72-9024

CHEAM, Venghuot, 1940-
VAPOR DENSITY AND PVT STUDIES OF MOLECULAR
INTERACTIONS OF POLAR SUBSTANCES.

The University of Oklahoma, Ph.D., 1971
Chemistry, physical

University Microfilms, A XEROX Company, Ann Arbor, Michigan

THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

VAPOR DENSITY AND PVT STUDIES OF MOLECULAR

INTERACTIONS OF POLAR SUBSTANCES

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

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Norman, Oklahoma

1971

VAPOR DENSITY AND PVT STUDIES OF MOLECULAR

INTERACTIONS OF POLAR SUBSTANCES

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ACKNOWLEDGEMENTS

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VAPOR DENSITY AND PVT STUDIES OF MOLECULAR

INTERACTIONS OF POLAR SUBSTANCES

CHAPTER I

INTRODUCTION

"Water . . . shows tendencies both to add and give up hydrogen, which are nearly balanced. Then . . . a free pair of electrons on one water molecule might be able to exert sufficient force on a hydrogen held by a pair of electrons on another water molecule to bind the two molecules together. Indeed the liquid may be made up of large aggregates of molecules, continually breaking up and reforming under the influence of thermal agitation."

Such an explanation amounts to saying that the hydrogen nucleus held between 2 octets constitutes a weak "bond." This was stated in J. Am. Chem. Soc., 42, 1431 (1920) by W. M. Latimer and W. H. Rodebush.[1]

So five decades ago the concept of the hydrogen bonding was first proposed, although it had been employed in vague form as early as 1910.[2,3] It seems somewhat surprising, therefore, that now in 1971 there is little direct information about the stoichiometry and structure of aggregates in water vapor; needless to say, the situation with respect to liquid water is even worse. Indeed, the field of hydrogen bonding is very complex and the evolution of satisfactory models for systems of polar molecules will probably require several more decades.

Extensive data have been accumulated on association reactions involving hydrogen-bonded components;[4-8] however, except for the association of carboxylic acids, which are generally agreed to form dimers in preference to other polymers, there is little general agreement regarding the nature of aggregates of hydroxylic compounds. Dimers of carboxylic acids in the vapor phase and most probably in dilute solutions are cyclic; their enthalpy of formation in the vapor phase is generally in the range (-14 ± 1) kcal/mole, and the enthalpy does not appear to depend strongly on the size of the acids or the substituents attached to the carboxyl group.

One must note, however, that in these acid systems, the percentage of the complex species is very high (20-60%) compared to other classes of hydrogen-bonded systems such as amines or alcohols (1-3%) in organic solvents or in gas; furthermore, with these other systems, there are most probably several types of polymers, not just dimers.

Presently, many of the most impressive scientific advances are occurring in the general area of the chemistry and biology of macromolecules such as DNA, RNA, and proteins. A molecular understanding of genetics and heredity appears to be within our grasp, although information about the exact molecular changes and structures involved is far from complete. There is a need for exact thermodynamic information about macromolecules which are important in life processes. We believe that studies of molecular complexes and interactions, performed in this laboratory and elsewhere, will provide the basis for a better understanding of these complicated subjects. Studies of association in solution, particularly in the dilute region, have been carried out more extensively than those

in vapor phase, in spite of the inherent problems of solvation effects and the need to know more about vapor phase systems. The major reason for this is the difficulty of obtaining data which are accurate enough to provide information about specific vapor phase complexes. Recently, techniques developed in this laboratory have been applied in several studies of molecular complexes in the vapor phase.

This research deals mainly with the self-association and hetero-association of polar molecules in the vapor phase for systems of immediate interest; i.e., the ones that could clarify the results of related systems and shed some new light on the behavior of more complicated systems in condensed phases. Different systems chosen for study were: methanol self-association; methanol-water; trimethylamine-sulfur dioxide; self-association of trifluoroacetic acid; trifluoroacetic acid-water; ammonia-water; self-association of triethylamine; triethylamine-water; pyridine-water; pyridine-methanol; pyridine-2,2,2-trifluoroethanol. Shorthand notations for these compounds are given in Appendix II and they will be used at convenient places. Each of the following sections gives a brief, pertinent literature survey concerning the above systems; work on chemically similar systems is also summarized.

Association of Methanol and Water Vapors

Recently in this laboratory, Farnham[13] has investigated the methanol system fairly extensively in vapor phase to almost 95% saturation, using the PVT expansion technique of Burnett at 3 temperatures: 15, 25, 35°C. Tucker, Farnham, and Christian[10] proposed the 1-3-8 self-association model for methanol in the vapor phase and in n-hexadecane. This model has been

successfully used to explain Fletcher and Heller's IR data[9] of 1-octanol

in n-decane in the overtone region, and those of Liddel and Becker[14] on

methyl-, ethyl-, and t-butyl alcohol in CCl_4 in the O-H stretching funda-

mental region; the model is also applied satisfactorily to NMR data of

ethanol in CCl_4 by Becker and colleagues[15] and Davis et al.[16]

Evidence of trimers was also reported by Kudchadker[17] who used

his smoothed values of compressibility factors to obtain formation con-

stants and enthalpies of formation of dimers, trimers and tetramers

using Wooley's model.[18] A PVT method using a Burnett-type apparatus was

employed to obtain raw compressibility factors of MeOH vapor in the

range $25°-200°C$ at $25°$ intervals and at corresponding pressures below

saturation; a graphical smoothing procedure was then used to get smoothed

internally consistent values of compressibility factors. The values of

2nd virial coefficients[17] are published in Reference 19; these values

agree very well with those of Kretschmer and Wiebe[20] and those of Russel

and Maass,[21] who also reported average molecular weights in terms of P

(up to 1 atm) and T $(75°-200°C)$.

Kell and McLaurin[22] have determined 2nd and 3rd virial coeffici-

ents of MeOH in the range of temperature $150-300°C$; their PVT measurements

indicated that trimers were definitely more important than tetramers,

hence the 1-2-3 model, an equilibrium mixture of monomers-dimers-trimers,

was proposed for MeOH vapor.

Bottomley and Spurling[23] measured the temperature variation of

virial coefficients of some polar gases and their mixtures, using an

unconventional apparatus, where absolute pressure determinations were

avoided by working differentially;[24] to obtain absolute values of the

virial coefficients, they used in addition a differential compressibi-
lity apparatus.[25] Their data indicated that the 3rd virial coefficient
contributes substantially to the total non-ideality of MeOH vapor.
Absolute values of B and C, 2nd and 3rd virial coefficients, were given
in the temperature range $50^{o}-150^{o}C$.[23]

Foz Gazulla et al.[26] found their data for ethanol, propanol and
butanol follow the monomer-dimer model; but for MeOH, the 1-2 model was
not adequate to explain their data without including the trimer terms.
However, Foz Gazulla and colleagues[27] later concluded that MeOH vapor
dimerizes, as indicated by the magnitude of 2nd virial coefficients ob-
tained from observed apparent molecular weights; the enthalpy of dimer
formation, ΔH_{2}, was found to be -6 kcal/mole.

In 1962 Scott and Dunlap[28] stressed the difficulties in the
numerical analysis of subatmospheric PVT data when the 3rd virial coef-
ficients cannot properly be neglected. Moreland, et al.,[29] found their
compressibility data fit best with the monomer-dimer-trimer model.
Kretschmer and Wiebe[20] could not distinguish between trimers and tetra-
mers as the larger polymers if they only used their vapor density data
for methanol, ethanol, and propanol; however, when their data were
combined with those of DeVries and Collins[30] and Sinke and DeVries,[31]
the 1-2-4 model (the equilibrium mixture of monomers-dimers-tetramers)
came out best.

Lambert, Staines and Woods[32] reported thermal conductivity data
on organic vapors, which showed the existence of polymers higher than
dimers in case of MeOH and acetone by the curved plots of thermal con-
ductivity against pressure. This view was later supported by Lambert's

curved Van't Hoff plots[33] for dimerization constants of MeOH, EtOH, and acetone. The heat capacity-temperature plot for MeOH vapor of DeVries and Collins[30] showed a flat minimum in the temperature range $110\text{-}150^\circ C$; the explanation for this was the assumption that dimers and possibly trimers were present. DeVries and Collins also reported the average molecular weights at different temperatures ($20\text{-}160^\circ C$) and pressures.

So far in this section, we have reviewed important studies of methanol vapor, that either propose or suggest the presence of trimers. We will now consider other work that seems to favor the presence of dimers only as associated species, or the more commonly assumed combination of monomers-dimers-tetramers, proposed in 1951 by Weltner and Pitzer.[34]

Lambert, Roberts, Rowlinson, and Wilkinson[35] used compressibility data to obtain 2nd virial coefficients of organic vapors, which they divided into two classes: a) those having observed 2nd virial coefficients agreeing with those calculated from Berthelot's critical data equation for vapors of ethane, ethylene, n-hexane, cyclohexane, benzene, ethyl ether, ethyl chloride, chloroform, and CCl_4,[35] and trimethylamine and triethylamine;[36] and b) those possessing 2nd virial coefficients larger than those predicted by the Berthelot equation: acetaldehyde, acetone, acetonitrite, and methanol. They concluded that the vapors of polar substances for which the energy of attraction between molecules, due to dipole interaction or to hydrogen bonding, is larger than kT undergo dimerization. It may be noted in passing that this concept of dimerization is somewhat different from that of Rice[37,67] or Christian and coworkers[59,60-62,66] in that the latter workers do not exclude, for

example, contributions from van der Waals forces to the value of the
dimerization constant.

Lambert et al.[35] and many authors[38-43,21] analyzed their data
using the state equation $PV/RT = 1 + B/V$ where all deviation from
ideality is incorporated into B, the 2nd virial coefficient. Claque
et al.[38] determined the heat of dimerization of MeOH in the temperature
range $60°-200°C$ and the concentration range $0.03-0.12$ mole/liter.
Curtiss and Hirschfelder[39] obtained B for MeOH, EtOH, water, NH_3, H_2S,
and many nonpolar molecules from heat of vaporization and vapor pressures;
also, in the saturation region, Ingle and Cady[42] used an improved Dumas
method to determine molecular weights of MeOH, EtOH, PrOH, BuOH, H_2O,
and D_2O at the boiling points. (For example, the average molecular
weight of methanol was found to be 33.82 gm/mole.) Dunken and Winde[40]
thought that methanol dimers are cyclic since the value of ΔH_2 they
determined from their IR data of MeOH vapor $(20-40°C)$ was equal to -15
kcal/mole, a value too large for a single hydrogen-bond.

Their heat capacity data of MeOH vapor at $346°K$ (at 755, 500,
260mm, and at the ideal gas state) convinced Weltner and Pitzer[34] that
they had the monomer-dimer-tetramer mixture, since inclusion of a term
involving pressure to the 4th power (in addition to the dimer term)
gave them a better fit than any other model tested. By combining nec-
essary data from References 30 and 41 with their own, they were able
to obtain ΔH and ΔS for dimers and tetramers. The 1-2-4 model was
therefore postulated to represent methanol vapor--an equilibrium mix-
ture of monomers, dimers and tetramers (cyclic tetramers~6kcal/bond).

This model has been more "popular" than any others for various

alcohols, and it has been supported by the work of several investigators including Fletcher,[44] Berman,[45] Barrow,[46] and others[47-51,20,31] employing diverse techniques such as heat capacity, IR, mass spectrometry, PVT, and ultrasonic dispersion.

Berman[45] concluded after reviewing the published results on heat capacities, viscosity, and entropy of vaporization that the 1-2-4 model is quite accurate in describing the alcohol vapors or solutes in dilute solutions, the tetramers being cyclic and very stable, as evident for six alcohols MeOH, EtOH, n-PrOH, 2-PrOH, 2-BuOH, and 2-methyl 2-propanol; also he concluded that in liquids the dimers are linear or cyclic and that the higher polymers are cyclic so that a limiting degree of association is reached at low temperatures. Fletcher[44] concluded from his IR study of MeOH vapor (40-120°) that the 1-2-4 representation adequately accounts for the non-ideality of this alcohol in vapor state.

Inskeep and Colleagues[51a] investigated the infrared spectra of MeOH vapor at 305°K and 335°K; their data were best fit with the 1-2-4 model. The tetramers were presumed to be cyclic and the trimers were not thought to be important at all. Deuterated methanol was also studied[51b] and the same model seemed to be the best. Barrow's ethanol heat capacity data,[46] too, were consistent with the 1-2-4 model.

Table 1 sums up briefly what has been discussed in this section about MeOH vapor. It is clear that there is a wide variation in results, even where the same model has been used. However, there seems to be a general agreement in that the average value of the association enthalpy per hydrogen bond is greater for the higher polymers than for dimers or trimers; this is probably due to the "cooperative effects" which will be discussed in Chapter V.

TABLE 1

POLYMERS OF MeOH VAPOR AND THEIR ENTHALPIES OF FORMATION, ΔH_n*

$-\Delta H_2$	$-\Delta H_3$	$-\Delta H_4$	$-\Delta H_8$	Method	Ref.
	12.5±0.1		67.8±0.3	PVT-Burnett type	10
3.3	4.59			PVT	22
3.5±0.1	**			Differential thermal expansion	23
4.3	15.1	26.0		PVT-Burnett type	17
6.0				Compressibility	27
7.1				Thermal Conductivity	26
3.2-7.3				Compressibility	35
4.1±.5				NMR	38
15.15±2.8				IR	40
3.2		24.2		Heat Capacity and PVT	34
4.0		22.1		VD, Heat Capacity	20
2.9±0.2		17±5		IR	51a
4.9±.2		14±1		IR (deuterated methanol)	51b

*ΔH in Kcal/mole; the subscript n stands for number of monomers in a polymer.

**Was not computed because their 3rd virial coefficients were probably in error according to Ref. 22 p. 4351.

The non-ideality of water vapor has not been studied as extensively as that of its counterpart methanol. Recently Christian et al.[7] reviewed the complexity of water in gas and in solution; it is evident that vapor phase studies of water are rare compared to those of solutions. Eucken[52] inferred the presence of relatively large aggregates of H_2O or D_2O from an examination of his isothermal compressibility data. Kell and McLaurin[53] interpreted their PVT studies of steam (150-450°C) in terms of the 2nd and 3rd virial coefficients. Luck and Ditter[54] observed the nonideality of steam up to $T/T_c \sim 1.1$ by infrared spectroscopy, while Kebarle and colleagues[55] examined the reactions of hydrogen ions with water molecules and calculated all the corresponding thermodynamic parameters. Rowlinson[56] employed the method of Stockmayer to calculate the 2nd virial coefficient of water, and used this value in calculating the lattice energy of ice. Van Thiel, Becker, and Pimentel[57] suggested the presence of cyclic water dimers in a nitrogen matrix at 20°K.

As far as the methanol-water reaction in gas is concerned, no previous work has been done to our knowledge. Farnham[13] obtained scattered data of 2 systems of water-alcohol: W-TFE and W-HFP at 25°C by isothermal expansion method. The respective 1:1 complex formation constants are $(4 \pm 2) \times 10^{-4}$ torr^{-1} and $(6 \pm 1)10^{-4}$ torr^{-1}. There is, however, comparatively more information about water and water-alcohol interactions in organic solvents.[7]

Charge-Transfer Complex Formation in Gas between
Trimethylamine and Sulfur Dioxide

Vapor phase studies of charge-transfer complexes are equally scarce compared to condensed phase studies. In the particular case of TMA-SO_2,

the only previous vapor phase studies were those by Burg[58] and Grundnes and Christian.[59,60] Burg obtained PVT properties of this system in the temperature range 65-100°C, from which equilibrium constants and the energy of formation for the 1-1 complex could be deduced.[59,60] Grundnes and Christian employed UV (276 mμ) absorption spectroscopy to determine K_{1-1} at 39.7°C and enthalpy of formation ΔH^o_{1-1} by measuring the absorbance variations with temperatures (39-60°C) at a constant composition of the gas mixture in the cell: $\Delta H^o_{1-1} = -9.7$ kcal/mole. This value agrees extremely well with that obtained from the treatment of Burg's data combined with those from this laboratory by Grundnes, Christian, Cheam and Farnham[61,62] using isothermal expansion of Burnett type and vapor density techniques.

This system has been studied in heptane solution.[60] An important conclusion, which is different from all other CT systems in this solvent known, is that the extinction coefficient and oscillator strength of the charge-transfer (CT) band of TMA-SO$_2$ are nearly the same in the gas phase as in heptane. The system has also been studied in chloroform and dichloromethane solutions.[63] Childs[64,65] obtained the crystal structure of the TMA-SO$_2$ complex; he also did solution work on weak complexes of I_2 with some aromatic hydrocarbons, pyridine, and diethyl ether in the solvent heptane, using two different methods: a conventional technique of the Benesi-Hildebrand type (UV-visible region) and a new solubility method involving tetramethyl ammonium polyiodide, which maintains a constant I_2 activity. In the vapor phase, Christian et al.[61] developed a new vapor phase isopiestic technique to study Et$_2$O-I$_2$ system, for which K_{1-1} was found to be 4.3±0.3 l/mole. This method was employed by Christian and

Grundnes[66] to investigate hexane-I_2 complex, which is thought to be stabilized solely by polarizability-polarizability interaction (K_{1-1}=3.4 l/mole); also in this paper an attempt was made to separate the effects of the different types of interaction (polarizability, CT) that might give rise to formation of complexes of I_2 with benzene, Et_2O and CO_2.

Rice[67] had previously attempted to distinguish between the effects of true charge-transfer forces and those attributable to simple van der Waals forces. The vapor phase complex benzene·I_2 was thought to be almost entirely held together by van der Waals forces; Christian, et al.,[66] consider that the force stabilizing the complex is composed of about 25% CT and 75% dispersion forces. For the Et_2O·I_2 complex, although there is undoubtedly some CT contribution, Rice[67] thought the binding force was largely of van der Waals type, while Christian considers it to be ∿50% CT and 50% dispersion. And for Et_2S·I_2, Rice took it as largely CT contribution, whereas Christian attributes almost all the binding force to dispersion in the case of the very weak complex CO_2·I_2. Rice also compared the stability of different complexes in gas and solution. For weak complexes, equilibrium constants and extinction coefficients generally decrease in going from vapor to solution; however, in the case of strong complexes these constants are frequently roughly the same in both phases.

Recently Tamres and Bhat[68] characterized the blue-shifted iodine band in the vapor phase of diethyl sulfide-I_2 complex for the first time. Previous vapor phase studies of CT reactions often involved use of the acceptor, I_2, complexing with donors benzene, Et_2O, Et_2S, p-xylene, mesitylene, Me_2S, or tetrahydrothiophem;[69-73] Kroll[73] also used the acceptor tetracyanoethylene reacting with p-xylene, o-xylene, mesitylene,

and durene, while Prochorow[74] studied carboxyl cyanide-common donor complexes. Spectroscopy was used in all cases except Reference 69 where the PVT method was employed. Extensive references on solution studies can be found in Childs' dissertation.[64] Moede and Curran[75] used dielectric measurements, UV absorption and density measurements to obtain different properties of addition compounds of SO_2 and SO_3 with trialkylamines and pyridine in solutions of benzene, CCl_4, chloroform, etc.; they obtained N-S bond moments, electric moments, and equilibrium constants, which reveal the following order of decreasing stability: $TMA \cdot SO_2 >$ $TEA \cdot SO_2 > t\text{-}BuA \cdot SO_2 > Pyr \cdot SO_2$. The very strong complexes $TMA \cdot SO_3$ and $TEA \cdot SO_3$ appear to be undissociated in benzene and chloroform.

TFA Self-association and Hetero-association with Water in Gas

Most of the studies of carboxylic acids in vapor phase have been single component systems; PVT-titration and vapor density techniques have been used[76-84] as well as electron diffraction,[85] dielectric polarization[86] and IR and Raman spectroscopy.[86-93]

Lundin, Harris and Nash[83] studied TFA vapor, at 150-560 Torr pressure in the temperature range 80-130°C; a new vapor density method using a magnetically operated silica balance[79] was employed. CCl_4 was used as the calibrating gas, since its density is well known. Then the densities of the gases of interest were determined as a function of the restoring current. The apparent molecular weights were determined at different temperatures and pressures, and thereby equilibrium constants were deduced. Although the dimers were predominant in all the acids studied, there was strong evidence that trimers, not tetramers, were

present as higher polymers in the case of acetic, trimethylacetic, butyric, and heptanoic acids.[79,82] Lundin, Harris and Nash[83] were able to obtain the subsequent thermodynamic parameters, and suggested that at particular temperature there is a small but significant correlation of the magnitude of K's with the nature of carboxyl substituents, and that the correlation is an entropy, rather than an enthalpy, effect as indicated by the following Table.

TABLE 2

DIMER DISSOCIATION OF ALIPHATIC ACID VAPORS*

Acid	Dissociation Constants at 160°C, in atm.	ΔH_2, Kcal/mole
TFA	7.4	14.0, 14.06[a],(13.7±.4)[b],14.01[e]
Formic	5.5	14.1[d]
Acetic	1.8	13.8
Butyric	1.6	13.9
Heptanoic	1.65	13.3
Trimethyl-acetic	1.1	14.0

*All data are from Ref. 83 except a = Ref. 84, b = Ref. 89, c = this work, d = Ref. 76.

This trend in the dissociation free energies was also observed in benzene solutions by Maryott, Hobbs, and Gross,[94] who generalized as follows: "In going through the aliphatic series from formic acid to stearic acid there is a progressive . . . increase in the tendency to associate."

