^\circ}\right) \left[\frac{V_1^\circ \frac{dV_2^\circ}{dT} - V_2^\circ \frac{dV_1^\circ}{dT}}{(V_1^\circ)^2}\right] - \left[\frac{V_1^\circ \frac{dV_2^\circ}{dT} - V_2^\circ \frac{dV_1^\circ}{dT}}{(V_1^\circ)^2}\right] \\ & - \left(\frac{V_2^\circ}{V_1^\circ}\right)^{1/2} \frac{\Delta W}{RT^2} + \frac{1}{RT} \left(\frac{V_2^\circ}{V_1^\circ}\right)^{1/2} \frac{d\Delta W}{dT} \\ & + \frac{\Delta W}{2RT} \left(\frac{V_2^\circ}{V_1^\circ}\right)^{-1/2} \left[\frac{V_1^\circ \frac{dV_2^\circ}{dT} - V_2^\circ \frac{dV_1^\circ}{dT}}{(V_1^\circ)^2}\right] \end{aligned} \qquad (136)$$

Now the cubical coefficient of expansion is defined as

$$\beta \equiv \frac{1}{V^\circ} \frac{dV^\circ}{dT} \qquad (137)$$

Multiplying Equation (136) by $-RT^2$ and substituting (31) and (137) yields

$$\begin{aligned} \Delta H_2^E = {} & \left(\frac{V_2^\circ}{V_1^\circ}\right)^{1/2} \left[\Delta W - \frac{T}{2}(\beta_2 - \beta_1)\Delta W - T \frac{d\Delta W}{dT}\right] \\ & - RT^2 \left(1 - \frac{V_2^\circ}{V_1^\circ}\right)(\beta_2 - \beta_1) \end{aligned} \qquad (138)$$

Also as

$$\Delta S_2^E = \frac{\Delta H_2^E}{T} - R \ln \gamma_2^\infty \tag{33}$$

one may utilize (135) and (138) to obtain

$$\Delta S_2^E = -R\left[\ln \frac{V_2^o}{V_1^o} + \left(1 - \frac{V_2^o}{V_1^o}\right)\right] - RT\left(1 - \frac{V_2^o}{V_1^o}\right)(\beta_2 - \beta_1)$$

$$- \left(\frac{V_2^o}{V_1^o}\right)^{1/2}\left[\frac{1}{2}(\beta_2 - \beta_1)\Delta W + \frac{d\Delta W}{dT}\right] \tag{139}$$

Thus the proposed model based on the lattice theory of liquids does provide relationships for determining the thermodynamic properties of a solute at infinite dilution in a binary solution. However, in order to test the assumptions made concerning the coordinate dependence and the form of the configurational potential energy, independent data for the activity coefficient and the partial molar excess enthalpy should be utilized. Although, as was anticipated, a certain degree of rigor was sacrificed, at least tractable relations result for the desired properties from the above treatment.

IV. EXPERIMENTAL PROGRAM

A. Description of Equipment

Experimentally the thesis was conducted on a highly modified F and M Model 609 Gas Chromatograph. This model is equipped with a flame ionization detector and a linear column temperature programmer. However, all runs made in this investigation were performed under isothermal conditions. The unit as received could maintain the column temperature control to ± 2°C at best. The heating circuit for the thermostated column chamber consisted of an on-off relay which alternately pulsed 110 volts to a 32 ohm resistance heater. This circuit was modified to give essentially a semi-proportional control by modifying the relay to a high-low operation and controlling the amount of voltage delivered to the heater. This voltage differed in the high and low modes of operation so that the high voltage circuit was only used occasionally to offset accumulated heat losses. In this manner the column temperature in the thermostated chamber could be maintained at ± 0.1°C of the desired temperature over prolonged periods of time. In addition to the temperature control of the chamber, separate variable controls existed for setting the temperature of the sample injection port and the flame ionization detector block independently.

The flow system on the original unit consisted of a Moore constant volume flow controller set with a precision needle valve, a Brooks floating ball flowmeter, the sample injection port with stream splitter, the actual chromatographic column, and the flame ionization detector. Brooks flowmeters were also provided for the hydrogen and air streams supplied to the flame ionization detector. As the solvents studied in this investigation were all quite volatile, having vapor pressures of the same order as the solutes studied, the flow system was modified to accomodate a presaturator. So as to prevent fogging in the flowmeter, the presaturator was installed following the flowmeter but prior to the sample injection port. This presaturator column was installed in the thermostated column chamber so that the helium carrier gas could equilibrate with the solvent in the presaturator prior to entry in the chromatographic column. As the inlet and outlet column pressures must also be known, a 0-10 psig Matheson pressure gage was installed following the presaturator. As the column outlet was located immediately adjacent to the flame ionization detector, the outlet pressure was taken as the prevailing atmospheric pressure as registered on a Princo Fortin-type mercurial barometer mounted near the apparatus. Following the flame ionization detector, provision was made to install a 25 cc soap bubble flowmeter. This flowmeter could be added to the flow system or not as desired. All Brooks flowmeters were calibrated with the soap bubble flowmeter, and the pressure gage was calibrated using a ten foot mercury column in the standards laboratory. The Brooks flowmeters were only used to approximately determine the flow rates, the actual determinations being made on the soap bubble flowmeter.

Due to the high volatility of the solvents studied the rate of solvent depletion was reasonably high. In the normal mode of operation of the flame ionization detector the unit is designed to detect of the order of 10^{-12} gram atoms of carbon per second. The mode of operation as described by Sternberg *et al.*(112) is one of chemi-ionization. Now with the constant solvent depletion the rate of carbon atoms flowing through the detector is considerably higher than the above mentioned value and the effect is to saturate the output current to the preamplifier. Therefore the detector geometry had to be modified. The platinum loop electrode was placed in much closer proximity to the electrically grounded combustion jet. In this manner much of the actual ion production occurred in the upper region of the flame envelope and was never collected by the upper electrode, as this operation took place above the electrode. Although the electrode became hotter in this region than in normal operation, it was assumed that the work function of platinum was sufficiently high so as not to contribute any secondary emission. Also to minimize the noise due to random fluctuations in the hydrogen flow rate, a precision needle valve was installed in the hydrogen flow stream prior to the Brooks flowmeter. Two stage diaphragm pressure regulators and appropriate check valves were installed on all compressed gas cylinders prior to connection with the gas chromatograph.

A Minneapolis-Honeywell recorder with a one millivolt full scale range output was utilized to record the detector output signal. This unit was equipped with a Disc Instruments recording integrator.

In addition to displaying the detector output, independent thermocouple readings could be displayed indicating the temperatures of the sample injection port, the thermostated column chamber, the flame ionization detector block and the actual combustion flame. All these thermocouples, with the exception of the latter one, were calibrated using standardized Princo thermometers. The calibrated thermocouples were of the iron-constantan type.

A brief description of the apparatus flow system will now be given following the schematic diagram as shown in Figure 1. The helium carrier gas is controlled by a two stage regulator and a check valve. Following this the helium passes through the Moore constant volume flow controller, through the Brooks flowmeter and into the thermostated column chamber. The column chamber is heated by a resistance element which warms the air circulated by a small blower located outside of and below the actual chamber. The helium then is presaturated with solvent in a forecolumn, its pressure being registered on the Matheson gage, and passes into the sample injection port sweeping out the volatilized sample. The samples were injected utilizing a Hamilton microsyringe with a Chaney adaptor or a Wahl-Henius syringe with volumetric spacers. Immediately adjacent to the sample injection port is the chromatographic column. The columns used in this study are 1/4 inch outside diameter aluminum tubing. All interconnecting fittings were Swagelok to reduce the possibility of leakage. Following the column the carrier gas is premixed with hydrogen and elutes through the combustion jet where it is ignited

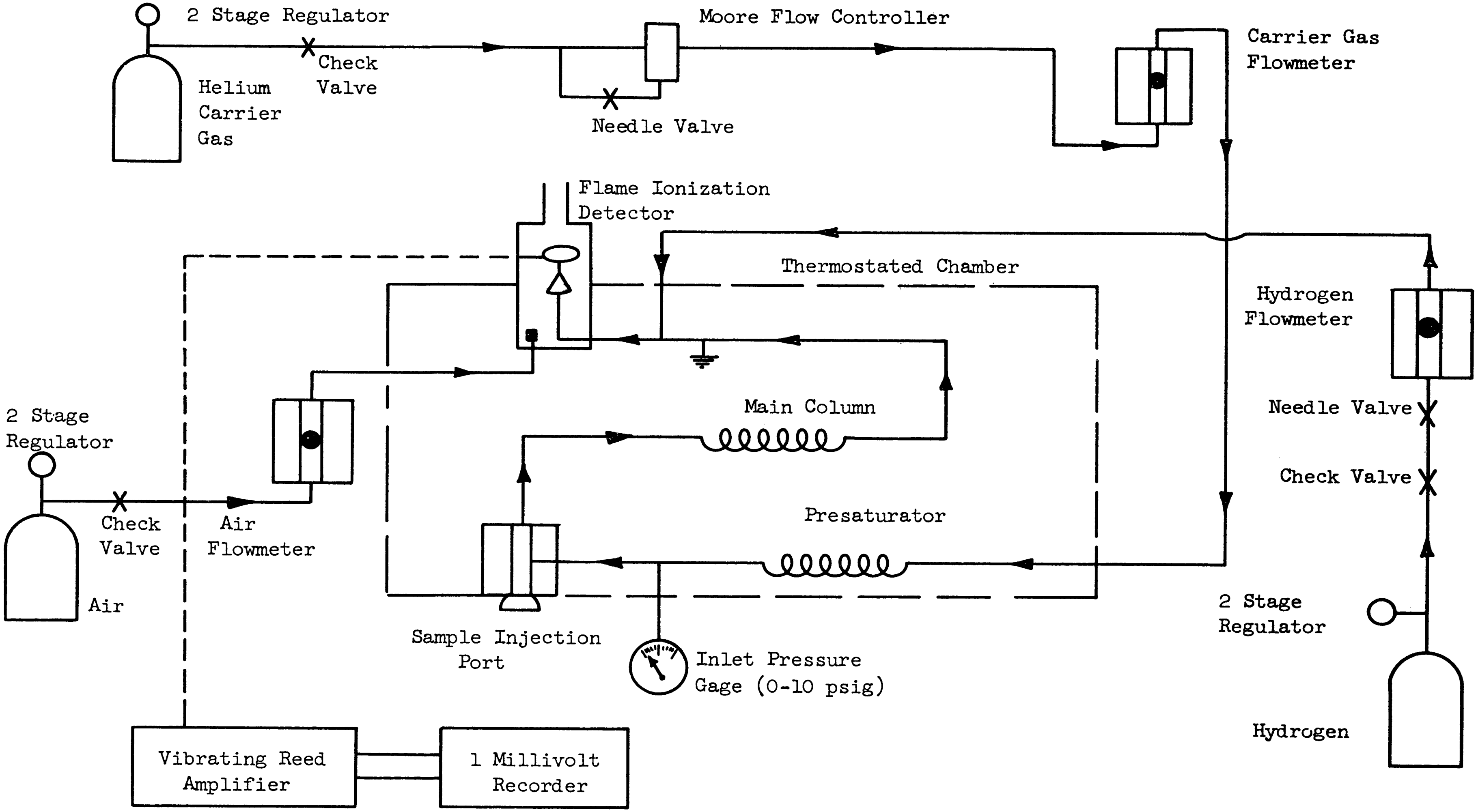


Figure 1. Schematic Diagram of Equipment.

and burned. The chemi-ionized radicals produce a current which is collected by the platinum electrode, amplified and displayed on the recorder. The remaining gases flow out of the detector chamber through the outlet port. Two additional gas streams are supplied to the flame ionization detector chamber. Hydrogen, premixed with the carrier gas stream, provides the combustion media. It flows through a two stage regulator and check valve to the Brooks flowmeter for the hydrogen. Prior to the flowmeter the flow rate is accurately controlled by a precision needle valve. The hydrogen then flows through the jet and is combusted. An air stream is also utilized in the flame ionization detector to support the combustion. The air flows through a two stage regulator and check valve, is metered through a Brooks flowmeter and then fed into the detector chamber through a diffuser to avoid turbulence near the flame envelope.

B. Choice of Systems

The systems chosen for investigation in this work represent the results of a very comprehensive study into the anticipated behavior of solutions and possible solute-solvent interactions. Rather than studying solutions normally of interest in GLC, it was decided to investigate binary systems of the normal type in which both components are volatile. As the intended purpose of the study was to provide a correlational technique valid for a large range of solutions, the solutes and solvents had to be such that all types of behavior were included. In order to cover all possible types of interactions some method or scheme of liquid classification was sought which would accomodate most conceivable nonelectrolyte liquids.

The earliest work uncovered in this study, and the one on which almost all subsequent work has been based, is that of Ewell, Harrison and Berg(28) in 1944. These workers in an attempt to classify liquids for predicting possible azeotrope formation, evolved a scheme based on hydrogen bonding and dispersion forces. They ascertained that these two solution interactions were responsible for the bulk of the deviations from ideality, the former being the more important effect. In hydrogen bonding a hydrogen atom can coordinate between two oxygen, nitrogen or fluorine atoms or between one of these donor atoms and a carbon atom provided that enough negative constituents are attached to the carbon atom. With these bond types the following classification of bond strengths can be made

Strong Bond	Weak Bond
$O \longrightarrow HO$	$N \longrightarrow HN$
$N \longrightarrow HO$	$\left.\begin{matrix}O\\N\end{matrix}\right\} \longrightarrow \left\{\begin{matrix}HCCl_2\\HCNO_2\\HCCN\end{matrix}\right.$
$O \longrightarrow HN$	

Based on this bond classification liquids may be categorized into five groups

Class I - Liquids capable of forming three dimensional networks of strong hydrogen bonds. -- e.g. water, glycols, glycerols, amino alchols, hydroxyl amines, hydroxy acids, polyphenols, amides.

Class II - Liquids with molecules containing active hydrogen atoms and donor atoms. -- e.g. alchols, acids, phenols, primary and secondary amines, oximes, nitro compounds with hydrogen atoms adjacent to the terminal carbon atom.

Class III - Liquids containing only donor atoms. -- e.g. ethers, ketones, aldehydes, esters, tertiary amines, pyridines, nitro compounds and nitriles with no hydrogen atoms adjacent to the terminal carbon atom.

Class IV - Liquids containing only active hydrogen atoms or pseudo active hydrogen atoms, i.e., mobile electrons. -- e.g. halogenated hydrocarbons with hydrogen atoms on the terminal carbon atom, aromatic compounds, olefins.

Class V - Liquids with no active hydrogen or donor atoms. -- e.g. hydrocarbons, CS_2, CCl_4, sulfides, mercaptans.

The first two classes are associated liquids in the sense that they hydrogen bond with themselves. Classes III and IV will form hydrogen bonds with the first two classes but not by themselves. The last class shows no tendency to hydrogen bond and thus the solution interactions are due mainly to dispersion forces.

Considering the possible interactions between classes of liquids, again leads to five general categories. The first class comprised of I-V and II-V interactions shows limited solubility and always positive deviations from ideality with hydrogen bonds being broken. The second class having only III-IV interactions always shows negative deviations from Raoult's law as hydrogen bonds are formed. The I-IV and II-IV interactions compose the third class.

This class again always shows positive deviations, but hydrogen bonds are broken and formed. However, the dissociation of the I or II component predominates. A fourth very extensive class is composed of I-I, I-II, I-III, II-II and II-III interactions and usually has activity coefficients greater than unity. However, the binary systems formed are quite complex and so negative deviations may occur. This is due to the simultaneous breaking and forming of hydrogen bonds. The fifth class comprising III-III, III-V, IV-IV, IV-V and V-V interactions behaves in a quasi-ideal manner as no hydrogen bonds are involved.

The above classification scheme, as mentioned earlier, seems to have gained wide acceptance. The work of Keulemans, Kwantes and Zaal,(53) described in the literature review, actually is patterned after the above classification. These authors studied C_3 and C_4 paraffins and olefins in transformer oil, dinonyl phthalate and dimethyl formamide. These three solvents fall respectively into Classes V, III and I. Dal Nogare and Juvet,(21) in their excellent text, utilize this scheme to relate solution behavior and the resulting thermodynamic properties. Pimentel and McClellan(83) propose a liquid classification system which is almost the same as that of Ewell _et al._ with the exception that they combine Classes I and II into a single group, as both these types exhibit self-association. This work also predicts the effect of hydrogen bonding on the partial molar excess enthalpy based on their liquid classification. Generally speaking, with the exception of the III-IV interaction, the thermal effect is endothermic. When compared with actual experimental results as done by Rowlinson,(101) it becomes clear that not only are the predictions of Pimentel concerning the thermal effects generally correct, but that quite often even III-IV binary solutions are endothermic. This would also tacitly imply that for certain of these solutions slightly positive deviations from ideality might exist as the strengths of the hydrogen bonds formed would be very weak. Rowlinson(103) in another study of hydrogen bonding investigated many groups of solutes in water, a Class I solvent. He found that ketones, nitriles, alcohols, ethers and amines all exhibited activity coefficients greater than unity as expected for Class II and III solutes. While in general all the solutions formed were endothermic, certain I-II systems at dilute solute concentrations were exothermic. This effect is a function of the number of bonds formed and the solution temperature, having an inflection point.

Based on the above discussion and classification scheme the systems for this work may now be chosen so as to encompass all possible types of solution behavior. The actual solutes and solvents chosen will also allow a comparison between the results of this work and existing literature values for certain selected systems. From a close appraisal of the possible classes of interactions it can be seen that by utilizing solvents from Classes I, III and V all anticipated types of behavior will be included with only the magnitude of the effect varying. As all solvents must be volatile and a desire existed to investigate water systems, the solvent choices are: Class I - water, Class III - 2 pentanone, and Class V - 2,3,4 trimethylpentane. All of these solvents have comparable vapor pressures and boil near 100°C. Thus unless all systems studied exhibit the same behavior, the hypothesis that similar boiling substances should exhibit similar behavior will be repudiated. Having determined the three solvents, the choice of solutes is largely a personal matter, so long as all classes of liquids are included. Therefore the solutes to be studied are: Class II - methanol, ethanol, propanol; ethylamine, propylamine, butylamine; Class III - methyl formate, ethyl formate, propyl formate; acetaldehyde, propionaldehyde, butyraldehyde; Class IV - dichloromethane, trichloromethane, tetrachloromethane; and Class V - pentane, hexane, heptane. These solutes should include all possible types of binary interactions as previously discussed. Although all solutes are chosen to be more volatile than the solvents, the technique is not restricted to such conditions and actually any solute could feasibly be studied in any solvent providing the solvent was normally in the liquid state at the conditions of operation.

C. Experimental Techniques

The following discussion will present the major operations in preparing for and conducting an actual experimental run. The effect of the GLC operating variables on the resultant thermodynamic properties as investigated in this work will be presented and a short accompanying analysis will be given. Other details of lesser significance for an understanding of the work but highly important for a continuing study will be found in the appendix.

1. Procedure

As water, 2 pentanone and 2,3,4 trimethylpentane are not standard partitioning liquids used in GLC, a few words will be said concerning the preparation of the chromatographic columns utilizing these solvents. Initially the solid support is weighed in a container of known mass. The solid support is then completely flooded with solvent and mixed thoroughly to insure complete coating of all particles. All solid supports used in this study were 40/60 mesh cuts, utilized as received. Following this thorough mixing the saturated support is carefully heated in a constant temperature oven, vaporizing the solvent. This process is continued with intermittent weighings until the desired amount of solvent, expressed percentagewise as grams of solvent per gram of solid support, is obtained. The container is then closed and the stationary phase is completed. To pack a column, the empty column and full packing container are weighed, some packing quickly transferred to the column, and then the full column and slightly depleted packing container are reweighed. In this manner the initial weight of the solvent in the column is determined and checked. At the conclusion of a run the column is reweighed and the lossage of solvent during the run is determined by difference. The presaturator columns utilized in this work were five and six feet in length while the main chromatographic columns were six and nine inches long. The rather short columns were necessitated by the long retention volumes of most of the solutes. However, due to this short length and the high volatility of the solvents, the columns had to be repacked for each run.

As the temperature of the sample injection port, the flame ionization detector and the thermostated column chamber could be controlled independently, each was set at an optimum value. In the case of the thermostated chamber, runs were made at 20°C, 30°C and 40°C. The sample injection port must be sufficiently hot to insure vaporization of the liquid sample. As all the solutes boiled below 100°C, the injection port temperature was sustained at 100°C. Similarly to prevent condensation of bleeding solvents and other material, the detector block temperature was held at 110°C. These latter two temperatures were maintained throughout the experimental work. Prior to making an actual run the column chamber was heated up and equilibrated at the desired temperature.

Due to the high depletion rate of solvent from the column, the normal operating mode of the flame ionization detector was unsuitable. In order to lessen the problem of current saturation, the carrier gas flow rate was maintained in the region of 15 to 20 cc per minute. Even with this low flow rate the operation was difficult. In actually carrying out a run, once all temperatures were equilibrated at the desired value, the presaturator and chromatographic column were quickly installed and the flame ionization detector ignited. Then the collector electrode to jet distance was varied until the amplifier background signal could be electrically balanced out. In this mode of operation the detector output may be nonlinear but as no quantitative analysis is being made, it makes no difference. Once equilibrium is reestablished and flow rates ascertained using the soap bubble flowmeter a sample is injected. Now in all runs in which the final data was obtained, 0.04 microliters of solute was injected. In this manner infinite dilution could actually be approached, i.e., liquid solute mole fractions of the order of 10^{-5}, and symmetric peaks resulted indicating linear absorption isotherms. The peaks obtained with such small sample sizes were quite sharp, exhibiting very little broadening. After each peak eluted another sample was injected and this process was continued until changing elution times indicated that the column was nearly depleted of solvent. The run was then terminated and the columns withdrawn from the thermostated chamber and reweighed.

Although the runs were continued until the column was nearly exhausted of solvent, no data was accepted for which the quantity of solvent in the column was less than 15% w/w. As the initial quantity of solvent in the column was approximately 40 to 50% w/w, this meant that a run would last about 60 to 90 minutes depending on the temperature of operation. These statements apply when water or 2 pentanone was used as the solvent. The limits differ for 2,3,4 trimethylpentane as will be explained shortly. To point up the effect of the presaturator, attempts were made to conduct a run without presaturation. After installation of the columns, approximately 20 to 25 minutes is required for thermal equilibrium to be reestablished. Without the presaturator, by the time equilibrium was reached the chromatographic column was depleted of solvent. In order to compute the desired properties from the GLC data, the weight of solvent must be known. Due to the constant temperature and carrier gas flow it is assumed that the depletion rate is constant and a linear change in amount of solvent present results. This assumption is verified by the fact that upon observing the recorder signal, although sporadic deviations occur above the background noise, no continual drift or trend in deviation can be observed. If a constantly drifting signal occurred this would indicate a varying amount of solvent bleed being ionized in the flame. As this does not happen the assumption is justified.

Concerning the remark about the double standard for solvent depletion depending on the solvent, this may be explained on the basis of solid support. With each solvent the most inert support was used, limited by the wetability of the support by the solvent. For water, the support chosen was Chromosorb W; for 2 pentanone, HMDS treated Chromosorb W was used; Fluoropak 80 was used to support the 2,3,4 trimethylpentane. Now the Fluoropak 80, a teflon polymer, has a much lower specific surface area than the other supports. Therefore less liquid can be coated on the support, but also less liquid is needed to insure coverage of the support. Thus for 2,3,4 trimethylpentane only 15 to 20% w/w of solvent existed initially and the data was taken until the quantity of solvent became less than 5% w/w. More will be said concerning the solid support in the following discussion.

2. Effect of Variables

Although the independence of the resulting thermodynamic properties from the GLC variables has been rather thoroughly investigated by other workers, some investigations were also conducted in the present study. Due to the relative ease of obtaining the water systems data, the studies were performed with water as the solvent. Chromosorb R, Firebrick, and Chromosorb W were all tried as solid supports, and provided that sufficient coating, i.e., 10% w/w or more, was maintained on the support no effect was noticed. Support adsorption effects only occur at low solvent concentrations and subambient operating temperatures. In the present work somewhat idealized calculations indicate that for a 20% w/w coating of water on Chromosorb W the liquid layer would be approximately 700 molecules thick, indicating a sufficient coverage of the solid support. Funk and Houghton(34) have derived a theoretical relation for the depth of penetration of the solute into the solvent and have used this model on the isobutylene-dinonyl phthalate system. They find that the fractional penetration varies from 0.60 to 0.84 of the total thickness as the coating varies from 10 to 24% w/w dinonyl phthalate. This indicates that for lower solvent concentrations the effect of solvent adsorption is much more feasible. Chueh(19) points out that if the solute remains near the surface of the solvent a high "effective" concentration of solute would result, which for a system exhibiting positive deviations from ideality causes activity coefficient values below the true results. As will be seen in the discussion of the results, if anything the contrary condition exists in the present study. Thus it is felt that both solid support and solvent adsorption effects are absent from the results obtained in this study and true equilibrium properties are obtained.

In addition to the solid support studies the other parameters involved were also varied. The helium flow rate was varied from 15 to 50 cc per minute with no noticeable change in the activity coefficient. The percentage coating of the solvent on the solid support was varied from 10 to 50% w/w and the total amount of solvent in the column was varied from 0.1 to 4.0 grams, all of which produced a constant value of the activity coefficient, within the experimental error. The values obtained for the thermodynamic properties remained the same whether or not a presaturator was used. Therefore the only effect of the presaturator is to retard the rate of solvent depletion and allow a longer run to be conducted. This is due to the fact that essentially laminar flow existed through the main column and thus no bulk flow of solvent occurred. In this mode of operation the solid support remained covered by solvent at all times. The effect of varying the column length from six inches to six feet was negligible as well as the effect of varying the inlet and outlet pressure over a narrow range. It should be recalled that varying the mean column pressure over a moderate range will result in a variation in the activity coefficient due to the gas phase nonideality correction. However, in this respect, helium was used throughout as the carrier gas and in the light of the theoretical development this choice tends to minimize the gas phase nonideality. Sample size variation has a very definite effect on the activity coefficient, as it is a function of concentration. However, in the runs made to obtain the present data, 0.04 microliter samples were used which was near the limit of detection with the noise level existent during the experiment. The sample injection time was instantaneous and so should have no effect. In contrast to the results of Stalkup,(110,111) the values of the gas phase volume in the column determined by the retention time of an unretained component and by geometrical calculations were essentially coincident. More will be said concerning this in the appendix. Thus it is felt from the above studies that the results obtained in this investigation are completely independent of the GLC variables and are true equilibrium properties.

V. RESULTS AND DISCUSSION

A. Presentation of Thermodynamic Properties

The actual process of determining thermodynamic properties from GLC consists of measuring the chromatographic parameters experimentally and then utilizing the relations derived in the theoretical development. The results obtained in this fashion from Equations (20) and (24), knowing the retention volume, are given in Table I for the three solvents at 20°, 30° and 40°C.

The data shown in Table I represents average values for a number of runs on each binary system. The general internal consistency of the data was quite good, the overall average error being ± 5%, with the 2,3,4 trimethylpentane systems being somewhat better while the 2 pentanone systems were slightly worse than this value. Due to the lengthy retention times of the alcohols and amines, as compared to the other solutes, more difficulty was experienced in obtaining the data for binary solutions with these solutes. As no carbon atoms are present in water, the flame ionization detector is oblivious to this solvent and thus although initially anticipated to provide the most trouble, the water binary systems were the easiest to study experimentally. Utilizing the data in Table I and Equation (28), the results in Table II are computed.