PVT studies of light and heavy TFA were carried out by Taylor and

Templeman[84] in the temperature range 30-150°C up to 150 Torr pressure. They also observed in studies of a series of acids the same trend as that noted above; namely, that the stronger the carboxylic acid, the greater the dissociation constant (see Table 2) i.e., the smaller the value of association constant, and that the enthalpies of dissociation are practically invariant for different carboxylic acids. The deuterium bond was found to be a bit weaker than the hydrogen bond (by $\sim$ 100 cal in ΔH).

Fuson, Josien, Jones and Lawson[91] used IR and Raman spectroscopy to study light and heavy TFA in the gas phase (which was shown to consist of a mixture of monomers and associated species), also in CCl_4 and in the liquid state at 25°C. They were able to assign different bands to the various bonding groups; the principal bands corresponding to vibrations of the COOH and COOD groups have been assigned for both the monomers and the associated species by means of a comparative study of the two acids in the three states. Kagarise[89] also obtained IR spectra of TFA vapor in the temperature range 20-100°C; he was able to calculate the dimer dissociation enthalpy from the temperature dependence of O-H stretching bands. His spectra, in the range 400-5000 cm^{-1}, showed that at room temperature both monomers and dimers are present, but at 100°C the dimers are almost completely dissociated. His band assignments generally agreed with those of Fuson and colleagues.[91]

Affsprung and Lin[95] obtained an equation relating K_2 and T of TFA vapor, by which dimerization constants were obtained for use in several studies of heterosystems.[96-98] Stevens,[99] who needed the vapor phase monomer absorptivity of TFA for his solution studies, obtained as a by-product a value of the dimerization constant equal to $(0.30\pm.02)mm^{-1}$ at 25°C,

which agrees with the value calculated from Affsprung and Lin's equation.

Dunken and Marx[100] interpreted IR data on acetic acid and TFA vapors in terms of monomer-dimer equilibrium also, but their ΔH_2 (-17 Kcal) is somewhat large in magnitude compared to that obtained from other studies. Karle and Brockway[85] obtained some information on TFA using electron diffraction; they found the lengths of OH-O bonds for formic, acetic, and trifluoroacetic acids to be the same; this may well be, as Mathews and Sheets[93] suggested, an indication that the dimer enthalpies of formation of carboxylic acids are nearly the same.

Stevens[99] carried out extensive solution studies of TFA in cyclohexane, CCl_4, benzene, and dichloroethane; he obtained the dimer thermodynamic constants by studying the O-H stretching region at 3 temperatures; also the dimerization enthalpies were obtained by studying the C=O absorbances at different temperatures. The ΔH_2's from the two studies agree very well. Also, Stevens used a vapor-solution method to get Henry's Law constants in all the four solvents. Solvation effects on the association parameters were interpreted in terms of the α-model proposed by Christian et al.[101] and a simple lattice theory of group or site interactions.[99,99b] The enthalpies of formation for the dimers predicted by the α-model and lattice calculations compared well with the experimental values in cyclohexane, CCl_4 and dichloroethane. TFA dimers in the vapor as well as in these solvents were believed to be cyclic as previously reported in the literature. However, Murty and Pitzer[102,103] recently presented IR spectral evidence for linear dimers in nonpolar solvents; this inference was rebutted by Kirszenbaum, Corset, and Josien,[104] and it is not supported by the work of Stevens.[99]

Apparently, the only vapor phase study of TFA-water interaction is that by Chii Lin et al.[105,96] They studied this system at $20^{\circ}C$ and suggested that up to the mixture pressure of $\sim$ 12mm, where $x_w \sim$ .5, the only hetero-complex species is the cyclic acid monomer dihydrate - namely

$$CF_3-C \begin{array}{c} O--H---O \overset{H}{\underset{H}{\diagdown}} \\ O---H---O \overset{H}{\underset{H}{\diagdown}} \end{array} \cdot$$
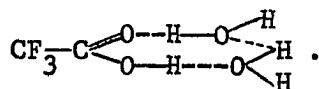
Other vapor complexes studied were the reaction of TFA with acetic acid and dioxane,[96,97] and with acetone and cyclopentanone;[98] thermodynamic constants for most of these reactions were obtained.

Villepin, Lauté, and Josien[106] used infrared spectroscopy to study this reaction in CCl_4; they found that there are two heterospecies present, TFA-W and $(TFA)_2$-W. Both the carbonyl stretching region and that of the three fundamental vibrations of water were analysed.

Amine Self-Association and Hetero-Association with
Water and Alcohol in Gas

Rowlinson[56] used statistical mechanical calculations (method of Stockmayer) to obtain 2nd virial coefficients of nine polar substances including ammonia, water, and methanol. His results on ammonia agreed reasonably well with observed values of Lambert and Strong,[36] who suggested that ammonia self-associates through hydrogen bonding rather than simple interactions between dipoles, in accordance with the evidence from crystal structure data that NH_3 forms hydrogen bonds.[107] Their[36] second virial coefficients of ammonia, obtained in the range of temperature $20-130^{\circ}C$ by the compressibility method, agreed very well with Stockmayer's[108] and Hirschfelder's[109] values. Pimentel, et al.,[110]

obtained infrared spectra of NH_3 suspended in a solid nitrogen matrix at $20^\circ K$; there was evidence of hydrogen bonding in ammonia dimers. Lowder[111] also employed infrared spectroscopy in the 3μ region, to study hydrogen bonding in ammonia, and obtained among other things the energy of formation of dimers. Kollman and Allen[112] used a quantum-mechanical method (CNDO/2 MO) to calculate dimerization energies of three different forms of ammonia dimers--linear, cyclic and bifurcated--the value for the linear dimer being in excellent agreement with experimental values of Lambert and Strong.[36]

Kollman and Allen also obtained the formation energies of the cross-dimers NH_3-H_2O, NH_3-HF and H_2O-HF; the values of these energies are, however, somewhat high: 10-13 kcal/mole. Experimentally, no one to our knowledge has studied this interaction of water with ammonia. The low temperature studies of heat capacity led Hildebrand and Giauque[113] to regard the crystalline hydrates of ammonia as ammonium salts = $(NH_4)OH$ and $(NH_4)_2O$. However, Waldron and Hornig[114] showed spectroscopically, by infrared spectra of crystals of the water-NH_3 system at $-195^\circ C$, that the above ionic structures didn't really exist as such but rather as bimolecular $(NH_3 \cdot H_2O)$ and trimolecular $(2NH_3 \cdot H_2O)$ crystals of ammonia hydrates; they then concluded that two types of hydrogen bonds were involved in the crystal, NH---O and OH---N. The vapor system NH_3-MeOH was studied by Millen and Zabicky;[115] the O-H frequency shift of MeOH was reported to be 170 cm^{-1}.

Apparently the only self-association study of triethylamine (TEA) in vapor phase is that by Lambert and Strong;[36] their 2nd virial coefficients agreed with those predicted by the Berthelot equation using the

critical constants. And to our knowledge the system TEA-water in vapor phase has not been studied by anyone. Hirano and Kozima[116] studied the hydrogen bonding interactions between TEA and MeOH in both vapor and condensed phase, by observing the O-H stretching band. The 1-1 enthalpy of formation, -8.2 kcal/mole, was obtained without getting the values of equilibrium constants. Three solvents of different dielectric constants were shown to affect the Δv_{O-H} and ΔH_{1-1}. The Δv_{O-H} value in CCl_4 compared well with that obtained by Arnett et al.,[117] 430 to 410 cm^{-1}.

Pyridine 2nd virial coefficients have been reported by various workers, including Cox and Andon,[118] Andon, Cox, Herington, and Martin,[119] and McCullough and colleagues.[120] The coefficients determined by the latter group were converted into equilibrium constants, from which the constant at 25°C was obtained by extrapolation for use in this research.

Hussein and Millen[121] observed the O-H stretching band of the 1:1 pyridine-water complex at approximately 3480 cm^{-1}, compared to 3390 cm^{-1}, the corresponding value in CCl_4 obtained by Mohr, Wilk, and Barrow.[122] Yarym-Agaev, et al.[121b] obtained a K_{1-1} value (0.00900 $torr^{-1}$ at 40°C) for the pyridine·water complex in the vapor phase; they used a differential equation for the dependence of pressure of a saturated vapor on the composition of the mixture. This K value is probably too large because at saturation pressures polymers higher than dimers most probably exist (as shown by this research, see Chapter V) and this will lead to an anomalously large value of K_{1-1} if corrections are not made for the larger aggregates. Studies of pyridine-alcohol systems in the vapor phase are also very rare; apparently the only work done was by Reece and Werner[123] who obtained the hydroxyl frequency shifts, Δv, and the approximate half-intensity band-widths ($v\frac{1}{2}$) of complexes with methanol, 2,2,2-trifluoroethanol and

2,2,3,3-tetrafluoropropan-1-ol.

Other vapor phase hetero-association studies include that of trimethylamine-MeOH by Fild, Swiniarski and Holmes,[124] who used infrared and vapor pressure techniques to obtain 1-1 equilibrium constants and enthalpy of formation, ΔH_{1-1} = -7.3 kcal/mole; experiments were performed at several temperatures in the range $\sim$10-50°C. Also, this system was studied by Claque, Govil and Bernstein,[38] employing NMR methods; these workers report ΔH_{1-1} = (-5.8±.7) kcal/mole. Millen and Zabicky[115] obtained $\Delta \nu_{O-H}$ and $\Delta \nu_{O-D}$ for methanol-ammonia and ammonia derivatives. Ginn and Wood[125] and Carlson et al.[126] used far IR to study the TMA-MeOH system among others; apparently no information was obtained about the vibration frequency of the bond OH----N. Tucker[127] obtained $-\Delta H_{1-1}$ = (7.31±0.02) kcal/mole for diethylamine-methanol complexes, while Cracco and Huyskens[128] gave ΔH_{1-1} = -8.9 kcal/mole for the formation of aggregate n-butanol·tri-n-butyl amine; both investigations employed vapor density methods. Tucker[127] also reported the formation enthalpy of the diethylamine-water complex: ΔH_{1-1} = -6.63±0.05 kcal/mole. Lin[105] reported the equilibrium constants for 1-1 and 2-2 complexes between ethylenediamine and water at 20°C. Hussein, Millen and Mines[121] also reported the bonded hydroxyl-stretching frequency of water hydrogen-bonded to trimethylamine, 2-methylpyridine and HFP.

Inskeep et al.[129] obtained $\Delta \nu_{O-H}$ and ΔH_{1-1} of MeOH reacted with diethyl ether in the vapor phase; respectively they are 124 cm^{-1} and (-4.7±0.7) kcal/mole. The dimethyl ether-hydrogen chloride complex formation reaction was investigated by Govil, Claque, and Bernstein;[130] they reported ΔH_{1-1} = (-7.1±0.8) kcal/mole, from measurement of the

temperature and pressure dependence of the proton NMR signals. The enthalpies of formation for this reaction (Me$_2$O-HCl) were also reported: -7.6[131] and -5.6[132] kcal/mole from pressure measurements and IR studies, respectively.

Farnham[13] studied the systems MeOH-TFE (2,2,2-trifluoroethanol) and MeOH-HFP (1,1,1,3,3,3-hexafluoro-2-propanol) using an isothermal expansion technique; the enthalpies of formation for the 1-1 complexes were given, (-7.3±0.2) and (-10.5±0.3) kcal/mole. Millen and Colleagues[133-136] reported the infrared frequency shifts of several vapor hetero-systems involving HF, HCl, HNO$_3$, ethers, carbonyl compounds. Reece and Werner[123] also gave $\Delta\nu_{O-H}$ values of different alcohols with several organic vapors. Lambert and colleagues[137] used a Boyle's law apparatus to obtain thermodynamic constants for the chloroform-ether and chloroform-diethylamine systems. Tables 3 and 4 show some constants related to the discussion of this section.

TABLE 3

ENTHALPY OF FORMATION OF AMINE DIMERS*

Gas	Dipole Moment μ, Debye**	$-\Delta H_2$ (kcal/mole)**
Ammonia	1.46	4.4, 3.7[a], 4.5±.4[b], 4.3[g]
Ethylamine	1.37	3.6
Methylamine	1.32	3.4
Diethylamine	1.10	3.3, 3.8[c]
Dimethylamine	1.02	3.1
Triethylamine	0.74	1.89±0.03[d], 1.88±0.08[e]
Trimethylamine	0.65	1.94±0.03[d]
Pyridine	2.2[h]	2.4±0.2[f]

*Data taken from Ref. 36 except a = Ref. 56, b = Ref. 111, c = Ref. 127 d = calculated from an equation by Lambert and Strong Ref. 36, e = this work, f = Ref. 120, g = Ref. 112, h = Ref. 138.

**There seems to be a general relation between μ and ΔH_2 (or ΔU) for ammonia and its derivatives: $\Delta U = 2\mu^e/r^3$ where r is the distance between the dipoles.[36] It is reasonable to assume that similar relations exist with other families of compounds, such as benzene, pyridine, etc.

TABLE 4

CONSTANTS OF SOME MIXED POLAR VAPORS*

Binary Mixture	$-\Delta H$, kcal/mole	$\Delta\nu$, cm^{-1}	K, mm^{-1}	Method	Reference
H_2O-NH_3 (linear)	11.1			MO	112
H_2O-HF (linear)	11.3			MO	112
H_2O-Pyridine		b^{O-H} 3480		IR	121
H_2O-Diethylamine	6.63±0.05		$4.2 \times 10^{-4}/25^{o}$	VD	127
H_2O-Ethylenediamine			$0.08/20^{o}$	VD	105
H_2O-TMA		b^{O-H} 3375		IR	121
H_2O-HFP		HFP()-H) 188		IR	121
MeOH-NH_3		O-H 170		IR	115
MeOH-TMA		O-H 330		IR	115
MeOH-TMA	5.8±0.7			NMR	38
MeOH-TMA	7.3	O-H 302	$9.4 \times 10^{-4}/27^{o}$	IR,VP	124
MeOH-TEA	8.2	O-H 370		IR	116
MeOH-Pyridine		O-H 210		IR	123
MeOH-Diethylamine	7.3±0.02		$7.3 \times 10^{-4}/25^{o}$	VD	127

TABLE 4 .cont'd

Binary Mixture	$-\Delta H$, kcal/mole	Δv, cm^{-1}	K, mm^{-1}	Method	Reference
MeOH-Et$_2$O	4.7±0.7	O-H 124		IR	129
MeOH-Et$_2$O		O-H 133		IR	123
MeOH-Tetrahydrofuran		O-H 124		IR	123
MeOH-HF		H-F 420		IR	135
MeOH-TFE	7.3±0.2		$10.9 \times 10^{-4}/25°$	PVT	13
MeOH-HFP	10.5±0.3		$41 \times 10^{-4}/25°$	PVT	13
TFE-Pyridine		O-H 370		IR	123
n-BuOH-(n-Bu)$_3$N	8.9			VD	128
Et$_2$O-CHCl$_3$	6.02			PVT	137
Me$_2$O-HCl	7.1±0.8			NMR	130
Me$_2$O-HCl	7.6			VP	131
Me$_2$O-HCl	5.6			IR	132
Diethylamine-CHCl$_3$	4.19			PVT	137
NH$_3$-HF	14.4			MO	112

*All values are for 1-1 complexes
VD = vapor density
VP = vapor pressure
$_b$O-H = frequency of the bonded O-H, not Δv values

CHAPTER II

OBJECTIVES AND METHODS

This research was performed with a primary objective in mind—to determine the most probable stoichiometries of complex species and the thermodynamic constants for association reactions in several systems of interest in the field of gas molecular interactions. To achieve this end, three kinds of classical methods were used: vapor density measurements using microbalance (buoyancy) and micropipette (volumetric addition) methods, and an isothermal expansion method of the Burnett type.

Reliable values of thermodynamic constants for molecular complexes in the vapor phase are scarce; and, in view of the importance of such information in the development of theories of weak molecular interactions, it is essential that accurate experimental results be obtained for numerous systems of associating vapors. The classical techniques to be employed here are in many cases capable of considerably greater accuracy than the conventional spectral methods for studying complexes. A combination of spectral and classical techniques should ultimately provide much more useful chemical information than any one type of method alone.

CHAPTER III

EXPERIMENTAL

Chemicals

All liquid chemicals were generally of reagent grade high purity as specified by different companies, distilled shortly before use to remove as much as possible[139,140] water and impurities and kept in desiccators above drierite (anhydrous $CaSO_4$) and/or anhydrous barium oxide with indicating $CaSO_4$.

Methanol, reagent grade purity higher than 99% sold by Malinkrodt Chemical Company, was fractionally distilled from magnesium methoxide in a 30-plate bubble-cap column at a reflux ratio 30:1 and stored with drierite. The forerun and the residue were 300-500 ml each.

Trimethylamine (TMA), sulfur dioxide, and ammonia were bought from Matheson Gas Products of respective purity > 99%, 99.8%, 99.99%. SO_2 and NH_3 were anhydrous grade while TMA was not specified by the company. When used, the gases were passed through a column of drierite or barium oxide.

Trifluoroacetic acid (TFA) was purchased from Matheson Coleman and Bell. P_2O_5 was used in the distilling pot to help remove water and columns of drierite were used at the openings of the 30-plate bubble-cap column; the reflux ratio was 30:1. Out of about 500 ml, only 200 ml was

collected, 150 ml being for the forerun and 150 ml for the residue. The distillate was then stored as in the case of methanol.

Triethylamine and pyridine were heated to reflux for several hours with and distilled from barium oxide, using a reflux ratio 30:1. Since pyridine is hygroscopic, it was allowed to stand over potassium hydroxide for 2-3 weeks before distillation; the main part of the distillate was collected in a flask containing KOH and stored this way in a desiccator with barium oxide and the indicating anhydrous $CaSO_4$. Again the forerun and the residue were about 400 ml. The quality was Pyridine Merck purchased from Merck and Company, Inc. Triethylamine was treated essentially the same way as pyridine except KOH was not used; it was obtained from Matheson Coleman and Bell.

2,2,2-Trifluoroethanol (TFE) was purified and distilled by Dr. S. B. Farnham.[13]