From the thermal variation of the activity coefficient, the partial molar excess enthalpy can be determined using Equation (32). In actuality the value of ΔH_2^E is determined from the slope

TABLE I

INFINITELY DILUTE ACTIVITY COEFFICIENTS FOR VARIOUS SOLUTES IN WATER, 2 PENTANONE AND 2,3,4 TMP AT 20°, 30° AND 40°C

	Water			2 Pentanone			2,3,4 TMP		
Solute	20°C	30°C	40°C	20°C	30°C	40°C	20°C	30°C	40°C
C_5H_{12}	945	796	517	5.27	3.99	5.36	0.99	0.97	0.97
C_6H_{14}	2940	2225	1465	6.53	4.65	6.16	1.10	1.13	1.09
C_7H_{16}	8050	6160	3925	8.51	5.36	7.36	1.07	0.98	0.98
CH_2Cl_2	209	201	153	1.18	0.95	1.21	2.26	1.97	2.23
$CHCl_3$	571	568	425	1.19	1.13	0.93	1.59	1.35	1.56
CCl_4	2870	2150	1490	3.61	2.73	2.41	5.51	6.48	8.63
MeFo	16.6	17.4	14.2	2.58	1.95	2.18	5.57	5.11	4.92
EtFo	46	51	41	2.66	1.96	2.25	3.52	3.40	3.78
PrFo	150	168	131	3.66	3.24	3.65	3.11	2.70	3.13
CH_3CHO	3.59	4.36	3.71	2.06	1.73	1.65	5.17	5.00	5.24
C_2H_5CHO	14.7	17.6	15.4	2.25	2.01	1.77	4.14	3.77	4.18
C_3H_7CHO	63	73	61	3.97	2.59	2.66	4.04	3.62	3.72
EtAm	0.37	0.69	0.44	0.50	0.41	0.50	2.18	1.80	1.85
PrAm	2.33	2.85	2.44	3.00	2.14	2.50	2.23	2.15	2.48
BuAm	4.00	4.70	3.70	4.40	4.31	4.58	1.76	1.45	1.84
MeOH	2.69	2.53	2.30	5.60	3.93	5.12	39.9	39.4	33.9
EtOH	6.51	6.15	5.50	6.52	4.24	6.01	28.1	22.6	22.4
PrOH	24	26	22	7.21	4.60	6.27	23.0	12.8	18.3

TABLE II

PARTIAL MOLAR EXCESS FREE ENERGY (CAL/MOLE) FOR VARIOUS SOLUTES IN WATER, 2 PENTANONE AND 2,3,4 TMP AT 20°, 30° AND 40°C

	Water			2 Pentanone			2,3,4 TMP		
Solute	20°C	30°C	40°C	20°C	30°C	40°C	20°C	30°C	40°C
C_5H_{12}	3990	4020	3880	970	830	1040	-10	-20	-20
C_6H_{14}	4650	4640	4530	1090	920	1130	60	70	50
C_7H_{16}	5230	5250	5140	1250	1010	1240	40	-10	-10
CH_2Cl_2	3110	3190	3130	100	-30	120	470	410	500
$CHCl_3$	3690	3820	3760	110	80	-50	270	180	280
CCl_4	4630	4620	4540	750	600	550	990	1120	1340
MeFo	1630	1720	1650	550	400	480	1000	980	990
EtFo	2230	2370	2310	570	410	500	730	740	830
PrFo	2920	3080	3030	750	710	800	660	600	710
CH_3CHO	740	890	810	420	330	310	960	970	1030
C_2H_5CHO	1560	1730	1700	470	420	350	830	800	890
C_3H_7CHO	2410	2580	2560	800	570	610	810	770	820
EtAm	-580	-220	-510	-400	-540	-430	450	350	380
PrAm	490	630	520	640	460	570	470	460	560
BuAm	810	960	850	860	880	950	330	220	380
MeOH	580	560	520	1000	820	1020	2150	2210	2190
EtOH	1090	1090	1060	1090	870	1110	1940	1880	1930
PrOH	1850	1960	1920	1150	920	1140	1820	1530	1810

of a plot of the logarithm of γ_2^{∞} as a function of reciprocal temperature. Now as the overall temperature range of this investigation was 20°C, and ΔH_2^E is being determined by graphical differentiation of the data, no attempt is made to analyze the temperature dependence of ΔH_2^E. Rather a best straight line fit of the three data points is utilized and ΔH_2^E is assumed constant over the 20°C range. As the anticipated change in ΔH_2^E with temperature is of the order of 5 cal/mole • °K for most organic binary solutions according to Littlewood,(68) the average error in γ_2^{∞} does not justify a more detailed interpretation on a 20°C range. The results of this procedure are presented in Table III. Knowing the values of ΔG_2^E and ΔH_2^E from Tables II and III and utilizing Equation (27), the partial molar excess entropies may be evaluated. These are tabulated in Table IV.

From an inspection of the activity coefficients in Table I it can be seen that the alkanes and chlorinated methanes are only slightly soluble in water, thus forming very non-ideal solutions. Also, as the number of methylenic groups increase in the hydrocarbon radical, any solubility tendencies created by the functional group in water are masked out and lost. As 2 pentanone has solution properties generally near the mean of the solutes studied, none of its binary solutions show a very large deviation from ideality. On the opposite end of the scale the alkanes form essentially ideal solutions with 2,3,4 trimethylpentane as both components are nonpolar and so little solute-solvent interaction exists. It should be noted that

TABLE III

PARTIAL MOLAR EXCESS ENTHALPY (CAL/MOLE) FOR VARIOUS SOLUTES IN WATER, 2 PENTANONE AND 2,3,4 TMP FROM 20° TO 40°C

Solute	Water 20° - 40°C	2 Pentanone 20° - 40°C	2,3,4 TMP 20° - 40°C
C_5H_{12}	6340	-90	180
C_6H_{14}	6550	540	80
C_7H_{16}	6480	1350	580
CH_2Cl_2	2760	880	210
$CHCl_3$	2650	2480	180
CCl_4	5950	3580	-3990
MeFo	1120	2240	860
EtFo	770	1920	-250
PrFo	960	1650	0
CH_3CHO	-110	2010	-90
C_2H_5CHO	-720	2170	-110
C_3H_7CHO	-130	5140	720
EtAm	-2490	-410	1390
PrAm	-1090	1390	-600
BuAm	106	-410	-550
MeOH	1450	310	1430
EtOH	1480	360	2270
PrOH	1060	320	1550

TABLE IV

PARTIAL MOLAR EXCESS ENTROPY (CAL/MOLE · °K) FOR VARIOUS SOLUTES IN WATER, 2 PENTANONE AND 2,3,4 TMP AT 20°, 30° AND 40°C

	Water			2 Pentanone			2,3,4 TMP		
Solute	20°C	30°C	40°C	20°C	30°C	40°C	20°C	30°C	40°C
C_5H_{12}	8.0	7.7	7.9	-3.6	-3.1	-3.6	0.7	0.7	0.7
C_6H_{14}	6.5	6.3	6.5	-1.9	-1.3	-1.9	0.1	0.0	0.1
C_7H_{16}	4.2	4.0	4.3	0.4	1.1	0.4	1.8	1.9	1.9
CH_2Cl_2	-1.2	-1.4	-1.2	2.7	3.0	2.4	-0.9	-0.7	-0.9
$CHCl_3$	-3.6	-3.9	-3.6	8.1	7.9	8.1	-0.3	0.0	-0.3
CCl_4	4.5	4.4	4.5	9.7	9.8	9.7	-17	-17	-17
MeFo	-1.7	-2.0	-1.7	5.8	6.1	5.6	-0.5	-0.4	-0.4
EtFo	-5.0	-5.3	-4.7	4.6	5.0	4.5	-3.4	-3.3	-3.5
PrFo	-6.7	-7.0	-6.6	3.0	3.1	2.7	-2.3	-2.0	-2.3
CH_3CHO	-2.9	-3.3	-3.0	5.4	5.6	5.5	-3.6	-3.5	-3.6
C_2H_5CHO	-7.8	-8.1	-7.7	5.8	5.8	5.8	-3.2	-3.0	-3.2
C_3H_7CHO	-8.7	-9.0	-8.6	14.8	15.1	14.5	-0.3	-0.2	-0.3
EtAm	-6.5	-7.5	-6.3	0.0	0.4	-0.1	3.2	3.4	3.2
PrAm	-5.4	-5.7	-5.1	2.6	3.1	2.6	-3.6	-3.5	-3.7
BuAm	-2.4	-2.8	-2.4	-4.3	-4.2	-4.3	-3.0	-2.5	-3.0
MeOH	3.0	2.9	3.0	-2.4	-1.7	-2.3	-2.5	-2.6	-2.4
EtOH	1.3	1.3	1.4	-2.5	-1.7	-2.4	1.1	1.3	1.1
PrOH	-2.7	-3.0	-2.7	-2.8	-2.0	-2.6	-0.9	0.1	-0.8

within any homologous series of solutes at a given temperature the acitivity coefficient increases with increasing size of the hydrocarbon chain. This result will be the basis of a very interesting correlation. As the partial molar excess free energy is related exponentially to the activity coefficient, the trends observable in Table I also exist in Table II but in a somewhat normalized fashion.

Although Equation (32) would indicate that at least for a narrow range of temperature ΔH_2^E should be a constant, this is not rigorously valid, as can be seen from an inspection of Table I as a function of temperature for any given binary system. In fact the accuracy of determining thermal effects of solutions from vapor liquid equilibrium has been questioned repeatedly in the past. The results obtained by this procedure never do fully concur with independent calorimetric data. Granted then that this procedure is suspect, and bearing in mind that the overall average error of the data is ± 5%, it is best to view the values of ΔH_2^E as semi-quantitative in nature. They are very useful in discerning trends and general patterns but no great significance should be placed on the absolute values. Only with exceedingly accurate vapor liquid equilibrium data can a reasonably accurate analysis of the thermal effect be made.

Anderson et al.(7) attribute ΔH_2^E to two sources, the physical forces always present which cause a positive thermal effect, and specific interactions or chemical forces which yield negative contributions to ΔH_2^E. This latter contribution decreases with increasing temperature. Thus a small ΔH_2^E does not necessarily indicate an ideal solution but may merely be a balancing of the two effects. The verification of this last conclusion can be seen in Table III for the amines and alchols in 2 Pentanone. A positive excess enthalpy also indicates the loss of cohesive energy of the solvent.

Upon viewing Table IV, it can be seen that ΔS_2^E is less than zero for most of the solutes in water. This may be attributed to the fact that the solute motion is more restricted due to specific interactions with the solvent than it was in the pure solute environment. The negative values of ΔS_2^E for all the solutes but the alkanes in 2,3,4 trimethylpentane are caused by geometric hinderances due to the much larger molecular size of the solvent with respect to the solutes. Other trends due to hydrogen bonding will be presented in the following discussion.

B. Comparison with Literature Data

As mentioned in the experimental program, certain of the systems studied were chosen to provide a comparison between the results of this work and data obtained by other vapor liquid equilibrium techniques. The majority of the systems to be compared involve water, as this is a commonly studied liquid. Copp and Everett(20) in a study correlating activity coefficients of various solutes in water have studied the amines in water at 25°C. They quote the excess free energies of solution as follows: ethylamine, -500 cal/mole; propylamine, 300 cal/mole; and butylamine, 800 cal/mole. As can be seen from Table II, these values agree quite well with the data. Davison, Hood and Harris(22) also studied amines in water. The only data at infinite dilution quoted by these authors is the partial molar excess enthalpy of ethylamine which is given as -6300 cal/mole. While this value differs considerably from that listed in Table IV, only semi-quantitative agreement can be anticipated, as was mentioned. Suffice to say that both values are exothermic and in the region of -5 kcal/mole.

Pierotti et al.(81) have studied alkanes in water by static techniques at 25°C. They obtain activity coefficients at infinite dilution for pentane and hexane. The values are 1,250 and 3,150 respectively as compared to 945 and 2,940 at 20°C obtained in this study. This verifies the present work and the conclusion drawn concerning limited solubility in these systems. The system methanol-water has been studied by Brown and Martin(17) and in the International Critical Tables.(119) Brown gives $\gamma_2^\infty = 2.3$ at 0°C, while the I.C.T. value at 40°C is $\gamma_2^\infty = 2.6$. These results agree quite favorably with the data in Table I, but the thermal dependence appears to be in the opposite direction. More will be said concerning this discrepancy later in this section.

Very little data for comparison exists other than the water binary systems. Studies made involving 2 pentanone have all been conducted at constant pressure and are thus unsuited for this purpose.

Likewise, no work apparently exists involving 2,3,4 trimethylpentane. However, Kretschmer, Nowakowska and Wiebe(57) have studied ethanol in 2,2,4 trimethylpentane, which is a more common solvent. The results, therefore, while not directly comparable could be useful in at least a qualitative sense. These authors quote an activity coefficient of 31 at 25°C, as compared to 28 for ethanol in 2,3,4 trimethylpentane at 20°C. This comparison for similar solvents is quite favorable. Likewise, the data obtained by Kwantes and Rijnders(58) for polar solutes in paraffin solvents can confirm the general validity of the results for 2,3,4 trimethylpentane. They study oxygenated hydrocarbons in hexadecane at 25°C and 40°C at infinite dilution by GLC. Their results are as shown below.

Solute	γ_2^∞ at 25°C	40°C
Methanol	71.5	45.0
Ethanol	47.0	30.5
Propanol	31.5	19.5
Acetaldehyde	7.3	6.1
Propionaldehyde	4.0	3.4
Ethyl Formate	3.7	3.2

Realizing that hexadecane has a longer hydrocarbon chain length but similar polarity properties, the analogy between the above data and that listed in Table I is exceptionally good. As 2,3,4 trimethylpentane has fewer methylenic groups, the corresponding values in Table I should be lower than those given by Kwantes. It should be noted that the trends in the activity coefficient as the chain length increases within a homologous series as well as the thermal effects correspond very well between the two works. In fact for the solutes which do not exhibit association with themselves, the values of the activity coefficient almost completely agree, indicating that the addition of methylenic groups to the solvent has little effect in this case.

The remaining system for which a comparison with the existing literature can be made is ethanol-water. As this system is of definite commercial interest much work has been spent studying the vapor liquid equilibrium properties. However, as will be pointed out in the following discussion, a rather large discrepancy exists among the various investigators as to the value of the activity coefficient of ethanol at infinite dilution. The International Critical Tables(119) quotes extensive data on this system. From a plot of the data given there, the activity coefficients at various temperatures are as follows: at 20°C, $\gamma_2^\infty = 4.5$; at 40°C, $\gamma_2^\infty = 6.1$; at 55°C, $\gamma_2^\infty = 6.8$; and at 75°C, $\gamma_2^\infty = 7.6$. They also report the only calorimetric data from which ΔH_2^E can be obtained independently. Comparing this data with that in Table I shows reasonable agreement but again the temperature dependence of the two sets are reversed. In 1943, Jones, Schoenborn and Colburn(49) in a careful study also examined this system. The activity coefficients reported by these workers are: at 50°C, $\gamma_2^\infty = 4.4$, while at 60°C, $\gamma_2^\infty = 5.2$. This data, while not agreeing with either the present work or the I.C.T. values, does agree with the calorimetric data also presented in the I.C.T. However, the interpretation and emphasis given to certain data points in the dilute region is questionable and it is believed that a better representation of the data would yield higher values than those given here. Rao, Acharya and Rao(99) studied ethanol-water by static techniques in the dilute region and obtained the following activity coefficients: at 65°C, $\gamma_2^\infty = 4.8$; at 70°C, $\gamma_2^\infty = 4.3$; and at 80°C, $\gamma_2^\infty = 3.2$. The temperature dependence of this work can be seen to correspond to the data of this study. However, the data of Rao et al. exhibit a maximum in the region of three mole percent ethanol. Altsheler, Unger and Kolachov(4) using an equilibrium still have obtained data for this system at extremely dilute concentrations. Unfortunately the data is at constant pressure rather than constant temperature, as is most data available in the literature. However, at 760 mm pressure and an ethanol mole fraction of 0.00043 they report $\gamma_2^\infty = 3.8$. Interestingly enough they too report a maximum in the data occurring at about 0.2 mole percent ethanol. The analysis technique utilized to determine phase concentrations by these workers is rather suspect of possible errors. One final study by Hansen and Miller(38) of this system yielded an activity coefficient value at 25°C of 4.0, concurring fairly well with the work of Jones et al.

As the above studies would indicate a range of values for γ_2^∞ from 4.0 to 6.1 in the temperature region of interest and the present data falls within the upper portion of this range, one might be content to let the situation pass. However, in an attempt to resolve this discrepancy a more extensive study was made of this binary system in which the variation of γ_2 with mole fraction of ethanol was investigated. This was accomplished with GLC by allowing the water in the column to become partly depleted, while still insuring coverage of the solid support, and by increasing the sample injection size in increments from 0.04 microliters to 1.0 microliters. In this manner the ethanol mole fraction was varied from 7.6×10^{-5} to 0.022. The results of this work are shown in Figure 2. As can be seen, the data can be fitted rather nicely by a smooth continuous curve in the entire region. Thus the value of γ_2 for any concentration may be obtained by interpolation. Now the above quoted literature values of γ_2^{∞} are all determined by extrapolating data obtained by static methods to infinite dilution. Generally the most dilute data point is obtained at a mole fraction of 0.02 to 0.03, such as in the study of Hansen and Miller or Jones et al. Now a comparison of their values at $x_2 = 0.02$ and Figure 2 indicate complete agreement, i.e., $\gamma_2 = 3.8$ at $x_2 = 0.02$ as compared to $\gamma_2 = 4.1$ at $x_2 = 0.02$ in this study. Being as $x_2 = 0.02$ represented a maximum value for this work and a minimum for the literature studies, it is felt that there is more justification for a smooth interpolation through the data of this study to infinite dilution than a very nonlinear extrapolation of the literature work to zero mole fraction.

A word will now be said concerning the reverse trends between this study and the literature data on the thermal effects.

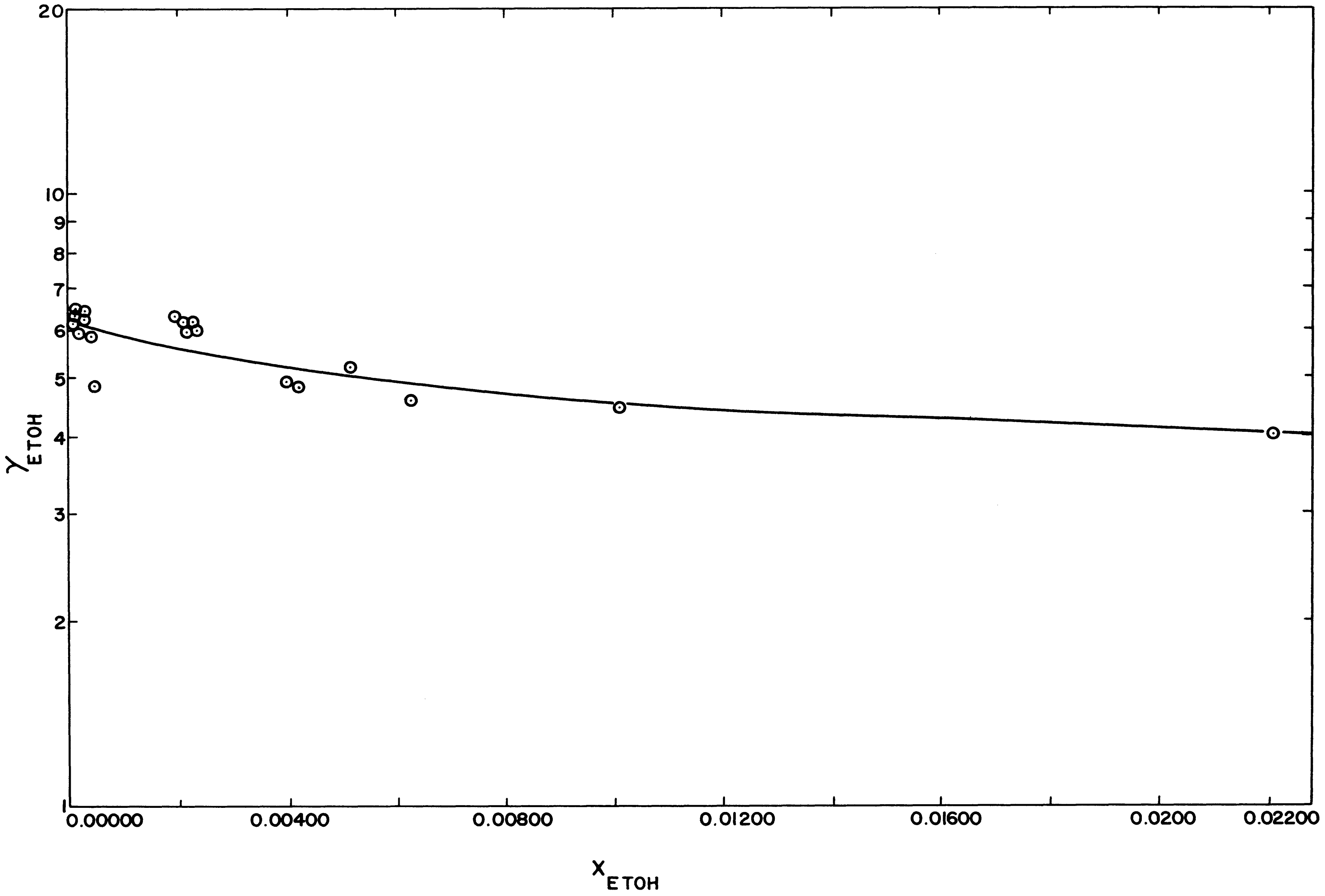


Figure 2. Activity Coefficient of Ethanol in Water as a Function of Concentration in the Dilute Solution Region at 30°C.

Again the fact must be brought out that most literature data is for solute mole fractions of the order of 0.02 to 0.05 and higher. From this point excess property plots are extrapolated to a zero value at zero concentration and the tangent-intercept method is used to determine the respective partial excess properties. Careful studies may often indicate devious behavior in these regions, however. Prigogine(94) while investigating the ethanol-water system in the very dilute water region observed inversions in the excess properties curves which would indicate an inverted thermal dependence of the partial excess properties. Also Lewis(64) has indicated that such behavior in very dilute solutions is not uncommon in liquid-liquid chromatography and ion exchange chromatography. Thus it may be that due to the existing data being at essentially high concentrations with respect to infinite dilution, such behavior has not been commonly observed. Further investigations into this area based on molecular concepts could provide fruitful if impractical research.

C. Discussion of Thermodynamic Results

As most of the discussion concerning the results of this work will accompany the correlation and analysis of the data, this section will be devoted to comparing the resultant thermodynamic properties with those anticipated in the experimental program. Trends and behavior of solutions will be discussed. Also the magnitude of the gas phase nonideality and its effect on the activity coefficient in the present study will be considered. Methods for determining the virial coefficients from other sources will be described.

1. Analysis Based on Hydrogen Bonding Theory

In the experimental program the classification scheme of Ewell(28) was presented and liquids were categorized into five types. The classification scheme of Pimentel(83) was then shown to be equivalent to that of Ewell if the self associating liquids were grouped into a single class. Thus Ewell's scheme, although postulated on azeotrope formation, is in reality based on hydrogen bonding, as was apparent by this point. Based on this scheme then certain interactions were postulated and anticipated deviations from ideality given. How well this anticipated behavior was substantiated by the present data will now be determined. According to the classification of interactions proposed, the interaction of Class I liquids with Class IV and Class V components should always result in positive deviations from ideality. The data on the alkanes and chlorinated methanes in water adequately bear this out, as shown in Table I. The I-II and I-III interactions are more complex but again should usually show positive deviations, as hydrogen bonds are both broken and formed but the breaking process is predominant. Again, upon viewing the water systems this hypothesis is fulfilled with the exception of the ethylamine-water mixture. In this case association between ethylamine and water must be the important effect.

Turning to the Class III solvent, 2 pentanone, its solutions with Class II and Class III solutes should in general have activity coefficients greater than unity due to hydrogen bond breakage. Again this effect is seen to be true with the exception of ethylamine-2 pentanone interactions which deviate negatively from ideality. Similarly Class V solutes form solutions with positive deviations, but this effect is due to physical forces such as dispersion, orientation and induction, rather than hydrogen bonding which does not occur in these solutions. The only interaction predicted to show negative deviations from ideality is the Class III-Class IV solution. However, Table I indicates this to be only partially true for the chlorinated methanes in 2 pentanone. This is most probably due to the formation of weak hydrogen bonds only, the effect of which is overridden by the magnitude of the physical forces.

As no hydrogen bonds can be formed with a Class V solvent, all deviations from ideality must be positive or quasi-ideal. The Class II solutes show the largest deviations as hydrogen bonds are broken as the solutes become surrounded by solvent. This can be seen to be the case for alcohols in 2,3,4 trimethylpentane. For Class III and Class IV solutes no hydrogen bonding exists and the positive deviations are due to physical forces interacting between the solutes and the 2,3,4 trimethylpentane. The alkanes represent the only true quasi-ideal solutions studied here and the activity coefficients are nearly unity as only very weak dispersion forces exist between solute and solvent. Thus the data very nicely confirms the behavior anticipated according to Ewell's classification.

Pimentel's hypotheses concerning the partial molar excess enthalpy will now be tested, bearing in mind that slight contradictions do not invalidate the conclusions due to the uncertainty in the values of ΔH_2^E determined in this study. For water binary systems, Class IV and Class V solutes should form endothermic solutions. Also Class II and Class III solutes should usually form endothermic solutions. From an inspection of Table III these predictions can be seen to hold quite well with the exception of the amines in water. Here again the hydrogen bond formed between the amine and water must be of a particularly strong nature although the trend decreases as the hydrocarbon radical in the amine increases, indicating a decreasing bond strength.

The value of ΔH_2^E for all the solute classes in 2 pentanone should be positive, i.e., endothermic solutions, with the exception of Class IV, with chlorinated methanes. Once again the data in Table III for III-IV interactions imply weak hydrogen bond formation between solute and solvent and so the physical forces dictate the solution behavior. As no hydrogen bonding is possible with 2,3,4 trimethylpentane all solutions formed should be endothermic regardless of the solute involved. The data in Table III confirm this postulate very well with the exception of CCl_4. The reason for this deviation is not understood. From the above discussion the conclusion may easily be drawn that the majority of binary nonelectrolyte solutions are endothermic and exhibit positive deviations from ideality, thus concurring with hydrogen bonding theory.

2. Effect of Gas Phase Nonideality

The activity coefficient discussed in the above analysis, as has already been mentioned, is actually a hybrid coefficient representing the deviations from ideality in both the liquid and the gas phases. In order to remove the gas phase nonideality, the relations derived in the theoretical development will be used to replace the ideal gas law assumption with the more accurate virial equation of state. However, the resulting expressions for γ_2^∞ involve the second virial coefficient, B_{ij}, which is not readily available for most pure substances, let alone the interaction virial coefficient B_{12}. Therefore some means of estimating this property must be utilized. The most general technique available is that of Guggenheim and McGlashan(36) and its extension by Fox and Lambert.(31) The method is based on the theory of corresponding states and expresses the results in terms of reduced properties. Therefore knowing the critical temperature and volume of a particular component, the virial coefficient may be evaluated at any given temperature. For interaction virial coefficients, pseudo-critical properties are obtained by using the geometric mean temperature and the arithmetic mean of the cube roots of the critical volumes. While this technique works well for nonpolar and slightly polar vapors, it does not adequately represent the virial coefficients of highly polar vapors as are considered in this study. For these vapors the method proposed by Rowlinson(100) must be used. This system is also based on reduced properties, but not in the usual sense. The reduced virial coefficient is tabulated for two reduced parameters, one a function of the dipole moment, the intermolecular distance, and the minimum potential energy, the other dependent on the minimum potential energy and the temperature. Again for interaction virial coefficients the pseudo-reduced properties based on geometric and arithmetic mean laws are used. At any rate utilizing one of the above two techniques, values of B_{ij} may be determined.

Knowing B_{ij} and utilizing Equation (64) the true value of γ_2^{∞} may be computed from GLC data. The two correction terms in Equation (64), involving the second virial coefficients, remove the gas phase nonideality. In the present study as both solute and solvent are volatile, in actuality a ternary system exists in the vapor phase. However, in order to determine the magnitude of the two correction terms to the value of γ_2^{∞} as listed in Table I, a worst possible binary system will be chosen typifying nonideal vapor behavior, and this will be used as representative. Although in the present work the carrier gas and the solvent are the two major components in the vapor phase, helium exhibits very little deviation from ideal behavior as has been verified by Desty _et al._(23) Therefore a solute-solvent binary mixture will be chosen which would be anticipated to be highly nonideal. Such a binary system is ethanol and water. In this case as both components are highly polar the method of Rowlinson was used to compute B_{12} and B_{22} at 40°C. Utilizing these values in Equation (64), the two correction terms amount to -0.024 or a 2.4% effect on the value of γ_2^{∞} in Table I due to the vapor phase nonideality. Now as the overall average error in the value of γ_2^∞ was ± 5%, and the present example is a worst possible case, the correction to γ_2^∞ due to the ideal gas law assumption was neglected in this work. However, it must be remembered that in instances where an alternate carrier gas which is less ideal is used or with long GLC columns for which the mean pressure is a larger value, the effect may become important and the data should be corrected. Also, when data of a higher order of accuracy is obtainable, Equation (69) may be used to obtain the value of B_{12} and thus study solute-solvent interactions directly by GLC.

VI. CORRELATION AND ANALYSIS OF DATA

A. Empirical Homologous Series Approach

In the discussion of the results, it was noted from an inspection of Table I than within any homologous series of solutes at a given temperature the activity coefficient increases with increasing size of the hydrocarbon chain. This fact was also noticeable in Table II, but here the increases were of a more uniform nature. Needless to say, this was not the first time that the relation was noted. Butler, Ramchandi and Thomson(18) while studying alcohols in water observed that a linear increase in the partial molar excess free energy occurred as each additional methylenic group was added to the -OH functional group. Bronsted and Koefoed(16) in their principle of congruence expressed the fact that in paraffin-paraffin systems the activity coefficient could be related to the difference in the number of carbon atoms between the solute and the solvent. The constant of proportionality was a function of temperature only, independent of hydrocarbon chain length of either species for the solutions they studied. Copp and Everett(20) extended the work of Butler *et al.* to include alcohols, amines, alkanes, aliphatic acids and alkyl acetates in water. Much of the data originated from sources already mentioned. The relation noted by Butler was verified for all these solutes in water. In addition Copp and Everett derived other parallelisms for the various solutes in water for more concentrated solutions.