Apparatus, Pressure Measurement and Temperature Control

The main apparatus used in this research is shown in Figure 1, which gives a general view from the front and the side and an illustration of the longitudinal section. As Figure 1b shows, the apparatus is essentially composed of 3 Pyrex bulbs, L, S_a, and S_b, and a silica microbalance MB supported by a Teflon stand. The large bulb L has a volume of about 3.5 l, while $V_{Sa} \sim 65$ cc and $V_{Sb} \sim 250$ cc. Vapor density studies can be done by adding substances quantitatively through the mercury-covered, sintered-glass disk D or by using the microbalance; the isothermal expansion study was carried out using L and S_b while adsorption studies used L and S_a. Necessary specifications will be given in the following sections, where each experiment is described separately.
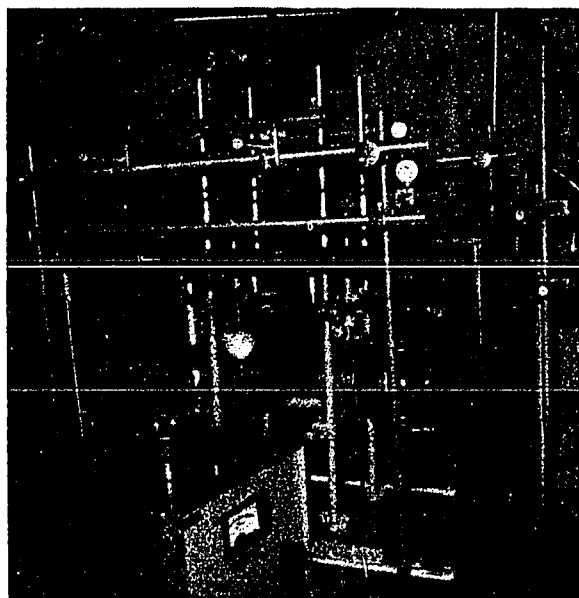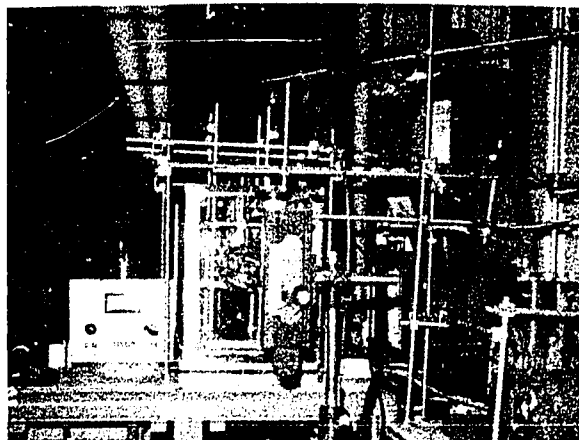
Figure 1a. General view of the apparatus: Top - photographed
from the front; Bottom - from the side.
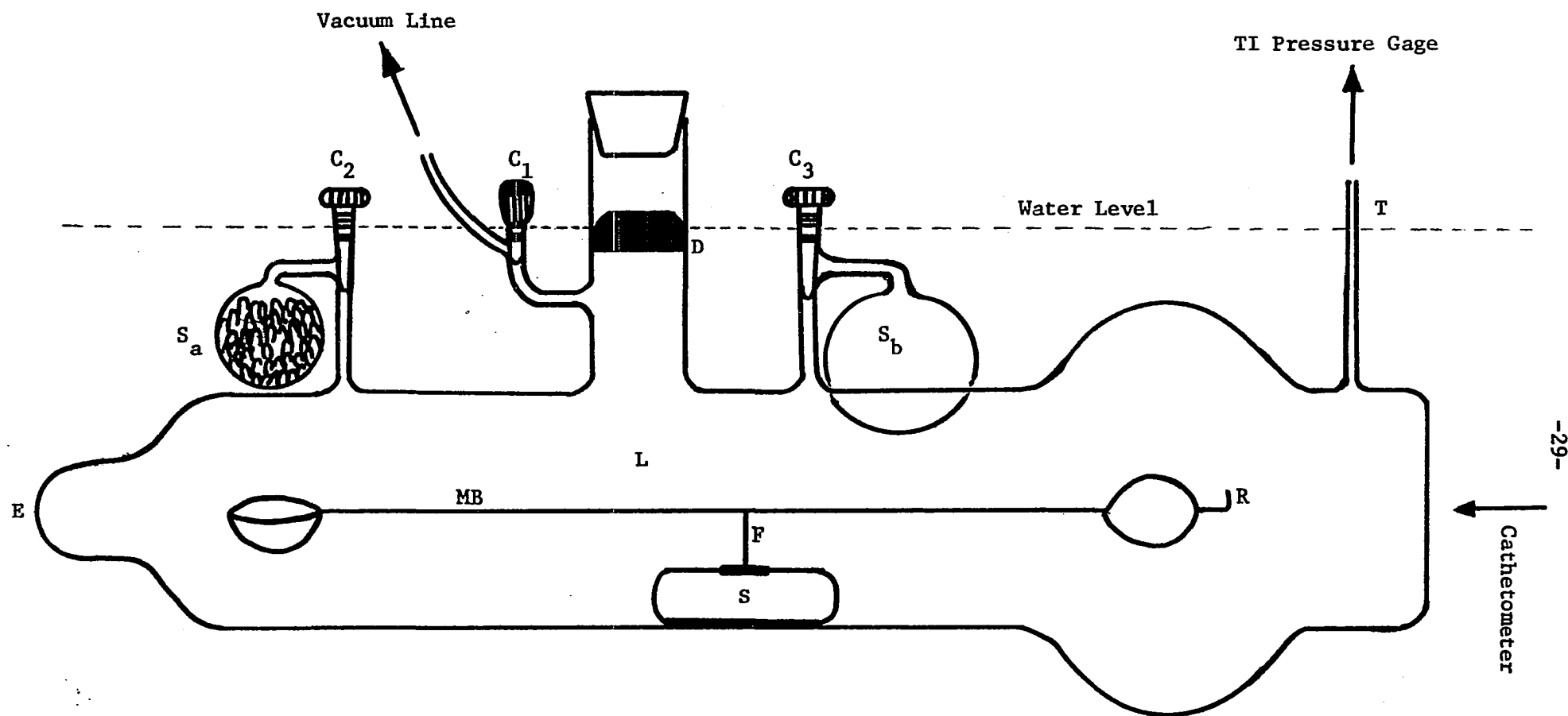
Figure 1b. Longitudinal Section of Apparatus for Vapor Density, PVT, Adsorption Studies. Different sizes aren't in proportion to each other.

In all types of experiments, however, the evacuation, the pressure measurement and the temperature control were done essentially the same way. The whole apparatus is connected to the vacuum line by a Rataflo stopcock, C_1, TF 6/13, Quickfit Inc. The pressures were read on a Fused Quartz Precision Pressure Gage,[13,127] model 140, obtained from Texas Instruments, Inc. The Gage Bourdon Tube is connected to the bulb L by a 1 mm i.d. Pyrex capillary tube, T, carefully wrapped around with a heating tape; this helps maintain the capillary tube at a temperature somewhat above $45^{\circ}C$, the temperature at which the gage was calibrated. The reference side of the Gage Bourdon Tube was continuously evacuated. When a gas exerts some pressure on the Bourdon Tube, the mirror rotates and the reflected light beam is detected by a photoelectric nulling mechanism. The pressure could be read to within 10^{-4} torr, but the reproducibility is approximately ±0.003 torr. A closed-end mercury manometer, instead of the TI Gage, was employed to study the self-association of methanol; for this a cathetometer was used to read the pressures to within ±0.025 mm.

The apparatus was submerged in a constant temperature bath--an aquarium containing about 20 gallons of water. The temperature control was achieved basically by using the thermoregulator-relay-light bulb system, a cooling coil in the bath if necessary, and the constant stirring of the bath. The mercury contact type thermoregulators were made by Precision Thermometers and Instruments Co. A Manostat Electronic Relay, Model 4, was used; two 200-300 watt bulbs, painted in black and/or wrapped around with aluminum foil served as heaters. A small refrigeration unit, outside the bath, provided and circulated the cold solution

through the copper cooling coil; this was necessary when the experiments were performed at 25°C. The stirring was vigorous enough to provide a fairly uniform temperature, but not so vigorous as to cause vibration of the microbalance and make it difficult to read the pointer R; a circulating pump, Model CP-5000 purchased from Little Giant Pump Co. was satisfactory for all experiments.

The studies were made at 25°, 35°, and 45°. Thermometers were made by Brooklyn Thermometer Co., Inc.; for 25° and 35° experiments a one degree thermometer was employed, while a ten degree thermometer was used at 45°C.

Vapor Density - Buoyancy

One of the earliest vapor density studies using a microbalance was by Edwards.[141] Dry air was used as calibrating gas; the determination of molecular weight of different gases was accomplished by bringing the pointer to a known position and known pressure. Johnson and Nash[79] used a magnetically operated silica balance to obtain vapor densities and thermodynamic constants of acetic and trimethylacetic acids. Bradley[143] and Carmichael[144] extensively described the operation, performance, and theory of various silica-balances.

Torsion-type silica microbalances have been used in this laboratory to determine activity coefficients of components in binary liquid mixtures,[142] vapor phase hetero-association constants by a new isopiestic technique,[61,66] and thermodynamic constants for vapor phase self- and hetero-association from buoyancy measurements,[12,61,62] which concern us here. These last three references include details of balance construction, data collection, and data analysis.

So briefly (see Figure 1b) the balance beam—connected to the balance frame, F, through two horizontal quartz fibers[143]—was about 30 cm long; the middle part of the beam (silica) was graded-sealed to Pyrex ends so that the two Pyrex bulbs could be easily connected to the beam. The closed bulb was 15-25 cc; the open bulb was made in such a way so that its total area nearly equalled the external area of the closed bulb. The areas were made as closely the same as possible to minimize adsorption effects. The weight of the whole balance was about 4.5 gm. The Teflon support, S, was grooved so that the balance base fitted in nicely; the support was inserted first into the large bulb L through E (open), then the balance was very carefully introduced and supported on S. The end E was then sealed with a torch, so that the entire apparatus was grease-free; vapors were in contact only with Pyrex and Teflon. With stopcocks C_2 and C_3 closed, the vapor density apparatus is ready for use.

After flushing and evacuating L with pure nitrogen N_2, the calibrating ideal gas, a series of pressures, P_{N_2}, and corresponding scale readings, R, was taken; these data were fit by linear least squares analysis in the form

$$R = a + bP_{N_2} + cP_{N_2}^2 + dP_{N_2}^3 \ . \ . \ . \ . \tag{1}$$

The empirical constants a, b, c, and d obtained were related to the force constant and rest position of the balance. Next, the system was evacuated and bulb L was flushed with the vapor of interest; the steps described above were repeated, i.e., a series of pairs of values of P and R was obtained in the same range of scale readings as that used with the N_2 gas.

Corresponding to each measured value of R, it was possible to calculate

P'_{N_2} (the pressure of N_2 required to give the same density as that of the

unknown vapor) by numerical interpolation of equation (1). This series

of calculated P'_{N_2} values was then used to compute the densities or to

calculate apparent molecular weights

$$<M> = P'_{N_2} \ M_{N_2} / P$$

and formal pressures

$$\pi = P'_{N_2} \ M_{N_2} / M_{MeOH} \ .$$

Either <M> or π could be analyzed for equilibrium constants and species

but the analysis involving π was more convenient; treatment of data will

be discussed in Chpater IV. This method was used to study the MeOH,

TMA-SO$_2$ and TFA systems. The limiting molecular weights used were

N_2 = 28.02, MeOH = 32.04, TMA = 59.11, SO$_2$ = 64.07, TFA = 114.02.

MeOH and TFA were added through the disk D from a micropipette

previously stored in a desiccator over drierite. In the case of TMA-SO$_2$

system, however, a different procedure was used as described in detail

by Grundnes, Christian, Cheam and Farnham.[62] Briefly, the 1:1 solid

adduct of TMA and SO$_2$ was prepared and stored in a bulb connected by a

Teflon-bore stopcock to the main apparatus (not shown in Fig. 1b).

After removing any excess of either component from the solid adduct (which

is a white, readily sublimable compound) the stopcock connecting the

storage bulb and L was opened and the total pressure in the main system

was brought to a desired value. Measurements were limited to pressures

less than 60-70% of saturation. All the changes in density were detected

by reading the height of the blackened pointer to ±0.001 mm with a precision cathetometer purchased from Gaertner Scientific Corporation.

PVT Studies - Isothermal Expansion

This technique has been used successfully in this laboratory by Farnham[13] and Tucker[127] for single-component and binary mixture systems. The apparatus is of the modified Burnett type; unique features of their method were that it was unnecessary to evacuate either bulb to a very low pressure at the start of a run[145] and that elaborate corrections were made to correct for the time-dependent adsorption processes occurring in the two bulbs.

In this research the large bulb, L, and the smaller one, S_b, were connected by a Fisher and Porter stopcock, C_3, (cat. no. 795-609-0004) see Fig. 1b; the respective volumes were about 3500 and 250 cc, S_a being closed; the volume ratio $V_L/(V_1 + V_{S_b})$ was determined very accurately using dry nitrogen (up to about 30 mm) as the ideal calibration gas. This ratio, X_L, was needed along with three pressures P_L, P_{S_b}, and P_F to calculate equilibrium constants. P_L, the pressure in the large bulb, was always greater than that of the small bulb, P_S; P_F is the final equilibrium pressure after the stopcock C_3 has been opened.

The three pressures are obtained as follows: After the two chambers are well flushed with the material of interest and pumped out to a convenient low pressure, the pumping is cut off by closing C_1; after a few minutes equilibration the pressure P_{S_b} is determined. Then stopcock C_3 is closed and a sample of volatile material is added to a desired pressure P_L, which is measured after a brief period of equilibration. Next C_3 is opened and the final equilibrium pressure, P_F, is measured.

Both bulbs are evacuated and the cycle is repeated. We will relate these observables quantitatively in Chapter IV. TEA systems at three temperatures were studied this way.

Vapor Density - Volumetric Addition Method

Methods involving the accurate volumetric addition of liquid samples by means of a micropipette have been employed frequently in this laboratory, for example by Lin,[105] Taha,[146] and Tucker[127] for vapor pressure or vapor density studies. The volumetric addition technique is one of the simplest and most direct means for getting information about molecular interactions in the vapor phase or in solution. In several respects, it is superior to the method employing the microbalance.

Micropipettes—built around a Swiss made micrometer and put out by Roger Gilmont Instruments, Inc., Model S3100A (0.25 ml, smallest division 0.0001 ml)—were employed to add liquids volumetrically. The pipettes, containing pure liquids ready to deliver, were stored in convenient cylindrical "desiccators" over drierite, and kept at a constant temperature in a thermostatted bath. To calibrate a pipette, a known volume of a substance A (to be later added quantitatively) is delivered into the evacuated bulb L through the mercury-covered, sintered-glass disk, D, of fine or medium-fine porosity;[147] then one reads the corresponding pressure, which should be in the ideal range. This is done several times and the average value of the ratio of the change in pressure to change in volume is determined.

Next, L is evacuated and flushed 3-4 times with another substance B; B is added to a certain desired pressure, using in this case a convenient plastic Roger Gilmont pipette, S1200A-2 ml. A is now added in

the same way as during the calibration run. At equilibrium any defi-
ciency is pressure is attributed to the formation of complexes. In
analyzing results (see Cahpter IV) the observed equilibrium pressure
is compared to that predicted from assumed constants and the known
values of π_A and π_B.

In this type of experiment, it is necessary to know in advance
the pressure-mole fraction phase diagrams to avoid condensation of
vapors. This information was usually found in Reference 148.

Adsorption studies for correcting vapor phase data are discussed
in the Appendix section; the adsorption balance and adsorption bulb are
described in detail.

CHAPTER IV

DATA: ANALYSIS AND RESULTS

Vapor Density - Buoyancy

As stated in the preceding chapter, a numerical interpolation technique can be used to obtain the equivalent nitrogen pressure, P'_{N_2}; in turn, knowledge of this pressure permits the calculation of the formal pressure, π, of a vapor A. Now, having the 2 known values of π and P, total pressure, one can in principle use least squares analysis to determine the stoichiometry of the most probable complex species and their equilibrium constants.

Assuming that all deviations from ideality are due to the formation of specific complexes and that each species behaves ideally one can write:

$$P = P_A + P_{A_2} + P_{A_3} + \ldots \qquad (1)$$

$$\pi = P_A + 2P_{A_2} + 3P_{A_3} + \ldots \qquad (2)$$

where P_A, P_{A_2}, and P_{A_3} are the partial pressures of the monomers, dimers, and trimers respectively; and π is the pressure the same molar amount of vapor would exert if it behaved ideally. These assumptions are made throughout this research.

The equilibrium constant for formation of a complex A_n, by the reaction:

$$nA \rightleftarrows A_n$$
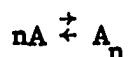
is defined as

$$K_n = \frac{P_{A_n}}{(P_A)^n} \tag{3}$$

where n stands for the number of monomers in the complex A_n.

Equations (1) and (2) can then be rewritten in terms of K_n as:

$$P = P_A + K_2 P_A^2 + K_3 P_A^3 + \ldots \tag{4}$$

$$\pi = P_A + 2K_2 P_A^2 + 3K_3 P_A^3 + \ldots \tag{5}$$

Equations (4) and (5) will be treated by a non-linear least squares procedure, using an optimum-seeking process.[149,150] Trial values of K_2, K_3, etc., are introduced into equation (4), which can now be solved linearly to give values of P_A. These monomer pressures are then used along with assumed values of K's to calculate π according to equation (5). The root mean square deviation in π, RMSD (π), is then

$$RMSD(\pi) = \sqrt{\frac{\sum_{i=1}^{N} (\pi_i - \pi_i^{calcd})^2}{N - p}}$$

where N is the number of π values and p is the number of parameters, K_n. The K values are systematically changed until RMSD is minimized; these values of equilibrium constants at minimum RMSD are taken as the most probable ones for a particular set of trial species; the constants derived in this way constitute a _fit_ for that set. The fit with the lowest minimum

RMSD is usually taken as best representing a system, unless the corresponding constants are chemically or physically meaningless.

Data for the methanol system, obtained in regions of pressure where adsorption studies have shown that adsorption is not important (see Appendix), were treated as described above. Table 5 gives RMSD for various choices of assumed associated species and corresponding values of association constants for MeOH vapor, inferred from data up to 90 Torr total pressure. Table 6 gives similar results for MeOH-water system at 25°. Data are tabulated at the end of this Chapter along with those of the remaining systems.

For the system trifluoroacetic acid, which was investigated during the early part of this research, an adsorption study was not performed; however, apparently adsorption occurs even at very low pressures in TFA vapors. To avoid such systematic errors, in computations, a difference technique was employed[62] where $\Delta\pi$ values are compared instead of π as in MeOH case. $\Delta\pi^{obs}$ was defined as:

$$\Delta\pi^{obs} = \pi^{obs}_{initial} - \pi^{obs}_{final}$$

where $\pi_{initial}$ was chosen to take the highest value of π in a data set, and π_{final} took on each of the remaining π values in the set. The calculated values of π were computed exactly the same way as explained above from equation (4) and (5), so that it was possible to write

$$\Delta\pi^{calcd}_{i} = \pi^{calcd}_{initial} - \pi^{calcd}_{final}$$

and

$$RMSD(\Delta\pi) = \sqrt{\frac{\sum\limits_{i=1}^{N} (\Delta\pi^{obs}_{i} - \Delta\pi^{calcd}_{i})^2}{N - p}}$$

TABLE 5

RMSD AND EQUILIBRIUM CONSTANT VALUES FOR VARIOUS SETS OF ASSUMED

METHANOL SPECIES AT 25°C AND UP TO 90 TORR TOTAL PRESSURE

Species	Equilibrium Constants[a]	RMSD, Torr
1-2	$K_2 = (7.46 \pm 0.17)\ 10^{-5}\ torr^{-1}$	0.0621
1-3	$K_3 = (4.61 \pm 0.08)\ 10^{-7}\ torr^{-2}$	0.0470
1-4	$K_4 = (3.69 \pm 0.08)\ 10^{-9}\ torr^{-3}$	0.0592
1-2-3	$K_2 = (3.8 \pm 11.5)\ 10^{-6}\ torr^{-1}$	0.0474
	$K_3 = (4.38 \pm 0.71)\ 10^{-7}\ torr^{-2}$	
1-3-4	$K_3 = (5.09 \pm 0.94)\ 10^{-7}\ torr^{-2}$	0.0473
	$K_4 = $ negative	
1-2-4	$K_2 = (3.52 \pm 0.69)\ 10^{-5}\ torr^{-1}$	0.0482
	$K_4 = (1.99 \pm 0.33)\ 10^{-9}\ torr^{-3}$	
1-3-6	$K_3 = (4.84 \pm 0.31)\ 10^{-7}\ torr^{-2}$	0.0473
	$K_6 = $ negative	
1-3-8	$K_3 = (4.8 \pm 0.3)\ 10^{-7}\ torr^{-2}$	0.0472
	$K_8 = $ negative	
1-3-9	$K_3 = (4.77 \pm 0.22)\ 10^{-7}\ torr^{-2}$	0.0472
	$K_9 = $ negative	
1-2-3-4	$K_2 = $ negative	0.0477
	$K_3 = (8.9 \pm 1.4)\ 10^{-7}\ torr^{-2}$	
	$K_4 = $ negative	

[a]Uncertainties in equilibrium constant values are standard errors.

TABLE 6

RMSD AND EQUILIBRIUM CONSTANT VALUES FOR VARIOUS SETS OF

ASSUMED METHANOL-WATER COMPLEXES AT $25^{\circ}C$

M-W	K	RMSD
One-Parameter Fits		
1-1	$(2.7\pm0.3)\ 10^{-4}\ torr^{-1}$	0.0774
1-2	$(1.11\pm0.09)\ 10^{-5}\ torr^{-2}$	.0636
2-1	$(2.8\pm0.2)\ 10^{-6}\ torr^{-2}$	.0628
2-2	$(1.56\pm0.07)\ 10^{-7}\ torr^{-3}$	.0406
3-1	$(3.5\pm0.2)\ 10^{-8}\ torr^{-3}$	.0580
1-3	$(5.6\pm0.4)\ 10^{-7}\ torr^{-3}$	.0617
3-2	$(2.24\pm0.07)\ 10^{-9}\ torr^{-4}$	.0292
2-3	$(8.9\pm0.4)\ 10^{-9}\ torr^{-4}$	.0362
3-3	$(1.36\pm0.03)\ 10^{-10}\ torr^{-5}$	.0209
4-1	$(4.8\pm0.3)\ 10^{-10}\ torr^{-4}$	.0600
1-4	$(3.0\pm0.2)\ 10^{-8}\ torr^{-4}$	.0641
4-2	$(3.3\pm0.1)\ 10^{-11}\ torr^{-5}$	.0316
2-4	$(5.2\pm0.2)\ 10^{-10}\ torr^{-5}$	.0397
4-3	$(2.06\pm0.05)\ 10^{-12}\ torr^{-6}$	.0234
3-4	$(8.3\pm0.2)\ 10^{-12}\ torr^{-6}$	.0259
Two-Parameter Fits		
1-1, 2-1	$(-2.5\pm1.1)\ 10^{-4}\ torr^{-1}$ $(5.2\pm1.0)\ 10^{-6}\ torr^{-2}$	.0588
1-1, 1-2	negative $(1.7\pm0.4)\ 10^{-5}\ torr^{-3}$	.0621
1-1, 2-2	negative $(2.8\pm0.1)\ 10^{-7}\ torr^{-3}$	.0223
1-1, 3-2	negative $(2.8\pm0.2)\ 10^{-9}\ torr^{-4}$	.0246

TABLE 6 cont'd

M-W	K	RMSD
1-1, 2-3	negative $(1.06\pm0.09)\ 10^{-8}$	.0345
1-1, 3-3	negative $(1.43\pm0.07)\ 10^{-10}\ torr^{-5}$	.0208
1-2, 2-1	$(5.4\pm2.8)\ 10^{-6}\ torr^{-2}$ $(1.5\pm0.7)\ 10^{-6}\ torr^{-2}$	.0602
2-2, 2-1	$(2.4\pm0.3)\ 10^{-7}\ torr^{-3}$ negative	.0364
2-2, 1-2	$(3.0\pm0.3)\ 10^{-7}\ torr^{-3}$ negative	.0301
2-2, 3-1	$(1.5\pm0.3)\ 10^{-7}\ torr^{-3}$ $(5\pm63)\ 10^{-10}\ torr^{-3}$	.0412
2-2, 1-3	$(2.0\pm0.3)\ 10^{-7}\ torr^{-3}$ negative	.0397
2-2, 3-2	negative $(2.7\pm0.5)\ 10^{-9}\ torr^{-5}$	.0292
2-2, 2-3	$(2\pm5)\ 10^{-8}\ torr^{-3}$ $(7.6\pm2.7)\ 10^{-9}\ torr^{-4}$	.0367
2-2, 3-3	negative $(1.5\pm0.2)\ 10^{-10}\ torr^{-5}$	.0209
2-2, 4-4	$(5.5\pm1.1)\ 10^{-8}\ torr^{-3}$ $(8.7\pm0.9)\ 10^{-14}\ torr^{-7}$	.0211
3-3, 2-1	$(1.39\pm0.09)\ 10^{-10}\ torr^{-5}$ negative	.0212
3-3, 1-2	$(1.48\pm0.09)\ 10^{-10}\ torr^{-5}$ negative	.0205
3-3, 3-1	$(1.31\pm0.09)\ 10^{-11}\ torr^{-5}$ $(1.4\pm2.5)\ 10^{-9}\ torr^{-3}$	.0211
3-3, 1-3	$(1.49\pm0.09)\ 10^{-10}\ torr^{-5}$ negative	.0205

TABLE 6 cont'd

M-W	K	RMSD
3-3, 3-2	$(1.2\pm0.2)\ 10^{-10}\ torr^{-5}$ $(4\pm4)\ 10^{-10}\ torr^{-4}$	.0212
3-3, 2-3	$(1.7\pm0.2)\ 10^{-10}\ torr^{-5}$ negative	.0203
3-3, 4-4	$(1.1\pm0.2)\ 10^{-10}\ torr^{-5}$ $(2\pm2)\ 10^{-14}\ torr^{-7}$	.0209

From here on the optimizing process is exactly the same as above. The TFA results are given in Tables 7 and 8 and in Figure 2. The 1-2 fit was definitely better than any other one, by about a factor of 2 in RMSD, and when another parameter was included along with the dimerization constant, that parameter was found to be negative.

In the case of the trimethylamine-sulfur dioxide system, which consisted of a 50-50 mixture, $\Delta\pi^{calcd}$ was inferred directly from $P_{initial}$ and P_{final}, P_i and P_f, using an assumed K_{1-1} value, without calculating the monomer pressures by equation (4). $\Delta\pi^{calcd}$ was derived to be

$$\Delta\pi^{calcd} = 2(P_i - P_f) - \frac{2}{K_{1-1}} \{\sqrt{P_i K_{1-1} + 1} - \sqrt{P_f K_{1-1} + 1}\}$$

and the error function was just

$$RMSD(\Delta\pi) = \sqrt{\frac{\sum\limits_{i=1}^{N} (\Delta\pi^{obs} - \Delta\pi^{calcd})^2}{N - 1}}$$

where p was set equal to 1. The TMA-SO_2 results are also given in Tables 7 and 8 along with those of MeOH and TFA.

Temperature dependence studies of equilibrium constants permitted calculation of enthalpy and entropy changes of the formation reactions through the usual thermodynamic relations

$$\Delta G^o = -RT \ln K_p$$

$$= \Delta H^o - T\Delta S^o$$

and

$$\frac{d \ln K_p}{d(\frac{1}{T})} = \frac{-\Delta H^o}{R}$$

where K_p is the pressure equilibrium constant. The Van't Hoff plot for

TABLE 7

FORMATION CONSTANTS OF METHANOL, METHANOL-WATER, TRIFLUOROACETIC ACID, TRIFLUOROACETIC ACID-WATER, AND TRIMETHYLAMINE-SULFUR DIOXIDE SYSTEMS

$T^{\circ}C$	System	Equilibrium Constant	RMSD, torr
25	MeOH	$K_3 = (4.61 \pm 0.08)\ 10^{-7}\ torr^{-2}$	0.0470
25	MeOH-W	$K_{3-3} = (1.36 \pm 0.03)\ 10^{-10}\ torr^{-5}$	.0209
25		$K_2 = (0.256 \pm 0.003)\ torr^{-1}$	.011
35	TFA	$K_2 = (0.119 \pm 0.001)\ torr^{-1}$	.017
44		$K_2 = (0.0621 \pm 0.0006)\ torr^{-1}$	.021
25		$K_{1-1} = (0.049 \pm 0.001)\ torr^{-1}$	.032
35	TFA-W	$K_{1-1} = (0.020 \pm 0.001)\ torr^{-1}$	.045
44		$K_{1-1} = (0.0147 \pm 0.0004)\ torr^{-1}$	.034
35	TMA-SO_2	$K_{1-1} = (0.0106 \pm 0.0019)\ torr^{-1}$	.035
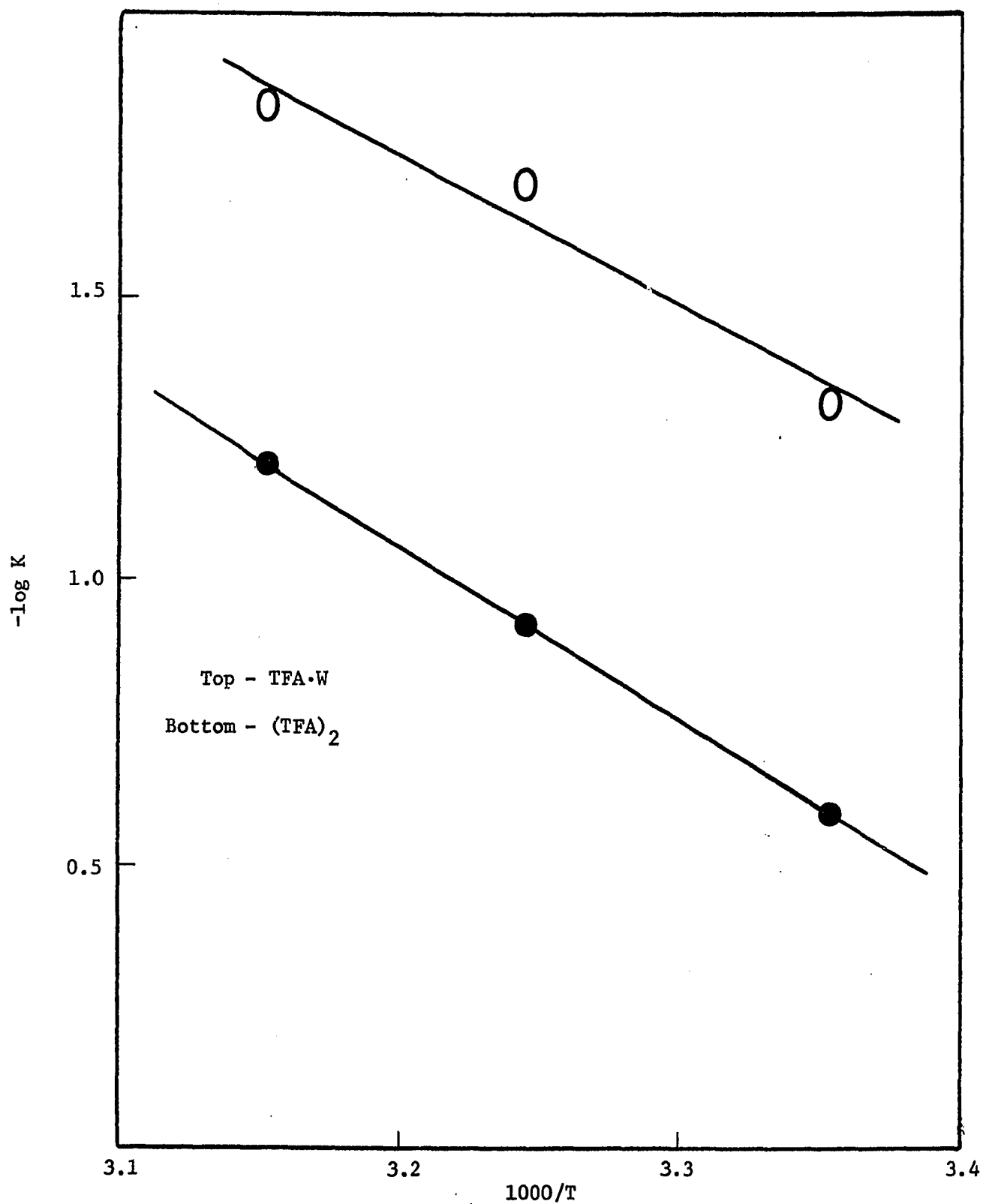
Figure 2. Van't Hoff Plots of the Temperature Dependence of the Dimer

Association Constants for TFA, and TFA-Water Systems.

TABLE 8

THERMODYNAMIC PARAMETERS FOR TRIFLUOROACETIC ACID, TRIFLUOROACETIC

ACID-WATER, AND TRIMETHYLAMINE-SULFUR DIOXIDE SYSTEMS

Complexes	Parameters	Reference
$(TFA)_2$	$\Delta H_2^o = (-14.01 \pm 0.02)$ Kcal/mole	This Work
	$\Delta S_2^o = (-49.70 \pm 0.06)$ e.u.	
$(TFA)_2$	$\log K_2 \ (torr^{-1}) = \dfrac{3062}{T} - 10.860$	This Work
	$= \dfrac{3053}{T} - 10.800$	83
	$= \dfrac{3071}{T} - 10.869$	84
	$= \dfrac{2847.2}{T} - 10.053$	95
TFA·W	$\Delta H_{1-1}^o = (-12.0 \pm 2.6)$ Kcal/mole	This Work
	$\Delta S_{1-1}^o = (-46.4 \pm 8.6)$ e.u.	
	1 Torr standard state was used.	
TMA·SO$_2$	$\Delta E_{1-1}^o = (-9.1 \pm 0.3)$ Kcal/mole	62
	$\Delta S_{1-1}^o = (-20.9 \pm 0.8)$ e.u.	
	1 mole/liter standard state was used.	

K_p's yields ΔH^O and ΔS^O. Recall that if the equilibrium constants are expressed in terms of concentration units, K_c, then the plot $\ln K_c$ vs. $1/T$ will yield as the slope $-\Delta E^O/R$, the internal energy change/R, rather than $-\Delta H^O/R$. Throughout this research K_p's are used unless other units are specified. Usually the standard state of 1 Torr is used.

Isothermal Expansion

As mentioned in the preceding chapter there are 4 observed quantities to be analyzed in this type of experiment--3 pressures P_L, P_S, and P_F and the volume ratio, X_L. In a one-component system, one can write

$$P_L = P_{A_L} + K_2 P^2_{A_L} + K_3 P^3_{A_L} \cdots$$

$$P_S = P_{A_S} + K_2 P^2_{A_S} + K_3 P^3_{A_S} + \cdots$$

$$P_F = P_{A_F} + K_2 P^2_{A_F} + K_3 P^3_{A_F} + \cdots \tag{6}$$

and the corresponding formal pressures are

$$\pi_L = P_{A_L} + 2K_2 P^2_{A_L} + 3K_3 P^3_{A_L} + \cdots$$

$$\pi_S = P_{A_S} + 2K_2 P^2_{A_S} + 3K_3 P^3_{A_S} + \cdots$$

$$\pi_F = P_{A_F} + 2K_2 P^2_{A_F} + 3K_3 P^3_{A_F} + \cdots \tag{7}$$

Having assumed that each species behaves ideally, one can then write the following mass balance equation

$$\pi_F = X_L \pi_L + X_S \pi_S \tag{8}$$

To get values of equilibrium constants out of these equations, one seeks again to minimize RMSD as a function of the K's. With assumed values of K's, P_{A_L} and P_{A_S} are calculated from equation (6); these monomer pressures are used along with assumed K values to compute π_L and π_S according to equation (7). In turn these formal pressures permit calculation of π_F from equation (8); π_F is then used along with assumed K values to solve linearly for P_{A_F} according to equation (7). Finally with P_{A_F} one can calculate P_F in equation (6). Next, this predicted final pressure, P_F^{calcd}, is compared with P_F^{obs} and the error function is written as

$$RMSD = \sqrt{\frac{\sum_{i=1}^{N} (P_F^{obs} - P_F^{calcd})^2}{N - p}}$$

This technique led to the determination of equilibrium constant values for triethylamine, needed in treating data for cross-association systems. The results are shown in Tables 9 and 10. The 1-2 fits were sufficient to represent the data at the three temperatures; Figure 3 illustrates the temperature dependence studies for TEA along with those of the TEA-W system, studied by the volumetric addition vapor density method to be discussed next.

Vapor Density - Volumetric Addition

Recall that there are 3 observed quantities to be treated--π_A, π_B, and P. Usually it is desirable to restrict the pressures of both components to ranges in which they do not self-associate, so that the computations are a bit simpler. To simplify, assume that in a mixture A self-associates but B doesn't, and the hetero-complexes are only of one kind;

TABLE 9

FORMATION CONSTANTS OF TRIETHYLAMINE, TRIETHYLAMINE-WATER, AND AMMONIA-WATER SYSTEMS

$T^{\circ}C$	K_2 (Torr^{-1})	K_{1-1} (Torr^{-1})	
	$(TEA)_2$	TEA·W	NH_3·W
25	$(8.83\pm1.23)\times10^{-5}$	$(5.11\pm0.22)\times10^{-4}$	
35	$(8.02\pm0.66)\times10^{-5}$	$(3.08\pm0.03)\times10^{-4}$	$(7.54\pm0.38)\times10^{-5}$
43.5	$(7.33\pm0.48)\times10^{-5}$	$(2.23\pm0.03)\times10^{-4}$	
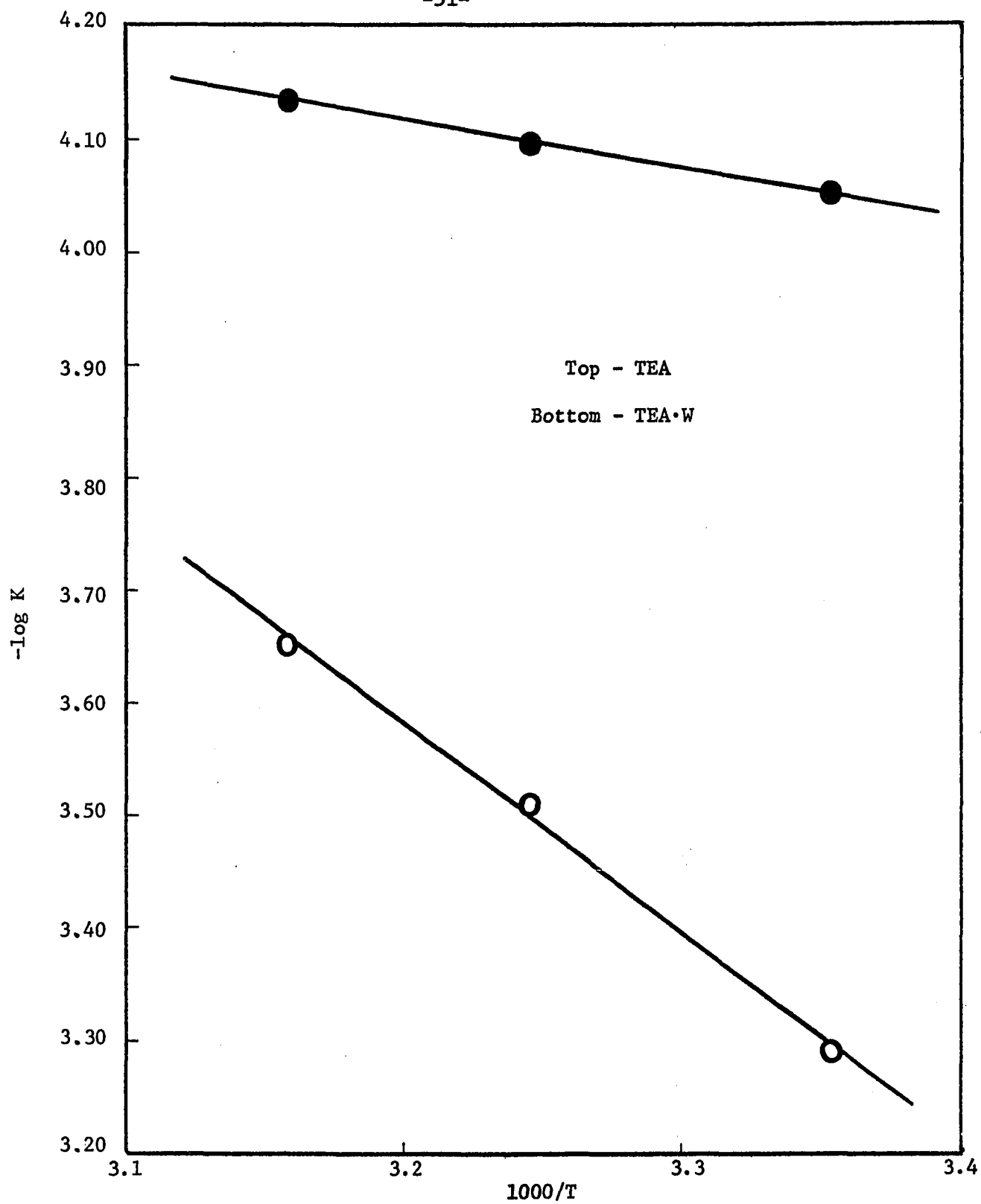
Figure 3. Van't Hoff Plot of the Temperature Dependence of the Dimer Associ-

ation Constants for TEA, and TEA-Water Systems.

TABLE 10

THERMODYNAMIC PARAMETERS FOR TRIETHYLAMINE, AND

TRIETHYLAMINE-WATER SYSTEMS

$(TEA)_2$

$\Delta H_2^o = (-1.88 \pm 0.08) \text{ Kcal/mole}$

$\Delta S_2^o = (-24.9 \pm 0.3) \text{ e.u.}$

TEA·W

$\Delta H_{1-1}^o = (-8.4 \pm 0.4) \text{ Kcal/mole}$

$\Delta S_{1-1}^o = (-43 \pm 2) \text{ e.u.}$

Standard state = 1 Torr

then we can write

$$nA \overset{\rightarrow}{\leftarrow} A_n \ , \ K_n = \frac{P_{A_n}}{P_A^n}$$

$$aP_A + bP_B \overset{\rightarrow}{\leftarrow} P_{AaBb} , \ K_{ab} = \frac{P_{AaBb}}{P_A^a P_B^b}$$

and also

$$\pi_A = P_A + nK_n P_A^n + aK_{ab} P_A^a P_B^b \qquad (9)$$

$$\pi_B = P_B + bK_{ab} P_A^a P_B^b$$

$$P = P_A + P_B + K_n P_A^n + K_{ab} P_A^a P_B^b$$

With a reasonable trial value of K_{ab}, P_A and P_B may be inferred

from values of π_A and π_B, with equation (9), using a numerical, Newton-

Raphson method for 2 equations in two unknowns.[151] These monomer pres-

sures together with the assumed K_{ab} value in turn permit calculation of

P according to the P equation of (9). Finally this predicted P value,

P^{calcd}, is compared to the observed P value, and the error function is

obtained and minimized as in the preceding sections. (In the earlier

treatment π^W values were compared instead of P.) The above treatment

can be extended to cases where there are two or more cross-species

and where B also self-associates. (In cases where a mixture is added

volumetrically, the treatment of data is also the same; the only system

studied this way was triethylamine-water at $25^\circ C$.) Systems studied by

this method were TFA-W (Tables 7 and 8 and Figure 2), TEA-W (Tables 9

and 10, and Figure 3), NH_3-W (Table 9), MeOH-W (Table 7), Pyr-W, MeOH,

TFE (Table 11). Data are tabulated in Tables 12-34.

TABLE 11

FORMATION CONSTANTS OF PYRIDINE-WATER, PYRIDINE-METHANOL, AND

PYRIDINE-2,2,2-TRIFLUOROETHANOL SYSTEMS AT 25°C

Complexes	Equilibrium Constant	RMSD(P), torr
Pyr · W	$K_{1-1} = (7.6 \pm 0.2) \times 10^{-4} \text{ torr}^{-1}$	0.0149
Pyr · M	$K_{1-1} = (9.33 \pm 0.21) \times 10^{-4} \text{ torr}^{-1}$	0.0212
Pyr · TFE	$K_{1-1} = (7.7 \pm 0.2) \times 10^{-3} \text{ torr}^{-1}$	0.0118

Observed and Calculated Data

The data treated in this Chapter are presented in the following tables. Sometimes a table is appended with the data which were not used in the calculations; in that case a star * indicates that only the data from the top of the page on down to the starred values (included) were used in the calculations; necessary explanations can be found in Chapter V.

All pressures are in torr units. P and π are total and formal pressures. P_M, P_N, and P_A are the monomer pressures of methanol, water, and amine or acid or alcohol, depending on the systems.