Discussions of the work of Herington(41) have indicated that the above observed linear relation in water binary solutions should not be expected to hold for nonaqueous solvents. The reasons behind this fact will be the subject of discussion in the next section. At any rate as water and 2,3,4 trimethylpentane are two of the solvents studied in this work, an attempt to correlate the data by this technique should prove interesting. In Figures 3 through 11 this correlation for all the solutes in each of the three solvents is presented at 20°, 30° and 40°C. An inspection of the graphs shows that the correlation represents the water binary systems very well and the 2,3,4 trimethylpentane binary systems quite satisfactorily. However, the 2 pentanone systems, with the exception of the alkanes and the alcohols, deviate considerably from the anticipated behavior. It is also interesting to note that the chlorinated methanes in water exhibit the same linear relation for the partial molar excess free energy when the number of chlorine atoms is used as the parameter in the homologous series in place of the number of carbon atoms. This effect is not observable with the other two solvents.

B. Homologous Series Approach Based on Group Interactions

It has been noted that the 2 pentanone binary systems do not follow the anticipated linear relation described above, and also that such a relation should only be expected to be valid for water as a solvent. The reasons for this behavior can be better understood

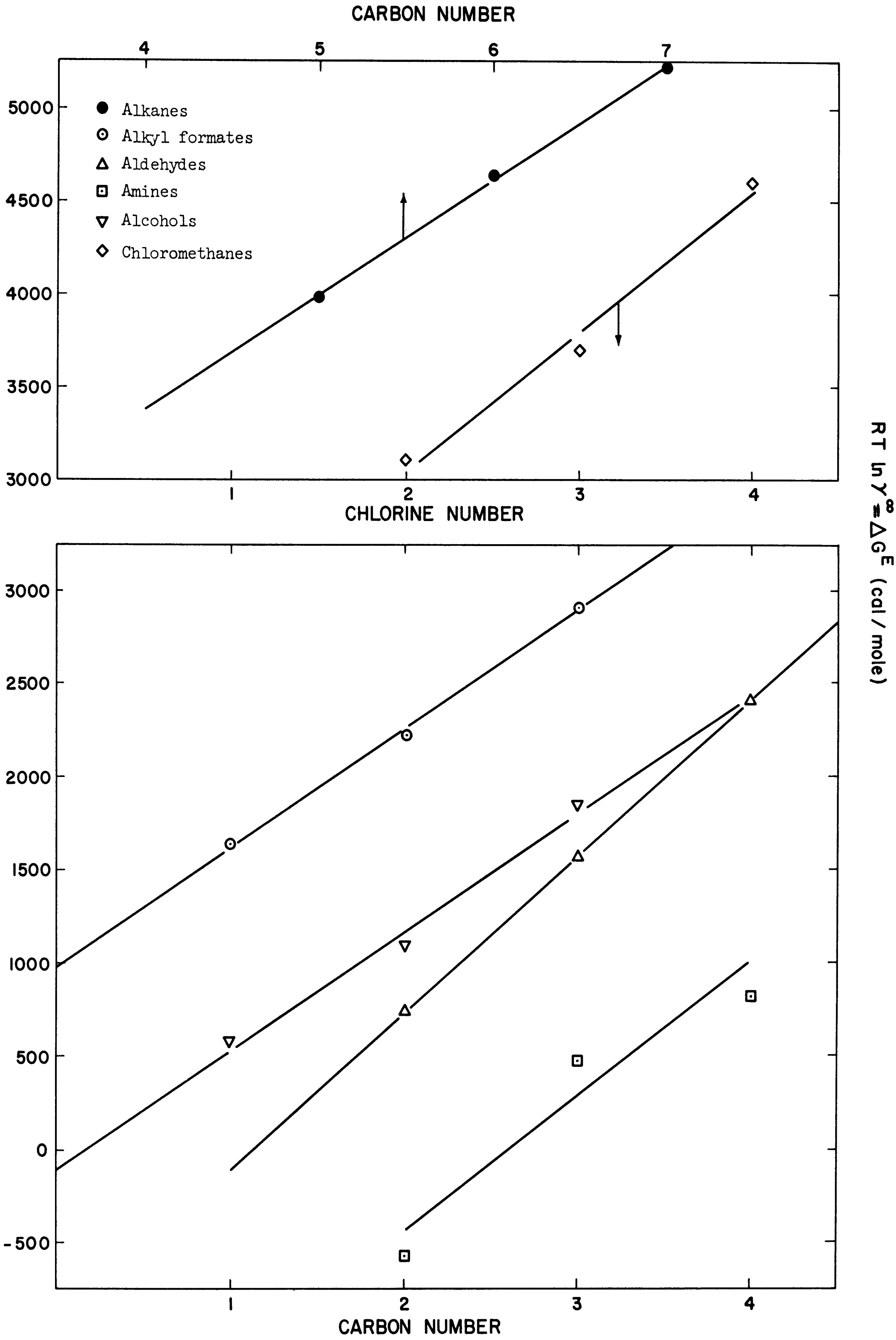


Figure 3. Incremental Relation Between Excess Free Energy and Molecular Structure for Solutes in Water at 20°C.

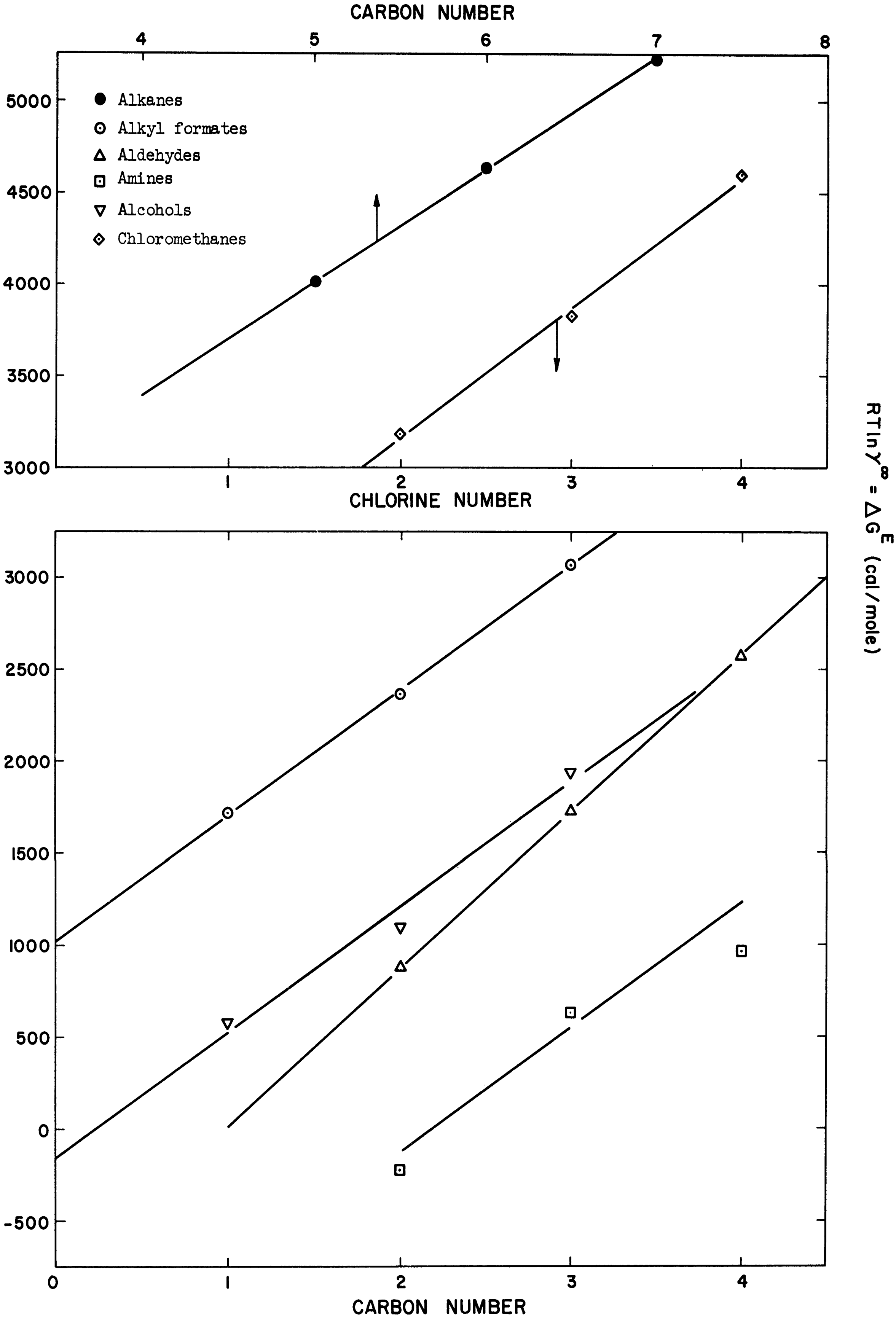


Figure 4. Incremental Relation Between Excess Free Energy and Molecular Structure for Solutes in Water at 30°C.

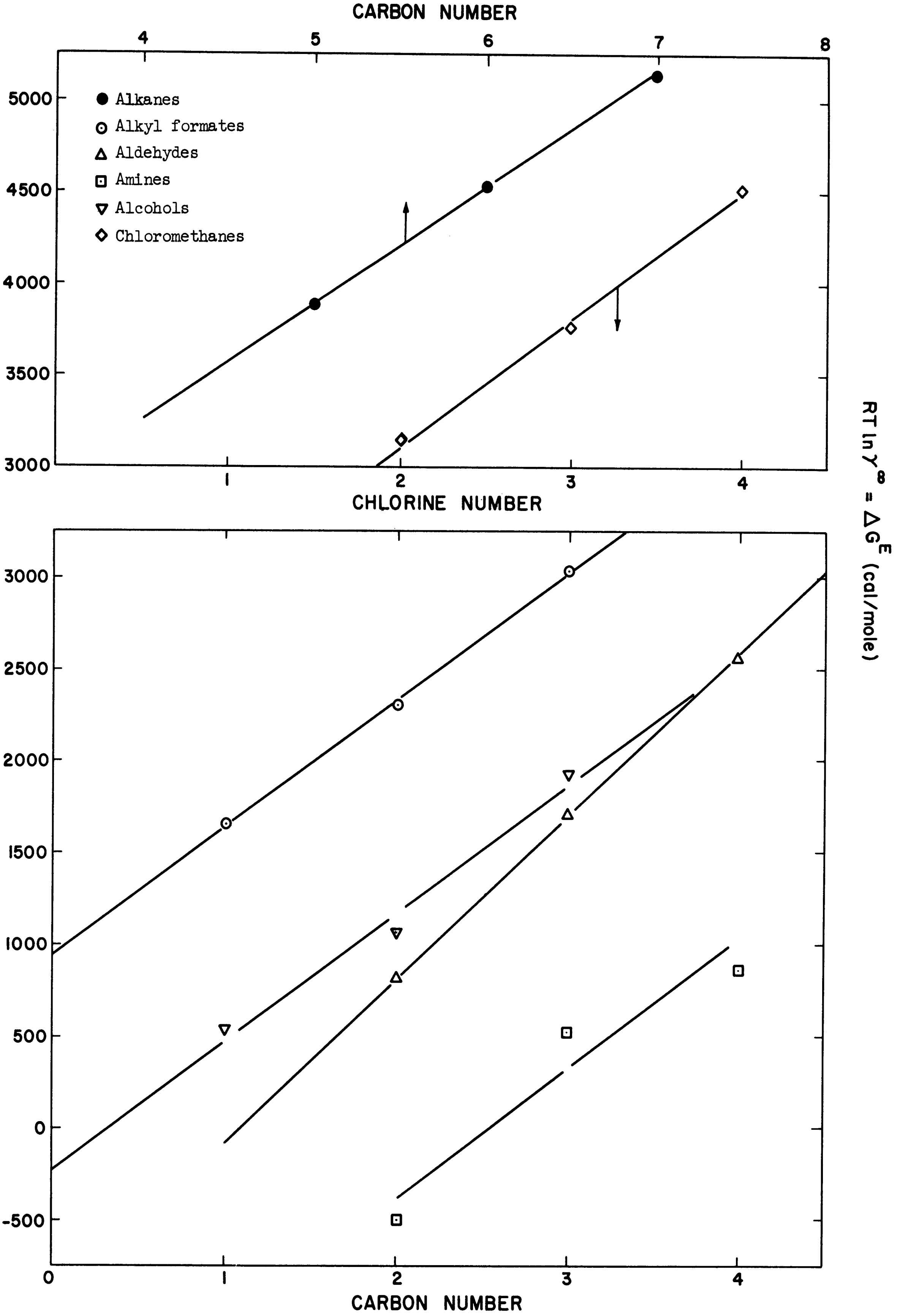


Figure 5. Incremental Relation Between Excess Free Energy and Molecular Structure for Solutes in Water at 40°C.

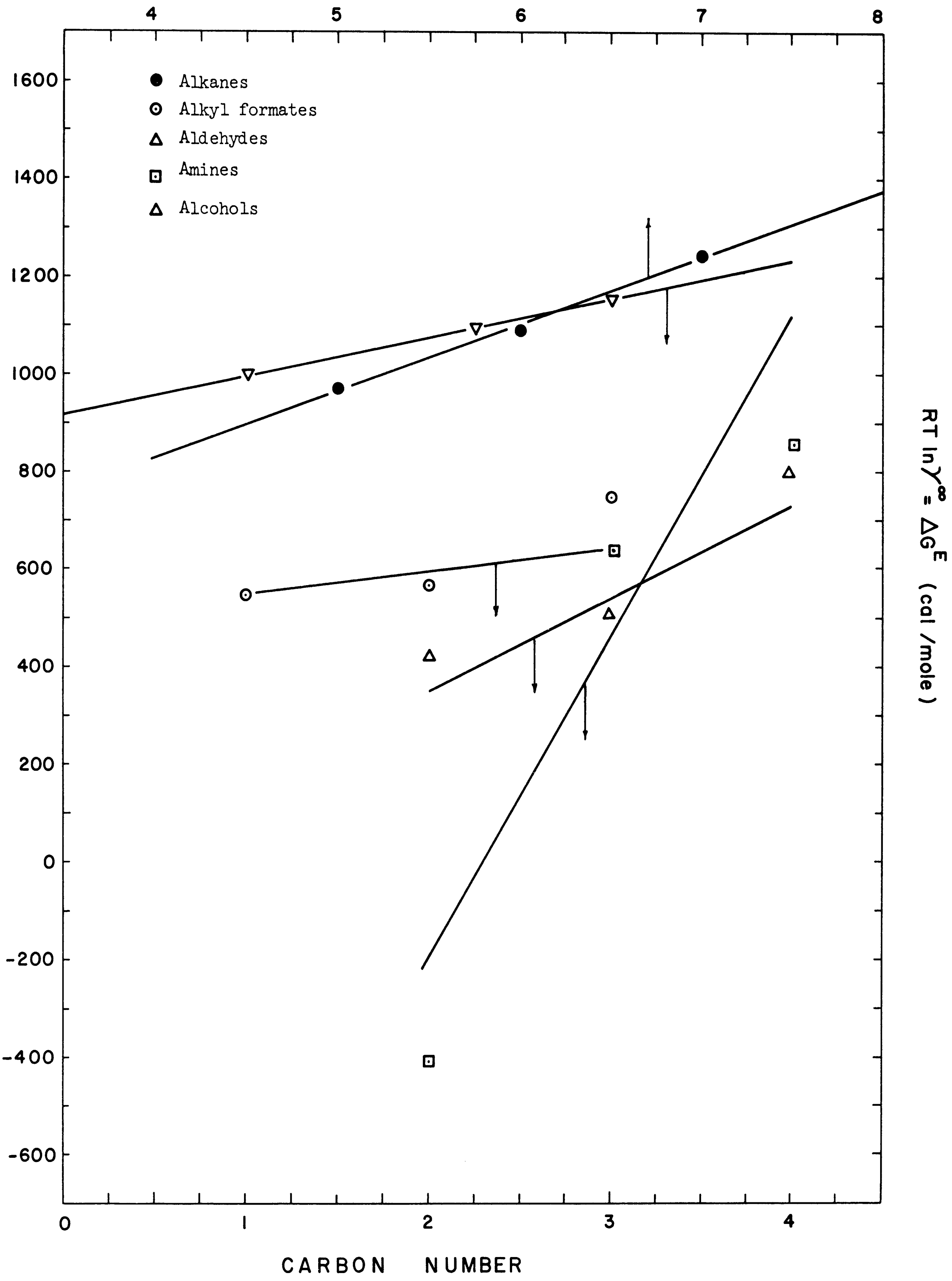


Figure 6. Incremental Relation Between Excess Free Energy and Molecular Structure for Solutes in 2 Pentanone at 20°C.

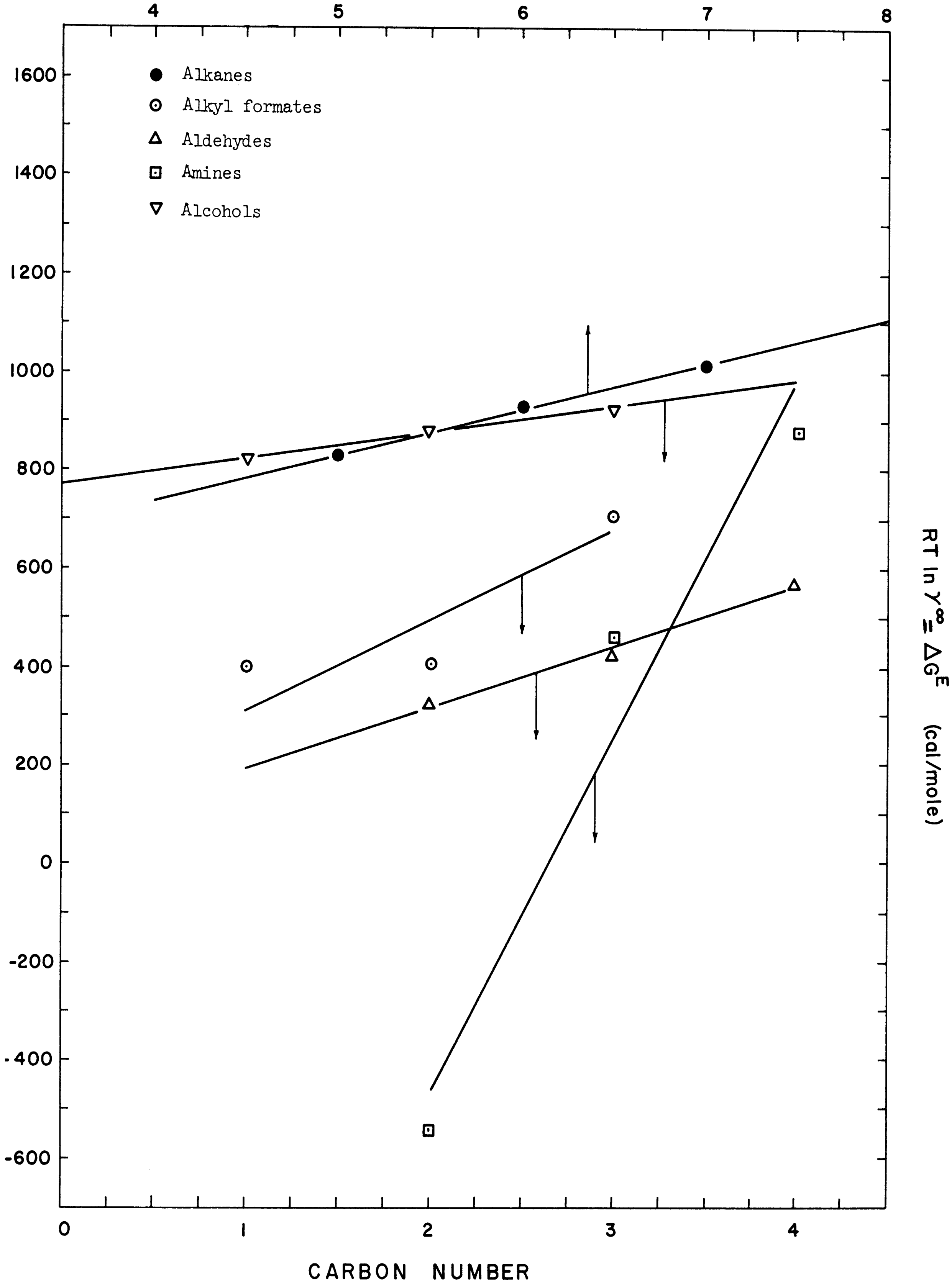


Figure 7. Incremental Relation Between Excess Free Energy and Molecular Structure for Solutes in 2 Pentanone at 30°C.

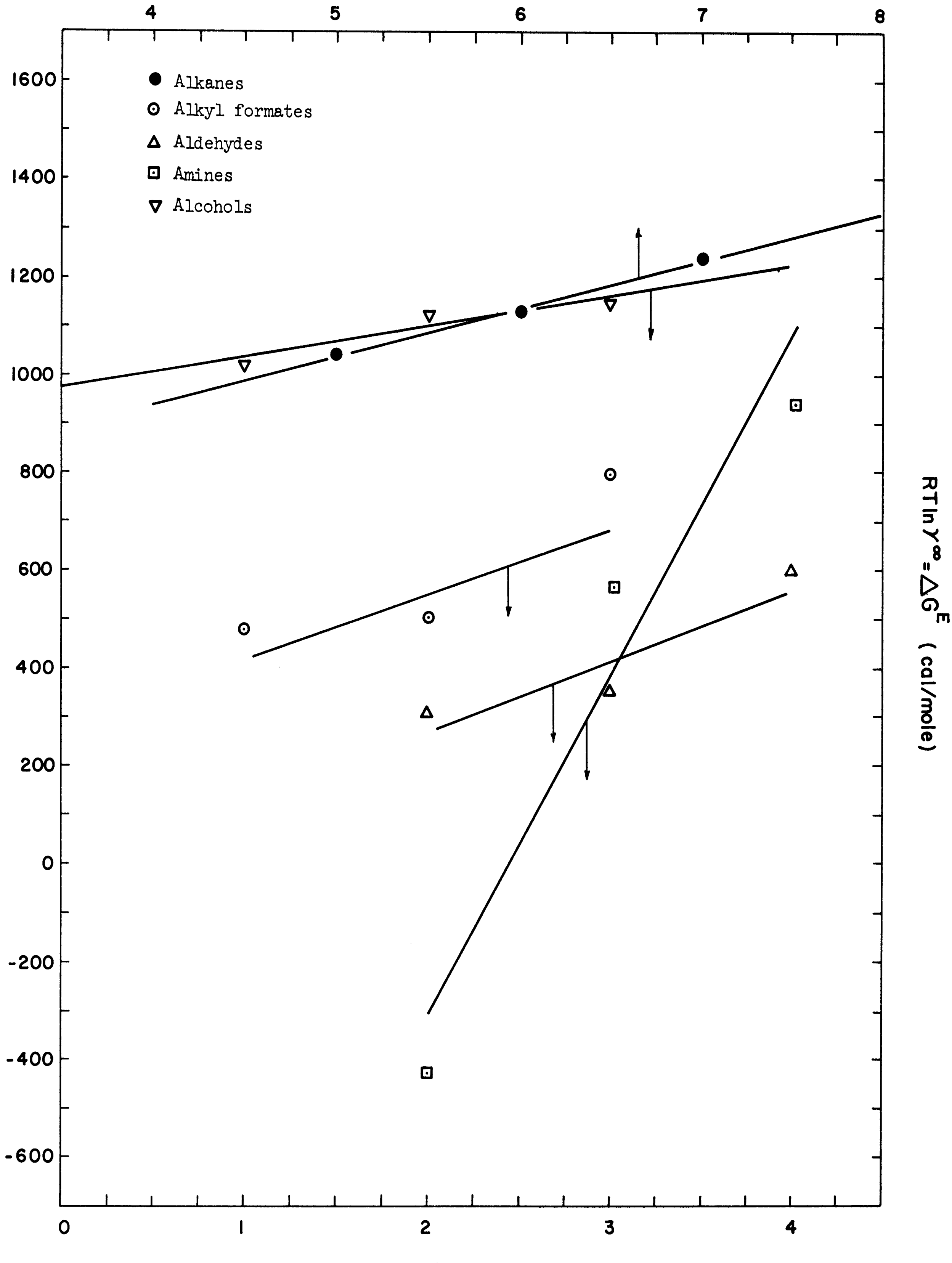


Figure 8. Incremental Relation Between Excess Free Energy and Molecular Structure for Solutes in 2 Pentanone at 40°C.

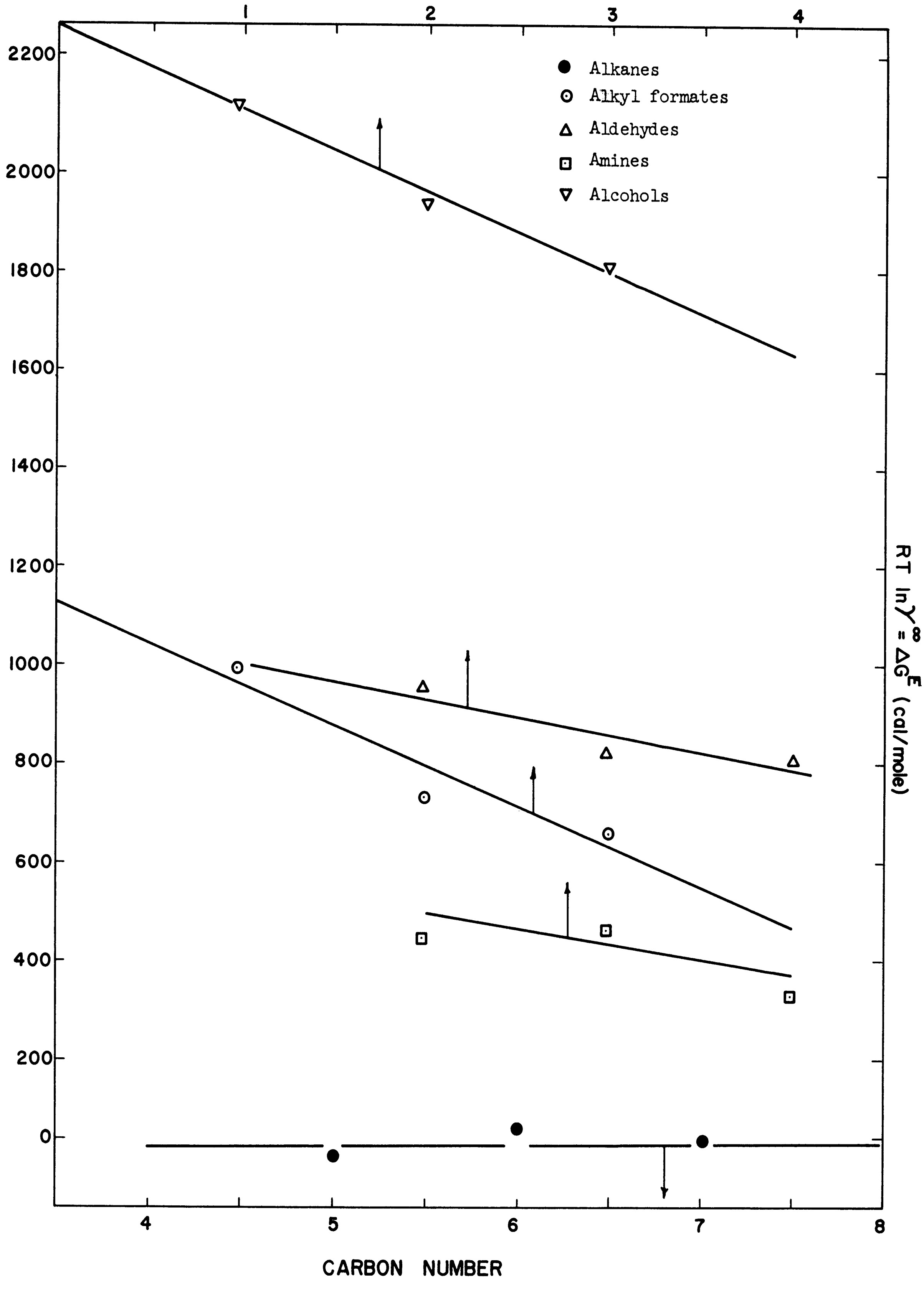


Figure 9. Incremental Relation Between Excess Free Energy and Molecular Structure for Solutes in 2,3,4 TMP at 20°C.