TABLE 12

OBSERVED BUOYANCY DATA FOR METHANOL SYSTEM AT 25°C

P	π	<M>
10.70	10.73	32.14
12.35	12.35	32.03
14.30	14.26	31.94
16.25	16.21	31.97
18.40	18.42	32.08
20.35	20.39	32.10
21.85	21.88	32.08
24.15	24.13	32.02
27.40	27.43	32.07
30.00	30.08	32.13
32.70	32.74	32.08
34.55	34.56	32.05
37.05	37.04	32.04
39.50	39.59	32.11
42.80	42.82	32.06
49.05	49.13	32.09
52.20	52.40	32.16
54.75	54.90	32.13
57.35	57.49	32.12
60.70	60.94	32.17
64.40	64.68	32.18
67.15	67.47	32.19
67.85	68.21	32.21
69.30	69.57	32.16
69.80	70.05	32.16
70.90	71.13	32.14
72.01	72.36	32.20
72.30	72.66	32.20
73.75	74.18	32.23
77.50	77.92	32.22
77.65	78.02	32.19
79.05	79.41	32.18
79.80	80.35	32.26
80.50	81.03	32.25
80.90	81.45	32.26
81.85	82.37	32.25
82.15	82.58	32.21
82.75	83.27	32.24
82.90	83.48	32.26
83.05	83.60	32.25
83.95	84.49	32.25
84.25	84.86	32.27
84.75	85.25	32.23

TABLE 12 cont'd

P	π	<M>
85.45	86.01	32.25
85.60	86.16	32.25
85.85	86.38	32.24
87.90	88.52	32.27
88.15	88.80	32.28
88.65	89.35	32.29
89.40	90.00	32.25
* 90.80	91.42	32.26
91.35	92.00	32.27
91.45	92.09	32.26
93.35	94.13	32.31
93.40	94.06	32.27
94.50	95.25	32.29
94.60	95.44	32.32
96.35	97.08	32.28
98.30	99.12	32.32
100.10	100.97	32.32
100.85	101.67	32.30
101.80	102.74	32.34
104.10	105.02	32.33
104.25	105.21	32.33
104.45	105.50	32.36
105.70	106.77	32.36
106.85	108.01	32.39
108.20	109.44	32.41
109.10	110.29	32.39
110.05	111.34	32.42
110.65	111.80	32.37
112.15	113.55	32.44
112.65	113.91	32.40
115.01	116.46	32.45
* 116.55	118.02	32.45
117.25	119.24	32.58
117.40	118.89	32.49
118.50	120.16	32.49
119.25	121.01	32.51
119.45	122.15	32.76
120.95	123.44	32.70
121.35	123.60	32.63
121.55	125.28	33.02
122.47	126.01	33.00
123.05	126.34	32.90
123.33	127.02	33.00

TABLE 13

OBSERVED AND CALCULATED BUOYANCY DATA FOR METHANOL SYSTEM

UP TO 90 TORR TOTAL PRESSURE AT 25°C

P	P_M	π	π^{calcd}
10.70	10.70	10.73	10.70
12.35	12.35	12.34	12.35
14.30	14.30	14.26	14.30
16.25	16.25	16.21	16.25
18.40	18.40	18.42	18.41
20.35	20.35	20.39	20.36
21.85	21.85	21.88	21.86
24.15	24.14	24.13	24.16
27.40	27.39	27.43	27.42
30.00	30.00	30.08	30.02
32.70	32.68	32.74	32.73
34.55	34.53	34.56	34.59
37.05	37.03	37.04	37.10
39.50	39.47	39.59	39.56
42.80	42.76	42.82	42.87
49.05	49.00	49.13	49.16
52.20	52.13	52.40	52.33
54.75	54.67	54.90	54.90
57.35	57.26	57.49	57.52
60.70	60.60	60.94	60.90
64.40	64.28	64.68	64.64
67.15	67.01	67.47	67.43
67.85	67.71	68.21	68.14
69.30	69.15	69.57	69.60
69.80	69.64	70.05	70.11
70.90	70.74	71.13	71.22
72.01	71.84	72.36	72.35
72.30	72.13	72.66	72.65
73.75	73.57	74.18	74.12
77.50	77.29	77.92	77.93
77.65	77.44	78.01	78.08
79.05	78.82	79.41	79.50
79.80	79.57	80.35	80.26
80.50	80.26	81.03	80.98
80.90	80.66	81.47	81.38
81.85	81.60	82.37	82.35
82.15	81.90	82.58	82.66
82.75	82.49	83.27	83.27
82.90	82.64	83.47	83.42
83.05	82.79	83.60	83.57
83.95	83.68	84.49	84.49
84.25	83.98	84.85	84.80

TABLE 13 cont'd

P	P_M	π	π^{calcd}
84.75	84.47	85.25	85.31
85.45	85.17	86.01	86.02
85.60	85.31	86.16	86.17
85.85	85.56	86.38	86.43
87.90	87.59	88.52	88.52
88.15	87.84	88.80	88.77
88.65	88.33	89.35	89.28
89.40	89.07	90.00	90.05
90.80	90.46	91.42	91.48

TABLE 14

VOLUMETRIC ADDITION DATA FOR METHANOL-WATER SYSTEM AT 25°C

P	π_M	π_W^{calcd}	π_W
57.996	50.388	7.792	7.795
64.024	50.383	14.012	14.006
56.913	49.292	7.793	7.798
62.926	49.288	13.984	13.988
38.188	30.380	7.849	7.833
44.328	30.378	14.034	14.042
69.428	62.043	7.724	7.788
68.113	60.612	7.819	7.809
73.961	60.605	13.985	14.009
65.619	58.069	7.831	7.817
71.553	58.056	14.059	14.027
38.855	31.044	7.855	7.821
44.995	31.042	14.042	14.026
48.793	41.104	7.790	7.794
54.902	41.100	14.006	14.009
49.352	41.623	7.834	7.820
55.468	41.621	14.061	14.043
48.226	40.474	7.848	7.834
54.349	40.472	14.074	14.039
47.745	40.010	7.828	7.809
53.861	40.007	14.043	14.011
40.058	32.277	7.830	7.829
46.205	32.275	14.029	14.047
38.617	30.820	7.839	7.820
44.758	30.818	14.027	14.033
65.128	57.580	7.823	7.811
71.045	57.567	14.024	14.018
66.449	58.927	7.815	7.814
72.334	58.920	13.995	14.027
55.636	48.007	7.788	7.805
61.675	48.002	13.994	14.013
56.999	49.335	7.833	7.835
63.052	49.330	14.073	14.057

TABLE 15

VOLUMETRIC ADDITION DATA FOR METHANOL-WATER SYSTEM AT $35^{\circ}C$

P	π_M	π_W^{calcd}	π_W
112.213	104.933	8.056	8.063
118.535	104.933	14.558	14.533
99.165	91.610	8.095	8.065
105.539	91.610	14.602	14.564
111.853	91.610	21.091	21.039
100.487	92.999	8.049	8.074
106.863	92.999	14.562	14.593
113.149	92.999	21.028	21.049
104.999	97.613	8.026	8.038
111.380	97.613	14.559	14.540
117.664	97.613	21.044	21.009
54.241	46.241	8.097	8.094
60.659	46.241	14.554	14.586
67.092	46.241	21.033	21.069
56.309	48.274	8.144	8.133
62.773	48.274	14.649	14.641
69.177	48.274	21.102	21.107
108.646	94.835	14.546	14.572
114.957	94.835	21.046	21.062
63.616	49.148	14.624	14.605
70.056	49.148	21.114	21.086
75.484	54.721	21.019	21.018
118.121	98.184	20.940	20.988

TABLE 16

VOLUMETRIC ADDITION DATA FOR METHANOL-WATER SYSTEM AT 45°C

P	π_M	π_W^{calcd}	π_W
125.164	114.232	11.497	11.476
135.045	114.221	21.485	21.504
116.874	105.873	11.459	11.424
126.813	105.862	21.491	21.455
121.225	110.433	11.305	11.383
131.141	110.422	21.321	21.443
121.848	110.960	11.408	11.395
131.749	110.949	21.411	21.428
122.262	111.358	11.430	11.395
132.179	111.348	21.448	21.432
124.787	114.025	11.322	11.343
134.680	114.014	21.322	21.377
124.022	112.794	11.776	11.740
133.946	112.783	21.805	21.778
123.533	112.374	11.701	11.702
133.443	112.364	21.714	21.723
122.728	111.505	11.754	11.699
132.660	111.494	21.789	21.730
123.945	112.623	11.869	11.860
133.882	112.612	21.910	21.928
123.026	111.823	11.737	11.710
132.960	111.813	21.775	21.765
91.878	80.377	11.718	11.733
101.875	80.369	21.771	21.778
96.678	85.194	11.738	11.738
106.633	85.185	21.755	21.778
90.186	78.675	11.715	11.718
100.145	78.668	21.728	21.747
101.916	90.508	11.707	11.689
111.284	90.500	21.140	21.126
87.285	75.712	11.757	11.739
93.948	75.703	18.457	18.437
63.675	52.072	11.671	11.728
73.699	52.068	21.719	21.769
71.537	59.836	11.799	11.744
81.601	59.830	21.896	21.781
70.562	58.934	11.722	11.733
80.547	58.930	21.737	21.791
68.749	57.081	11.754	11.746
78.783	57.077	21.817	21.800

TABLE 16 cont'd

P	π_M	π_W^{calcd}	π_W
65.722	54.043	11.753	11.744
75.778	54.039	21.836	21.810
66.659	55.059	11.679	11.725
76.668	55.055	21.714	21.748
64.842	53.143	11.770	11.746
74.878	53.139	21.832	21.803
64.649	52.967	11.753	11.742
74.663	52.963	21.792	21.774

TABLE 17

BUOYANCY DATA FOR TRIFLUOROACETIC ACID SYSTEM AT 25°C

P	P_A	$\Delta\pi^{calcd}$	$\Delta\pi$
2.217	1.578	0	0
2.212	1.575	0.008	0.021
2.136	1.533	0.118	0.125
2.043	1.481	0.250	0.267
2.036	1.477	0.260	0.262
1.913	1.406	0.436	0.441
1.886	1.391	0.474	0.486
1.862	1.376	0.508	0.532
1.774	1.324	0.632	0.623
1.693	1.276	0.745	0.758
1.632	1.239	0.830	0.818
1.617	1.230	0.851	0.861
1.484	1.147	1.034	1.023
1.475	1.141	1.047	1.065
1.379	1.080	1.178	1.184
1.332	1.050	1.241	1.227
1.318	1.040	1.261	1.271
1.201	0.963	1.418	1.423
1.165	0.939	1.464	1.457
1.011	0.833	1.666	1.669
1.002	0.827	1.679	1.671
0.857	0.723	1.864	1.853
0.803	0.683	1.934	1.942
0.722	0.623	2.034	2.027
0.575	0.509	2.214	2.206
0.566	0.501	2.226	2.234
0.442	0.401	2.373	2.379
0.424	0.386	2.394	2.385

TABLE 18

BUOYANCY DATA FOR TRIFLUOROACETIC ACID SYSTEM AT 35°C

P	P_A	$\Delta\pi^{calcd}$	$\Delta\pi$
2.806	2.220	0	0
2.804	2.219	0.002	0.040
2.719	2.163	0.117	0.121
2.656	2.121	0.201	0.208
2.622	2.099	0.246	0.287
2.613	2.093	0.258	0.268
2.531	2.037	0.367	0.371
2.465	1.993	0.455	0.465
2.460	1.990	0.460	0.496
2.395	1.945	0.547	0.550
2.371	1.929	0.579	0.591
2.280	1.866	0.698	0.731
2.279	1.865	0.699	0.708
2.209	1.817	0.790	0.803
2.194	1.806	0.810	0.814
2.109	1.746	0.920	0.952
2.089	1.732	0.946	0.957
2.033	1.692	1.018	1.030
2.009	1.676	1.048	1.049
1.908	1.603	1.178	1.187
1.862	1.569	1.236	1.270
1.834	1.549	1.272	1.261
1.822	1.540	1.288	1.303
1.697	1.448	1.445	1.470
1.666	1.425	1.484	1.483
1.642	1.406	1.515	1.503
1.627	1.396	1.533	1.541
1.503	1.301	1.687	1.713
1.426	1.243	1.782	1.781
1.401	1.223	1.813	1.794
1.335	1.172	1.893	1.896
1.294	1.139	1.943	1.961
1.234	1.092	2.016	2.016
1.209	1.072	2.046	2.028
1.149	1.024	2.118	2.122
1.090	0.977	2.188	2.201
1.031	0.928	2.258	2.242
1.005	0.907	2.289	2.280
0.895	0.816	2.417	2.429
0.872	0.797	2.444	2.445

TABLE 18 cont'd

P	P_A	$\Delta\pi^{calcd}$	$\Delta\pi$
0.831	0.762	2.491	2.465
0.829	0.760	2.494	2.479
0.693	0.644	2.649	2.644
0.655	0.611	2.692	2.697
0.636	0.594	2.714	2.684
0.629	0.588	2.722	2.712
0.483	0.458	2.884	2.888
0.463	0.440	2.906	2.902
0.428	0.408	2.944	2.914
0.275	0.267	3.108	3.107
0.268	0.260	3.116	3.125
0.268	0.260	3.116	3.113
0.246	0.240	3.138	3.140

TABLE 19

BUOYANCY DATA FOR TRIFLUOROACETIC ACID SYSTEM AT $44°C$

P	P_A	$\Delta\pi^{calcd}$	$\Delta\pi$
3.594	3.025	0	0
3.389	2.876	0.259	0.291
3.358	2.853	0.299	0.263
3.335	2.836	0.328	0.323
3.273	2.789	0.406	0.424
3.179	2.720	0.524	0.557
3.155	2.702	0.554	0.521
3.143	2.693	0.569	0.564
3.081	2.646	0.646	0.662
2.967	2.560	0.789	0.828
2.932	2.533	0.832	0.803
2.914	2.520	0.854	0.846
2.765	2.405	1.038	1.043
2.759	2.401	1.045	1.082
2.717	2.368	1.098	1.089
2.715	2.367	1.100	1.071
2.589	2.269	1.253	1.259
2.563	2.249	1.285	1.321
2.515	2.211	1.344	1.322
2.508	2.205	1.353	1.342
2.394	2.115	1.491	1.498
2.348	2.079	1.546	1.575
2.300	2.041	1.604	1.592
2.236	1.990	1.681	1.654
2.180	1.945	1.747	1.752
2.148	1.919	1.785	1.819
2.104	1.884	1.838	1.834
2.064	1.851	1.885	1.857
1.982	1.784	1.983	1.987
1.920	1.733	2.056	2.092
1.909	1.725	2.068	2.058
1.819	1.650	2.174	2.147
1.712	1.561	2.299	2.295
1.707	1.557	2.305	2.296
1.680	1.534	2.336	2.369
1.613	1.477	2.414	2.388
1.511	1.391	2.531	2.521
1.458	1.346	2.592	2.622
1.461	1.348	2.589	2.579
1.399	1.295	2.659	2.633

TABLE 19 cont'd

P	P_A	$\Delta\pi^{calcd}$	$\Delta\pi$
1.316	1.223	2.754	2.741
1.281	1.193	2.793	2.788
1.233	1.151	2.847	2.870
1.151	1.079	2.939	2.916
1.081	1.017	3.017	3.013
1.073	1.010	3.026	3.014
1.005	0.949	3.101	3.134
0.940	0.891	3.173	3.155
0.858	0.817	3.263	3.256
0.851	0.810	3.271	3.267
0.767	0.734	3.362	3.388
0.746	0.714	3.385	3.371
0.653	0.629	3.485	3.483
0.601	0.580	3.541	3.540
0.543	0.526	3.602	3.593
0.476	0.462	3.674	3.700
0.367	0.359	3.787	3.791
0.304	0.299	3.853	3.862

TABLE 20

VOLUMETRIC ADDITION DATA FOR TFA-WATER SYSTEM AT $25^{\circ}C$

P	π_A	π_W^{calcd}	π_W
3.639	2.751	1.570	1.549
5.147	2.751	3.150	3.116
6.660	2.751	4.732	4.686
8.138	2.751	6.274	6.257
9.623	2.751	7.819	7.828
3.709	2.860	1.565	1.541
5.201	2.860	3.131	3.112
6.681	2.860	4.679	4.682
8.158	2.860	6.222	6.252
9.623	2.860	7.748	7.823
3.736	2.856	1.596	1.582
5.253	2.856	3.187	3.152
6.756	2.856	4.760	4.719
8.239	2.856	6.310	6.287
9.275	2.856	7.858	7.858
3.721	2.874	1.568	1.565
5.223	2.874	3.144	3.134
6.719	2.874	4.710	4.702
8.214	2.814	6.271	6.282
9.696	2.874	7.817	7.860
3.745	2.894	1.579	1.593
5.254	2.894	3.163	3.184
6.767	2.894	4.746	4.778
3.692	2.803	1.587	1.580
5.211	2.803	3.180	3.160
6.736	2.803	4.775	4.739
8.225	2.803	6.329	6.313
9.707	2.803	7.873	7.885

TABLE 21

VOLUMETRIC ADDITION DATA FOR TFA-WATER SYSTEM AT 35°C

P	π_A	π_W^{calcd}	π_W
4.556	3.617	1.640	1.595
6.163	3.617	3.297	3.236
7.744	3.617	4.929	4.880
9.330	3.617	6.564	6.524
10.922	3.617	8.205	8.167
12.530	3.617	9.860	9.811
4.582	3.643	1.644	1.589
6.161	3.643	3.276	3.232
7.716	3.643	4.881	4.875
9.269	3.643	6.483	6.519
10.829	3.643	8.090	8.166
12.402	3.643	9.710	9.816
4.368	3.391	1.613	1.582
5.934	3.391	3.229	3.222
7.516	3.391	4.860	4.865
9.100	3.391	6.492	6.507
10.685	3.391	8.123	8.148
12.252	3.391	9.734	9.794
4.420	3.438	1.631	1.590
6.022	3.438	3.285	3.233
7.599	3.438	4.910	4.871
9.182	3.438	6.541	6.515
10.775	3.438	8.181	8.159
12.355	3.438	9.806	9.797
13.934	3.438	11.430	11.442

TABLE 22

VOLUMETRIC ADDITION DATA FOR TFA-WATER SYSTEM AT $44^{\circ}C$

P	π_A	π_W^{calcd}	π_W
5.117	4.023	1.688	1.666
6.766	4.023	3.390	3.358
8.393	4.023	5.069	5.060
10.030	4.023	6.757	6.765
11.671	4.023	8.448	8.469
13.353	4.023	10.179	10.186
14.989	4.023	11.862	11.889
5.106	3.989	1.703	1.662
6.790	3.989	3.442	3.389
8.430	3.989	5.134	5.094
10.095	3.989	6.850	6.803
11.725	3.989	8.530	8.505
13.362	3.989	10.215	10.206
15.072	3.989	11.973	11.988
4.969	3.832	1.689	1.661
6.622	3.832	3.394	3.356
8.244	3.832	5.066	5.054
9.898	3.832	6.770	6.756
11.576	3.832	8.497	8.461
13.254	3.832	10.223	10.174
14.948	3.832	11.964	11.903
5.226	4.167	1.684	1.663
6.858	4.167	3.371	3.367
8.489	4.167	5.055	5.077
10.124	4.167	6.742	6.782
11.769	4.167	8.438	8.491
13.402	4.167	10.120	10.189
15.044	4.167	11.811	11.894
4.967	3.841	1.680	1.659
6.611	3.841	3.376	3.358
8.254	3.841	5.069	5.063
9.901	3.841	6.766	6.766
11.563	3.841	8.477	8.475
13.214	3.841	10.175	10.178
14.871	3.841	11.878	11.876

TABLE 23

BUOYANCY DATA FOR TRIMETHYLAMINE-SULFUR DIOXIDE SYSTEM AT 35°C

P_i	P_f	$\Delta\pi$	$\Delta\pi^{calcd}$
6.175	5.604	0.630	0.589
5.604	5.009	0.641	0.611
5.009	4.637	0.356	0.381
4.637	4.227	0.417	0.419
4.227	3.756	0.462	0.481
5.654	5.181	0.464	0.486
5.181	4.790	0.382	0.401
4.790	4.281	0.534	0.521
4.281	3.675	0.606	0.618
3.675	3.172	0.516	0.513
3.172	2.816	0.349	0.361
2.816	1.648	1.221	1.181
6.175	5.604	0.636	0.589
5.604	5.009	0.637	0.611
5.009	4.637	0.351	0.381
4.637	4.227	0.410	0.419
4.227	3.756	0.452	0.481
5.654	5.181	0.458	0.486
5.181	4.790	0.378	0.410
4.790	4.281	0.525	0.521
4.281	3.675	0.593	0.618
3.675	3.172	0.501	0.513
3.172	2.816	0.336	0.361
2.816	1.648	1.154	1.181
6.175	5.604	0.629	0.589
5.604	5.009	0.642	0.611
5.009	4.637	0.356	0.381
4.637	4.227	0.416	0.419
4.227	3.756	0.459	0.481
5.654	5.181	0.461	0.486
5.181	4.790	0.382	0.410
4.790	4.281	0.533	0.521
4.281	3.675	0.602	0.618
3.675	3.172	0.507	0.513
3.172	2.816	0.339	0.361
2.816	1.648	1.159	1.181
5.589	5.151	0.474	0.449
5.151	4.817	0.406	0.343
4.817	4.491	0.336	0.334
4.491	3.677	0.831	0.832