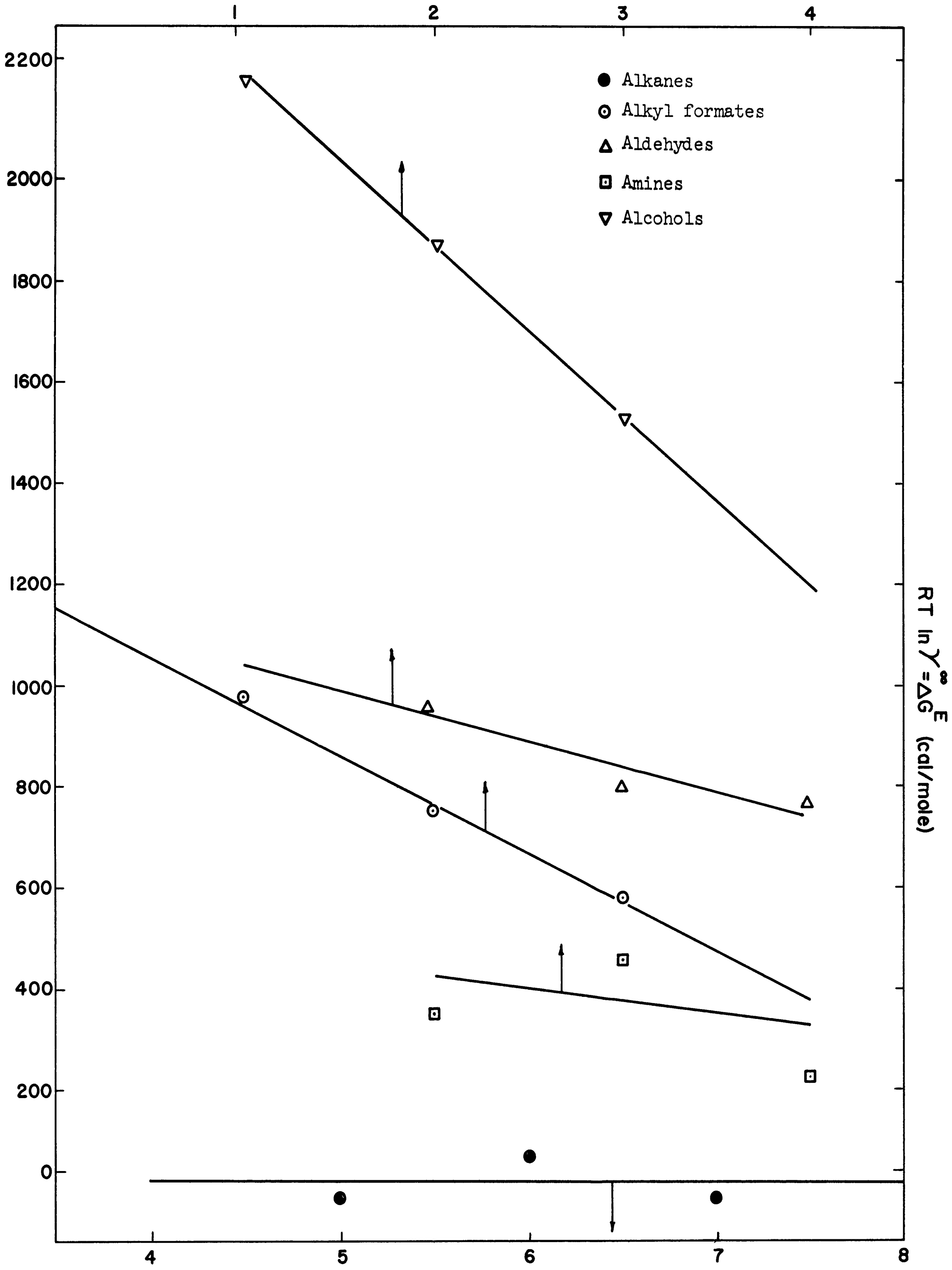


Figure 10. Incremental Relation Between Excess Free Energy and Molecular Structure for Solutes in 2,3,4 TMP at 30°C.

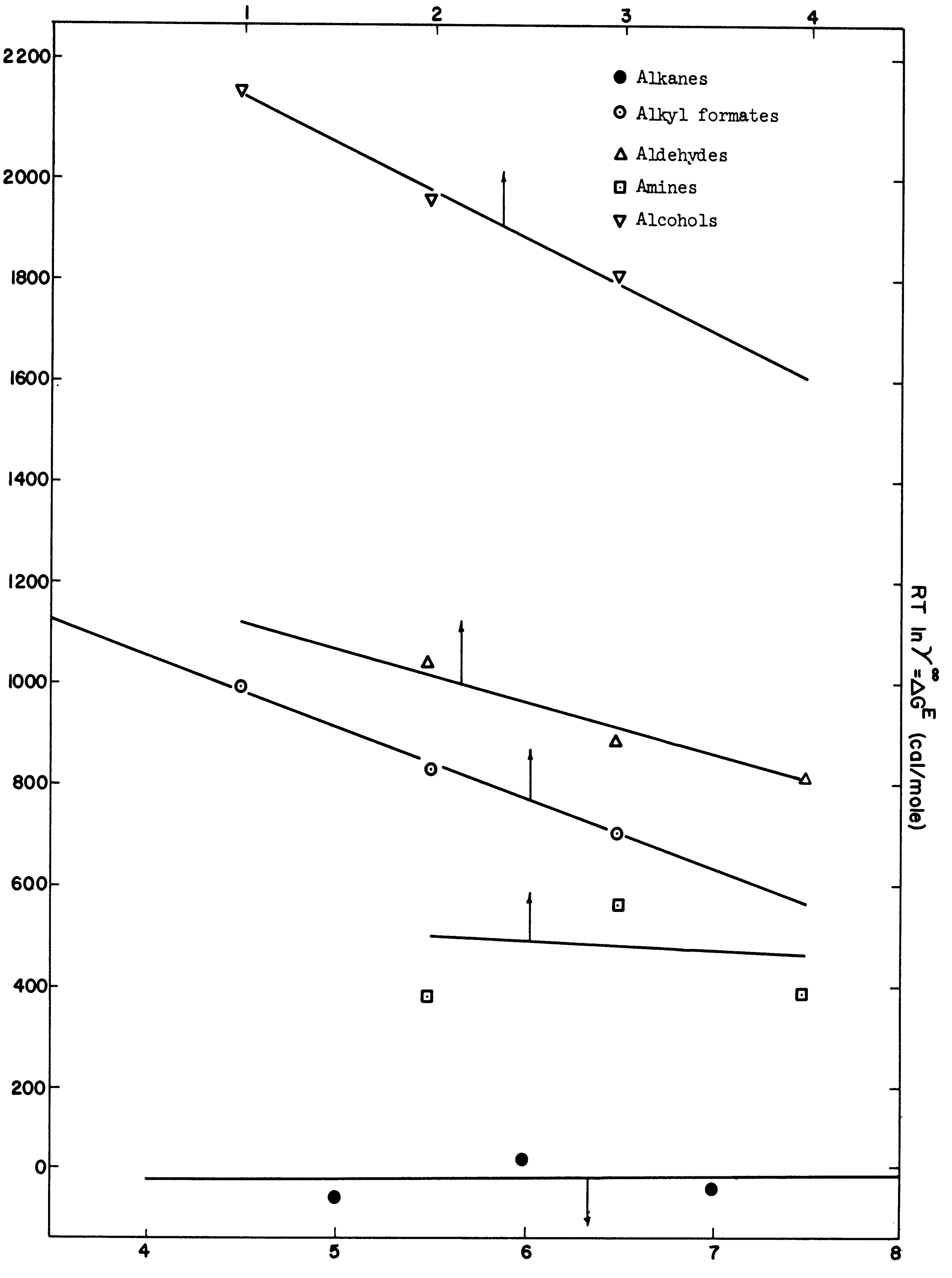
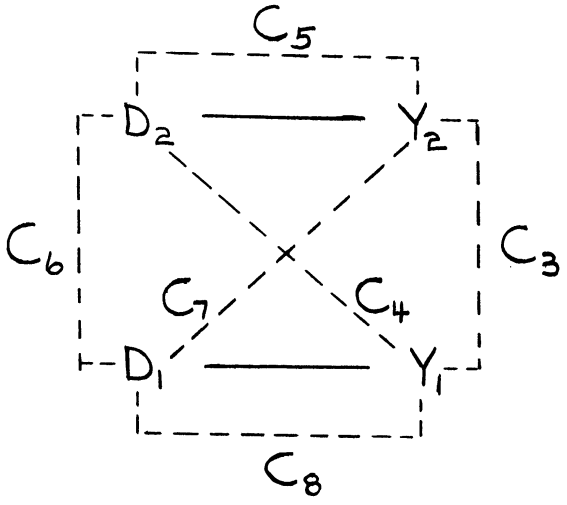


Figure 11. Incremental Relation Between Excess Free Energy and Molecular Structure for Solutes in 2,3,4 TMP at 40°C.

by considering the problem on a molecular level and examining the possible interactions which can occur. For a solute molecule D_2Y_2 and a solvent molecule D_1Y_1 the possible interactions are as shown.



In this case D_i represents the nonfunctional hydrocarbon radical and Y_i represents the functional terminal group. The possible molecular interactions are represented by C_3 through C_8. The following treatment is due to Pierotti, Deal and Derr.(82) They assume that the contribution of each interaction to the logarithm of the activity coefficient is additive and dependent only on the number of methylenic groups in the solute and in the solvent. The postulated relation is

$$\ln \gamma_2^\infty = C_3 + C_4\frac{\ell_2}{\ell_1} + \frac{C_5}{\ell_2} + C_6(\ell_2-\ell_1)^2 + C_7\frac{\ell_1}{\ell_2} + \frac{C_8}{\ell_1} \qquad (140)$$

The above quoted works of Butler *et al.*(18) and Bronsted and Koefoed(16) were used to determine the exact form of some of these terms. From an inspection of Equation (140) and the proposed interaction scheme, certain conclusions may be drawn. For a given solvent C_8/ℓ_1 and C_4/ℓ_1 are constants while for a given solute C_5/ℓ_2 is a constant. Therefore when studying a homologous series of solutes in a particular solvent, many terms are fixed. The various constants in Equation (140) are functions of temperature only, being independent of the number of methylenic groups under consideration. The experimental results of Pierotti have also indicated that slight branching of the D_i radical not immediately adjacent to Y_i has a negligible effect on γ_2^{∞}.

The exact form of Equation (140) applicable to the particular binary systems of interest in this work will now be considered. For the alkanes in water, as no D_1 or Y_2 groups exist, C_5, C_6, C_7 and C_8 are zero and

$$\ln \gamma_2^{\infty} = C_3 + C_4' \ell_2 \tag{141}$$

This is the equation of a straight line and therefore the behavior exhibited in the empirical correlations shown in Figures 3, 4 and 5 can actually be substantiated by the present development based on group interactions. For other solutes in water the C_5 term is nonzero and

$$\ln \gamma_2^{\infty} = C_3 + C_4' \ell_2 + C_5/\ell_2 \tag{142}$$

However, judging from the linear relations obtained for all the solutes in water the effect of the third term must be of a second order. Proceeding in this fashion for alkanes in 2 pentanone, Equation (140) becomes

$$\ln \gamma_2^\infty = C_3 + C_4' \ell_2 + C_6 (\ell_2 - \ell_1)^2 + C_8' \qquad (143)$$

while for all other solutes in 2 pentanone all possible interactions exist and the full form of Equation (140) is needed. The alkanes in 2,3,4 trimethylpentane show the least interactions. They can be represented by

$$\ln \gamma_2^\infty = C_6 (\ell_2 - \ell_1)^2 \qquad (144)$$

The remaining solutes in 2,3,4 trimethylpentane follow the relation

$$\ln \gamma_2^\infty = C_3 + C_5/\ell_2 + C_6 (\ell_2 - \ell_1)^2 + C_7'/\ell_2 \qquad (145)$$

At this point the reason why the 2 pentanone systems do not follow the empirical correlation should be quite clear. Equation (140) is not a linear relation in ℓ_2. The values of C_6 used by Pierotti are those given by Bronsted. As the term $C_6(\ell_2 - \ell_1)^2$ is always considerably smaller than the other group interactions, it can be seen that Equations (143) and (145) reduce to a pseudo-linear relation in ℓ_2. This fact is the underlying reason why the alkanes in 2 pentanone and all the solutes in 2,3,4 trimethylpentane show nearly linear relations in the previous correlation. That a linear relation also results for alcohols in 2 pentanone is purely fortuitous.

Using the above relations, Pierotti calculated the values of the constants from data obtained by static techniques for many systems. However, two discrepancies exist in his application of the above theory which cannot be resolved satisfactorily. First, he assumes that the interaction represented by C_7 is negligible or can be included in the C_8 interaction and second, the conclusions drawn concerning the constancy of C_8/ℓ_1 and C_4/ℓ_1 for a given solvent and C_5/ℓ_2 for a given solute are disregarded. Now in an infinitely dilute solution the solute molecule is completely surrounded by a matrix of solvent molecules, and therefore no reason can be seen at all for neglecting the C_7 interactions. Likewise the second discrepancy is an unnecessary inconsistency. For these two reasons, the constants in Equations (140) through (145) were determined independently utilizing the data of this study, and are given in Table V. These constants are devoid of the discrepancies described above. Since in a given solvent certain terms are constant, most systems of homologous series are over defined, in a mathematical sense, and thus a best fit of the constants is used. Because of this fact, Equation (140) with the constants of Table V actually represents the experimental data only to within ± 15%.

C. Infinitely Dilute Solution Theory

This section will parallel the theoretical development for nonelectrolyte solutions and therefore will consist of two parts, the athermal and the thermal contributions to the activity coefficient.

TABLE V

CORRELATION CONSTANTS FOR INFINITELY DILUTE ACTIVITY COEFFICIENTS

$$\ln \gamma_2^{\infty} = C_3 + C_4 \frac{\ell_2}{\ell_1} + C_5/\ell_2 + C_6(\ell_2-\ell_1)^2 + C_7 \frac{\ell_1}{\ell_2} + C_8/\ell_1$$

Solute Series	Solvent Series	Temp. °C	C_3	C_4	C_5	C_6	C_7	C_8
Alkanes	Water	20	1.15	1.14				
		30	1.58	1.02				
		40	1.05	1.04				
Alkyl Formates	Water	20	1.43	1.14	0.24			
		30	1.94	1.02	-0.10			
		40	1.65	1.04	-0.04			
Aldehydes	Water	20	0.68	1.14	-0.54			
		30	1.21	1.02	-0.76			
		40	1.03	1.04	-0.76			
Amines	Water	20	-3.07	1.14	0.85			
		30	-2.57	1.02	1.23			
		40	-2.70	1.04	0.69			
Alcohols	Water	20	-0.29	1.14	0.14			
		30	0.35	1.02	-0.44			
		40	0.06	1.04	-0.27			
Alkanes	Ketones	20	0.00	0.17		-.00110		0.42
		30	0.00	0.12		-.00115		0.44
		40	0.00	0.11		-.00120		0.74
Alkyl Formates	Ketones	20	0.03	0.17	0.24	-.00110	-0.03	0.42
		30	0.21	0.12	-0.10	-.00115	-0.08	0.44
		40	-0.25	0.11	-0.04	-.00120	-0.04	0.74
Aldehydes	Ketones	20	0.16	0.17	-0.54	-.00110	0.06	0.42
		30	-0.15	0.12	-0.76	-.00115	0.18	0.44
		40	-0.46	0.11	-0.76	-.00120	0.13	0.74
Amines	Ketones	20	2.40	0.17	0.85	-.00110	-2.26	0.42
		30	2.47	0.12	1.23	-.00115	-2.45	0.44
		40	2.18	0.11	0.69	-.00120	-2.24	0.74
Alcohols	Ketones	20	0.72	0.17	0.14	-.00110	0.02	0.42
		30	0.44	0.12	-0.44	-.00115	0.16	0.44
		40	0.49	0.11	-0.27	-.00120	0.07	0.74
Alkanes	Alkanes	20				-.00110		
		30				-.00115		
		40				-.00120		
Alkyl Formates	Alkanes	20	0.85		0.24	-.00110	0.08	
		30	0.75		-0.10	-.00115	0.13	
		40	1.04		-0.04	-.00120	0.06	
Aldehydes	Alkanes	20	1.25		-0.54	-.00110	0.12	
		30	1.09		-0.76	-.00115	0.17	
		40	1.19		-0.76	-.00120	0.16	
Amines	Alkanes	20	0.39		0.85	-.00110	0.02	
		30	0.37		1.23	-.00115	-0.04	
		40	0.65		0.69	-.00120	-0.04	
Alcohols	Alkanes	20	2.88		0.14	-.00110	0.10	
		30	2.01		-0.44	-.00115	0.27	
		40	2.62		-0.27	-.00120	0.16	

The athermal contribution, as derived earlier, is rather straightforward. However, many variants exist for the thermal contribution, primarily based on the work of Hildebrand. The advantages and disadvantages of each of these variants will be presented, as well as a comparison between the activity coefficient as predicted by the particular techniques and those measured experimentally.

1. Athermal Contribution to Nonideality

Since the athermal contribution to the activity coefficient is dependent on the geometry and the spatial orientation and distribution of the solute with respect to the solvent, Guggenheim's treatment based on the cell theory of liquids has been shown to provide the best approach to evaluating this effect. The method is a very plausible one to evaluate geometric dependency, as the cell theory provides a rigid structure for liquids for which definite dimensions and orientations can be visualized. Also this development appears to be the only one for evaluating this effect which has been reduced to a form where practical calculations can be made. Work done in the theory of high polymers considers this type of contribution, but the final results are essentially coincident with the treatment of Guggeheim for a large number of nearest neighbors.

The two relations derived from this theory are

$$\ln \gamma_2^{ath} = \ln \frac{1}{r} + 6 \ln \frac{6r}{5r+1} \qquad (78)$$

when the solute molecule is smaller than the solvent molecule, and

$$\ln \gamma_2^{ath} = \ln r + (5r+1) \ln \frac{5r+1}{6r} \qquad (84)$$

when the solute molecule is larger than the solvent molecule. The results of this prediction for the various solutes in the three solvents are presented in Table VI. As can be seen in the table, the values of $\ln\gamma_2^{ath}$ are always negative indicating that the size contribution to ΔS_2^E is always positive. It can also be noted that with the exception of the water binary systems the solute and the solvent have approximately the same molecular dimensions. Therefore a really thorough evaluation of the theory for the athermal effect is not possible. Nevertheless, as it represents the only available method for predicting this contribution to nonideality, the values in Table VI will be used in conjunction with the results of the next section to attempt to predict the infinitely dilute activity coefficients determined experimentally by GLC.

2. Thermal Contribution to Nonideality

Two alternatives exist for evaluating the thermal contribution to the activity coefficient. One may either use the work of Hildebrand or one of the later modifications of his work, or the theory of intermolecular forces may be employed. However, even when using the latter technique, analogies to Hildebrand's work must be used to formulate the complete relationship. Conceptually the two

TABLE VI

ATHERMAL CONTRIBUTION TO THE ACTIVITY COEFFICIENT AT INFINITE DILUTION FOR VARIOUS SOLUTES IN WATER, 2 PENTANONE AND 2,3,4 TMP

	Water			2 Pentanone			2,3,4 TMP		
Solute	r	ln γ_2^{ath}	γ_2^{ath}	r	ln γ_2^{ath}	γ_2^{ath}	r	ln γ_2^{ath}	γ_2^{ath}
C_5H_{12}	6.45	-3.19	0.04	1.09	-.01	0.99	1.42	-.06	0.94
C_6H_{14}	7.25	-3.81	0.02	1.23	-.02	0.98	1.27	-.02	0.98
C_7H_{16}	8.14	-4.48	0.01	1.38	-.05	0.95	1.13	-.01	0.99
CH_2Cl_2	3.53	-1.10	0.33	1.67	-.11	0.90	2.59	-.33	0.72
$CHCl_3$	4.43	-1.71	0.18	1.33	-.05	0.95	2.07	-.21	0.81
CCl_4	5.36	-2.38	0.09	1.10	-.01	0.99	1.71	-.13	0.88
MeFo	3.40	-1.04	0.35	1.73	-.14	0.87	2.70	-.34	0.71
EtFo	4.46	-1.71	0.18	1.32	-.04	0.96	2.06	-.21	0.81
PrFo	5.43	-2.43	0.09	1.08	-.01	0.99	1.69	-.13	0.88
CH_3CHO	3.12	-0.85	0.43	1.89	-.17	0.84	2.94	-.40	0.67
C_2H_5CHO	4.00	-1.42	0.24	1.47	-.07	0.93	2.29	-.26	0.77
C_3H_7CHO	4.90	-2.05	0.13	1.20	-.01	0.99	1.87	-.16	0.85
EtAm	3.55	-1.13	0.32	1.66	-.10	0.90	2.58	-.32	0.73
PrAm	4.57	-1.80	0.17	1.29	-.03	0.97	2.01	-.18	0.85
BuAm	5.49	-2.46	0.10	1.07	-.01	0.99	1.67	-.11	0.90
MeOH	2.24	-0.38	0.68	2.62	-.33	0.72	4.09	-.62	0.54
EtOH	3.24	-0.95	0.39	1.82	-.14	0.87	2.83	-.36	0.70
PrOH	4.15	-1.53	0.22	1.42	-.06	0.94	2.21	-.22	0.80

methods are also closely linked. In Hildebrand's original relation, it was assumed that the only solute-solvent interactions occurring in solution were dispersion forces. Although the primary solution interactions are of this type, many other solutions exhibit other interactions due to the polarity of the components. This is especially true of the solutions examined in this work. In the following discussion in order to show the effect of the various modifications, each of the variants will briefly be presented followed by a tabulation which will illustrate the effectiveness of the method in predicting the thermal contribution to nonideality.

The basic relation first postulated by Hildebrand(42) is

$$\ln \gamma_2^{th} = \frac{v_2}{RT}(\delta_1 - \delta_2)^2 \Phi_1^2 \qquad (91)$$

It was postulated assuming a regular solution. Although some theoretical basis can be attributed to its formulation, it is largely empirical being quite closely related to Van der Waals' equation. Nevertheless, it provided a practical method for determining the activity coefficient and worked quite well provided that the solution components were not very polar and no specific interactions occurred. The results utilizing Equation (91) are presented in Table VII. As the temperature dependence of many of the physical properties are unknown and the values available are at 25°C, all subsequent calculations will be made at this temperature.

TABLE VII

THERMAL CONTRIBUTION TO NONIDEALITY USING HILDEBRAND'S FORMULATION FOR VARIOUS SOLUTES IN WATER, 2 PENTANONE AND 2,3,4 TMP

Solute	Water			2 Pentanone			2,3,4 TMP		
	$(\delta_1-\delta_2)^2$	$\ln \gamma_2^{th}$	γ_2^{th}	$(\delta_1-\delta_2)^2$	$\ln \gamma_2^{th}$	γ_2^{th}	$(\delta_1-\delta_2)^2$	$\ln \gamma_2^{th}$	γ_2^{th}
C_5H_{12}	243	47.7	$6x10^{20}$	1.96	0.39	1.48	0.09	0.02	1.02
C_6H_{14}	243	53.7	$2x10^{23}$	1.96	0.43	1.54	0.09	0.02	1.02
C_7H_{16}	243	60.2	$2x10^{26}$	1.96	0.49	1.65	0.09	0.02	1.02
CH_2Cl_2	164	17.6	$5x10^{7}$	1.96	0.21	1.23	9.61	1.03	2.80
$CHCl_3$	185	24.9	$7x10^{10}$	0.36	0.05	1.05	5.29	0.71	2.04
CCl_4	205	33.3	$3x10^{14}$	0.01	0.00	1.00	2.56	0.41	1.51
MeFo	156	16.2	$1x10^{7}$	2.89	0.30	1.35	11.6	1.20	3.33
EtFo	180	24.3	$4x10^{10}$	0.64	0.09	1.09	6.25	0.85	2.34
PrFo	196	32.4	$1x10^{14}$	0.04	0.01	1.01	3.61	0.59	1.81
CH_3CHO	161	15.3	$4x10^{6}$	2.25	0.21	1.23	10.2	0.97	2.64
C_2H_6CHO	174	21.2	$2x10^{9}$	1.00	0.12	1.13	7.29	0.89	2.44
C_3H_7CHO	188	28.0	$1x10^{12}$	0.25	0.04	1.04	4.84	0.72	2.06
EtAm	166	18.0	$6x10^{7}$	1.69	0.18	1.20	9.00	0.97	2.64
PrAm	185	25.7	$1x10^{11}$	0.36	0.05	1.05	5.29	0.73	2.08
BuAm	199	33.2	$3x10^{14}$	0.01	0.00	1.00	3.24	0.54	1.72
MeOH	74	5.1	$2x10^{2}$	31.4	2.14	8.50	53.3	3.63	37.7
EtOH	104	10.3	$3x10^{4}$	16.0	1.58	4.86	32.5	3.21	24.8
PrOH	130	16.4	$1x10^{7}$	7.8	0.99	2.70	20.3	2.56	13.0

From an inspection of the data in Table VI and Table VII it can be seen that by and large the athermal contribution to non-ideality is negligible compared to the thermal contribution. This is true because in most instances the solute and solvent are of the same order of molecular dimensions. However, in solutions usually studied by GLC the solvent is much larger than the solutes and the athermal effect is the predominant one. Such is not the case here. Also by comparing the values in Table I and Table VII, already reasonable agreement is obtained for the 2 pentanone and 2,3,4 trimethylpentane binary systems. This does indicate that dispersion forces are a predominant effect. However, for the water binary systems the predicted values deviate widely from the experimental data. This is due primarily to hydrogen bonding, about which more will be said later.

At an early point workers began to realize that in solutions in which the solute or solvent possessed a sizeable dipole moment the Hildebrand formulation was inadequate. In addition to dispersion forces, orientation forces also existed. Van Arkel(116) appears to be the first to propose a modification of Equation (91) to account for this interaction. Based on the form of this relation he proposed

$$\ln \gamma_2^{th} = \frac{V_2}{RT}\left[(\delta_1 - \delta_2)^2 + (\omega_1 - \omega_2)^2\right]\Phi_1^2 \qquad (92)$$

The additional term was to account for the dipole-dipole interactions. The improvement gained by utilization of this relation may be seen in Table VIII. Here the first column for each solvent is the magnitude of the added term while the second and third column represents the entire equation for $\ln\gamma_2^{th}$ including all the terms.

By comparison of Table VII and Table VIII the effect of dispersion forces and orientation forces as empirically formulated by Hildebrand's techniques may be ascertained. Generally for water binary systems the orientation forces are about 60% of the dispersion forces, while for 2 pentanone binary systems the orientation effect is usually twice as large as the dispersion forces. The results for the 2,3,4 trimethylpentane binary systems are quite variable but the orientation forces always make a sizeable contribution to the activity coefficient. Utilizing Van Arkel's modification greatly improves the predicted deviation from ideality when compared with the experimental results for 2 pentanone and 2,3,4 trimethylpentane systems with the exception of the alcohol solutes. The values for the water systems, however, become even larger. This further exemplifies the importance of hydrogen bonding and the inability of this technique to account for specific interactions. Also it should be noted that in the present modification it is still impossible to predict a negative deviation from ideality. This will be the topic of the following discussion.

Martire(73) in an attempt to account for weak specific interactions proposed a modification of Hildebrand's work which

TABLE VIII

THERMAL CONTRIBUTION TO NONIDEALITY USING VAN ARKEL'S FORMULATION FOR VARIOUS SOLUTES IN WATER, 2 PENTANONE AND 2,3,4 TMP

Solute	Water			2 Pentanone			2,3,4 TMP		
	$(\omega_1-\omega_2)^2$	$\ln \gamma_2^{th}$	γ_2^{th}	$(\omega_1-\omega_2)^2$	$\ln \gamma_2^{th}$	γ_2^{th}	$(\omega_1-\omega_2)^2$	$\ln \gamma_2^{th}$	γ_2^{th}
C_5H_{12}	45.6	56.8	$5x10^{24}$	5.97	1.58	4.86	0.00	0.02	1.02
C_6H_{14}	34.3	61.2	$4x10^{26}$	4.82	1.49	4.44	0.00	0.02	1.02
C_7H_{16}	26.0	66.2	$1x10^{29}$	4.36	1.56	4.76	0.00	0.02	1.02
CH_2Cl_2	90.3	27.3	$7x10^{11}$	4.85	0.70	2.02	2.53	1.30	3.67
$CHCl_3$	48.2	31.3	$4x10^{13}$	5.56	0.82	2.27	1.22	0.88	2.41
CCl_4	45.6	40.7	$5x10^{17}$	6.32	1.03	2.80	0.00	0.41	1.51
MeFo	51.8	21.6	$3x10^{9}$	4.63	0.78	2.18	3.34	1.54	4.67
EtFo	29.9	28.4	$2x10^{12}$	3.06	0.52	1.69	3.15	1.27	3.56
PrFo	25.2	36.6	$8x10^{15}$	3.12	0.79	2.21	2.21	0.96	2.61
CH_3CHO	8.58	16.1	$1x10^{7}$	3.87	0.57	1.77	8.12	1.74	5.70
C_2H_5CHO	3.57	21.7	$3x10^{9}$	0.52	0.18	1.20	5.69	1.58	4.86
C_3H_7CHO	5.78	28.9	$4x10^{12}$	0.08	0.05	1.05	4.31	1.37	3.94
EtAm	64.2	24.9	$6x10^{10}$	6.72	0.90	2.46	1.70	1.14	3.16
PrAm	49.0	32.5	$1x10^{14}$	5.69	0.84	2.32	1.18	0.90	2.98
BuAm	37.4	39.4	$1x10^{17}$	5.03	0.84	2.32	0.89	0.69	2.00
MeOH	66.3	9.7	$2x10^{4}$	11.0	2.89	18.0	5.14	3.99	54.1
EtOH	52.2	15.4	$5x10^{6}$	9.04	2.48	11.9	3.31	3.53	34.1
PrOH	44.3	21.9	$3x10^{9}$	9.19	2.16	8.7	2.36	2.85	17.3

allowed for negative deviations from ideality. The formulation, however, involves an empirical constant which must be determined from independent experimental data. It is only dependent on the solvent and therefore once determined for a given solvent, say 2 pentanone, it is applicable for any solute. In actuality although only one experimental data point was needed to evaluate the constant, as it is still empirical in nature a mean constant was determined by averaging the best constants for each solute in a given solvent. The results of this technique are tabulated in Table IX. Again the first column for each solvent represents the value of J, the empirical constant as defined by Equations (94) through (96), while the second and third columns represent the entire value of $\ln\gamma_2^{th}$ as obtained from

$$\ln \gamma_2^{th} = \frac{v_2}{RT}\left[(\delta_1 - \delta_2)^2 + (\omega_1 - \omega_2)^2 - J\right] \Phi_1^2 \qquad (93)$$

From the values listed in Table IX for J three definite conclusions can be reached. For the water systems no single correlational constant will suffice to represent the data. This is due to the strong hydrogen bonding role dominating the solution behavior. As the J value is negative for the 2 pentanone systems this indicates that in actuality the systems deviate more positively from ideality than the dispersion and orientation forces alone would predict. Finally, for the 2,3,4 trimethylpentane systems since no

TABLE IX

THERMAL CONTRIBUTION TO NONIDEALITY USING MARTIRE'S FORMULATION FOR VARIOUS SOLUTES IN WATER, 2 PENTANONE AND 2,3,4 TMP

	Water			2 Pentanone			2,3,4 TMP		
Solute	J	ln γ_2^{th}	γ_2^{th}	J	ln γ_2^{th}	γ_2^{th}	J	ln γ_2^{th}	γ_2^{th}
C_5H_{12}	326	- 7.3	$7x10^{-4}$	-.84	1.72	5.59	0	0.02	1.02
C_6H_{14}	367	-19.6	$3x10^{-9}$	-.45	1.70	5.47	0	0.02	1.02
C_7H_{16}	411	-35.1	$6x10^{-16}$	-.99	1.79	6.00	0	0.02	1.02
CH_2Cl_2	128	13.5	$8x10^5$	-.33	0.77	2.16	0	1.30	3.67
$CHCl_3$	175	7.9	$3x10^3$	-.45	0.86	2.36	0	0.88	2.41
CCl_4	229	3.5	$3x10^1$	-.59	1.13	3.10	0	0.41	1.51
MeFo	118	9.3	$1x10^4$	-.31	0.81	2.25	0	1.54	4.67
EtFo	171	5.3	$2x10^2$	-.44	0.56	1.76	0	1.27	3.56
PrFo	223	- 0.31	$7x10^{-1}$	-.58	0.62	1.86	0	0.96	2.61
CH_3CHO	111	5.6	$3x10^2$	-.29	0.60	1.83	0	1.74	5.70
C_2H_5CHO	149	3.5	$3x10^1$	-.39	0.23	1.26	0	1.58	4.86
C_3H_7CHO	194	- 0.08	$9x10^{-1}$	-.50	0.12	1.13	0	1.37	3.94
EtAm	130	10.9	$5x10^4$	-.34	0.94	2.56	0	1.15	3.16
PrAm	179	7.7	$2x10^3$	-.46	0.90	2.46	0	0.90	2.98
BuAm	229	1.2	$3x10^0$	-.59	0.94	2.56	0	0.69	2.00
MeOH	56	5.7	$3x10^2$	-.15	2.90	18.2	0	3.99	54.1
EtOH	91	6.4	$6x10^2$	-.24	2.49	18.2	0	3.53	34.1
PrOH	130	5.6	$3x10^2$	-.34	2.19	8.9	0	2.85	17.3

specific interactions between solute and solvent are anticipated, J is set at zero. The effect of J for the water systems has been to normalize the data about an activity coefficient of unity, but the spread in the values remains equally as great as in the previous tabulations. The 2,3,4 trimethylpentane systems remain unchanged from Van Arkel's treatment as J is zero. On the other hand, the 2 pentanone systems are predicted more closely to the actual experimental results than in the other modifications of Hildebrand. Nevertheless, this technique is limited by the fact that an empirical constant has been introduced which must be evaluated with at least one independent data point. In an attempt to remove the empiricism of the above correlation and yet maintain the possibility of predicting negative deviations from ideality, recourse will now be made to the theory of intermolecular forces. In the theoretical development, expressions were derived relating dispersion, orientation, and induction forces to the polarizabilities, dipole moments, ionization potentials and intermolecular separation of the solute and solvent. These expressions were then combined by analogy to the generalized form of Hildebrand's equation to yield

$$\ln \gamma_2^{th} = \frac{V_2}{RT}\left(Z_{11} + Z_{22} - 2Z_{12}\right)\phi_1^2 \qquad (106)$$

where Z_{11} , Z_{22} and Z_{12} are as defined in Equation (108). As Z_{12} is not the geometric mean of Z_{11} and Z_{22} , the activity coefficient determined from Equation (106) may be less than unity. The values predicted by this technique based on intermolecular forces are given in Table X. Arithmetic mean values are used to compute σ_{12} and v_{12}.

From a comparison between Table I, Table IX and Table X it can be seen that the values for the activity coefficients predicted from the theory of intermolecular forces are in poor agreement with the experimentally determined values and therefore do not compare well with Martire's formulation either. As the relation between the activity coefficient and the intermolecular forces was formulated by analogy to Hildebrand's expression and both methods are considering dispersion, orientation, and induction forces, this lack of agreement at first seems strange. This anomaly, however, disappears after further considerations illustrate the two methods not to be so congruent. From a comparison of Equations (104) through (109) it can be shown that not only does Hildebrand use the geometric mean values for Z_{12} but also for σ_{12} and v_{12}. As the more common arithemetic mean was used in compiling Table X, the only way to remove the differences between Table IX and Table X would be to equate the two averaging techniques. This implies that $\sigma_{11} = \sigma_{22}$ and $v_{11} = v_{22}$. However, these conditions are not even closely met in the binary systems studied in this work. Therefore the two techniques, Hildebrand's modification and the theory of intermolecular forces, should not be anticipated to produce essentially similar results.

TABLE X

THERMAL CONTRIBUTION TO NONIDEALITY USING THE THEORY OF INTERMOLECULAR FORCES FOR VARIOUS SOLUTES IN WATER, 2 PENTANONE AND 2,3,4 TMP

		Water Z_{11} = 605			2 Pentanone Z_{11} = 9.44			2,3,4 TMP Z_{11} = 3.96		
Solute	Z_{22}	Z_{12}	$\ln\gamma_2{}^{th}$	$\gamma_2{}^{th}$	Z_{12}	$\ln\gamma_2{}^{th}$	$\gamma_2{}^{th}$	Z_{12}	$\ln\gamma_2{}^{th}$	$\gamma_2{}^{th}$
C_5H_{12}	6.13	16.74	113	$2x10^{49}$	5.59	0.86	2.36	4.82	0.09	1.09
C_6H_{14}	5.22	13.59	129	$1x10^{55}$	5.48	0.82	2.27	4.54	0.02	1.02
C_7H_{16}	4.58	10.74	146	$3x10^{64}$	4.77	1.11	3.04	4.27	0.00	1.00
CH_2Cl_2	14.96	54.60	54.9	$8x10^{23}$	10.25	0.42	1.53	6.38	0.66	1.94
$CHCl_3$	11.37	34.49	73.8	$1x10^{32}$	9.02	0.37	1.45	6.14	0.41	1.51
CCl_4	9.89	19.56	93.9	$6x10^{40}$	7.41	0.74	2.10	6.03	0.29	1.34
MeFo	16.16	68.76	50.1	$6x10^{21}$	12.45	0.07	1.07	5.96	0.85	2.34
EtFo	12.47	55.09	68.8	$1x10^{30}$	10.49	0.13	1.14	5.73	0.67	1.96
PrFo	9.02	31.95	91.0	$4x10^{39}$	8.84	0.13	1.14	5.32	0.39	1.48
CH_3CHO	35.92	121.8	37.8	$3x10^{16}$	16.51	1.17	3.23	5.36	2.77	16.0
C_2H_5CHO	17.85	47.57	64.2	$1x10^{28}$	12.60	0.25	1.29	5.23	1.38	3.98
C_3H_7CHO	12.16	31.76	82.6	$9x10^{35}$	10.68	0.04	1.04	5.02	0.91	2.49
EtAm	13.87	45.34	57.1	$8x10^{24}$	10.15	0.01	1.01	6.31	0.56	1.76
PrAm	10.11	32.55	76.4	$2x10^{33}$	8.64	0.32	1.38	5.80	0.34	1.41
BuAm	6.06	24.00	94.1	$1x10^{41}$	7.83	0.00	1.00	5.57	-.19	0.83
MeOH	23.92	94.58	30.0	$1x10^{13}$	13.46	0.44	1.56	5.71	1.12	3.07
EtOH	15.97	68.66	47.8	$6x10^{20}$	11.62	0.21	1.24	5.94	0.79	2.21
PrOH	11.52	43.18	67.0	$2x10^{29}$	9.61	0.22	1.25	4.68	0.77	2.16

In addition, in determining the dispersion forces which are generally the dominant solute-solvent interaction, the use of Equation (99) was made. As was pointed out in the theoretical development this relation may be in error by a factor of two or three, holding only for molecules with closed sp shells. In an attempt to cope with this problem Finch and Van Winkle(30) have introduced a structural constant into Equation (109) to gain equivalence. An analysis of the present systems under study also indicates the need for such a constant. However, as the determination of this parameter is purely empirical and the effect of this empiricism would only reduce the method to an equivalent position with that of the previous technique, no such constant will be introduced. It is doubtful even with the introduction of this constant if the values in Table X could be made to approach the experimental data as well as the results presented in Table IX due to the other factors brought out in the above discussion.

At this point three general results have become clear. Due to hydrogen bonding the predictive techniques based on physical forces alone seem to fail when applied to the water binary systems. The modification proposed by Van Arkel seems to fit the data for the 2,3,4 trimethylpentane systems as well as any other correlational technique. From an inspection of Martire's method for the 2 pentanone systems it is clear that as J is a negative value the dispersion and orientation forces alone are insufficient to accurately represent the experimental facts. With these results in mind a final modification will be proposed which conbines the advantageous features of the previous techniques. As induction forces, although generally negligible, can sometimes be important, Van Arkel's relation will be modified to include this effect. As a geometric mean representation is clearly insufficient for these forces, the form derived in the theory of intermolecular forces will be used, employing geometric mean values for v_{12} and σ_{12} to insure overall consistency. The resulting expression is

$$\ln \gamma_2^{th} = \frac{v_2}{RT}\left[(\delta_1-\delta_2)^2+(\omega_1-\omega_2)^2+\mathrm{I.T.}\right]\phi_1^2 \qquad (110)$$

where I.T. is defined by Equation (111). In Equation (110) no empirical constants are employed and providing the induction forces are the deciding factor in solution behavior, even negative deviations from ideality are possible. This formulation represents a very generalized variation of Hildebrand's technique incorporating molecular interactions. As this method should provide the optimum correlational technique the full results are presented for all three solvents in Table XI.

Comparing the values of γ_2^{th} in Table IX and Table XI it can be seen that the results obtained from Equation (110) are in each case at least as good and in most instances much better than those predicted by Martire's method. Therefore the former method is to be preferred as the predictive technique is based solely on theoretical development and necessitates no empirical parameters. Again, however,

TABLE XI

THEORETICAL DETERMINATION OF INFINITELY DILUTE ACTIVITY COEFFICIENTS FOR VARIOUS SOLUTES IN WATER, 2 PENTANONE AND 2,3,4 TMP

				Water				
Solute	$(\delta_1-\delta_2)^2$	$(\omega_1-\omega_2)^2$	I.T.	$\ln \gamma_2^{th}$	γ_2^{th}	$\ln \gamma_2^{ath}$	γ_2^{∞}	γ_2^{∞}(xptl.)
C_5H_{12}	243	45.6	18.4	58.1	$2x10^{26}$	-3.19	$7x10^{24}$	871
C_6H_{14}	243	34.3	19.3	65.7	$4x10^{28}$	-3.81	$7x10^{26}$	2582
C_7H_{16}	243	26.0	19.8	71.3	$1x10^{31}$	-4.48	$1x10^{29}$	7105
CH_2Cl_2	164	90.3	15.0	28.8	$3x10^{12}$	-1.10	$1x10^{12}$	205
$CHCl_3$	185	48.2	16.1	33.6	$4x10^{14}$	-1.17	$7x10^{13}$	570
CCl_4	205	45.6	17.0	43.4	$8x10^{18}$	-2.38	$7x10^{17}$	2510
MeFo	156	51.8	14.4	23.0	$1x10^{10}$	-1.04	$4x10^{9}$	17.0
EtFo	180	29.9	17.3	30.6	$2x10^{13}$	-1.71	$4x10^{12}$	49
PrFo	196	25.2	17.3	39.1	$1x10^{17}$	-2.43	$1x10^{16}$	159
CH_3CHO	161	8.58	13.8	17.7	$5x10^{7}$	-0.85	$2x10^{7}$	4.0
C_2H_5CHO	174	3.57	15.6	23.7	$2x10^{10}$	-1.42	$4x10^{9}$	16.1
C_3H_7CHO	188	5.78	16.7	31.3	$4x10^{13}$	-2.05	$5x10^{12}$	68
EtAm	166	64.2	14.4	26.5	$3x10^{11}$	-1.13	$1x10^{11}$	0.5
PrAm	185	49.0	15.8	34.5	$1x10^{15}$	-1.80	$2x10^{14}$	2.6
BuAm	199	37.4	16.7	42.1	$2x10^{18}$	-2.46	$2x10^{17}$	4.4
MeOH	74	66.3	13.5	10.6	$4x10^{4}$	-0.38	$3x10^{4}$	2.6
EtOH	104	52.2	14.7	16.8	$2x10^{7}$	-0.95	$8x10^{6}$	6.3
PrOH	130	44.3	16.1	24.2	$3x10^{10}$	-1.53	$6x10^{9}$	25

TABLE XI (CONT'D)

2 Pentanone

Solute	$(\delta_1-\delta_2)^2$	$(\omega_1-\omega_2)^2$	I.T.	$\ln \gamma_2^{th}$	γ_2^{th}	$\ln \gamma_2^{ath}$	γ_2^{∞}	γ_2^{∞}(xptl.)
C_5H_{12}	1.96	5.97	-0.06	1.54	4.66	-0.01	4.6	4.6
C_6H_{14}	1.96	4.82	0.00	1.49	4.44	-0.02	4.4	5.6
C_7H_{16}	1.96	4.36	0.03	1.56	4.76	-0.05	4.6	6.9
CH_2Cl_2	1.96	4.85	-0.17	0.71	2.04	-0.11	1.8	1.1
$CHCl_3$	0.36	5.56	-0.17	0.77	2.16	-0.05	2.1	1.2
CCl_4	0.01	6.32	-0.20	1.00	2.72	-0.01	2.7	3.2
MeFo	2.89	4.63	-0.12	0.77	2.16	-0.14	1.9	2.3
EtFo	0.64	3.06	0.12	0.52	1.69	-0.04	1.6	2.3
PrFo	0.04	3.12	0.06	0.53	1.70	-0.01	1.7	3.5
CH_3CHO	2.25	3.87	0.20	0.60	1.83	-0.17	1.5	1.9
C_2H_5CHO	1.00	0.52	0.03	0.19	1.21	-0.07	1.1	2.1
C_3H_7CHO	0.25	0.08	0.06	0.06	1.06	-0.01	1.1	3.3
EtAm	1.69	6.72	-0.14	0.89	2.44	-0.10	2.2	0.5
PrAm	0.36	5.69	-0.20	0.81	2.25	-0.03	2.2	2.6
BuAm	0.01	5.03	-0.09	0.83	2.30	-0.01	2.3	4.3
MeOH	31.4	11.0	0.09	2.90	18.2	-0.33	13.1	4.8
EtOH	16.0	9.04	-0.09	2.46	11.8	-0.14	10.2	5.4
PrOH	7.8	9.19	0.06	2.16	8.7	-0.06	8.2	5.9

TABLE XI (CONT'D)

Solute	$(\delta_1-\delta_2)^2$	$(\omega_1-\omega_2)^2$	I.T.	$\ln \gamma_2^{th}$	γ_2^{th}	$\ln \gamma_2^{ath}$	γ_2^{∞}	γ_2^{∞}(xptl.)
				2,3,4 Trimethylpentane				
C_5H_{12}	0.09	0.00	0.00	0.02	1.02	-0.06	1.0	1.0
C_6H_{14}	0.09	0.00	0.00	0.02	1.02	-0.02	1.0	1.1
C_7H_{16}	0.09	0.00	0.00	0.02	1.02	-0.01	1.0	1.0
CH_2Cl_2	9.61	2.53	0.17	1.32	3.75	-0.33	2.7	2.1
$CHCl_3$	5.29	1.20	0.09	0.89	2.44	-0.21	2.0	1.5
CCl_4	2.56	0.00	0.00	0.42	1.52	-0.13	1.3	6.0
MeFo	11.6	3.34	0.20	1.56	4.76	-0.34	3.4	5.3
EtFo	6.25	3.15	0.37	1.32	3.75	-0.21	3.0	3.5
PrFo	3.61	2.21	0.23	1.00	2.72	-0.13	2.4	2.9
CH_3CHO	10.2	8.12	0.55	1.80	6.05	-0.40	4.1	5.1
C_2H_5CHO	7.29	5.69	0.26	1.61	5.01	-0 26	3.9	4.0
C_3H_7CHO	4.84	4.31	0.20	1.39	4.02	-0.16	3.4	3.8
EtAm	9.00	1.70	0.29	1.19	3.29	-0.32	2.4	2.0
PrAm	5.29	1.18	0.12	0.92	2.51	-0.18	2.1	2.2
BuAm	3.24	0.89	0.14	0.71	2.04	-0.11	1.8	1.6
MeOH	53.3	5.14	0.52	4.02	55.8	-0.62	30.0	39.6
EtOH	32.5	3.31	0.26	3.56	35.2	-0.36	24.6	25.3
PrOH	20.3	2.36	0.20	2.88	17.9	-0.22	14.3	17.9

the predicted values for the activity coefficients in the water systems are grossly in error due to the hydrogen bonding effect. Thus one conclusion to be drawn from this development is the inability of the technique to properly account for strong specific interactions. For the 2 pentanone and 2,3,4 trimethylpentane systems the agreement between predicted and experimental activity coefficients is quite good, considering that the only parameters used in predicting the deviations from ideality are the physical properties of the pure components. Utilizing Equation (70) the optimum thermal and athermal contributions are combined and also tabulated in Table XI. The predicted values for the 2,3,4 trimethylpentane systems concur with the experimental results within an average deviation of 18% while the discrepancy between predicted and experimental values for the 2 pentanone systems is 39%. This discrepancy is larger than that in the 2,3,4 trimethylpentane systems due to the hydrogen bonding effect between many of the solutes and 2 pentanone.

D. Specific Interactions

In the above development it became rather obvious that in systems which exhibited hydrogen bonding interactions the theory based only on physical forces was unable to properly predict the deviations from ideality. This is clearly pointed up for the water systems in Table XI and to a lesser extent for the amines and alcohols in 2 pentanone. The present state of understanding concerning hydrogen bonding allows a very adequate qualitative description of the problem but unfortunately no quantitative analysis has been successful as yet. The problem existing is two-fold, one half of which has been solved. In order to be able to quantitatively evaluate hydrogen bonding effects one must know the strength of the bond involved and the number of bonds formed or broken. The strength of a hydrogen bond, in actuality the energy of formation or dissociation, has been determined by various techniques. Lambert (59) studied association in pure components and binary mixtures by determining the virial coefficients in the vapor state. Assuming an equilibrium between the associated and dissociated states, he computed enthalpies and entropies of bond formations in various polar substances. Becker(11) has used spectroscopic techniques to study polar solutes in nonpolar solvents and determined enthalpies of bond formation from shifts in known spectroscopic lines due to changes in vibrational and rotational frequencies between the associated and unassociated species. Problems, however, exist with both of these techniques. One is not sure if the actual species of interest is the species measured in the vapor state. Also, the effect of the nonpolar solvent in spectroscopic studies is unclear. Suffice to say that the energies of bond formation for both pure component self association and solute-solvent association can be determined. Pimentel and McClellan(83) provide a large compilation of these bond energies.

The second part of the quantitative problem is as yet unsolved. The prediction of the number of bonds formed or broken represents a sizeable task. When two self associating components are mixed there are two types of hydrogen bonds being broken and at least a third type being formed. The extent to which bonds are broken and formed depends on the new environment the solution creates for both components as well as the degree of association existing in the pure liquids prior to mixing. Paraskevopoulos and Missen(78) while studying alcohols in CCl_4, benzene and hexane noted that the partial molar excess enthalpies and entropies of the alcohols were independent of the hydrocarbon chain length in the alcohols and only dependent on the choice of solvent. They studied methanol through octanol. They attributed the positive excess properties to the breaking of hydrogen bonds of the alcohol as the solution was formed. This effect should be predominant as any solute-solvent bonds formed utilizing these particular solvents would be of a weaker nature. Benjamin and Benson(13) in an investigation of the methanol-water system obtained negative values for ΔH_2^E and ΔS_2^E. This was due to the formation of hydrogen bonds between the methanol and water which were of a stronger nature than those existing in either pure liquid. Although the formal number of hydrogen bonds present must necessarily be reduced when mixing water and molecules with inert hydrocarbon groups, these workers postulated that the mean number of bonds may actually increase due to stabilization of aggregates around the hydrocarbon group. This work was done at higher solute mole fractions and is thus not directly applicable to the present study. The point to be made here is that for a given binary solution in which hydrogen bonding is anticipated to be a major interaction, it is not always clear whether bonds are formed or broken let alone the number of bonds involved which are being formed or broken.

Even though the above dilemma exists quantitatively, much can be said concerning hydrogen bonding in a qualitative sense. Prausnitz and Blanks(91) have summed up the above development in the following general rules. For solutes exhibiting self association, as a non-self associating solvent is added hydrogen bonds are broken and a positive partial excess enthalpy results. If the solute is not self associating then as the solvent is added hydrogen bonds are formed and the partial excess enthalpy is less than zero, indicating evolution of energy. Consequently from the net value of ΔH_2^E one may determine whether hydrogen bond breaking or formation is predominant, as was done in the discussion of the results.

As mentioned previously, solution behavior due to hydrogen bonding cannot be predicted solely on the basis of bond strengths. Moelwyn-Hughes and Thorpe(77) in a study of hydrogen bonding found that although N-H ... O bonds are weaker than N-H ... N bonds in association, both types formed endothermic solutions. Also, although oxygen is more electronegative than nitrogen, tetrahydropyran mixed endothermally with piperidine. Therefore the nature of hydrogen bonding is not simply predictable and is dependent on other factors besides bond strengths and electronegativity. The local polarizability of lone pair orbitals appears to be an important factor. Also, hydrogen bonding requires a more precise orientation of the molecules involved than that needed for dipole-dipole interactions.

The reasoning put forward in the above discussion can only qualitatively explain the behavior of the water binary systems. In order to bring the predicted deviations as shown in Table XI into closer agreement with the experimental results it would be necessary to postulate the breaking of a number of hydrogen bonds in most cases. For very dilute solutions, the solute is essentially surrounded only by solvent molecules and so any self association would undoubtedly be reduced freeing the solute and solvent molecules within the solution environment. As in the majority of the binaries formed only water is self associating, the effect would not be so pronounced as there are few solute molecules. However, qualitatively it would appear that consideration of hydrogen bonding should reduce the predicted values into a closer accord with the experimental facts. Unfortunately, except for this qualitative reasoning no further analysis of the water systems can be made. Thus it appears that the initial correlation utilizing the empirical homologous series approach is the best method of representing the experimental water systems data of this work. Although empirical in nature it is felt that the technique, based on the group interaction theory of Pierotti, is justified and in fact very adequately correlates the water systems data. For systems in which specific interactions are not expected to play a major role, the theory based on physical forces is to be preferred.

E. Statistical Mechanical Analysis

Utilizing the principles of statistical mechanics as applied to a binary solution in which the components are of different molecular sizes, the following relations were derived in the theoretical development for the solute at infinite dilution

$$\ln \gamma_2^{\infty} = \ln \frac{V_2^{\circ}}{V_1^{\circ}} + \left(1 - \frac{V_2^{\circ}}{V_1^{\circ}}\right) + \left(\frac{V_2^{\circ}}{V_1^{\circ}}\right)^{1/2} \frac{\Delta W}{RT} \qquad (135)$$

$$\Delta H_2^E = \left(\frac{V_2^{\circ}}{V_1^{\circ}}\right)^{1/2} \left[\Delta W - \frac{T}{2}(\beta_2 - \beta_1)\Delta W - T\frac{d\Delta W}{dT}\right] - RT^2\left(1 - \frac{V_2^{\circ}}{V_1^{\circ}}\right)(\beta_2 - \beta_1) \qquad (138)$$

and

$$\Delta S_2^E = -R\left[\ln \frac{V_2^{\circ}}{V_1^{\circ}} + \left(1 - \frac{V_2^{\circ}}{V_1^{\circ}}\right)\right] - RT\left(1 - \frac{V_2^{\circ}}{V_1^{\circ}}\right)(\beta_2 - \beta_1) - \left(\frac{V_2^{\circ}}{V_1^{\circ}}\right)^{1/2}\left[\frac{1}{2}(\beta_2 - \beta_1)\Delta W + \frac{d\Delta W}{dT}\right] \qquad (139)$$

However, as was also pointed out at that time, in order to test the validity of the underlying assumptions made to simplify the mathematical treatment, independent vapor-liquid equilibrium data and calorimetric data should be used. As no independent calorimetric data is available for most of the systems studied in this work, instead an evaluation of the contributions of the various factors to the thermodynamic properties, as indicated in the above relations, will be made. From this result qualitative conclusions regarding solution behavior can be drawn.

1. Geometric Effects

The procedure to be followed in this analysis is to use both the activity coefficient and the partial molar excess enthalpy from the experimental results in conjunction with the above three relations to determine three unknowns. The three unknowns in this case are the interaction energy Δw, its temperature dependence, and the partial molar excess entropy, ΔS_2^E. Let us define three terms as follows

$$C_9 \equiv R\left[\ln \frac{V_2^\circ}{V_1^\circ} + \left(1 - \frac{V_2^\circ}{V_1^\circ}\right)\right] \tag{146}$$

$$C_{10} \equiv RT(\beta_2 - \beta_1)\left(1 - \frac{V_2^\circ}{V_1^\circ}\right) \tag{147}$$

and

$$C_{11} \equiv \left(\frac{V_2^\circ}{V_1^\circ}\right)^{1/2}\left[\frac{1}{2}(\beta_2 - \beta_1)\Delta w + \frac{d\Delta w}{dT}\right] \tag{148}$$

From a comparison of Equations (146), (147), (148) and Equation (139) it can be seen that ΔS_2^E may be expressed as

$$\begin{aligned} \Delta S_2^E &= -(C_9 + C_{10}) - C_{11} \\ &= (\Delta S_2^E)_G + (\Delta S_2^E)_E \end{aligned} \tag{149}$$

where C_9 and C_{10} are functions of molar volumes and cubical coefficients of expansion only and C_{11} is dependent on the interaction energy as well. Thus a clear distinction may be made of the contributions to the partial molar excess entropy by geometric effects and energetric effects. From Equation (135) and the values of the activity coefficient given in Table I, the interaction energy is computed. Then utilizing the data of Table III together with Equation (138) the temperature dependence of the interaction energy is determined. Finally C_9 , C_{10} and C_{11} can be calculated. As this section is concerned only with the geometric effect, i.e., C_9 and C_{10} , the magnitude of these terms as well as the partial molar excess entropy, assuming the interaction energy to be zero, are given in Table XII. Again due to a limited knowledge of the physical properties, all values are for 25°C.

An inspection of Table XII reveals a number of interesting facts. The C_9T term is negative for all binary systems. As this term is a function of the molar volumes of the solute and solvent alone, it is analogous to the athermal contribution to the deviation from ideality discussed in the earlier correlations. The two terms are both always negative yielding a positive contribution to the partial molar excess entropy. This result is in accord with the theoretical development of the two methods. The magnitude of both the C_9T and $C_{10}T$ terms for the water systems is quite large. This is due to the small molar volume and cubical coefficient of expansion of water. Thus the geometric effect for the water systems

TABLE XII

GEOMETRIC CONTRIBUTION TO THE PARTIAL MOLAR EXCESS ENTROPY FOR VARIOUS SOLUTES IN WATER, 2 PENTANONE AND 2,3,4 TMP

	Water			2 Pentanone			2,3,4 TMP		
Solute	C_9T	$C_{10}T$	$(T\Delta S_2^E)_G$	C_9T	$C_{10}T$	$(T\Delta S_2^E)_G$	C_9T	$C_{10}T$	$(T\Delta S_2^E)_G$
C_5H_{12}	-2125	-1393	3518	-2	-7	9	-34	21	13
C_6H_{14}	-2527	-1389	3916	-14	-11	25	-15	7	8
C_7H_{16}	-2980	-1472	4452	-34	-12	46	-4	2	2
CH_2Cl_2	-752	-530	1282	-66	14	52	-196	14	182
$CHCl_3$	-1148	-642	1790	-23	3	20	-126	0	126
CCl_4	-1587	-775	2362	-3	0	3	-74	-4	78
MeFo	-699	-572	1271	-74	27	47	-215	32	183
EtFo	-1160	-736	1896	-20	9	11	-120	11	109
PrFo	-1622	-828	2450	-2	1	1	-70	0	70
CH_3CHO	-580	-572	1152	-98	45	53	-248	55	193
C_2H_5CHO	-953	-650	1603	-39	14	25	-154	17	137
C_3H_7CHO	-1368	-763	2131	-10	4	6	-98	4	94
EtAm	-758	-727	1485	-66	45	21	-196	60	136
PrAm	-1214	-793	2007	-19	11	8	-114	18	96
BuAm	-1652	-918	2570	-2	2	0	-66	8	58
MeOH	-255	-229	484	-206	7	199	-395	-1	396
EtOH	-628	-343	971	-88	-10	98	-237	-22	259
PrOH	-1024	-417	1441	-34	-13	47	-147	-30	177

will play a major role in the overall excess entropy of the solute. On the other hand, the molar volumes and expansion coefficients of the other solvents are quite similar to the majority of the solutes studied and therefore the C_9T and $C_{10}T$ terms are quite small, often partially canceling each other. Thus it is anticipated that the geometric effect in these binary systems on ΔS_2^E will be of much smaller magnitude.