TABLE 23 cont'd

P_i	P_f	$\Delta\pi$	$\Delta\pi^{calcd}$
3.677	2.411	1.299	1.285
2.411	1.515	0.883	0.905
1.515	0.862	0.637	0.657
0.862	0.286	0.479	0.577
6.102	5.589	0.604	0.529
5.589	5.151	0.467	0.449
5.151	4.817	0.394	0.343
4.817	4.491	0.324	0.334
4.491	3.677	0.795	0.832
3.677	2.411	1.245	1.285
2.411	1.515	0.868	0.905
1.515	0.862	0.651	0.657
0.862	0.286	0.481	0.577
0.862	0.286	0.510	0.577
6.102	5.589	0.586	0.529
5.589	5.151	0.463	0.449
5.151	4.817	0.397	0.343
4.817	4.491	0.329	0.334
4.491	3.677	0.817	0.832
3.677	2.411	1.284	1.285
2.411	1.515	0.878	0.905
1.515	0.862	0.636	0.657
7.788	6.773	1.079	1.053
6.773	5.735	1.078	1.070
5.735	4.614	1.149	1.151
4.614	3.665	0.972	0.969
7.649	6.375	1.339	1.319
6.375	5.400	1.028	1.004
5.400	4.318	1.111	1.109
4.318	3.154	1.197	1.186
3.154	1.943	1.243	1.227
7.888	1.943	6.113	6.094
7.888	6.751	1.152	1.178
5.654	3.756	1.821	1.944

TABLE 24

PVT DATA FOR TRIETHYLAMINE SYSTEM AT 25°C

P_L	P_S	P_F	P_F^{calcd}
8.048	1.879	7.642	7.643
12.133	2.042	11.469	11.471
13.824	0.868	12.969	12.973
19.506	2.418	18.388	18.384
23.091	4.710	21.883	21.885
28.374	1.925	26.634	26.640
33.020	2.081	30.992	30.992
34.571	2.923	32.493	32.497
36.036	0.295	33.685	33.694
39.067	4.528	36.799	36.804
40.621	6.954	38.424	38.415
42.829	8.548	40.583	40.583
46.295	1.687	43.366	43.375
46.627	7.642	44.063	44.073
48.717	0.510	45.562	45.562
49.373	4.563	46.446	46.439
52.404	7.972	49.495	49.495
53.585	8.740	50.644	50.649
55.813	7.512	52.661	52.652
55.816	4.236	52.445	52.441
56.031	1.472	52.461	52.462
56.335	7.444	53.140	53.135
59.408	19.192	56.783	56.774

TABLE 25

PVT DATA FOR TRIETHYLAMINE SYSTEM AT 35°C

P_L	P_S	P_F	P_F^{calcd}
92.819	0.968	86.839	86.824
88.034	23.764	83.856	83.831
85.941	1.526	80.422	80.429
82.201	0.178	76.845	76.844
80.998	2.035	75.839	75.839
77.983	0.830	72.933	72.943
75.962	0.897	71.055	71.057
72.599	10.453	68.536	68.534
68.207	9.644	63.746	63.754
66.462	0.542	62.154	62.152
62.650	0.407	58.580	58.579
60.898	1.037	56.973	56.982
57.240	1.176	53.566	53.572
51.365	1.773	48.116	48.118
49.230	1.136	46.077	46.081
46.904	0.842	43.880	43.888
43.962	0.940	41.147	41.144
39.070	0.501	36.543	36.543
35.974	1.279	33.694	33.701
32.940	0.944	30.842	30.843
25.214	3.020	23.764	23.758
23.062	1.006	21.608	21.615
18.932	0.432	17.717	17.718
17.763	1.143	16.677	16.672
14.441	1.080	13.563	13.564
11.109	1.124	10.453	10.454

TABLE 26

PVT DATA FOR TRIETHYLAMINE SYSTEM AT 43.5°C

P_L	P_S	P_F	P_F^{calcd}
11.206	2.994	10.667	10.667
16.679	2.908	15.774	15.775
22.591	1.584	21.209	21.212
28.112	1.811	26.385	26.387
29.701	3.992	28.009	28.015
34.148	3.581	32.143	32.143
40.836	2.901	38.347	38.350
43.393	3.564	40.778	40.783
48.530	4.063	45.613	45.617
49.394	2.220	46.306	46.304
50.430	4.207	47.401	47.403
51.372	4.078	48.269	48.275
53.950	3.520	50.635	50.648
58.098	2.594	54.466	54.465
59.083	3.585	55.439	55.450
60.297	0.433	56.373	56.380
63.495	11.580	60.091	60.096
64.314	3.710	60.338	60.349
65.025	10.667	61.473	61.466
65.847	2.087	61.676	61.676
70.096	2.883	65.690	65.700
73.799	2.000	69.101	69.104
74.741	15.774	70.886	70.882
78.354	4.357	73.503	73.516
80.726	2.481	75.609	75.612
84.342	2.975	79.024	79.025
85.531	3.172	80.144	80.150
89.258	2.168	83.568	83.569
95.728	3.249	89.690	89.689
103.176	4.244	96.723	96.718.
114.203	1.024	106.846	106.822

TABLE 27

VOLUMETRIC ADDITION DA_A FOR TRIETHYLAMINE-WATER SYSTEM AT 25°C

(MIXTURE ADDED VOLUMETRICALLY, X_{TEA} = 0.887)

P	π_A	π_W	π_W^{calcd}
0.343	0.305	0.039	0.039
2.763	2.466	0.299	0.303
5.191	4.615	0.580	0.588
7.600	6.748	0.859	0.859
12.422	11.035	1.405	1.405
0.378	0.335	0.043	0.043
5.198	4.614	0.588	0.588
10.020	8.894	1.138	1.133
11.909	10.558	1.368	1.345
0.861	0.764	0.097	0.097
5.694	5.043	0.656	0.642
10.513	9.321	1.206	1.187
12.939	11.467	1.493	1.460
17.710	15.735	2.013	2.004
22.522	20.003	2.581	2.547
24.940	22.166	2.848	2.822
29.727	26.437	3.396	3.365
34.498	30.707	3.933	3.909
36.922	32.871	4.214	4.184
41.686	37.153	4.740	4.728
46.475	41.433	5.299	5.272
48.852	43.584	5.552	5.546
53.603	47.869	6.076	6.090
58.351	52.159	6.596	6.635
60.734	54.299	6.872	6.907
0.340	0.302	0.039	0.039
5.181	4.577	0.608	0.583
10.003	8.854	1.161	1.128
5.948	5.260	0.693	0.670
10.781	9.532	1.264	1.214
13.190	11.677	1.535	1.487
5.456	4.828	0.632	0.615
10.265	9.092	1.186	1.158
12.677	11.235	1.461	1.431
6.255	5.537	0.722	0.705
11.056	9.807	1.264	1.249
13.472	11.948	1.545	1.521
18.265	16.224	2.081	2.066

TABLE 27 cont'd

P	π_A	π_W	π_W^{calcd}
23.054	20.488	2.630	2.609
25.450	22.632	2.896	2.881
30.238	26.900	3.448	3.424
34.983	31.144	3.985	3.964
37.396	33.296	4.266	4.238
42.191	37.597	4.806	4.785
46.984	41.881	5.367	5.329
49.363	44.030	5.624	5.602
54.138	48.324	6.163	6.148
58.892	52.621	6.683	6.694
61.262	54.768	6.939	6.967
5.868	5.197	0.675	0.622
10.693	9.477	1.230	1.207
13.107	11.607	1.520	1.478
5.528	4.876	0.656	0.621
10.351	9.149	1.215	1.165
5.012	4.453	0.562	0.567
9.808	8.719	1.100	1.110
14.626	13.001	1.651	1.656
19.448	17.261	2.233	2.198
24.259	21.560	2.770	2.745
29.062	25.852	3.312	3.291
31.486	28.013	3.592	3.566
36.279	32.307	4.129	4.112
41.057	36.598	4.659	4.658
43.449	38.751	4.924	4.931
48.239	43.054	5.462	5.478
52.972	47.312	5.993	6.020
55.359	49.480	6.243	6.295

TABLE 28

VOLUMETRIC ADDITION DATA FOR TRIETHYLAMINE-WATER SYSTEM AT 25°C

π_A	π_W	P^{calcd}	P
37.252	8.959	45.926	45.932
39.054	8.761	47.514	47.530
49.690	8.683	57.948	57.922
20.801	8.718	29.391	29.403
21.841	8.719	30.423	30.415
25.381	8.829	34.042	34.046
15.358	8.832	24.101	24.090
30.586	8.584	38.958	38.932
30.379	8.674	38.842	38.834
40.301	9.010	48.992	49.046
44.905	8.576	53.118	53.114
12.892	8.855	21.675	21.655

TABLE 29

VOLUMETRIC ADDITION DATA FOR TRIETHYLAMINE-WATER SYSTEM AT $35^{\circ}C$

π_A	π_W	P^{calcd}	P
63.636	7.776	70.948	70.954
63.636	11.386	74.490	74.498
63.636	15.188	78.221	78.232
63.636	18.838	81.802	81.792
75.632	7.287	82.309	82.312
75.632	11.122	86.059	86.061
75.632	14.993	89.845	89.852
76.842	7.998	84.198	84.213
76.842	11.886	87.999	88.026
76.842	15.486	91.518	91.518
77.904	7.373	84.634	84.635
77.904	11.028	88.206	88.214
77.904	15.229	92.311	92.299
78.591	7.241	85.182	85.198
78.591	14.264	92.044	92.048
80.813	3.639	83.856	83.856
80.813	7.326	87.456	87.461
80.813	14.502	94.462	94.454
80.813	18.077	97.954	97.942
82.915	7.193	89.396	89.409
82.915	11.046	93.156	93.156
82.915	14.998	97.013	96.965
83.042	7.529	89.850	89.859
83.042	11.504	93.728	93.747
83.042	15.568	97.694	97.676
83.198	7.012	89.500	89.509
83.198	10.598	92.998	93.010
83.198	14.083	96.399	96.398

TABLE 30

VOLUMETRIC ADDITION DATA FOR TRIETHYLAMINE-WATER SYSTEM AT 43.5°C

π_A	π_W	P^{calcd}	P
90.084	7.630	96.988	96.996
90.084	11.480	100.765	100.769
90.084	15.363	104.574	104.556
90.084	19.305	108.440	108.398
90.084	23.035	112.099	112.073
97.984	4.020	101.236	101.245
97.984	8.157	105.287	105.301
97.984	12.172	109.219	109.224
97.984	15.898	112.868	112.871
97.984	19.741	116.632	116.619
97.984	23.822	120.628	120.590
104.597	7.728	111.376	111.395
104.597	11.868	115.425	115.441
104.597	15.801	119.272	119.298
104.597	19.682	123.067	123.076
104.597	23.439	126.742	126.744
114.275	3.816	117.073	117.071
114.275	7.576	120.743	120.749
114.275	11.299	124.377	124.408
114.275	15.190	128.174	128.186
114.275	19.024	131.917	131.927
114.275	22.648	135.455	135.473

TABLE 31

VOLUMETRIC ADDITION DATA FOR AMMONIA-WATER SYSTEM AT 35°C

P	π_A	π_W^{calcd}	π_W
120.104	108.795	11.431	11.423
131.945	123.839	8.220	8.183
138.410	123.839	14.746	14.710
144.834	123.839	21.229	21.213
131.583	123.879	7.815	7.818
138.017	123.879	14.308	14.303
144.446	123.879	20.797	20.795
116.993	108.920	8.168	8.127
123.423	108.920	14.651	14.603
129.855	108.920	21.136	21.073
145.196	134.102	11.251	11.205
154.825	134.102	20.977	20.921
139.105	131.448	7.776	7.766
145.522	131.448	14.256	14.246
152.200	131.448	21.000	21.015
137.120	129.091	8.148	8.107
143.553	129.091	14.644	14.588
149.930	129.091	21.082	21.043
136.202	128.576	7.740	7.763
142.616	128.576	14.217	14.250
148.993	128.576	20.655	20.706
137.619	129.912	7.824	7.801
144.028	129.912	14.296	14.283
150.403	129.912	20.734	20.744
40.375	35.481	4.910	4.931
43.651	35.481	8.196	8.216
46.911	35.481	11.464	11.494
50.164	35.481	14.726	14.784
53.470	35.481	18.041	18.109
56.727	35.481	21.307	21.395
41.512	35.788	5.743	5.729
44.785	35.788	9.025	9.011
48.062	35.788	12.311	12.299
51.350	35.788	15.607	15.587
54.606	35.788	18.873	18.875
57.849	35.788	22.124	22.168
128.690	123.757	5.017	5.028
131.936	123.757	8.293	8.314
135.182	123.757	11.569	11.593
138.422	123.757	14.840	14.920
141.650	123.757	18.097	18.237

TABLE 31 cont'd

P	π_A	π_W^{calcd}	π_W
111.734	108.538	3.252	3.243
113.344	108.538	4.874	4.881
115.004	108.538	6.548	6.539
116.645	108.538	8.203	8.185
118.276	108.538	9.847	9.833
119.916	108.538	11.500	11.484
121.512	108.538	13.109	13.126
123.142	108.538	14.752	14.770

TABLE 32

VOLUMETRIC ADDITION DATA FOR PYRIDINE-WATER SYSTEM AT $25^{\circ}C$

π_{pyr}	π_W	P^{calcd}	P
8.142	10.145	18.219	18.239
9.044	10.032	19.000	18.996
9.974	10.052	19.942	19.925
9.973	10.056	19.943	19.945
9.932	10.089	19.936	19.959
10.656	6.780	17.370	17.381
10.791	8.507	19.217	19.214
10.982	8.522	19.421	19.417
10.845	8.540	19.304	19.312
10.980	8.607	19.503	19.524
10.877	8.650	19.445	19.462
10.075	9.995	19.985	19.985
10.165	10.007	20.086	20.084
10.069	10.009	19.992	19.970
10.123	10.035	20.072	20.062
10.082	10.049	20.045	20.021
10.021	10.059	19.994	19.971
10.098	10.062	20.074	20.087
10.052	10.069	20.035	20.051
10.067	10.072	20.053	20.054
10.105	10.116	20.133	20.122
10.055	10.139	20.107	20.129
10.116	10.142	20.171	20.189
10.085	10.152	20.150	20.152
10.067	10.165	20.146	20.170
10.379	10.225	20.514	20.500
11.660	6.728	18.315	18.327
11.498	8.387	19.800	19.819
11.751	8.417	20.080	20.065
11.900	8.473	20.283	20.298
12.286	6.912	19.118	19.129
12.055	8.374	20.338	20.317
12.054	8.387	20.351	20.331
12.132	8.417	20.458	20.460
12.063	8.454	20.425	20.431
12.197	8.477	20.581	20.575
12.170	8.480	20.557	20.563
12.167	8.484	20.558	20.550
12.191	8.484	20.582	20.595
12.233	8.533	20.673	20.654
12.285	8.554	20.745	20.731
12.247	8.557	20.710	20.689
16.041	7.708	23.629	23.604

TABLE 32 cont'd

π_{pyr}	π_W	P^{calcd}	P
13.534	6.783	20.229	20.228
13.686	6.808	20.405	20.412
13.598	6.875	20.384	20.384
* 13.628	6.892	20.430	20.446
15.020	10.312		25.062
15.018	10.295		25.009
15.316	10.225		25.228
15.537	10.139		25.357
15.007	10.059		24.781
15.887	10.125		25.556
15.001	10.025		24.734
15.106	8.617		23.556
15.134	8.560		23.508
15.122	8.503		23.436
15.052	8.462		23.333
15.107	8.387		23.337
15.095	7.012		21.985
15.107	6.928		21.910
15.025	6.778		21.681
14.848	10.335		24.923
14.879	10.215		24.814
14.103	10.076		23.944
14.042	8.580		22.492
14.058	8.444		22.368
14.541	8.415		22.808
14.415	8.380		22.630
14.107	8.360		22.328
14.122	8.344		22.353
13.971	10.222		23.980
13.474	10.035		23.306
13.372	8.637		21.880
13.362	8.390		21.627
12.744	10.352		22.918
12.759	10.349		22.951
12.765	10.302		22.927
12.668	10.269		22.781
12.796	10.205		22.844
12.740	10.071		22.650
12.769	10.059		22.652
12.926	83.437		21.162
11.592	10.094		21.572
11.732	10.049		21.625
10.126	9.989		19.988

TABLE 33

VOLUMETRIC ADDITION DATA FOR PYRIDINE-METHANOL SYSTEM AT 25°C

π_{pyr}	π_M	P^{calcd}	P
5.792	18.494	24.188	24.189
11.703	18.494	30.001	30.000
5.824	20.780	26.493	26.515
11.690	20.780	32.250	32.281
5.771	19.501	25.170	25.194
11.530	19.501	30.827	30.803
5.924	17.729	23.557	23.595
11.519	17.729	29.062	29.083
7.503	22.727	30.075	30.074
11.261	22.727	33.756	33.736
7.530	18.954	26.354	26.354
11.508	18.954	30.264	30.267
7.835	17.818	25.526	25.532
11.712	17.818	29.340	29.325
5.863	17.459	23.228	23.224
11.600	17.459	28.875	28.868
4.667	17.778	22.368	22.382
9.246	17.778	26.874	26.909
6.064	17.803	23.768	23.801
11.412	17.803	29.030	29.054
5.224	18.524	23.659	23.666
10.491	18.524	28.839	28.853
5.232	19.364	24.504	24.513
10.547	19.364	29.725	29.771
5.270	19.495	24.672	24.668
10.488	19.495	29.798	29.747
5.288	20.670	25.858	25.825
10.617	20.670	31.087	31.067
5.286	20.582	25.768	25.750
10.567	20.582	30.951	30.940
5.327	20.551	25.778	25.776
10.712	20.551	31.063	31.052
5.361	22.872	28.122	28.117
10.725	22.872	33.374	33.347
5.467	17.811	23.189	23.186
10.813	17.811	28.449	28.433
10.632	17.516	27.978	27.977
5.423	17.504	22.840	22.853
10.712	17.504	28.045	28.066
5.313	17.492	22.721	22.729
10.644	17.492	27.967	27.939

TABLE 34

VOLUMETRIC ADDITION DATA FOR PYRIDINE-TFE SYSTEM AT 25°C

π_{pyr}	π_{TFE}	P^{calcd}	P
5.434	0.835	6.236	6.247
5.434	1.674	7.041	7.040
5.434	2.096	7.447	7.443
6.779	0.835	7.573	7.572
6.779	1.670	8.367	8.360
6.779	2.567	9.221	9.202
5.451	0.839	6.256	6.258
5.451	1.675	7.059	7.058
5.451	2.118	7.484	7.483
5.604	0.833	6.402	6.419
5.604	1.667	7.203	7.211
5.604	2.510	8.012	8.014
5.594	0.833	6.392	6.394
5.594	1.666	7.191	7.183
5.594	2.503	7.995	7.986
4.106	0.838	4.919	4.926
4.106	1.671	5.727	5.716
4.106	2.540	6.570	6.548
4.099	0.837	4.911	4.920
4.099	1.670	5.718	5.729
4.099	2.503	6.527	6.540
4.174	0.810	4.959	4.965
4.174	1.651	5.774	5.790
4.174	2.488	6.586	6.611
4.217	0.836	5.026	5.035
4.217	1.707	5.870	5.884
4.217	2.187	6.336	6.355
4.220	0.849	5.042	5.030
4.220	1.726	5.892	5.878
4.220	2.566	6.706	6.682
4.235	0.842	5.051	5.061
4.235	1.676	5.859	5.866
4.235	2.514	6.671	6.690
4.258	0.831	5.063	5.060
4.258	1.666	5.872	5.875
4.258	2.506	6.686	6.694
5.513	0.834	6.313	6.312
5.513	1.673	7.118	7.111
5.513	2.515	7.927	7.917

CHAPTER V

DISCUSSION AND CONCLUSIONS

Association of Methanol and Water Vapors

Methanol vapor has been the subject of extensive investigations for at least three decades now as is evident by the numerous works cited in the introductory Chapter (References 10-51). Yet the reported stoichiometry and the thermodynamic constants for association reactions of methanol vary from author to author (see Table 1). Recently, in this laboratory, Farnham, et al.[10] reported some new data on methanol vapor and we thought it might be worthwhile to study this problem by our buoyancy technique also.

Let us first recall how Weltner and Pitzer[34] decided that the methanol vapor can be adequately represented by a mixture of monomers, dimers, and tetramers. Their heat capacity equation ($C_p = C_p^o + aP + cP^{n-1}$) was "clearly fitted better by n = 4 than any other integral value, consequently the higher polymer was assumed to be a tetramer"; however, this was true only for data at 345.6° K and the importance of the dimer as the first associated species was assumed. However, this 1-2-4 fit was not any better than the 1-2-3-4 or 1-2-3-5 fits, and as Weltner and Pitzer noted, "Actually our data do not distinguish between the formation of tetramers and the formation of an appropriate mixture of trimer, tetramer,

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pentamer, etc. . . ." Having so determined n, Weltner and Pitzer used values of ΔH_2 and ΔS_2 of Reference 41, partial heat capacity data of Reference 30 and their own C_p values (both at about one atmosphere) to compute the changes in enthalpy and entropy of dimers and tetramers. A successive approximation method involving their equations (4), (5), and (6) was employed in fitting data.