2. Energetic Effects

From the above development the energetic term has been defined as C_{11}. In actuality this term represents a conglomeration of all the effects, as it is a function of the molar volume ratio and the difference in expansion coefficients as well as the interaction energy and its temperature derivative. Nevertheless, as no method exists to completely isolate the energetic term, C_{11} will be taken as representative of this effect. In Table XIII, results are presented for the interaction energy and its temperature dependence as well as for $C_{11}T$, the energetic contribution to the partial molar excess entropy. Also included are values for $T\Delta S_2^E$, which is the algebraic sum of the two effects.

As anticipated from the results of Table XII, the energetic contribution to the excess entropy represents a major portion of the total. Even in the water binary systems the energetic contribution is larger than the geometric contribution. However, the two effects for these systems are approximately the same magnitude. In

TABLE XIII

ENERGETIC CONTRIBUTION TO THE PARTIAL MOLAR EXCESS ENTROPY FOR VARIOUS SOLUTES IN WATER, 2 PENTANONE AND 2,3,4 TMP

	Water				2 Pentanone				2,3,4 TMP			
Solute	Δw	$\frac{d\Delta w}{dT}$	$(T\Delta S_2^E)_E$	$T\Delta S_2^E$	Δw	$\frac{d\Delta w}{dT}$	$(T\Delta S_2^E)_E$	$T\Delta S_2^E$	Δw	$\frac{d\Delta w}{dT}$	$(T\Delta S_2^E)_E$	$T\Delta S_2^E$
C_5H_{12}	2415	-0.2	-1189	2329	871	3.0	-1004	-995	40	-0.7	170	183
C_6H_{14}	2657	0.8	-2020	1896	931	1.4	-501	-476	80	-0.1	16	24
C_7H_{16}	2888	2.0	-3117	1335	1006	-0.6	161	207	4	-2.1	575	577
CH_2Cl_2	2076	1.7	-1669	-387	158	-3.4	774	825	1017	2.1	-411	-229
$CHCl_3$	2325	3.4	-2965	-1175	150	-9.1	2348	2367	532	0.9	-185	-58
CCl_4	2692	0.2	-1061	1301	724	-10.2	2891	2894	1493	22.7	-5126	-5048
MeFo	1291	2.5	-1836	-565	746	-7.7	1702	1783	1972	1.4	-310	-127
EtFo	1639	4.5	-3427	-1531	590	-5.5	1419	1430	1231	5.2	-1106	-996
PrFo	1984	5.4	-4506	-2056	775	-3.2	900	901	909	3.1	-700	-631
CH_3CHO	792	3.4	-2083	-931	654	-7.5	1582	1635	2073	6.6	-1243	-1049
C_2H_5CHO	1301	5.9	-3963	-2360	580	-7.0	1699	1724	1478	5.3	-1073	-935
C_3H_7CHO	1749	6.3	-4762	-2631	779	-16.2	4378	4384	1216	0.7	-161	-68
EtAm	209	6.3	-3609	-2124	-445	0.2	-21	0	971	-4.8	846	982
PrAm	833	5.2	-3651	-1644	664	-3.2	819	827	819	5.4	-1156	-1059
BuAm	1082	4.2	-3341	-771	896	4.4	-1272	-1272	444	3.8	-882	-824
MeOH	552	-1.2	387	871	1836	4.4	-817	-617	5251	7.9	-1144	-748
EtOH	955	0.7	-578	393	1467	3.4	-733	-636	3643	-0.2	98	356
PrOH	1436	3.2	-2280	-839	1291	3.3	-769	-722	2769	2.1	-334	-157

the 2 pentanone systems the geometric effect is completely negligible. As the cubical expansion coefficient of 2 pentanone is nearly equal to that of the majority of the solutes, and the interaction energy for these systems is quite small by comparison to the other binary systems, the energetic contribution is in actuality composed primarily of the temperature derivative of the interaction energy. Thus for 2 pentanone systems the partial molar excess entropy is due mainly to the temperature dependence of the interaction energy. From Table XIII one may also deduce that the energetic effect is predominant in the 2,3,4 trimethylpentane systems. However, in these systems the interaction energy is generally quite large and so the energetic effect is evenly distributed among its components. It is interesting to note that for the alkanes in 2,3,4 trimethylpentane the interaction energy is extremely small implying quasi-ideal solutions. Many other deductions may be reached from an analysis of the results in Table XII and Table XIII and this will be the topic of the following discussion.

3. Solution Behavior Implications

The analysis of the binary systems studied by statistical mechanics can shed a good deal of light on the behavior of nonelectrolyte solutions. Wood(121) has shown on statistical mechanical grounds that the partial molar excess entropy may originate from three sources: (1) difference in molecular volumes of the components of the solution, (2) relative spatial distribution of the molecules about a given reference molecule, and (3) relative orientational distribution of the molecules about some reference molecule. The spatial distribution effect is the smallest of the three and is usually negligible. On the other hand the partial molar excess enthalpy is strongly dependent on this effect, receives some contribution from the orientational distribution of the molecules, and is completely independent of the first effect. The physical interpretation of the first effect is quite straightforward. The arrangement of molecules of different sizes is less uniform or more disorderly and so gives rise to a larger number of distinguishable configurational arrangements than would result with molecules of equal size. Thus it should always produce a positive partial molar excess entropy. Although this effect is discernible, it is still usually quite small as can be seen for the majority of the systems in Table XII. In many instances the thermal expansion effect actually tends toward compensation of the volume differences, nullifying the disorder resulting from a mixed population of molecules.

The orientational distribution of the molecules is the largest effect and accounts for 60 to 90% of the total excess entropy according to the results in Table XIII. The orientational effect may be postulated to be due to the degree of mobility which the solute gains or looses in going from the pure liquid to the solution. If the randomness of orientation becomes greater in the solution than in the pure liquid a positive excess entropy will result, and conversely a negative excess entropy indicates a loss in randomness of orientation in forming the solution. As in Table XIII for the water systems the energetic contribution to the excess entropy is negative, a gain in orientational order in the formation of the solution is indicated. This implies that pure solute and solvent hydrogen bonds are broken and new solute-solvent interactions are formed. Nonbonding solutes are also restrained in the three dimensional lattice formed by the self associated water. This restricts their mobility and increases the orientational order. In the other solvents the results of Table XIII indicate that generally a gain in randomness of orientation occurs from solution formation, implying breakage of any pure solute hydrogen bonding and also the lack of strong solute-solvent specific interactions. Thus the results obtained from a statistical mechanical analysis of the data can be seen to be very useful in explaining the behavior of the binary solutions studied in this work.

VII. SUMMARY AND CONCLUSIONS

The two-fold objective of this work was to determine the thermodynamic properties of infinitely dilute binary solutions, in which both components were appreciably volatile by means of gas-liquid chromatography, and to study the behavior of nonelectrolyte solutions with the desired goal of using the data obtained by the above method to formulate a predictive or correlative technique, applicable to a wide range of solutes and solvents, which was based on molecular interactions.

In order to achieve the first goal, GLC was first substantiated as a valid method for studying vapor-liquid equilibrium. This fact was established repeatedly in the literature review by a presentation of other studies utilizing GLC for the same general purpose and the resulting comparison with data obtained by static techniques. That the data obtained represents true equilibrium was further confirmed by a comparison between the results of this work and literature values obtained by conventional methods. For the binary systems for which this comparison could be made the results were very favorable. Finally in the appendix a discussion is provided which explains the concept of the dynamic equilibrium in a chromatographic column and how this type of equilibrium differs from the time invariant static equilibrium. It is thus felt that GLC has been more than adequately verified as a method for obtaining equilibrium thermodynamic properties of solutions.

To insure that the desired correlations would be valid for a wide range of solutes and solvents, a systematic classification scheme was used to aid in determining the systems to be studied in this work. The classification scheme, which is based on the theory of hydrogen bonding and intermolecular forces, groups liquids into five categories depending on their ability to contribute donor or acceptor atoms or both to a potential hydrogen bond. Utilizing this scheme and considering possible solute-solvent interactions, the solvents chosen for study were water, 2 pentanone, and 2,3,4 trimethylpentane. Homologous series of alkanes, chlorinated methanes, alkyl formates, aldehydes, amines, and alcohols were then studied in each of the three solvents. In order to determine other thermodynamic properties, the studies were conducted at 20°, 30° and 40°C. The upper temperature limit was set by the high volatility of the solvents and the added experimental difficulties which this caused. When studying two component volatile systems by GLC the upper temperature will be one of the limiting factors of the technique.

The experimental program consisted of modifying an existing chromatograph to meet the present needs, and then investigating the GLC operating parameters for a range of variables to insure that the results were independent of any effects except for temperature, pressure and concentration. Once it had been verified that the results were independent of these GLC parameters, the experimental data for all possible binary systems was obtained. Each run was repeated both on the same column and in a second independent column to guarantee the precision of the data. The overall accuracy of the data was ± 5% based on the mean values of these repetitive determinations.

Compilations are presented for the activity coefficient at infinite dilution, the excess partial molar free energy, the excess partial molar enthalpy and the excess partial molar entropy for all the solutions studied. Tha analysis of the data based on the earlier mentioned hydrogen bonding theory shows an excellent agreement between the experimental and the anticipated thermodynamic properties. The GLC variables are related to the thermodynamic solution properties by the following relations

$$\gamma_2^\infty = \frac{RT}{\bar{V}_R M p_2^\circ} \tag{24}$$

$$\Delta G_2^E = RT \ln \gamma_2^\infty \tag{28}$$

$$\Delta H_2^E = R \frac{d \ln \gamma_2^\infty}{d(1/T)} \tag{32}$$

and

$$\Delta S_2^E = \frac{\Delta H_2^E - \Delta G_2^E}{T} \tag{27}$$

An attempt was made to correct the activity coefficients for the gas phase nonideality by utilizing the expression

$$\ln \gamma_2^\infty = \ln \frac{RT}{\bar{V}_R M p_2^\circ} + \frac{\bar{P}}{RT}(2B_{12} - v_2^\circ) - \frac{p_2^\circ}{RT}(B_{22} - v_2^\circ) \tag{64}$$

However, as helium was used in this study as the carrier gas the correction for a worst possible binary system amounted to 2.4%. Since this correction was less than the overall accuracy of the data, no attempt was made to incorporate this factor in the results of the experimental work, as the effect is insignificant. When using other carrier gases or higher mean column pressures the effect does become significant and must be taken into account.

Utilizing the solution theory for nonelectrolytes, various correlational techniques were attempted to predict the experimental results. As early workers had noticed a linear relation within a homologous series between the partial molar excess free energy and the number of carbon atoms in a solute, this technique was tried with the present data. The results were quite satisfactory for the water and 2,3,4 trimethylpentane binary systems but the correlation failed for the 2 pentanone solutions. The reasons for the success or failure of this homologous series approach can be clearly understood by considering the possible group interactions on a molecular level as done by Pierotti. Applying his general technique but eliminating the inconsistencies, the data was used to obtain the constants in the following relation

$$\ln \gamma_2^{\infty} = C_3 + C_4 \frac{\ell_2}{\ell_1} + \frac{C_5}{\ell_2} + C_6 (\ell_2 - \ell_1)^2 + C_7 \frac{\ell_1}{\ell_2} + \frac{C_8}{\ell_1} \qquad (140)$$

for all the various solutes in the three solvents. This technique reproduces the data to ± 15%.

Alternately the activity coefficients at infinite dilution may be predicted from the theory of Hildebrand and its modifications. The activity coefficient may be expressed as

$$\ln \gamma_2^{\infty} = \ln \gamma_2^{ath} + \ln \gamma_2^{th} \qquad (70)$$

From Guggenheim's cell theory the athermal contribution is given by

$$\ln \gamma_2^{ath} = \ln \frac{1}{r} + 6 \ln \frac{6r}{5r+1} \qquad (78)$$

when $v_2^o > v_1^o$ and by

$$\ln \gamma_2^{ath} = \ln r + (5r+1) \ln \frac{5r+1}{6r} \qquad (84)$$

when $v_1^o > v_2^o$. In any instance γ_2^{ath} is always negative causing a positive excess entropy. Hildebrand's basic theory as well as early modifications, both theoretical and empirical, are considered for γ_2^{th}. However, each of these omit some phase of solute-solvent interaction and thus do not represent the experimental data well. The theory of intermolecular forces is employed, which avoids some of the earlier limitations, but does not coincide with the data established in this work. This is partially due to the lack of accurate characterization of the dispersion forces which are a dominant solute-solvent interaction. Therefore a modification of the above treatments is proposed which accounts for all the major physical interactions as follows

$$\ln \gamma_2^{th} = \frac{v_2}{RT}\left[(\delta_1-\delta_2)^2+(\omega_1-\omega_2)^2+I.T.\right]\Phi_1^2 \qquad (110)$$

where

$$I.T. \equiv \frac{2\alpha_1\mu_1^2}{\sigma_{11}^6\, v_{11}} + \frac{2\alpha_2\mu_2^2}{\sigma_{22}^6\, v_{22}} - \frac{2(\alpha_1\mu_2^2+\alpha_2\mu_1^2)}{\sigma_{12}^6\, v_{12}} \qquad (111)$$

and

$$\omega_i^2 \equiv \frac{2\mu_i^4}{3kT\sigma_{ii}^6\, v_{ii}} \qquad (104)$$

Equation (110) when used in conjunction with either Equation (78) or (84) predicts infinitely dilute activity coefficients which are within 18% of the experimental results for the 2,3,4 trimethylpentane systems and 39% for the 2 pentanone binary systems. This result is quite satisfactory considering that the technique utilizes only the physical properties of the pure components to predict binary solution properties.

The above technique predicts results which are in gross error for the water solutions. This is because of the failure of the theory to account for specific interactions such as hydrogen bonding which is so very prevalent in water systems. As the present state of hydrogen bonding theory is yet unable to provide a quantitative interpretation of the effect, the initial empirical homologous series correlation most adequately represents the experimental results for water solutions. This approach is justifiable based on molecular group interactions, and correlates the data quite well. Thus in synopsis, when strong specific interactions such as hydrogen bonding are absent the above method based primarily on intermolecular forces is to be preferred for predicting activity coefficients. It is better than empirical approaches as the entire relation is theoretically derived and depends only on pure component properties. No such generalized relations exist for solutions which exhibit strong interactions, but for the water binary systems the empirical homologous series correlation very adequately represents the data.

A statistical mechanical analysis of the data based on the lattice theory of liquids leads to the conclusion that the partial molar excess entropy is composed of two effects, the energetic contribution depending on the interaction energy between solute and solvent molecules, and the geometric contribution which depends on the molecular volumes and expansion coefficients of the solute and the solvent. Depending on the sign of the partial molar excess entropy, many conclusions may be drawn about the orientational distribution and mobility of the solute in the solution based on the above analysis. The contribution to ΔS_2^E from both of these effects, utilizing the data of this work to determine the interaction energy, is tabulated for the various systems. Generally the energetic effect is predominant as the molar volumes of the components studied in this work are quite similar, with the exception of water.

In conclusion then, based on the above findings, the technique of GLC has been justified as providing true vapor-liquid equilibrium. The predictive methods outlined herein may be used in GLC to determine the best solvent to separate a given solute mixture. The activity coefficients may be calculated for each solute-solvent pair and the relative volatility determined by

$$\psi_{AB} = \frac{\gamma_A^{\infty} P_A^{0}}{\gamma_B^{\infty} P_B^{0}} \tag{26}$$

The solvent providing the largest ψ_{AB} value for a given pair of solutes will yield the best resolution. Usually the best solvent for a given separation is one in which the solute solubilities increase with decreasing vapor pressures. Fortunately in GLC systems of common interest hydrogen bonding does not play the major role so this technique should be very useful in these instances. The GLC technique of establishing vapor-liquid equilibrium is also quite valuable for studying very dilute solutions and in this respect may supplement normal static equilibrium methods. In fact the ability to study very dilute solutions, coupled with the short equilibration time and the lack of need for liquid phase analysis are the primary advantages of the GLC technique. Based on the above considerations it is thus felt that this work has achieved both of its initial objectives.

APPENDICES

APPENDIX A

EXPERIMENTAL DATA

TABLE XIV

CHROMATOGRAPHIC COLUMN PROPERTIES

Run No.	Solvent (W,P,T)	Run Time (min)	T (°C)	p_i (psig)	p_o (mmHg)	F (cc/min)	m_s (gms.)	m_f (gms.)	V_G (cc)
29	W	200	29.5	8.5	730.1	57.72	2.682	2.392	26.15
30	W	164	29.7	8.5	746.0	57.72	2.392	2.259	26.44
31	W	152	30.2	1.3	747.5	48.24	0.177	0.032	4.85
32	W	140	29.5	0.6	745.4	45.90	0.173	0.077	4.87
33	W	156	29.7	0.6	745.9	47.76	0.170	0.034	4.87
34	W	132	30.2	0.7	742.3	46.02	0.175	0.074	4.87
35	W	212	20.8	7.2	737.4	47.94	2.257	2.182	26.31
36	W	208	21.9	7.2	739.0	49.32	2.182	2.111	26.65
37	W	184	21.1	0.5	728.0	49.20	0.151	0.052	4.92
38	W	196	21.0	0.6	727.6	47.64	0.174	0.067	4.87
40	W	188	41.3	7.0	738.5	43.98	2.111	1.969	26.72
41	W	180	40.1	6.9	727.1	44.64	1.969	1.857	26.86
42	W	152	40.0	0.9	739.8	38.94	0.188	0.056	4.83
43	W	140	39.8	0.7	739.3	39.36	0.182	0.055	4.85
48	P	180	29.2	0.3	731.5	18.42	0.497	0.186	5.52
49	P	204	30.7	0.3	740.2	18.30	0.500	0.232	5.51
50	P	124	29.4	0.3	743.4	17.88	0.258	0.030	4.64
51	P	120	29.7	0.3	746.1	18.30	0.270	0.048	4.61
52	P	120	29.7	0.3	747.0	16.92	0.280	0.042	4.59
53	P	120	30.2	0.3	735.9	17.16	0.274	0.043	4.60
54	P	124	31.3	0.3	742.7	18.78	0.288	0.046	4.57
55	P	128	29.6	0.3	745.1	18.30	0.295	0.069	4.55
56	P	144	29.6	0.3	733.9	6.66	0.294	0.167	4.56
57	P	128	29.2	0.3	737.8	18.06	0.294	0.068	4.56
58	P	116	29.0	0.3	743.3	15.60	0.291	0.106	4.56

TABLE XIV (CONT'D)

Run	Solvent (W,P,T)	Run Time (min)	T (°C)	p_i (psig)	p_o (mmHg)	F (cc/min)	m_s (gms.)	m_f (gms.)	V_G (cc)
59	P	136	29.5	0.3	736.8	16.38	0.268	0.122	4.61
60	P	152	29.7	0.3	742.5	17.34	0.276	0.148	4.60
61	P	184	29.7	0.3	736.3	18.30	0.296	0.195	4.55
62	P	160	20.6	0.3	734.5	17.34	0.280	0.071	4.59
63	P	184	20.1	0.3	742.4	15.48	0.277	0.091	4.59
64	P	140	19.4	0.3	733.9	18.06	0.277	0.078	4.59
65	P	144	18.9	0.3	740.8	17.64	0.281	0.092	4.58
66	P	148	22.6	0.3	736.1	17.34	0.274	0.102	4.60
67	P	176	20.8	0.3	738.5	17.52	0.281	0.128	4.58
68	P	108	39.8	0.3	739.4	17.76	0.275	0.091	4.60
69	P	104	39.6	0.4	745.2	17.88	0.280	0.114	4.58
70	P	136	19.8	0.3	745.9	17.16	0.271	0.152	4.62
71	P	100	41.0	0.4	732.3	17.16	0.279	0.111	4.59
72	P	92	39.2	0.5	743.4	18.00	0.276	0.125	4.60
73	P	100	40.8	0.3	738.1	17.10	0.268	0.134	4.62
74	P	104	20.8	0.3	745.8	17.94	0.072	0.047	4.91
75	P	248	20.8	0.3	735.4	25.44	0.4[illegible]	0.036	4.54
76	P	160	41.4	0.3	733.0	24.84	0.429	0.015	4.56
77	P	168	41.0	0.3	744.3	22.50	0.473	0.007	4.51
78	P	116	40.1	0.3	745.0	26.04	0.509	0.001	4.67
79	P	144	40.8	0.3	745.4	23.10	0.486	0.045	4.64
80	T	156	20.5	2.3	740.6	17.70	0.213	0.028	3.99
81	T	152	20.8	0.4	745.1	22.74	0.170	0.007	4.16
82	T	104	30.2	0.3	740.0	19.86	0.158	0.001	4.30
83	T	112	30.7	0.3	735.4	18.30	0.174	0.007	4.21
84	T	112	30.9	0.5	742.4	17.10	0.342	0.192	4.80
85	T	260	41.1	1.1	746.5	17.22	0.352	0.079	4.70
86	T	92	20.4	0.5	745.9	22.74	0.232	0.144	5.16

TABLE XV

SOLUTE RETENTION VALUES

Run No.	Solute	t_R (min)	m (gms)	Solute	t_R (min)	m (gms)	Solute	t_R (min)	m (gms)	Solute	t_R (min)	m (gms)
29	C_3H_7CHO	6.80	2.415	C_3H_7CHO	6.72	2.403	MeFo	5.08	2.539	MeFo	5.08	2.530
	C_2H_5CHO	9.38	2.446	C_2H_5CHO	9.23	2.428	EtFo	4.33	2.555	EtFo	4.30	2.547
	CH_3CHO	12.43	2.487	CH_3CHO	12.43	2.467	PrFo	3.91	2.580	PrFo	3.77	2.571
	PrFo	3.77	2.564	CH_2Cl_2	1.04	2.600	$CHCl_3$	0.89	2.596	CCl_4	0.65	2.590
	C_5H_{12}	0.58	2.622	C_6H_{14}	0.60	2.615	C_7H_{16}	0.61	2.606			
30	C_3H_7CHO	6.77	2.266	C_2H_5CHO	9.28	2.272	MeFo	4.91	2.292	MeFo	4.88	2.297
	CH_3CHO	12.12	2.281	EtFo	4.13	2.307	EtFo	4.13	2.311	PrFo	3.67	2.315
	PrFo	3.63	2.318	CH_2Cl_2	1.01	2.330	$CHCl_3$	0.87	2.326	CCl_4	0.65	2.323
	C_5H_{12}	0.57	2.343	C_6H_{14}	0.60	2.337	C_7H_{16}	0.62	2.334			
31	PrOH	4.88	0.158	EtOH	6.73	0.150	MeOH	7.47	0.139			
32	BuAm	4.80	0.146	BuAm	5.17	0.138	BuAm	5.08	0.131	PrAm	2.76	0.126
	PrAm	2.63	0.120	PrAm	2.45	0.115	EtAm	2.70	0.111	EtAm	2.93	0.107
33	EtAm	3.75	0.141	EtAm	3.87	0.131	EtAm	3.33	0.122	EtAm	3.00	0.113
	EtAm	2.93	0.109	EtAm	2.70	0.104	PrAm	1.92	0.090	PrAm	1.87	0.085
	BuAm	2.83	0.071									
34	PrOH	4.42	0.153	PrOH	4.38	0.149	EtOH	6.12	0.143	MeOH	7.12	0.135
	BuAm	4.75	0.129	BuAm	4.60	0.120	BuAm	6.46	0.112	BuAm	6.25	0.103
	BuAm	3.92	0.094	BuAm	3.25	0.089	BuAm	2.83	0.083			
35	CH_3CHO	20.75	2.185	C_2H_5CHO	16.58	2.194	MeFo	7.35	2.214	MeFo	7.37	2.211
	C_3H_7CHO	12.45	2.206	C_3H_7CHO	12.33	2.201	EtFo	6.63	2.220	EtFo	6.58	2.217
	PrFo	6.00	2.225	PrFo	6.00	2.223	CCl_4	0.78	2.228	$CHCl_3$	1.16	2.230
	CH_2Cl_2	1.35	2.234	C_7H_{16}	0.74	2.235	C_6H_{14}	0.70	2.238	C_5H_{12}	0.68	2.241
36	CH_3CHO	21.42	2.115	C_2H_5CHO	17.17	2.124	MeFo	7.42	2.141	MeFo	7.42	2.143
	C_3H_7CHO	12.83	2.130	C_3H_7CHO	12.92	2.135	EtFo	6.62	2.146	EtFo	6.60	2.149
	PrFo	6.17	2.151	PrFo	6.22	2.154	CCl_4	0.78	2.157	$CHCl_3$	1.18	2.158
	CH_2Cl_2	1.36	2.160	C_7H_{16}	0.74	2.161	C_6H_{14}	0.71	2.163	C_5H_{12}	0.70	2.167
37	EtAm	7.62	0.117	EtAm	6.75	0.111	EtAm	7.25	0.105	PrAm	4.13	0.100
	PrAm	3.72	0.096	PrAm	3.22	0.093	BuAm	6.50	0.087	BuAm	7.08	0.080
	BuAm	5.05	0.076									

TABLE XV (CONT'D)

Run	Solute	t_R (min)	m (gms)	Solute	t_R (min)	m (gms)	Solute	t_R (min)	m (gms)	Solute	t_R (min)	m (gms)
38	MeOH	12.25	0.151	MeOH	11.50	0.130	EtOH	10.47	0.144	EtOH	9.67	0.123
	PrOH	8.00	0.137	PrOH	7.60	0.117	EtAm	7.83	0.111	PrAm	3.73	0.099
	PrAm	4.25	0.095	PrAm	3.37	0.091	BuAm	6.55	0.086	BuAm	5.05	0.081
	BuAm	5.75	0.076									
40	C_3H_7CHO	5.27	1.976	C_3H_7CHO	5.38	1.981	PrFo	3.27	2.016	PrFo	3.27	2.020
	C_2H_5CHO	7.12	1.987	C_2H_5CHO	7.08	1.993	PrFo	3.25	2.023	EtFo	3.68	2.027
	CH_3CHO	9.65	1.999	CH_3CHO	9.87	2.009	EtFo	3.70	2.030	MeFo	4.43	2.034
	MeFo	4.42	2.037	CCl_4	0.80	2.047	CCl_4	0.79	2.051	$CHCl_3$	0.98	2.057
	CH_2Cl_2	1.11	2.063	C_7H_{16}	0.76	2.068	C_6H_{14}	0.75	2.074	C_5H_{12}	0.74	2.082
	C_5H_{12}	0.74	2.088									
41	C_3H_7CHO	5.72	1.865	C_3H_7CHO	5.83	1.870	PrFo	3.43	1.900	PrFo	3.24	1.904
	C_2H_5CHO	7.62	1.875	C_2H_5CHO	7.67	1.880	PrFo	3.40	1.906	EtFo	3.83	1.910
	CH_3CHO	10.17	1.885	CH_3CHO	10.10	1.893	EtFo	3.83	1.913	MeFo	4.50	1.916
	MeFo	4.50	1.920	CH_2Cl_2	1.12	1.936	$CHCl_3$	1.00	1.931	CCl_4	0.80	1.927
	C_5H_{12}	0.74	1.950	C_6H_{14}	0.75	1.944	C_7H_{16}	0.77	1.940			
42	MeOH	7.67	0.165	MeOH	7.50	0.157	EtOH	5.58	0.150	EtOH	5.45	0.143
	PrOH	3.73	0.139	PrOH	3.75	0.135	EtAm	4.87	0.117	EtAm	3.87	0.110
	EtAm	4.50	0.104	EtAm	3.57	0.100	PrAm	1.92	0.087	PrAm	1.60	0.083
	PrAm	1.53	0.082	BuAm	2.67	0.070	BuAm	2.67	0.064			
43	MeOH	7.75	0.155	EtOH	5.72	0.147	PrOH	3.78	0.142	EtAm	3.17	0.111
	EtAm	3.38	0.105	EtAm	3.00	0.101	PrAm	1.93	0.091	PrAm	1.98	0.084
	PrAm	2.20	0.083	BuAm	3.33	0.076	BuAm	3.08	0.072	BuAm	3.12	0.067
48	MeFo	4.08	0.418	MeFo	3.67	0.406	MeFo	3.77	0.395	EtFo	8.36	0.380
	EtFo	8.17	0.367	C_5H_{12}	1.42	0.271	C_5H_{12}	1.38	0.265	C_6H_{14}	3.40	0.257
	C_6H_{14}	3.37	0.246	C_7H_{16}	8.08	0.229	C_7H_{16}	7.67	0.208			
49	C_5H_{12}	2.60	0.473	C_5H_{12}	2.58	0.470	C_6H_{14}	6.33	0.458	C_6H_{14}	6.08	0.445
	$CHCl_3$	10.30	0.396	CH_2Cl_2	9.00	0.375	MeFo	2.70	0.329	MeFo	2.68	0.320
	CH_2Cl_2	8.83	0.361	EtFo	5.60	0.311	EtFo	5.53	0.291	EtFo	5.50	0.280
50	C_5H_{12}	1.32	0.212	C_5H_{12}	1.32	0.206	C_5H_{12}	1.30	0.203	C_6H_{14}	3.17	0.193
	C_6H_{14}	3.05	0.184	C_7H_{16}	6.62	0.149	C_7H_{16}	4.00	0.107			

TABLE XV (CONT'D)

Run No.	Solute	t_R (min)	m (gms)	Solute	t_R (min)	m (gms)	Solute	t_R (min)	m (gms)	Solute	t_R (min)	m (gms)
51	CH_2Cl_2	3.35	0.157	CH_2Cl_2	3.38	0.152	C_7H_{16}	6.67	0.185	C_7H_{16}	6.17	0.168
	CH_2Cl_2	3.08	0.140	$CHCl_3$	6.62	0.127	$CHCl_3$	5.42	0.113			
52	MeFo	2.08	0.196	MeFo	1.83	0.183	EtFo	3.88	0.171	EtFo	3.66	0.161
	C_7H_{16}	9.31	0.210									
53	CH_2Cl_2	7.00	0.222	CH_2Cl_2	6.17	0.207						
54	CH_3CHO	1.50	0.243	CH_3CHO	1.55	0.237	PrFo	4.20	0.133	PrFo	3.75	0.122
	CH_3CHO	1.52	0.231	CH_3CHO	1.48	0.227						
	C_2H_5CHO	3.70	0.217	C_2H_5CHO	3.30	0.206						
	C_2H_5CHO	3.08	0.196	C_3H_7CHO	7.30	0.178						
	C_3H_7CHO	5.30	0.159	C_3H_7CHO	4.75	0.145						
55	CH_3CHO	1.58	0.265	CH_3CHO	1.48	0.245	PrFo	6.07	0.180	$CHCl_3$	6.38	0.149
	CH_3CHO	1.45	0.242	C_2H_5CHO	3.42	0.233						
	C_2H_5CHO	3.52	0.226	C_3H_7CHO	7.25	0.209						
	C_3H_7CHO	6.65	0.194									
56	$CHCl_3$	27.56	0.244	$CHCl_3$	24.38	0.234	CCl_4	17.17	0.213	CCl_4	16.87	0.205
	CCl_4	14.96	0.195	CCl_4	16.38	0.186	CCl_4	16.09	0.177			
57	CCl_4	9.17	0.227	CCl_4	7.68	0.202	CCl_4	6.50	0.184	$CHCl_3$	7.17	0.135
	$CHCl_3$	4.67	0.120									
58	CH_3CHO	2.12	0.258	PrAm	3.83	0.187	PrAm	3.80	0.179	PrAm	2.60	0.171
	PrAm	3.38	0.165	PrAm	3.63	0.155	EtOH	4.75	0.127			
59	PrAm	2.92	0.199	PrAm	2.92	0.194	MeOH	3.75	0.182	MeOH	3.67	0.169
	MeOH	3.37	0.162	EtOH	6.25	0.153	EtOH	5.81	0.144	PrOH	11.67	0.128
60	PrAm	4.50	0.241	PrAm	4.67	0.235	BuAm	5.33	0.229	BuAm	4.95	0.219
	MeOH	4.67	0.200	MeOH	4.58	0.192	EtOH	7.67	0.181	EtOH	7.25	0.173
61	BuAm	6.83	0.257	BuAm	6.42	0.241	BuAm	5.08	0.236	PrOH	22.72	0.221
	PrOH	19.40	0.212	EtAm	4.67	0.205	EtAm	4.25	0.201	EtAm	4.67	0.198
62	CH_3CHO	2.30	0.242	CH_3CHO	2.18	0.236	MeFo	2.42	0.208	MeFo	2.33	0.203
	C_2H_5CHO	6.00	0.226	C_2H_5CHO	5.50	0.213	EtFo	5.00	0.193	EtFo	4.75	0.183
	PrFo	7.83	0.148	PrFo	6.92	0.131	PrFo	6.08	0.119			

TABLE XV (CONT'D)

Run No.	Solute	t_R (min)	m (gms)	Solute	t_R (min)	m (gms)	Solute	t_R (min)	m (gms)	Solute	t_R (min)	m (gms)
63	CH_3CHO	2.42	0.249	CH_3CHO	2.33	0.245	MeFo	2.75	0.224	MeFo	2.75	0.220
	C_2H_5CHO	6.33	0.237	C_2H_5CHO	6.08	0.228	EtFo	6.17	0.212	EtFo	5.72	0.202
	CH_2Cl_2	6.74	0.193	CH_2Cl_2	6.72	0.187	PrFo	12.75	0.168	PrFo	10.17	0.153
	C_3H_7CHO	6.67	0.138									
64	C_5H_{12}	1.42	0.212	C_5H_{12}	1.40	0.208	C_6H_{14}	3.40	0.201	C_6H_{14}	3.33	0.193
	CH_2Cl_2	5.88	0.184	CH_2Cl_2	5.50	0.172	C_7H_{16}	6.53	0.158	C_7H_{16}	5.75	0.148
	C_3H_7CHO	6.42	0.137	C_3H_7CHO	5.42	0.122						
65	C_5H_{12}	1.60	0.234	C_5H_{12}	1.58	0.230	C_6H_{14}	4.15	0.224	C_6H_{14}	3.95	0.216
	MeOH	5.83	0.205	MeOH	5.08	0.196	C_7H_{16}	8.47	0.182	C_7H_{16}	7.50	0.166
	$CHCl_3$	11.50	0.144	$CHCl_3$	9.75	0.136	$CHCl_3$	8.69	0.131	CCl_4	6.67	0.117
	CCl_4	4.50	0.103									
66	MeOH	6.17	0.227	MeOH	3.50	0.164	$CHCl_3$	7.72	0.130	EtOH	8.50	0.184
	EtOH	7.75	0.169	CCl_4	5.53	0.155	CCl_4	4.83	0.145	PrOH	13.40	0.113
67	MeOH	5.51	0.236	EtOH	5.84	0.185	EtOH	5.58	0.174	PrAm	2.88	0.167
	PrAm	2.46	0.163									
68	CH_3CHO	1.45	0.233	CH_3CHO	1.37	0.228	MeFo	1.42	0.202	MeFo	1.38	0.197
	C_2H_5CHO	3.42	0.221	C_2H_5CHO	3.12	0.210	EtFo	2.83	0.190	EtFo	2.67	0.183
	CH_2Cl_2	2.92	0.176	CH_2Cl_2	2.75	0.169	PrFo	3.67	0.141	PrFo	2.83	0.130
	C_3H_7CHO	4.20	0.158	C_3H_7CHO	3.70	0.148	PrFo	2.33	0.123			
69	CH_3CHO	1.23	0.240	CH_3CHO	1.20	0.236	MeFo	1.32	0.217	MeFo	1.25	0.214
	C_2H_5CHO	2.97	0.230	C_2H_5CHO	2.75	0.223	EtFo	2.62	0.207	EtFo	2.48	0.201
	CH_2Cl_2	2.68	0.194	CH_2Cl_2	2.48	0.184						
70	MeOH	6.33	0.238	MeOH	5.83	0.229	EtOH	12.17	0.216	EtOH	11.00	0.203
71	C_5H_{12}	0.87	0.227	C_5H_{12}	0.85	0.224	C_6H_{14}	1.97	0.219	C_6H_{14}	1.83	0.214
	C_7H_{16}	4.18	0.202	C_7H_{16}	3.67	0.194						
72	C_5H_{12}	0.83	0.228	C_5H_{12}	0.82	0.227	C_6H_{14}	1.83	0.222	C_6H_{14}	1.73	0.219
	C_3H_7CHO	4.08	0.193	C_7H_{16}	3.88	0.211	C_7H_{16}	3.63	0.202			
73	MeOH	2.22	0.231	MeOH	1.75	0.225						
74	PrOH	5.50	0.060	PrOH	5.25	0.058	PrOH	4.88	0.056			

TABLE XV (CONT'D)

Run No.	Solute	t_R (min)	m (gms)	Solute	t_R (min)	m (gms)	Solute	t_R (min)	m (gms)	Solute	t_R (min)	m (gms)
75	C_5H_{12}	1.70	0.414	C_5H_{12}	1.80	0.409	C_5H_{12}	1.17	0.259	C_5H_{12}	0.80	0.162
	C_5H_{12}	0.40	0.058	C_5H_{12}	0.29	0.029	C_5H_{12}	0.32	0.037	MeOH	5.17	0.365
	CH_3CHO	2.52	0.399	CH_3CHO	2.30	0.389	MeOH	5.06	0.343	MeOH	5.01	0.313
	CH_3CHO	2.28	0.382	MeOH	4.63	0.289	MeOH	4.41	0.269	MeOH	3.78	0.238
	MeOH	3.94	0.220	MeOH	4.17	0.199	EtOH	3.02	0.089	EtOH	2.91	0.074
	PrAm	0.83	0.056	PrAm	0.82	0.054	PrAm	0.82	0.053	EtAm	1.10	0.052
	EtAm	1.02	0.050	EtAm	1.26	0.046	EtAm	1.10	0.043	BuAm	0.90	0.036
	BuAm	1.00	0.035	BuAm	1.10	0.033	BuAm	1.15	0.031	BuAm	0.97	0.035
	BuAm	1.40	0.036	PrOH	2.99	0.030	PrOH	3.17	0.032	PrOH	3.13	0.034
76	C_5H_{12}	0.58	0.231	C_5H_{12}	0.57	0.224	C_5H_{12}	0.33	0.085	C_5H_{12}	0.28	0.056
	CH_3CHO	1.47	0.402	CH_3CHO	1.35	0.393	C_5H_{12}	0.23	0.026	MeOH	2.08	0.371
	CH_3CHO	1.35	0.384	CH_3CHO	0.23	0.015	MeOH	2.57	0.348	MeOH	2.53	0.335
	EtAm	2.17	0.213	EtAm	1.67	0.198	EtAm	1.75	0.186	BuAm	0.96	0.115
	BuAm	1.07	0.100	BuAm	1.10	0.093						
77	C_5H_{12}	1.08	0.441	C_5H_{12}	1.00	0.401	C_5H_{12}	0.90	0.350	C_5H_{12}	0.75	0.275
	CH_3CHO	1.78	0.469	CH_3CHO	1.80	0.467	C_5H_{12}	0.53	0.164	C_5H_{12}	0.35	0.073
	CH_3CHO	0.23	0.008	PrAm	3.33	0.462	PrAm	3.33	0.459	PrAm	3.20	0.453
	PrAm	0.35	0.023	$CHCl_3$	10.39	0.340	$CHCl_3$	7.60	0.230	$CHCl_3$	5.08	0.179
	CCl_4	2.60	0.140	CCl_4	2.33	0.110	CCl_4	2.05	0.086			
78	CH_2Cl_2	4.28	0.462	CH_2Cl_2	3.78	0.430	$CHCl_3$	8.25	0.331	$CHCl_3$	7.00	0.265
	CH_2Cl_2	3.88	0.397	CH_2Cl_2	1.67	0.159	$CHCl_3$	5.75	0.212	$CHCl_3$	4.27	0.173
	CH_2Cl_2	1.58	0.150	CH_2Cl_2	0.90	0.077	CCl_4	2.22	0.121	CCl_4	1.83	0.106
	C_3H_7CHO	1.05	0.057	C_3H_7CHO	0.92	0.043	CCl_4	1.58	0.084	MeOH	0.33	0.023
	C_3H_7CHO	0.93	0.037	MeOH	0.18	0.001	EtOH	0.32	0.015	EtOH	0.30	0.013
	EtOH	0.32	0.011									
79	CH_3CHO	1.50	0.438	CH_3CHO	1.66	0.422	MeOH	2.75	0.366	MeOH	2.48	0.343
	CH_3CHO	1.70	0.414	MeOH	2.53	0.327	MeOH	1.17	0.136	MeOH	0.90	0.098
	MeOH	0.87	0.094	MeOH	0.61	0.070	MeOH	0.67	0.066	MeOH	0.57	0.052
	MeOH	0.53	0.046	MeOH	0.52	0.045	PrOH	8.23	0.283	PrOH	7.57	0.239
	PrOH	6.50	0.196	PrOH	4.25	0.160	PrOH	2.85	0.086	PrOH	2.72	0.078

TABLE XV (CONT'D)

Run No.	Solute	t_R (min)	m (gms)	Solute	t_R (min)	m (gms)	Solute	t_R (min)	m (gms)	Solute	t_R (min)	m (gms)
80	CH_3CHO	0.60	0.172	CH_3CHO	0.58	0.167	PrOH	2.80	0.113	PrOH	2.75	0.109
	CH_3CHO	0.58	0.166	C_2H_5CHO	1.58	0.161	PrOH	2.70	0.101	EtFo	1.32	0.089
	C_2H_5CHO	1.57	0.158	C_2H_5CHO	1.55	0.155	EtFo	1.28	0.087	EtFo	1.25	0.085
	C_3H_7CHO	4.25	0.147	C_3H_7CHO	4.00	0.140	PrFo	3.33	0.080	PrFo	3.17	0.074
	C_3H_7CHO	3.83	0.134	PrFo	3.17	0.069	C_5H_{12}	1.50	0.064	C_5H_{12}	1.42	0.061
	C_5H_{12}	1.38	0.058	C_6H_{14}	3.75	0.052	C_6H_{14}	3.32	0.046	C_7H_{16}	7.92	0.035
81	C_5H_{12}	2.55	0.135	C_5H_{12}	2.42	0.131	C_5H_{12}	2.35	0.126	EtAm	0.65	0.124
	EtAm	0.63	0.120	EtAm	0.63	0.117	PrAm	1.65	0.109	PrAm	1.60	0.106
	PrAm	1.58	0.102	BuAm	5.28	0.095	BuAm	5.00	0.088	BuAm	4.75	0.081
	CH_2Cl_2	0.90	0.076	CH_2Cl_2	0.88	0.074	$CHCl_3$	2.22	0.069	$CHCl_3$	2.00	0.065
	CH_2Cl_2	0.88	0.072	$CHCl_3$	2.02	0.061	CCl_4	1.20	0.058	CCl_4	0.97	0.055
	CCl_4	0.97	0.054	C_6H_{14}	2.67	0.047	C_6H_{14}	2.42	0.043	C_6H_{14}	2.25	0.040
	C_7H_{16}	5.25	0.031	C_7H_{16}	4.67	0.022	C_7H_{16}	3.18	0.017	C_7H_{16}	2.50	0.012
82	C_2H_5CHO	0.78	0.100	C_2H_5CHO	0.78	0.098	C_5H_{12}	1.75	0.121	C_5H_{12}	1.68	0.115
	C_2H_5CHO	0.80	0.095	C_3H_7CHO	1.68	0.092	C_5H_{12}	1.68	0.110	PrOH	1.37	0.060
	C_3H_7CHO	1.75	0.086	C_3H_7CHO	1.75	0.082	PrOH	1.43	0.057	PrOH	1.30	0.052
	MeFo	0.32	0.049	EtFo	0.50	0.034	EtFo	0.50	0.032	EtFo	0.48	0.031
	PrFo	0.85	0.028	PrFo	0.87	0.023	PrFo	0.82	0.021	PrFo	0.78	0.018
	C_6H_{14}	0.75	0.015	C_6H_{14}	0.65	0.012	C_6H_{14}	0.57	0.011	C_7H_{16}	1.08	0.008
83	C_5H_{12}	2.12	0.138	C_5H_{12}	2.23	0.134	C_5H_{12}	0.42	0.013	$CHCl_3$	3.12	0.118
	CH_2Cl_2	1.28	0.131	CH_2Cl_2	1.28	0.128	$CHCl_3$	3.05	0.110	$CHCl_3$	2.95	0.104
	CH_2Cl_2	1.27	0.124	CCl_4	1.13	0.101	CCl_4	1.13	0.098	CCl_4	1.17	0.096
	PrAm	0.97	0.072	PrAm	0.93	0.069	BuAm	3.00	0.063	BuAm	3.05	0.057
	BuAm	2.75	0.051	C_6H_{14}	2.05	0.042	C_6H_{14}	1.92	0.038	C_7H_{16}	4.52	0.030
	C_7H_{16}	3.67	0.023	C_7H_{16}	3.17	0.016						
84	CH_3CHO	0.73	0.290	CH_3CHO	0.72	0.286	C_5H_{12}	4.17	0.302	C_5H_{12}	4.17	0.294
	CH_3CHO	0.65	0.284	CH_3CHO	0.65	0.282	C_5H_{12}	2.77	0.199	C_5H_{12}	2.75	0.194
	CH_3CHO	0.65	0.281	CH_3CHO	0.65	0.277	MeOH	0.58	0.263	MeOH	0.58	0.262
	C_2H_5CHO	1.77	0.273	C_2H_5CHO	1.77	0.270	MeOH	0.58	0.260	EtOH	1.30	0.258
	C_2H_5CHO	1.72	0.266	EtOH	1.27	0.255	EtOH	1.25	0.252	MeFo	0.80	0.250
	MeFo	0.80	0.247	MeFo	0.80	0.244	EtFo	1.95	0.240	EtFo	1.87	0.237
	EtFo	1.83	0.233	EtAm	1.02	0.231	EtAm	0.98	0.226	EtAm	0.95	0.224
	EtAm	0.95	0.222	PrAm	2.32	0.213	PrAm	2.20	0.209	PrAm	2.22	0.205

TABLE XV (CONT'D)

Run No.	Solute	t_R (min)	m (gms)	Solute	t_R (min)	m (gms)	Solute	t_R (min)	m (gms)	Solute	t_R (min)	m (gms)
85	C_5H_{12}	3.58	0.319	C_5H_{12}	3.57	0.312	C_5H_{12}	1.33	0.093	C_5H_{12}	1.18	0.086
	CH_3CHO	0.60	0.309	CH_3CHO	0.60	0.307	C_5H_{12}	1.13	0.083	MeOH	0.57	0.305
	CH_3CHO	0.60	0.306	MeOH	0.58	0.304	MeOH	0.57	0.303	MeFo	0.83	0.300
	MeFo	0.78	0.299	MeFo	0.77	0.298	MeFo	0.77	0.296	EtAm	0.93	0.294
	EtAm	1.03	0.292	EtAm	1.02	0.290	EtAm	0.97	0.288	PrAm	2.10	0.284
	PrAm	2.07	0.282	PrAm	2.00	0.278	EtOH	1.08	0.275	EtOH	1.05	0.274
	C_2H_5CHO	1.33	0.270	C_2H_5CHO	1.37	0.268	EtOH	1.00	0.273	EtFo	1.70	0.263
	C_2H_5CHO	1.35	0.266	EtFo	1.58	0.261	EtFo	1.65	0.258	CCl_4	1.55	0.255
	CH_2Cl_2	1.62	0.248	CH_2Cl_2	1.62	0.245	CCl_4	1.53	0.253	CCl_4	1.50	0.251
	CH_2Cl_2	1.55	0.243	PrOH	2.57	0.235	PrOH	2.33	0.232	PrOH	2.43	0.229
	C_3H_7CHO	3.18	0.224	C_3H_7CHO	3.07	0.219	PrFo	4.00	0.209	PrFo	3.75	0.204
	C_3H_7CHO	2.95	0.214	PrFo	3.65	0.199	$CHCl_3$	3.37	0.194	$CHCl_3$	3.28	0.189
	BuAm	4.72	0.178	BuAm	4.85	0.171	BuAm	4.52	0.165	$CHCl_3$	3.30	0.185
	C_6H_{14}	5.08	0.158	C_6H_{14}	4.75	0.151	C_6H_{14}	4.53	0.145	C_7H_{16}	12.18	0.130
	C_7H_{16}	11.67	0.116	C_7H_{16}	10.75	0.101						
86	C_5H_{12}	3.75	0.204	C_5H_{12}	3.75	0.199	C_5H_{12}	2.78	0.153	C_5H_{12}	2.85	0.150
	MeOH	0.60	0.195	MeOH	0.60	0.193	MeOH	0.62	0.192	MeOH	0.60	0.191
	MeFo	0.75	0.189	MeFo	0.75	0.188	MeFo	0.73	0.187	MeFo	0.73	0.185
	EtOH	1.32	0.183	EtOH	1.30	0.181	EtOH	1.30	0.179	EtOH	1.30	0.177
	PrOH	3.58	0.174	PrOH	4.03	0.168	PrOH	3.75	0.162	PrOH	3.70	0.157

APPENDIX B

EXPERIMENTAL DETAILS

From the discussion in the experimental program, the main experimental difficulties seem to center around the possible adsorption of the solute, and the determination of the gas phase volume. In addition, working with solvents of appreciable volatility caused a number of problems both in detection, as has already been discussed, and in the actual column operation. Therefore these effects will be discussed here in detail and the methods of alleviating these problems outlined.

The adsorption of the solute can occur in three ways, all of them undesirable. The solute may be adsorbed on the column walls, by the active sites on the uncovered support, or by the solvent itself rather than being absorbed. The possible effect of adsorption by the column metal itself has been investigated by Beckman and Bevenue.(12) These authors studied columns made of copper, stainless steel, aluminum and quartz. The percentage recovery of halogenated hydrocarbons was determined in each of these columns. Although quartz had the lowest solute retentivity, aluminum was the best metal investigated. The experience of the present writer in adsorption of trace hydrocarbon constituents also indicates aluminum to be the most preferrable choice for column material. Therefore in the present study all columns were constructed of aluminum.

The possibility of solute adsorption by the solvent surface has been discussed in the main portion of this work. Based on Funk and Houghton's penetration factor,(34) the possibility of solvent adsorption was seen to be highest for very low solvent coatings on the solid support. As in the present study only coatings greater than 15% w/w were used to obtain experimental data, the possibility of solvent adsorption should be minimized. Also static equilibrium studies conducted with the solvent in bulk phase or coated on a solid support gave the same result, as described earlier. If solvent adsorption had occurred this result could not have been reached. Finally the works performed which indicate the possibility of this effect,(71,72,79) also indicate that upon utilization of a more inert support the effect very noticeably decreases or becomes negligible. From the above reasoning it can be concluded that the possibility of solvent adsorption effects occurring in this work is quite minute.

On the contrary to the preceeding conclusion, the effect of solid support adsorption is a very real and probable event. Thus care must be taken to insure that this effect does not interfere with the experimental results. In this respect one must utilize the most inert support possible and be sure that the entire surface is covered with solvent. Scholz and Brandt(105) have investigated solid support effects and concluded that at least 10% w/w minimum coating must be used to nullify solid support interactions. This is due to the hydrogen bonding sites which exist on most diatomaceous earth supports in the form of silanol and siloxane groups. They concluded that the flux calcined diatomaceous earth support is to be preferred for oxygenated or polar solutes in nonpolar solvents. Perrett and Purnell(80) have investigated the possibility of reacting the hydrogen bonding sites with hexamethyl disilazane (HMDS) to deactivate them according to the following reaction

$$(CH_3)_3SiNHSi(CH_3)_3 + 2(\cdot OH) \longrightarrow 2\left[\cdot OSi(CH_3)_3\right] + NH_3$$

The resultant support shows much less adsorptive tendencies and the pores of the support remain unaffected.

In order to insure total surface coverage of the support, investigations have been conducted of the surface and pores of the support particles by Janak and Staszewski(48) and Smith.(107) These investigators used electron microscopy to study the surface coverage for various percentage liquid coatings. They conclude that the interstices are essentially filled with solvent for a 20% w/w coating and that the solvent is uniformly distributed over the surface in multilayer coatings providing complete coverage. Thus the possibility of uncoated support with a 20% w/w solvent loading seems very unlikely. Sawyer and Barr(104) in a very exhaustive investigation of solid supports studied Chromosorb R, Chromosorb W, Glass Beads, Carborundum, Stainless Steel, Nichrome, and Fluoropak 80. They measured retention volumes for all types of solutes both in an empty column and a column packed with the uncoated supports. Their conclusion was that the most inert possible support was Fluoropak 80. Based on the above studies and considering the solvent polarity and wetability of the various solid supports, the following supports were chosen for this study: water - Chromosorb W, a flux calcined diatomaceous earth was used; 2 pentanone - HMDS treated Chromosorb W, as described above, was employed; and 2,3,4 trimethylpentane - Fluoropak 80, a teflon polymer, was chosen as the most inert support. With these supports and the studies conducted concerning the effect of GLC variables, it is felt that the results of this work are devoid of support adsorption effects and are true equilibrium values.

The determination of the gas phase volume, although a minor consideration, has attracted attention due to the general inaccuracies connected with its determination. Stalkup,(110,111) attempts to determine V_G by the retention time of an unretained component and by calculation based on column geometry and system dead volume measurements, and gets poor agreement. When using a katharometer detector the normal unretained component studied is air. However, as air is not chemi-ionized in the flame ionization detector some other component must be chosen. Smith(106) has pointed out that the substance generally employed, methane, is actually retained, in some instances quite well, and thus should not be used for this purpose. For the solvents under consideration in this study methane is partially retained and so can not be used.

To circumvent this problem a somewhat different technique was utilized in this work. As the solubility of helium in pure hydrocarbons is quite low, pure methane was employed as the carrier gas and a small sample of helium was injected. The helium essentially preferentially displaced a momentary slug of methane which was registered by the flame ionization detector. As the helium is unretained by the solvents of interest this method should provide a true determination of the gas phase volume. A second method of determining V_G consisted of using an empty column of known dimensions and measuring the retention volume of methane. From this value the system dead volume may be determined. Then for a given column knowing the dimensions, the density of the solid support, and the density of the solvent, the value of the gas phase volume may be computed. Utilizing the above two procedures carefully, the values of V_G obtained in each case were coincident with each other. Therefore in the experimental program, as utilizing pure methane carrier gas presents a safety hazard, the geometric method of determining the gas phase volume was employed.

The distinction of this work from that of previous investigators was the thorough investigation of two component volatile systems by GLC. Concomitant with this distinction are the added experimental problems incurred with the utilization of a volatile solvent. Three general methods exist to cope with such a situation. The first and simplest technique consists of reducing the operating temperature to some subambient value where the solvent volatility is also reduced and obtaining the data at this temperature. This approach was attempted by Porter and Johnson.(90) The partial molar excess enthalpy data is then assumed constant and the results may be extrapolated back to the temperature region of normal interest. Two problems existing here are the long retention times at subambient temperatures and the constancy of ΔH_2^E. The first is avoided by utilizing a low percentage coating on the support but then solid support effects arise again. Thus the technique has basic limitations which are not, however, insurmountable.

An alternate approach also put forward by Porter and Johnson(88,89) is designated as circular GLC. In this method the inlet and outlet of the column are joined by a peristaltic pump and the carrier gas is constantly recirculated. In this manner the carrier gas becomes saturated with solvent and the remaining solvent remains in place on the support. In fact the support may be coated in situ by this technique but the uniformity of coating is questionable. The main disadvantage of this method is that the solute never elutes from the column but is constantly recirculated until it becomes an integral part of the carrier gas. Thus if it is desired to remain near infinite dilution, every few solute injections the system must be emptied out and replaced with a new solvent charge.

The method actually employed in this study is that of Kwantes and Rijnders.(58) In this approach a forecolumn is inserted into the flow system prior to the sample injection point. The purpose of this forecolumn is to presaturate the carrier gas with the solvent of interest and reduce "bleeding" in the main column. The presaturator packing is support material coated essentially at saturation with the solvent. The presaturator column is then thermostated at the same temperature as the main column so as to avoid solvent build up in the main column. The method is quite effective but not perfect, as the associated pressure drop across the main column changes the carrier gas saturation conditions and some solvent still is depleted. Thus as this latter technique seemed to have fewer limitations, it was chosen as the preferred method.

APPENDIX C

PHYSICAL PROPERTIES OF MATERIALS

A short discussion of the various physical properties of the solutes and solvents employed in this study seemed in order as often these are derived properties rather than those directly measurable and tabulated in the common sources. The complete tabulation of all the properties discussed below is given in Table XVI.