Fletcher[44] has argued that the 1-2-4 representation is entirely adequate for treating non-ideality in methanol vapor, and that infrared spectra reveal the presence of no other polymers than the dimer and tetramer. But Figure 6 in his paper[44] obviously does not exclude the 1-3 model for MeOH at 25° C up to 90 Torr or even 110 Torr (this Figure is the plot of average molecular weights vs. P for MeOH data found in this research and published in Reference 12; in the Figure, curves which represent the 1-3, 1-2-4, and 1-3-8 fits are drawn.) Actually the curve representing the 1-3 fit is somewhat better than the 1-2-4 fit up to 110 Torr. Since 1-2-3-4 fit gives negative values for K_2 and K_4 and a somewhat high value of K_3 (Table 5) we suggest that 1-3 fit quite adequately describes the MeOH vapor at 25°C up to 90 Torr where adsorption is not a problem (see Appendix I). Higher temperature studies tend to favor the amount of dimers, thereby the 1-2-3 or 1-2-4 models might be superior to the 1-3 model.

The preponderance of trimers over tetramers has been demonstrated by Kell and McLaurin[22] studying the PVT behavior of MeOH vapor in the temperature range 150 - 300° C. Farnham[13] has also argued that the trimers are predominant relative to the dimers or tetramers. Perhaps the best question up to this point, though, concerns not the presence

but the quantity of the dimers, "How much does it dimerize?" The answer

is "not much, at most $K_2 = 5 \times 10^{-5}$ Torr^{-1}" as it can be shown from the

plot of the average molecular weight, $\langle M \rangle$, vs. P (Fig. 4). Since

$P = P_M + K_2 P_M^2 + K_3 P_M^3 + \ldots$, it follows that $\langle M \rangle = (P_M M_m + 2K_2 P_M^2 M_m +$

$3K_3 P_M^3 M_m + \ldots)/P$, where M_m is the molecular weight of the monomer.

Then,

$$\langle M \rangle = M_m \left(\frac{1 + 2K_2 P_M + 3K_3 P_M^2 + \ldots}{1 + K_2 P_M + K_3 P_M^2 + \ldots} \right)$$

$$= M_m \{1 + K_2 P_M + (2K_3 - K_2^2) P_M^2 + \ldots\} .$$

The derivative of $\langle M \rangle$ with respect to P may be written

$$\frac{d\langle M \rangle}{dP} = \frac{d\langle M \rangle/dP_M}{dP/dP_M} = \frac{M_m \{K_2 + (4K_3 - 2K_2^2) P_M + \ldots\}}{\{1 + 2K_2 P_M + 3K_3 P_M^2 + \ldots\}} ;$$

but in the limit as P_M and P both go to zero, $\lim_{P \to 0} d\langle M \rangle/dP = M_m K_2$.

Consequently, the limiting slope of a plot of $\langle M \rangle$ vs. P, divided by M_m,

will equal K_2. It is difficult to see how the upper limit of the limiting

slope of the plot $\langle M \rangle$ vs. P could be greater than about 0.15/100; then

the dimerization constant could not be more than about 5×10^{-5} Torr^{-1}.

We therefore suggest that, for MeOH vapor at 25°C, $K_2 \leq 5 \times 10^{-5}$ Torr^{-1}

(or $K_2 \leq 1$ 1/mole).

In passing, Devries and Collins[30] also reported the average mole-

cular weights of methanol vapor in the temperature range 20-160°C. $\langle M \rangle$

at 20° and at 96.0 Torr was reported equal to 32.3, which compares well

with $\langle M \rangle$ values found in this study: 32.28 and 32.32 at pressures
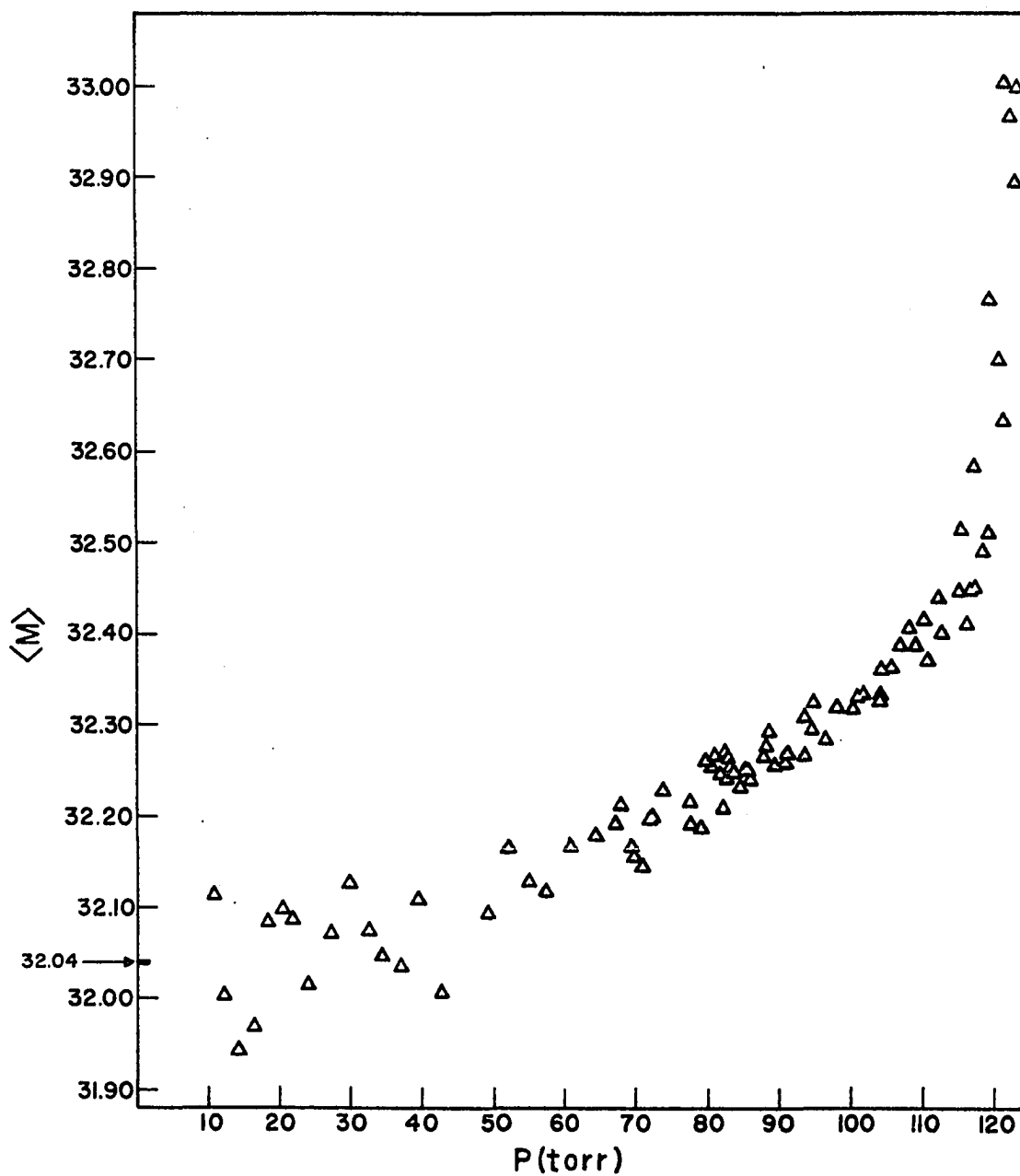
96.35 and 98.30 Torr, respectively.

Figure 4. Molecular weight of methanol vapor as a function of pressure at 25°.

The MeOH data up to 116 Torr, where adsorption might have played some role (Appendix I), were also fitted and given in Table 35. Notice that the K_3 value for the 1-3 fit is exactly the same as that in Table 5 (total pressure up to 90 Torr only); also, the 1-3 fit is definitely better than the 1-2 or 1-4 fits and certainly comparable to any of the two constant fits. Furthermore, the K_3 value is practically invariant in all the fits. Therefore, assuming that the adsorption effects on both bulbs of the balance cancel each other out, the trimer is interpreted to be the major associated species present throughout a wide range of pressures. Data above 116 Torr were not used in the calculations because adsorption probably played a definite role in leading to systematic errors in the values of observed densities.

The study of hetero-association between methanol and water in the gas phase is the first one reported to our knowledge. Table 6 presents the standard deviations and corresponding equilibrium constants of several fits at 25°. The choice of the 3-3 fit is definitely the best and simplest. The RMSD is not improved even if we go to the two-parameter fits; furthermore in the latter case, the K_{3-3} value comes out basically invariant (as in the case of K_3 for MeOH data) while the other constant is either negative or the standard error is the same order of magnitude as the constant itself. We therefore suggest that in this particular binary mixture (Y_{MeOH} ~ 0.7 - 0.9, and the total pressures ~ 0.65 - 0.85 of saturation pressures; see Figure 5) the aggregate composed of three molecules of water and three of methanol is quite sufficient to account for the non-ideality of the mixture. Figure 6 relates the 3-3 calculated lines and the experimental points; ΔP^W is the pressure deficiency when water is

TABLE 35

RMSD AND EQUILIBRIUM CONSTANT VALUES FOR VARIOUS SETS OF ASSUMED

METHANOL SPECIES AT $25^{\circ}C$ AND UP TO 116 TORR TOTAL PRESSURE

| Species	Equilibrium Constants	RMSD (π), Torr
1-2	$K_2 = (8.97 \pm 0.18)\ 10^{-5}\ Torr^{-1}$	0.1140
1-3	$K_3 = (4.61 \pm 0.04)\ 10^{-7}\ Torr^{-2}$	.0537
1-4	$K_4 = (3.00 \pm 0.05)\ 10^{-9}\ Torr^{-3}$	.0899
1-2-3	$K_2 = $ negative	.0538
	$K_3 = (4.88 \pm 0.30)\ 10^{-7}\ Torr^{-2}$	
1-2-4	$K_2 = (3.81 \pm 0.32)\ 10^{-5}\ Torr^{-1}$	.0529
	$K_4 = (1.79 \pm 0.11)\ 10^{-9}\ Torr^{-3}$	
1-3-4	$K_3 = (4.16 \pm 0.36)\ 10^{-7}\ Torr^{-2}$	.0535
	$K_4 = (2.95 \pm 2.35)\ 10^{-10}\ Torr^{-3}$	
1-3-6	$K_3 = (4.40 \pm 0.14)\ 10^{-7}\ Torr^{-2}$	.0532
	$K_6 = (7.75 \pm 5.03)\ 10^{-15}\ Torr^{-5}$	
1-3-8	$K_3 = (4.45 \pm 0.10)\ 10^{-7}\ Torr^{-2}$	.0530
	$K_8 = (3.84 \pm 2.16)\ 10^{-19}\ Torr^{-7}$	
1-3-9	$K_3 = (4.46 \pm 0.09)\ 10^{-7}\ Torr^{-2}$	.0528
	$K_9 = (2.91 \pm 1.55)\ 10^{-21}\ Torr^{-8}$	
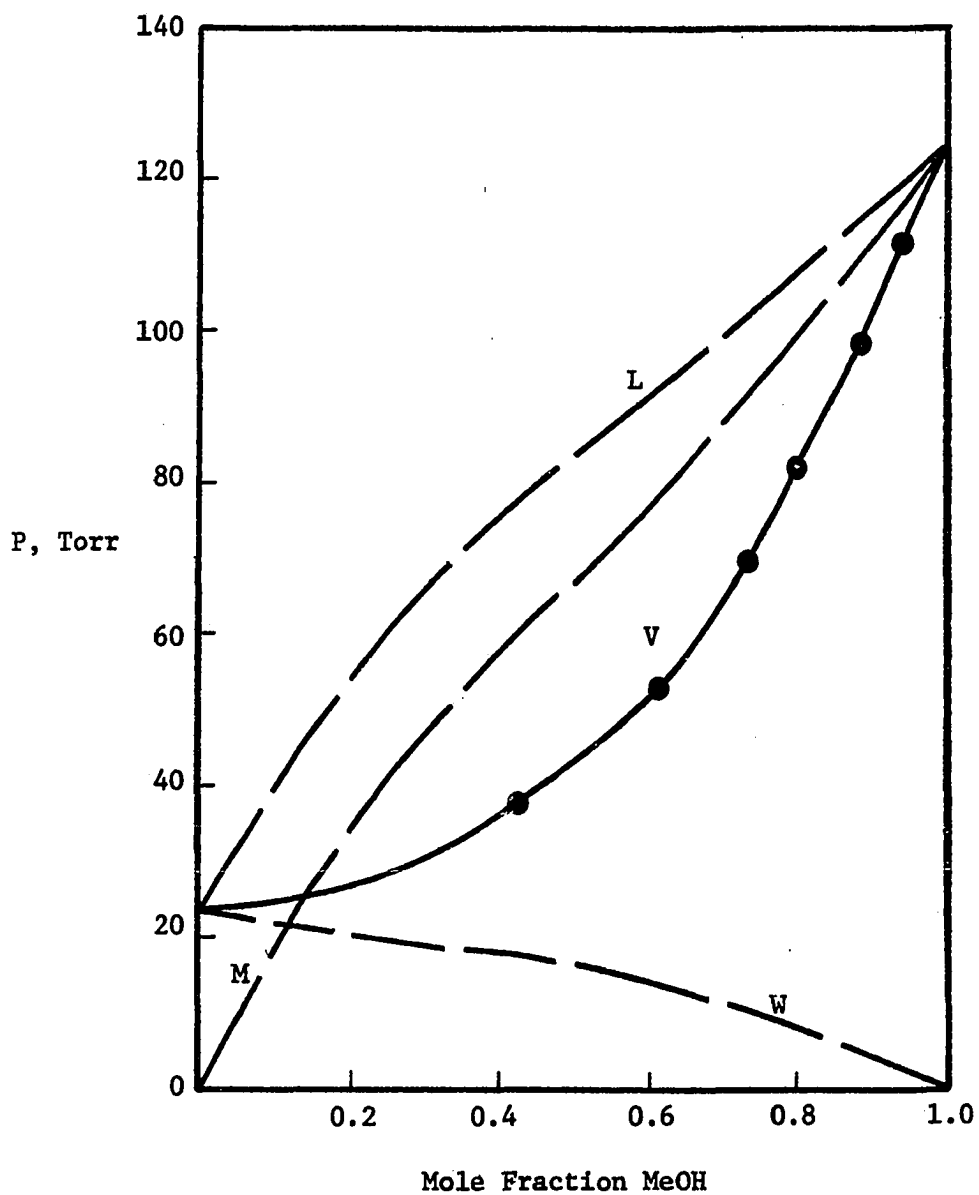
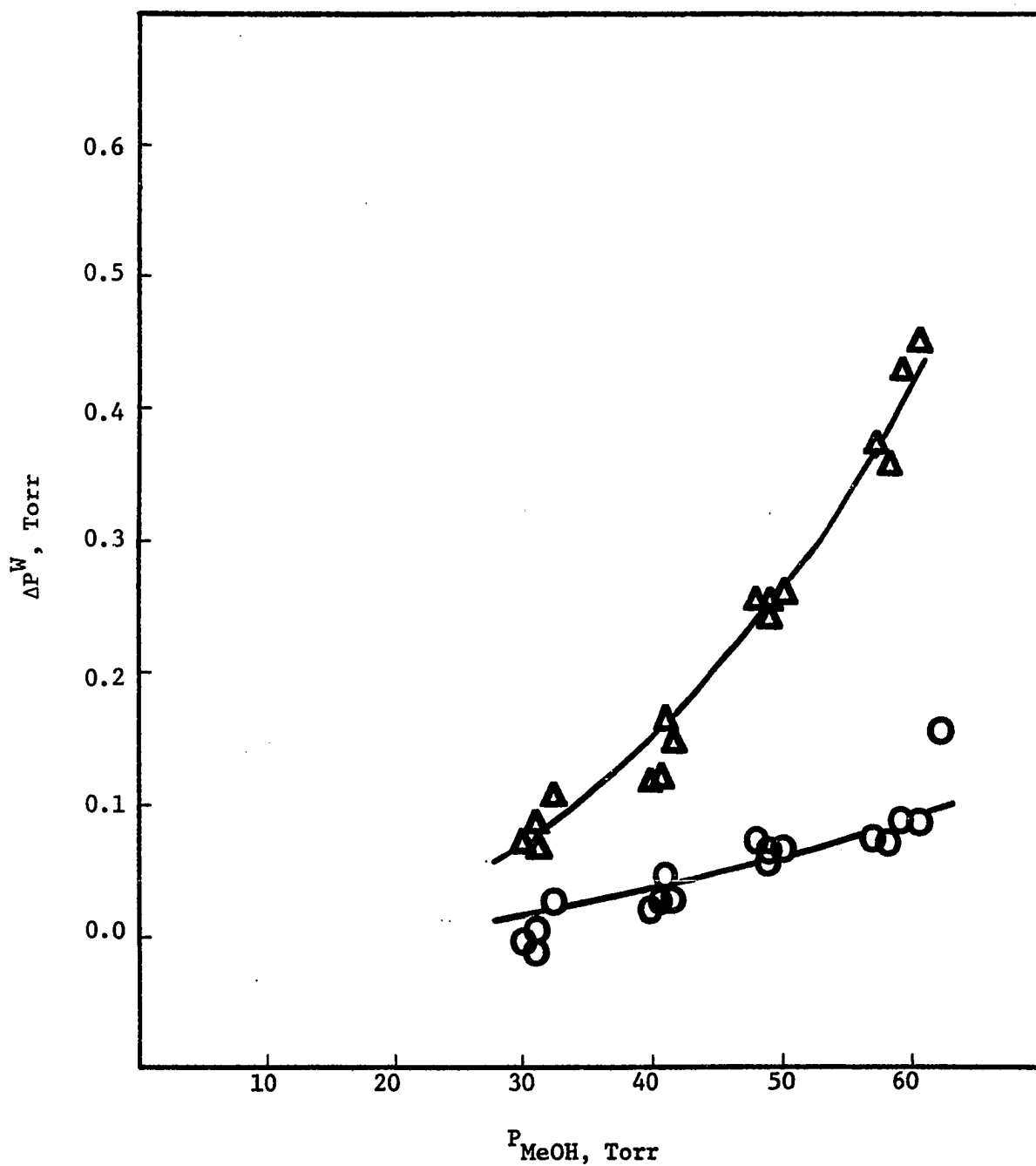Figure 5. Pressure-Mole Fraction Phase Diagram for Methanol-Water System at 25° (Ref. 148)
● P-y, --- p-x

Figure 6. Pressure Deficiency in Function of Total Pressure of MeOH, and Total Pressure of Water: $\Delta\pi_W \sim 14$ Torr, $o\pi_W \sim 7.8$ Torr

added volumetrically to methanol, i.e., the difference between the pressure

predicted assuming no association and the actual observed pressure. At

35° and particularly at 45° C where the total pressures are around one

half of saturation pressures, smaller aggregates seem to be more favored.

For all practical purposes the species $M_2 \cdot W$ quite accurately represents

the cross-polymers of methanol-water system at 45°C and up to half satu-

ration pressures where $Y_{MeOH} \sim 0.7 - 0.9$ (Table 36). At 35°, where

$Y_{MeOH} \sim 0.7 - 0.9$, and at total pressures up to about 0.6 - 0.8 satura-

tion pressures, the choice is a bit harder to make (Table 37). The fit

(1-1, 3-2) seems to be the best with the smallest RMSD = 0.0274; it is

definitely an improvement over the 2-2 fit (RMSD = 0.0395) which is the

best among one-constant fits. Also the fits (1-1, 3-3) and (2-2, 2-1)

are very good. Regardless of the choices, it appears that a cross-

complex bigger than the trimer is present; for the sake of simplicity

the 2-2 fit has been chosen to represent the non-ideality at 35° (this

is very reasonable as far as the size of the aggregate is concerned).