A word will now be said about the origin of each of these properties. Essentially all the values in Table XVI are at 25°C or very near this value. The dipole moments tabulated there have been taken from the compilations of Wesson(120) primarily and LeFevre.(63) The values of the ionization potentials for removal of the first electron from the molecule are from the work of Field and Franklin.(29) In order to compute the cubical coefficient of expansion the variation in density of the component with temperature over a small region was needed. This data was obtained from Dreisbach,(25) Friend and Hargreaves,(33) and Hodgman.(46) Hildebrand's solubility parameter is defined as the energy of vaporization per unit volume. To compute this quantity heats of vaporization and molar volumes were determined from Hodgman,(46) Dreisbach(25) and Washburn.(119)

The polarizabilities proved to be the most difficult property to ascertain. Some values were available from investigations by Smith(108) and Stuart.(114) These values are determined by secondary methods from experimental data. An attempt was made to

TABLE XVI

PHYSICAL PROPERTIES OF MATERIALS

Material	$\beta x 10^3$ ($°C^{-1}$)	$T_{Boil.}$ ($°C$)	μ (Debye)	ϵ	ΔH_{vap} (cal/gm)	I (ev)	v° (cc/mole)	σ (A°)	δ $(cal/cc)^{\frac{1}{2}}$	α x 10^{24} (cc/mole)
Water	0.21	100.0	1.85	78.5	539.6	12.67	18.0	2.6	22.5	1.5
2 Pentanone	1.20	103.3	2.71	15.5	90.0	9.59	106.1	5.6	8.3	9.9
2,3,4 TMP	1.27	113.6	0.00	2.0	68.4	9.90	165.1	6.4	6.6	16.2
MeOH	1.26	64.7	1.66	32.6	262.8	10.88	40.4	4.0	13.9	3.2
EtOH	1.08	78.4	1.74	24.3	204.3	10.60	58.4	4.5	12.3	5.3
PrOH	0.96	97.8	1.65	20.1	164.4	10.42	74.7	4.9	11.1	7.3
EtAm	1.83	16.6	1.28	6.9	146.0	9.32	63.9	4.6	9.6	6.8
PrAm	1.47	48.5	1.26	5.5	120.2	9.17	82.2	5.0	8.9	8.7
BuAm	1.38	77.8	1.20	5.3	104.9	9.19	98.8	5.3	8.4	10.7
CH_3CHO	1.74	20.2	2.70	21.1	136.2	10.28	56.2	4.5	9.8	4.4
C_2H_5CHO	1.44	48.8	2.54	18.5	118.8	10.06	72.0	4.9	9.3	6.3
C_3H_7CHO	1.32	75.7	2.57	13.4	104.4	10.01	88.2	5.3	8.8	8.3
MeFo	1.56	32.0	1.77	8.5	112.4	(10)	61.2	4.5	10.0	5.6
EtFo	1.42	54.3	1.94	7.2	97.2	(10)	80.2	4.9	9.1	7.5
PrFo	1.27	81.3	1.89	7.7	88.1	(10)	97.8	5.3	8.5	9.5
CH_2Cl_2	1.40	40.7	1.55	9.1	78.6	11.40	63.6	4.7	9.7	6.5
$CHCl_3$	1.27	61.3	1.27	4.8	59.0	11.35	79.7	5.0	8.9	8.2
CCl_4	1.22	76.7	0.00	2.2	46.4	11.10	96.5	5.3	8.2	10.5
C_5H_{12}	1.66	36.1	0.00	1.9	85.4	10.55	116.1	5.5	6.9	10.4
C_6H_{14}	1.47	68.7	0.00	1.9	80.5	10.43	130.5	5.8	6.9	12.0
C_7H_{16}	1.38	98.4	0.00	1.9	76.5	10.35	146.5	6.1	6.9	13.9

determine the remaining values employing the commonly accepted Clausius-Mosotti relation, which is dependent on the dielectric constant. The values of the dielectric constant were obtained from the tabulation of Maryott and Smith(75) and the polarizabilities calculated. Due to the highly polar nature of the majority of the materials involved, the relation failed miserably when compared with the available experimental values. Therefore the method of computing polarizabilities by summing the contributions of the individual bond polarizabilities as outlined by Hirschfelder, Curtiss and Bird(44) was used. The calculated results agreed very well with the above experimentally determined properties.

The intermolecular distance between molecules i and j was determined as suggested by Hirschfelder _et al._(44) using critical volumes as tabulated by Hodgman(46) and Lange.(60) This method may be questioned as the constant of proportionality varies from author to author. However, at least the method used here is consistent. All other commonly determined physical properties were obtained from Dreisbach,(25) Hodgman,(46) Lange(60) and Washburn.(119) In addition to those properties listed in Table XVI a knowledge of the variation of vapor pressure with temperature was needed. Graphs with this information were very excellently compiled by Jordan(50) and so are not reproduced here.

APPENDIX D

DATA PROCESSING AND EVALUATION METHODS

The actual process for determining m , V_G , V_R , j , $\bar{V}_R$, γ_2^∞ , ΔG_2^E , ΔH_2^E and ΔS_2^E will be outlined in detail both in principle and with a sample calculation. The method for determining the thermal contribution, including dispersion, orientation and induction forces, will also be presented and substantiated with numerical results. Finally the technique for obtaining the interaction energy based on statistical mechanics and its temperature derivative will be delineated. The constants for Pierotti's homologous series correlation will also be determined.

As the ethanol-water system has been used as an example system previously at 40°C, it will again serve the same purpose. From Table XIV, consider Run 42. Knowing m_s and m_f and the time of the run and assuming a linear rate of solvent depletion the value for m at any given time in the run may be calculated. Specifically the rate is

$$\text{Rate} = \frac{0.188 - 0.056}{152} = 0.00087 \text{ gms/min}$$

Now from the actual chromatogram for EtOH , the time of emergence of the peak maximum was 52 minutes after the run had begun so

$$m = 0.188 - (52)(.00087) = 0.143 \text{ gms}$$

which is the value tabulated in Table XV along with the retention time. This is how m values were computed. To determine V_G, the sum of the void volume within the column and the system dead volume, as ascertained according to the method outlined in Appendix B, is calculated.

$$V_G = \text{Void Volume} + \text{System Dead Volume}$$

The system dead volume of the F and M Model 609 Gas Chromatograph as modified was 2.36 cc. The internal volume of the six inch aluminum column was 2.89 cc. As the density of the Chromosorb W was 2.30 gms/cc and the water was 1.0 gms/cc, the void volume was determined by subtracting the volume of the support and the solvent from the column internal volume. In this case as a 36% w/w coating was used, 0.188 gms of water and 0.527 gms of Chromosorb W were contained in the column. Therefore

$$\text{Void Volume} = 2.89 - \frac{0.527}{2.30} - \frac{0.188}{1.00} = 2.47\,\text{cc}$$

and

$$V_G = 2.47 + 2.36 = 4.83\,\text{cc}$$

This is the result given in Table XIV and the above procedure represents the process of determining this quantity.

Now to determine the retention volume, the retention time in Table XV is multiplied by F from Table XIV.

$$V_R = t_R F = (5.45)(38.94) = 212.2 \text{ cc}$$

Next the factor j is determined using Equation (21)

$$j = \frac{3}{2}\left[\frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1}\right] = \frac{3}{2}\left[\frac{\left(\frac{786.2}{739.8}\right)^2 - 1}{\left(\frac{786.2}{739.8}\right)^3 - 1}\right] = 0.974$$

Now $\bar{V}_R$ is calculated using Equation (20) multiplied by j

$$\bar{V}_R = j\left(\frac{V_R - V_G}{m}\right) = 0.974\left(\frac{212.2 - 4.8}{0.143}\right) = 1412.6 \text{ cc/gm}$$

and from Equation (24) knowing M = 18 and R = 82.06 and obtaining p_2^o from Jordan(50) as 0.184 atm

$$\gamma_2^{\infty} = \frac{RT}{\bar{V}_R M p_2^o} = \frac{(82.06)(313)}{(1412.6)(18)(.184)} = 5.48$$

From this point on the remaining properties to be calculated are thermodynamic in nature and no longer need be related to the GLC variables. From Equation (28)

$$\Delta G_2^E = RT \ln \gamma_2^{\infty} = (1.99)(313)(1.7047) = 1061.8 \text{ cal/mole}$$

According to Equation (32)

$$\frac{d \ln \gamma_2^{\infty}}{d(1/T)} = \frac{\Delta H_2^E}{R} \qquad (32)$$

and a plot of $\ln \gamma_2^{\infty}$ as a function of (1/T) using the data in Table I should yield a straight line such that

$$\Delta H_2^E = (\text{Slope})\, R$$

For example at 40°C, $\gamma_2^{\infty} = 5.50$ and at 20°C, $\gamma_2^{\infty} = 6.51$ so

$$\Delta H_2^E \approx \left(\frac{\ln 6.51 - \ln 5.50}{1/293 - 1/313} \right) (1.99) \approx 1480 \text{ cal/mole}$$

In actuality the slopes are determined graphically by a best fit of the three available data points. From Equation (27)

$$\Delta S_2^E = \frac{\Delta H_2^E - \Delta G_2^E}{T} = \frac{1480 - 1060}{313} = 1.32 \frac{\text{cal}}{\text{mole} \cdot {}^\circ\text{K}}$$

Having determined all the thermodynamic solution properties at infinite dilution, the methods used in attempting to predict and correlate these properties will be presented. To determine the athermal contribution to nonideality either Equation (78) or Equation (84) will be used depending on the relative sizes of the solute and solvent. For EtOH-water, as $v_2^o > v_1^o$ then

$$\ln \gamma_2^{ath} = \ln r + (5r+1) \ln \frac{5r+1}{6r} \qquad (84)$$

and

$$\ln \gamma_2^{ath} = \ln 3.24 + \left[5(3.24)+1\right] \ln \frac{5(3.24)+1}{6(3.24)} = -0.95$$

or $\gamma_2^{ath} = 0.39$. To determine the thermal contribution many variants were presented in the correlation and analysis of data. However, in this discussion only the final proposed correlation, as presented in Table XI, will be considered as it represents the best predictive technique and also embodies all the other calculational methods. The relations are

$$\ln \gamma_2^{th} = \frac{v_2}{kT}\left[(\delta_1-\delta_2)^2+(\omega_1-\omega_2)^2+I.T.\right]\phi_1^2 \quad (110)$$

$$I.T. \equiv \frac{2\alpha_1\mu_1^2}{\sigma_{11}^6 v_{11}} + \frac{2\alpha_2\mu_2^2}{\sigma_{22}^6 v_{22}} - \frac{2(\alpha_1\mu_2^2+\alpha_2\mu_1^2)}{\sigma_{12}^6 v_{12}} \quad (111)$$

and

$$\omega_i^2 = \frac{2}{3} \cdot \frac{\mu_i^4}{kT\sigma_{ii}^6 v_{ii}} \quad (104)$$

As the solutions studied are essentially at infinite dilution, $\phi_1 \approx 1$ and $v_2 \approx v_2^o$. Also geometric mean values are used to calculate σ_{12} and v_{12} . Proceeding in a stepwise approach the proper conversion units must be incorporated to produce homogeneous results. Molecular units must be transformed to molar quantities throughout. Recalling that $R = \mathcal{N}_0 k$, 1 Debye = 10^{-18} esu·cm, and 1 cal = 4.186×10^7 ergs results in

$$(\omega_1-\omega_2)^2=\frac{2\,N_0^2}{3RT\,\sigma_{12}^6(4.186\times10^7)^2}\left[\frac{\mu_1^2}{\sqrt{V_{11}^{\circ}}}-\frac{\mu_2^2}{\sqrt{V_{22}^{\circ}}}\right]^2$$

where v_{ii}° is in cc/mole and σ_{12} is in cm. Grouping all constant terms together one obtains

$$(\omega_1-\omega_2)^2=\frac{2(6.02\times10^{23})^2(10^{-72})(10^{48})}{3(1.99)(298)(4.186\times10^7)^2\,\sigma_{12}^6}\left[\frac{\mu_1^2}{\sqrt{V_{11}^{\circ}}}-\frac{\mu_2^2}{\sqrt{V_{22}^{\circ}}}\right]^2$$

or

$$(\omega_1-\omega_2)^2=\frac{2.32\times10^5}{\sigma_{12}^6}\left[\frac{\mu_1^2}{\sqrt{V_{11}^{\circ}}}-\frac{\mu_2^2}{\sqrt{V_{22}^{\circ}}}\right]^2$$

where σ_{12} is in Å, v_{ii}° in cc/mole, and μ_i in Debye. Utilizing the same procedure for the induction term yields

$$\text{I.T.}=\frac{2(10^{-24})(10^{-36})(10^{48})(6.02\times10^{23})}{(4.186\times10^7)}\left[\frac{\alpha_1\mu_1^2}{\sigma_{11}^6V_{11}^{\circ}}+\frac{\alpha_2\mu_2^2}{\sigma_{22}^6V_{22}^{\circ}}-\frac{\alpha_1\mu_2^2+\alpha_2\mu_1^2}{\sigma_{12}^6V_{12}^{\circ}}\right]$$

or

$$\text{I.T.}=2.88\times10^4\left[\frac{\alpha_1\mu_1^2}{\sigma_{11}^6V_{11}^{\circ}}+\frac{\alpha_2\mu_2^2}{\sigma_{22}^6V_{22}^{\circ}}-\frac{\alpha_1\mu_2^2+\alpha_2\mu_1^2}{\sigma_{12}^6V_{12}^{\circ}}\right]$$

where σ_{ij} is in Å, v_{ij}° in cc/mole, μ_i in Debye and α_i in cc/mole x 10^{24}.

The above terms will now be calculated for the EtOH-water system

$$(\omega_1-\omega_2)^2=\frac{2.32\times10^5}{\left(\sqrt{(2.6)(4.5)}\right)^6}\left[\frac{(1.85)^2}{(18)^{1/2}}-\frac{(1.74)^2}{(58.4)^{1/2}}\right]$$

$$(\omega_1-\omega_2)^2=52.2\ \text{cal/cc}$$

$$\text{I.T.}=2.88\times10^4\left[\frac{(1.5)(1.85)^2}{(2.6)^6(18)}+\frac{(5.3)(1.74)^2}{(4.5)^6(58.4)}-\frac{(1.5)(1.74)^2+(5.3)(1.85)^2}{\left(\sqrt{(2.6)(4.5)}\right)^6\sqrt{(18)(58.4)}}\right]$$

or

$$\text{I.T.}=14.7\ \text{cal/cc}$$

and

$$(\delta_1-\delta_2)^2=(22.5-12.3)^2=104.0\ \text{cal/cc}$$

Substituting these terms into Equation (110)

$$\ln\gamma_2^{th}=\frac{58.4}{(1.99)(298)}\left[104.0+52.2+14.7\right]=16.83$$

and

$$\gamma_2^{th}=2.0\times10^7$$

Now from Equation (70)

$$\ln\gamma_2^{\infty}=\ln\gamma_2^{th}+\ln\gamma_2^{ath}=-0.95+16.83=15.88$$

and

$$\gamma_2^{\infty} = 8.3 \times 10^6$$

To calculate the separate terms for the various other correlative techniques, the individual contributions computed above are used separately or in partial summation in the corresponding relation.

The statistical mechanical development allows the interaction energy and its temperature dependence to be evaluated, as well as the geometric and energetic contributions to the partial molar excess entropy. From Equation (135) the interaction energy is given by

$$\Delta W = RT\left[\ln \gamma_2^{\infty} - \left(1 - \frac{V_2^o}{V_1^o}\right) - \ln \frac{V_2^o}{V_1^o}\right]\left(\frac{V_2^o}{V_1^o}\right)^{-1/2}$$

or

$$\Delta W = (1.99)(298)\left[1.845 - (1 - 3.24) - 1.176\right](3.24)^{-1/2} = 955 \text{ cal/mole}$$

Now from Equation (138)

$$\frac{d\Delta W}{dT} = \frac{\Delta W}{T} - \frac{1}{2}(\beta_2 - \beta_1)\Delta W - \left(\frac{V_2^o}{V_1^o}\right)^{-1/2}\left[\frac{\Delta H_2^E}{T} + RT\left(1 - \frac{V_2^o}{V_1^o}\right)(\beta_2 - \beta_1)\right]$$

or

$$\frac{d\Delta W}{dT} = \frac{955}{298} - \frac{10^{-3}}{2}(1.08 - 0.21)(955) - (3.24)^{-1/2}\left[\frac{1480}{298} + (1.99)(298)(1 - 3.24)(10^{-3})(1.08 - 0.21)\right]$$

and

$$\frac{d\Delta W}{dT} = 0.66 \text{ cal/mole}\cdot{}^{\circ}\text{K}$$

To calculate the geometric contribution to ΔS_2^E one must know C_9, C_{10} and C_{11} defined by Equations (146), (147) and (148). From Equation (146)

$$C_9 = R\left[\ln \frac{V_2^\circ}{V_1^\circ} + \left(1 - \frac{V_2^\circ}{V_1^\circ}\right)\right] = (1.99)\left[1.176 + (1 - 3.24)\right]$$

or

$$C_9 = -2.11 \text{ cal/mole}\cdot{}^{\circ}\text{K}$$

and From Equation (147)

$$C_{10} = RT(\beta_2 - \beta_1)\left(1 - \frac{V_2^\circ}{V_1^\circ}\right) = (1.99)(298)(10^{-3})(1.08-0.21)(1-3.24)$$

or

$$C_{10} = -1.15 \text{ cal/mole}\cdot{}^{\circ}\text{K}$$

Finally from Equation (148)

$$C_{11} = \left(\frac{V_2^\circ}{V_1^\circ}\right)^{1/2}\left[\frac{1}{2}(\beta_2 - \beta_1)\Delta W + \frac{d\Delta W}{dT}\right] = (3.24)^{1/2}\left[\frac{(1.08-0.21)(955)}{(2)(10^3)} + 0.66\right]$$

or

$$C_{11} = 1.94 \text{ cal/mole}\cdot{}^{\circ}\text{K}$$

Now from Equation (149)

$$\Delta S_2^E = -C_9 - C_{10} - C_{11} = 2.11 + 1.15 - 1.94 = 1.32 \text{ cal/mole}\cdot{}^\circ K$$

where $C_9 + C_{10}$ is the geometric contribution, 3.26 cal/mole $\cdot{}^\circ$K , and C_{11} is the energetic contribution.

To compute the constants for Pierotti's homologous series correlation the correct equation for the system studied must be employed. For alcohols in water, Equation (142) should be used.

$$\ln \gamma_2^\infty = C_3 + C_4' \ell_2 + C_5/\ell_2 \tag{142}$$

At 40°C from the alkanes in water data, the value of C_4' has been determined as 1.04, i.e., see Table V. Thus two data points are needed to determine C_3 and C_5 . From Table I for MeOH-water, $\gamma_2^\infty = 2.30$ while for PrOH-water, $\gamma_2^\infty = 22$. Therefore

$$\ln 2.30 = C_3 + 1.04 + C_5/1$$

$$\ln 22 = C_3 + 3.12 + C_5/3$$

and solving the two relations simultaneously yields $C_3 = 0.06$ and $C_5 = -0.27$. In certain instances the system of equations is overdefined in that more data points exist than equations. In that case a "best" set of constants is determined to fit all the data.

APPENDIX E

VAPOR-LIQUID EQUILIBRIUM IN GAS LIQUID CHROMATOGRAPHY

At first the concept of vapor liquid equilibrium in the normal static sense seems a bit foreign when applied to GLC. The transient nature of the process, which on a macroscopic scale is in unsteady state, immediately causes one to think of the process as a nonequilibrium occurrence. The burden of proof that in fact vapor-liquid equilibrium does exist within the column may take one or both of two paths. By a logical consistent set of arguments, one's intuitive insight and feeling may be appealed to concerning the actual transfer of solute between the vapor and liquid phase and the equilibration which takes place. Alternately one may show supporting work which substantiates the hypothesis and concurs completely with equilibrium data obtained by other well accepted techniques. In order to confirm that equilibrium truly exists within the GLC column, both of these approaches will be used in the present discussion. The latter technique has already widely been used throughout this text to validate the method.

In the normal static sense vapor liquid equilibrium does not exist in a chromatographic column. In essence this is the crux of the entire problem. As the carrier gas is constantly flowing through the column sweeping the solute toward the exit during a short fraction of the total residence time, one must realize that a dynamic equilibrium exists here and not a static time invariant phenomena. In viewing a flow system one may adopt one of two points of view. The Eulerian approach may be used and one may situate his Maxwell's demon at one point along the column waiting for reports concerning the solute from time to time. One report would note the presence of the solute while the remaining reports would note nothing. Alternately one may adopt the LaGrangian view, correctly so, and order his demon to jump on a solute molecule and report back his findings irrespective of time interval. This is the approach to be pursued if the nature of the dynamic equilibrium in GLC is to be understood.

Consider a chromatographic column divided along its length into a number of very small yet distinct zones which shall be referred to as plates, as shown in Figure 12. Let us adopt this plate model of the column and imagine that initially a particular solute is all contained in the first plate, i.e., Figure 12(a). On passing an incremental volume of carrier gas, δV , some of the solute in the gas phase is swept onto the second plate where it equilibrates with the solvent. That equilibration occurs is logical during the short time period because the solvent is spread quite thinly having a high surface to volume ratio. Thus the solute does not have to penetrate far into the liquid phase to insure adequate contact with the solvent. Also very little solute is present initially so the process occurs on a microscopic or molecular level and the equilibration is very rapid, i.e., dynamic. Meanwhile the solute remaining in the liquid phase on the first plate equilibrates with the solute-free carrier gas entering the column as shown in Figure 12(b). On passing further increments of carrier gas this process repeats itself, see Figure 12(c), and slowly the vanguard of the solute moves along the column while the concentration on the first plate decreases until essentially no solute remains and the whole zone of solute

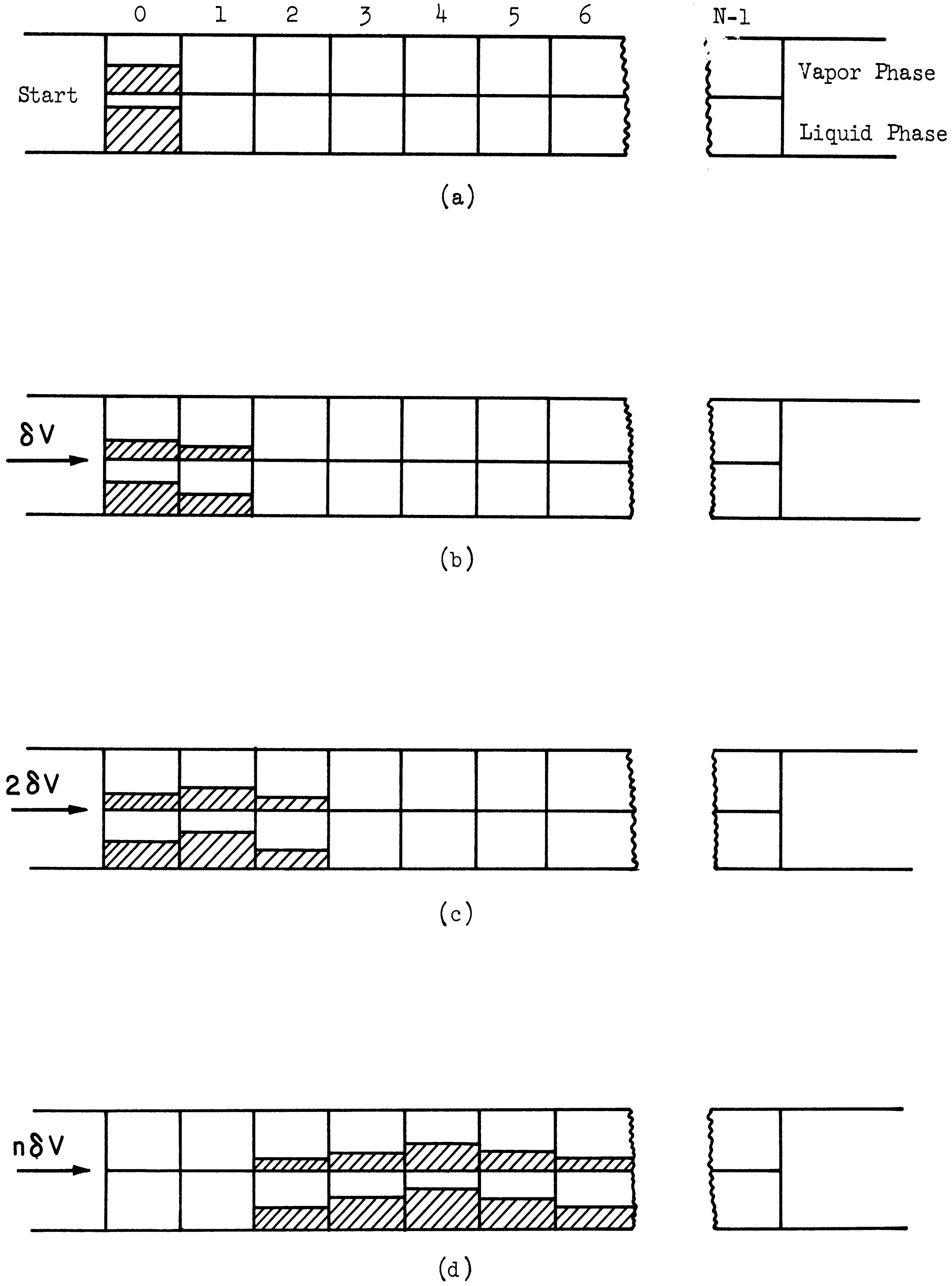


Figure 12. Elution Progress in a Column Composed of Plates.

has effectively moved along the column as in Figure 12(d). The way in which the solute is distributed among the plates after passage of a given number of increments of carrier gas depends on the relative crossections occupied by each phase and upon k , the equilibrium partition coefficient. Using the above type of intuitive argument led Martin and Synge(70) to derive the plate equation

$$V_R = V_G + k V_L \tag{1}$$

which relates the equilibrium GLC properties to the volume of carrier gas needed to elute the solute from the column.

As mentioned initially each plate or zone, although very small, remained distinct. More recent theoretical developments have reduced or eliminated the plate height. Lapidus and Amundson(62) and Van Deemter, Zuiderweg and Klinkenberg(117) while considering the effects of mass transfer resistance and longitudinal diffusion adopted a rate approach to deriving Equation (1). In these theories, the concept of local or point equilibrium is utilized. This concept is validated by the relatively fast mass transfer rates achieved and the low linear velocities through the chromatographic column. The fast mass transfer rates are due to the small support particle size providing the large surface area for the solvent. These authors show that for most normal conditions existing in a chromatographic column the theoretically more appealing rate approach reduces to a form equivalent to that obtainable from the less elegant plate theory. Thus regardless of approach the same result is obtained and therefore the concept of vapor-liquid equilibrium in a chromatographic column, be it on an infinitesimally small plate or at a local point, has been substantiated.

At the risk of repetition the alternate approach of substantiating GLC results by comparision with static equilibrium data will now be discussed in a bit more detail. In the literature review countless instances were cited quoting agreement between GLC data and static results. Also in the discussion of the results many cases were given showing excellent agreement between the data of this study and results in the literature determined by other methods. A short recapitulation of the more significant works will now be given which have been deemed highly pertinent.

Porter, Deal and Stross(87) studied the effect of the GLC variables on the resulting thermodynamic solution properties and conclusively showed that they were dependent solely on temperature, pressure and concentration. These workers also show that effects such as longitudinal diffusion should have no effect on Equation (1). They also studied the same systems by bulk equilibrium techniques which they had investigated by GLC and obtained very good agreement between the data determined by the two different methods. Kobayashi and Mellado(55) studied hydrocarbon vapor-liquid equilibrium by GLC and related the equilibrium constant to the partition coefficient used in GLC. The two are related by the ratio of N_L/N_G , being inversely proportional. The data obtained by Kobayashi showed good agreement with the standard N.G.A.A. tabulations.

Everett and Stoddart(27) studied normal and branched hydrocarbon solutes in dinonyl phthalate by GLC. The results they obtained compared exceptionally well with the static studies on the same systems conducted by Ashworth and Everett.(8) These latter authors examined the hydrocarbons in dinonyl phthalate both in the bulk phase and with the solvent spread on a solid support. The values of the partition coefficient derived from the two methods of studying static equilibrium were identical. The only effect of the solid support was to enhance the rate of attainment of equilibrium over that achieved in the bulk state. This, as was mentioned above, is due to the higher solvent contact area with the solute reducing the resistance to mass transfer.

Stalkup and Kobayashi,(111) in a continuation of Kobayashi's earlier study, investigated binary and ternary hydrocarbon vapor liquid equilibrium at pressure up to 2000 psia. Again comparison between the GLC derived equilibrium constants and those determined from static equilibrium stills was quite favorable. Koonce(56) in a further study in this area extended the work of Stalkup and conducted independent solubility studies on the same systems. The agreement obtained between the GLC data, the solubility studies, and the N.G.A.A. values is remarkably good. This work substantiates GLC as a vapor-liquid equilibrium technique valid for high pressures, finite concentrations, and multicomponent systems.

Finally Adlard, Khan and Whitham(2) have studied cyclohexane, benzene and CCl_4 in dinonyl phthalate by GLC used normal packed chromatographic columns. The resultant activity coefficients agree very well with the data the same authors(3) obtained at a later date using capillary columns. Also, both these results concur with the study of Freeguard and Stock(32) on the same systems using static measurements. These results again show the validity of GLC as a technique for obtaining equilibrium data, and that the solid support, present in normal packed columns, has no effect on the resultant properties. From the above discussion and substantiation it is felt that GLC has definitely been proven to be an equilibrium process, in a dynamic sense, capable of providing the same data obtainable by the more common static techniques in a quicker more straightforward manner.

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