Then it is clear that the polymers of smaller size become more important

as the temperature increases from 25° to 45° at total pressures ranging

from (0.65 - 0.85) $\rightarrow$ 0.5 of saturation. Since the range of pressures

extend to a greater per cent of saturation at 25° than at the higher

temperatures, it is expected that higher-order species will be relatively

more important for the 25° C data. However, the data at 35° and 45° are

not as consistent as those at 25°, as is indicated by the following plot

(Figure 7); systematic errors may lead to difficulties in interpreting

the nature of polymeric species. Had these points (35° and 45°) not been

so scattered, it might have been possible to obtain thermodynamic results

TABLE 36

RMSD AND EQUILIBRIUM CONSTANT VALUES FOR VARIOUS SETS OF

ASSUMED METHANOL-WATER COMPLEXES AT 45°

M-W	K	RMSD, Torr
One-parameter fits		
1-1	$(7.52 \pm 0.45) \ 10^{-5} \ \text{Torr}^{-1}$	0.0475
1-2	$(1.88 \pm 0.12) \ 10^{-6} \ \text{Torr}^{-2}$	.0509
2-1	$(3.81 \pm 0.18) \ 10^{-7} \ \text{Torr}^{-2}$	.0395
2-2	$(1.27 \pm 0.07) \ 10^{-8} \ \text{Torr}^{-3}$	.0434
3-2	$(8.91 \pm 0.50) \ 10^{-11} \ \text{Torr}^{-4}$	.0449
2-3	$(4.44 \pm 0.29) \ 10^{-10} \ \text{Torr}^{-4}$	.0518
3-3	$(3.31 \pm 0.22) \ 10^{-12} \ \text{Torr}^{-5}$	.0529
Two-parameter fits		
1-1, 2-1	negative	.0398
	$(4.25 \pm 0.93) \ 10^{-7} \ \text{Torr}^{-2}$	
1-1, 1-2	$(5.89 \pm 2.13) \ 10^{-5} \ \text{Torr}^{-1}$	.0477
	$(4.24 \pm 5.41) \ 10^{-7} \ \text{Torr}^{-2}$	
1-1, 2-2	$(2.66 \pm 1.38) \ 10^{-5} \ \text{Torr}^{-1}$	.0422
	$(8.50 \pm 2.30) \ 10^{-9} \ \text{Torr}^{-3}$	
1-1, 3-2	$(3.48 \pm 1.00) \ 10^{-5} \ \text{Torr}^{-1}$	.0404
	$(5.14 \pm 1.17) \ 10^{-11} \ \text{Torr}^{-4}$	

TABLE 36 cont'd

M-W	K	RMSD, Torr
1-1, 2-3	$(4.66 \pm 1.09) \; 10^{-5} \; \text{Torr}^{-1}$ $(1.87 \pm 0.65) \; 10^{-10} \; \text{Torr}^{-4}$	.0442
1-1, 3-3	$(4.64 \pm 0.88) \; 10^{-5} \; \text{Torr}^{-1}$ $(1.46 \pm 0.39) \; 10^{-12} \; \text{Torr}^{-5}$	.0422
2-2, 2-1	$(3.18 \pm 2.95) \; 10^{-9} \; \text{Torr}^{-3}$ $(2.89 \pm 0.87) \; 10^{-7} \; \text{Torr}^{-2}$	.0394
2-2, 1-2	$(1.44 \pm 0.35) \; 10^{-8} \; \text{Torr}^{-3}$ negative	.0438
2-2, 3-2	$(1.00 \pm 0.53) \; 10^{-8} \; \text{Torr}^{-3}$ $(1.92 \pm 3.73) \; 10^{-11} \; \text{Torr}^{-4}$	.0438
2-2, 2-3	$(2.88 \pm 0.48) \; 10^{-8} \; \text{Torr}^{-3}$ negative	.0393
2-2, 3-3	$(1.92 \pm 0.37) \; 10^{-8}$ negative	.0425

TABLE 37

RMSD AND EQUILIBRIUM CONSTANT VALUES FOR VARIOUS SETS OF

ASSUMED METHANOL-WATER COMPLEXES AT $35^{\circ}C$

M-W	K	RMSD, Torr
One-parameter fits		
1-1	$(2.01 \pm 0.10)\ 10^{-4}\ Torr^{-1}$	0.0566
1-2	$(5.43 \pm 0.27)\ 10^{-6}\ Torr^{-2}$	.0601
2-1	$(1.13 \pm 0.04)\ 10^{-6}\ Torr^{-2}$	.0425
2-2	$(4.13 \pm 0.13)\ 10^{-8}\ Torr^{-3}$	.0395
3-2	$(3.29 \pm 0.14)\ 10^{-10}\ Torr^{-4}$	.0523
2-3	$(1.55 \pm 0.09)\ 10^{-9}\ Torr^{-4}$	.0701
3-3	$(1.32 \pm 0.08)\ 10^{-11}\ Torr^{-5}$	.0767
Two-parameter fits		
1-1, 2-1	$(4.76 \pm 3.54)\ 10^{-5}\ Torr^{-1}$	.0417
	$(8.73 \pm 1.97)\ 10^{-7}\ Torr^{-2}$	
1-1, 1-2	$(1.15 \pm 0.41)\ 10^{-4}\ Torr^{-1}$	.0524
	$(2.39 \pm 1.10)\ 10^{-6}\ Torr^{-2}$	
1-1, 2-2	$(7.12 \pm 1.85)\ 10^{-5}\ Torr^{-1}$	.0309
	$(2.75 \pm 0.37)\ 10^{-8}\ Torr^{-3}$	
1-1, 3-2	$(9.83 \pm 1.28)\ 10^{-5}\ Torr^{-1}$	.0274
	$(1.81 \pm 0.21)\ 10^{-10}\ Torr^{-4}$	

TABLE 37 cont'd

M-W	K	RMSD, Torr
1-1, 2-3	$(1.21 \pm 0.17)\ 10^{-4}\ \text{Torr}^{-1}$	.0382
	$(6.85 \pm 1.30)\ 10^{-10}\ \text{Torr}^{-4}$	
1-1, 3-3	$(1.25 \pm 0.12)\ 10^{-4}\ \text{Torr}^{-1}$	.0314
	$(5.77 \pm 0.80)\ 10^{-12}\ \text{Torr}^{-5}$	
2-2, 2-1	$(2.24 \pm 0.45)\ 10^{-8}\ \text{Torr}^{-3}$	.0295
	$(5.32 \pm 1.24)\ 10^{-7}\ \text{Torr}^{-2}$	
2-2, 1-2	$(3.63 \pm 0.68)\ 10^{-8}\ \text{Torr}^{-3}$	.0399
	$(6.80 \pm 9.02)\ 10^{-7}\ \text{Torr}^{-2}$	
2-2, 3-2	$(4.69 \pm 1.16)\ 10^{-8}$	.0402
	negative	
2-2, 2-3	$(6.88 \pm 0.71)\ 10^{-8}\ \text{Torr}^{-3}$	.0307
	negative	
2-2, 3-3	$(6.22 \pm 0.61)\ 10^{-8}$	.0322
	negative	
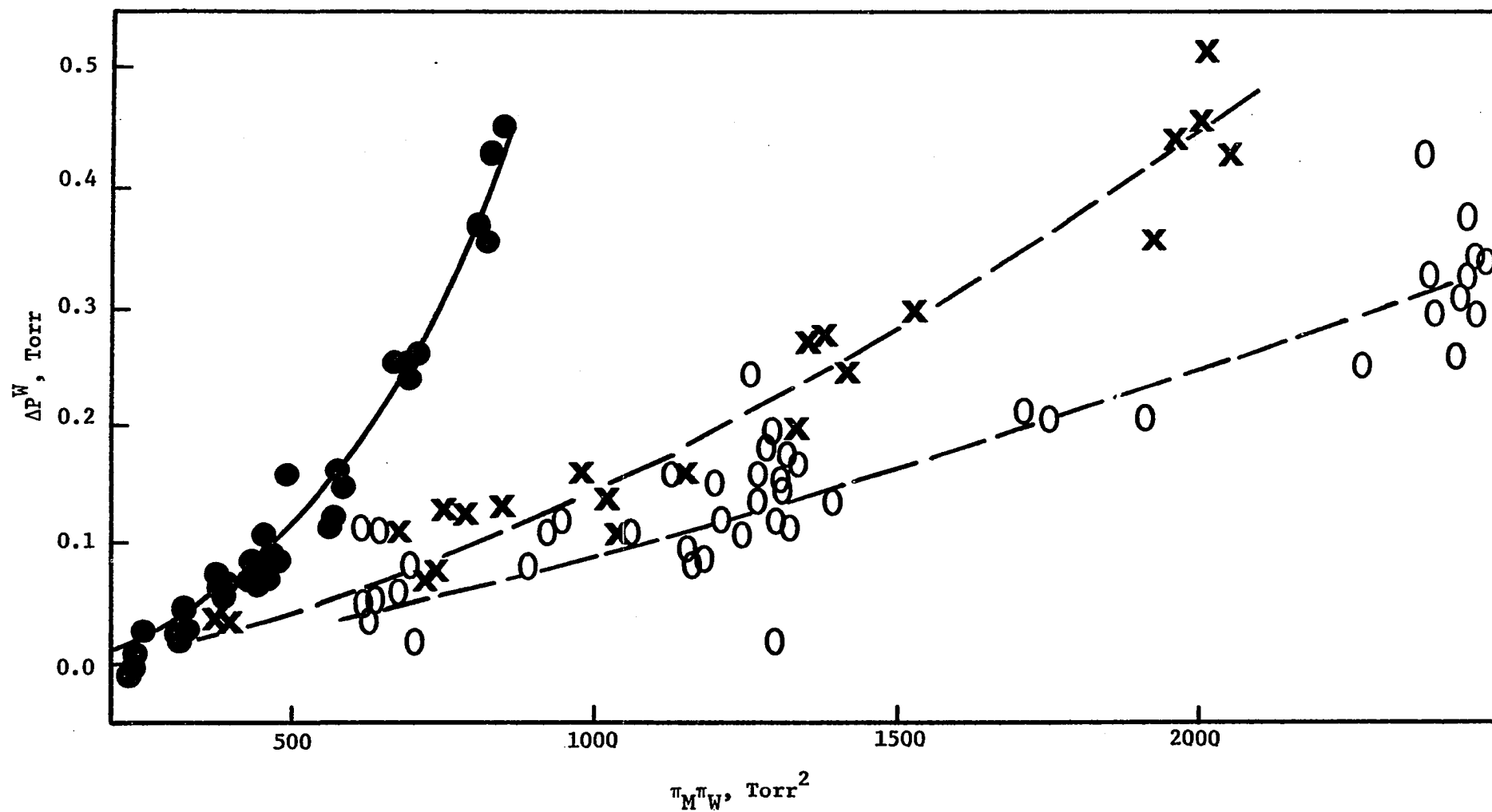
Figure 7. Pressure Deficiency in Function of Product of Formal Pressures of Methanol and Water: ● 25°, x 35°, 0 45°.

from the temperature dependence of ΔP^W, using the isoplectic enthalpy

concept introduced by Farnham (see Ref. 13, page 50ff).

Perhaps the single important thing we learn from the methanol-

water system is that the cross-polymers higher than dimers do exist.

Roach and Christian[152] showed from their infrared data that indeed polymers

higher than 1-1 exist. Possibly this ease of high polymer formation can

be explained by the "cooperative effect" proposed by Frank and Wen[153] in

discussing hydrogen-bonding in liquid water. Because of the cooperative

inductive effect, the water dimer is thought to be capable of forming a

more stable hydrogen bond than the starting monomers. Similarly, Bellamy

and Pace[154] found in studying the hydrogen-bonding of alcohols and

phenols that: ". . . the free OH groups of these dimers are able to

form stronger hydrogen bonds than the original monomers." Tucker[127] did

actually find experimentally values of the ratio, $\Delta H_{2-1}/\Delta H_{1-1}$, signifi-

cantly greater than 2 for the methanol-diethylamine system in different

solvents. These three authors, then, agree that the sites (on the dimers)

capable of forming a new hydrogen bond are more reactive than the corre-

sponding sites on the monomers. In our case it may be illustrated as

follows:
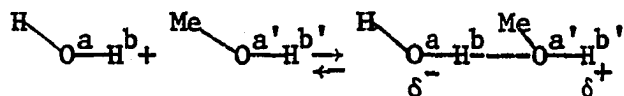
so that, on the dimer the oxygen a becomes more basic and the hydrogen

b' more acidic, thereby increasing the energy of interaction between the

dimer and a monomer bonding at either end position.

Bellamy and Pace also suggested that the dimers are linear where

the lone bond is of ordinary hydrogen bond strength while the higher

polymers are cyclic with stronger average bond strength for alcohols and phenols. It seems reasonable that the larger mixed polymers of methanol and water are also cyclic; nearly linear hydrogen bonds could be formed in cyclic species containing four or more monomer units. The reactive end groups would tend to add additional monomer units or join to close the cycle. Recall that Berman[45] concluded that in liquid alcohols the polymers larger than dimers are cyclic so that a limiting degree of association is reached. The hexamer may possibly be a 12-membered ring with alternating molecules of water and methanol, although direct evidence for such a species is lacking.

CT Reaction between TMA and SO_2 in Gas

The TMA-SO_2 complex is a relatively strong charge-transfer complex, and is in fact one of the strongest for which reliable gas phase thermodynamic and spectral data are available. In the gas phase the energy of formation of TMA·SO_2 is -9.1 Kcal/mole (Table 8). The dipole moment of the complex was concluded[60,75] to be much larger than the vector sum of dipole moments of the individual monomers (5D to 2.5D). An additional indication of the polarity and strength of the TMA-SO_2 interaction is given by the large value of α ($\approx$ 1.2) for the transfer processes of each species from vapor to heptane. The α value was calculated by Grundnes and Christian,[60] using the α-model proposed by Christian, et al.[101] They defined α as the ratio of transfer energy of a complex species to the sum of individual transfer energies of the monomers making up the above complex species, all these transfer processes going from a reference medium (vapor in this case) to another solvent (here heptane).

Childs[65] has determined the crystal structure of this complex and found that the CT bond N------S makes an angle of $22°$ with the perpendicular to the plane of SO_2 molecule, as pictured below. It is assumed that the vapor phase complex has the same configuration.
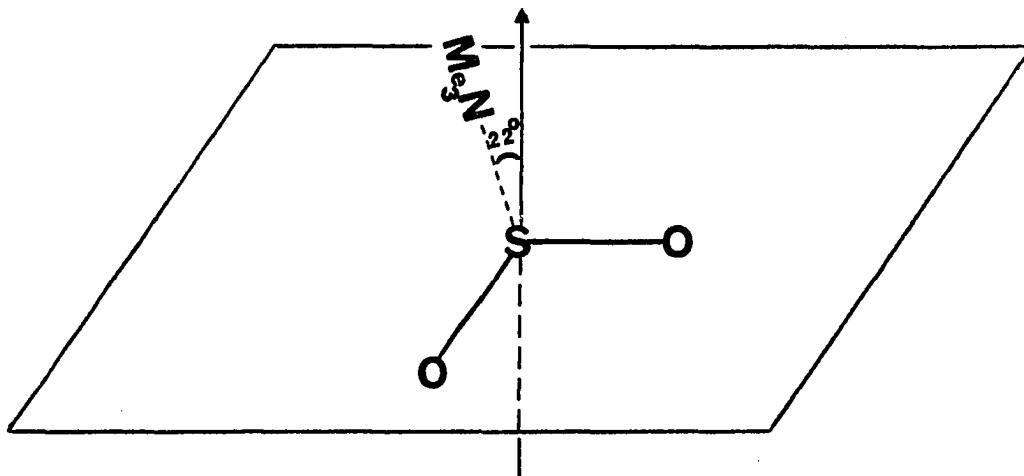

An interesting conclusion made by Grundnes and Christian[60] regarding the TMA-SO_2 system was that the extinction coefficient and oscillator strength of the CT band are nearly the same in the gas phase as in the solvent heptane; this is different from all other CT complexes known, where much lower intensities for the CT band are observed in gas as compared to solution.[70,71,73,74] However Grundnes and Christian reported the gas phase results at only one temperature $39.7°C$; in spite of the reliability of the reported value of product $K_c\varepsilon$ (ε is extinction coefficient), each individual value of K_c and ε might be questionable due to the inherent problem of separating these two values in any type of vapor phase spectral studies. So if it were possible to obtain reliable values of K_c from an independent experiment (for example using classical techniques) then from the known value of the product $K_c\varepsilon$ it would be feasible to compute ε and to compare this value with the spectrally determined ε value.

All this led us to investigate the TMA-SO$_2$ system classically by the buoyancy technique, for which results are reported in Tables 7, 8 and 23. Also to this end, an isothermal expansion technique of the Burnett type was used by Grundnes, et al.[62] to attack the problem. The Van't Hoff plot,[62] $\ln K_c$ vs. 1/T, of the results from these two classical techniques combined with those of Burg[58] do definitely show that the spectral K_c reported by Grundnes and Christian[60] is reliable and therefore that their ε value was also correctly determined. The present work therefore supports their conclusions regarding the near-equivalence of properties of the CT-band in the vapor phase and in solution.

TFA Self- and Cross- Association with Water in Gas

Apparently up to total pressures of 2-4 Torr of TFA, self-associated polymers other than dimers are not present in significant concentrations. The dimers (as shown below) are most probably cyclic for several reasons:
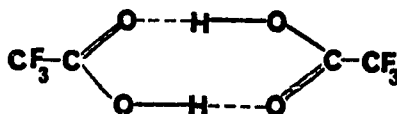
1. Costain and Srivastava[155] presented microwave spectral evidence that the hetero-dimers—TFA·HCOOH, TFA·CH$_3$COOH, TFA·CH$_2$FCOOH—are cyclic. Making necessary assumptions concerning various structural parameters of the monomers published in the literature, and the planarity of the cyclic dimers, they were able to calculate rotational constants which agree extremely well with the observed constants (from microwave spectra). These constants are related to each of the two O—O distances in the O—H—O bonds. There is no reason why the TFA molecules should behave differently from those of HCOOH, CH$_3$COOH and CH$_2$FCOOH as far as the ability of forming

mixed or unmixed cyclic dimers is concerned. In other words if one were

to replace HCOOH in the cyclic bimolecules TFA·HCOOH by TFA, these new

unmixed dimers TFA·TFA would very likely be cyclic. Besides, the very

fact that the self-associated dimers cannot be studied by microwave

methods strongly suggest that the dipole moments of these dimers are ∿ 0

(hence they must be cyclic; if they were linear they would almost certainly

be polar.)

2. The enthalpy of formation of carboxylic acid dimers (-14.01

Kcal/mole) would be too large for a single hydrogen bond.

3. Stevens,[99] using the α-model[101] to study solvation effects on

the TFA system, found values of α approximately equal to 0.5 for the four

solvents cyclohexane, CCl_4, benzene, and dichloroethane. A value of α = 0.5

indicates that the energy of solvation of the dimer is only half that of

two isolated monomer molecules. This α-value is among the lowest so far

determined and this supports the view that the TFA dimer is cyclic in both

vapor and condensed phases. If the dimers in solutions were open-chain,

one would expect the active sites on these dimers (C=O and O-H) more re-

active than the corresponding sites on the monomers by virtue of induc-

tive effects; therefore these open-chain dimers would be much more easily

solvated than the monomers, and this should give a high α-value. Since α

was determined to be only ∿ 0.5,[99] the active sites on the dimers (C=O and

O-H) could not be freely solvated but would interact to give cyclic dimers.

So cyclization essentially reduces both the number of active sites and the

dipole moment.

The value of enthalpy changes obtained here agree very well with

that reported by most workers (Table 2): -14 Kcal/mole. This ΔH_2 value

possibly holds for most, if not all, carboxylic acids to within 1 Kcal/mole

if proper adsorption corrections are taken care of as did Mathews and Sheets.[93] The entropy change value of -49.70 e.u. (standard state 1 mm) compares very well with those calculated from References 83 and 84 using the same standard state: -49.42 and -49.74 e.u.. The excellent agreement of these thermodynamic constants with those cited in the literature indicates that our difference technique discussed in Chapter III and used to analyze the TFA and TMA-SO_2 buoyancy data is quite reliable. The values of self-association constants of TFA are needed for the hetero-study of TFA-water system. Needless to say, these constants must be used to correct for the non-ideality of TFA in this hetero-system where water is volumetrically added. (On the other hand, we will see in the next section that the self-association constant of an amine could be neglected if water is added quantitatively to the amine, because both self- and hetero-association constants are small.)

It appears that the only vapor phase work on the TFA-water system is that by Ling, et al.,[96] who report the results at only one temperature, 20°. We thought it might be worthwhile to pursue this study further to other temperatures, 25°, 35°, and 44°. The temperature dependence study of this system in gas apparently is the first one to be reported. Although the accuracy of the data leaves something to be desired (see Fig. 2 and Table 8), there is good evidence that it is one of the strongest hydrogen-bonding reactions involving water. Ling, et al.[96] reported a value of K_{AW_2} = 0.01 Torr^{-2} at $20^{\circ}C$, which is indeed a large constant; these authors observed that when water is added to an infrared cell containing anhydrous TFA, both the carbonyl and the hydroxyl monomer stretching frequencies are shifted to lower values. This and the fact that the $-\Delta H_{1-1}$ value is quite

large suggest that the TFA·W complex might be cyclic as shown below. The
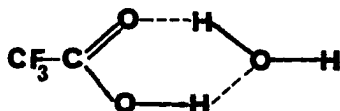
hydrogen atom of the acid would probably attack the water oxygen first;

then the cooperative effects would render the water hydrogen acidic enough

to react with carbonyl oxygen.

Table 38 indicates that the choice of the 1-1 complex is the best;

however the RMSD's of the 2-1 parameter fit are close to the 1-1 standard

deviations. Since the partial pressures of TFA are very low (2-4 Torr)

at all three temperatures, 2-1 complexes wouldn't be expected to be im-

portant anyway. The 1-2 fits for the species TFA·W_2 are not very good at

all compared to others. An α value obtained from the α-model coupled

with dipole moment measurements would be very helpful in deciding whether

this suggested dimer structure is correct. Lin[105] reported a constant for

the 1-1 complex of the ethylenediamine-water system at 20°C, K_{1-1} = 0.08

Torr^{-1}; it is interesting to note the order of magnitude agreement between

this value and the constant obtained here for the TFA-W reaction: K_{1-1} =

0.049 Torr^{-1} at 25°C.

Amine Self-Association and Hetero-Association with

Water and Alcohol in the Vapor Phase

Tucker[127] has recently investigated the systems diethylamine and

diethylamine-water at 25°, 35°, and 45°. One expects triethylamine to be

a bit more basic, and therefore to form stronger hydrogen-bond with water,

TABLE 38

RMSD AND EQUILIBRIUM CONSTANT VALUES FOR

TRIFLUOROACETIC ACID-WATER SYSTEM

T^oC	TFA-W	Equilibrium Constant	RMSD, Torr
25	1-1	(0.049 ± 0.001) Torr^{-1}	0.0280
	1-2	(0.0030 ± 0.0001) Torr^{-2}	.0522
	2-1	(0.0168 ± 0.0005) Torr^{-2}	.0310
	2-2	(0.00148 ± 0.00007) Torr^{-3}	.0479
	1-3	(0.00026 ± 0.00002) Torr^{-3}	.0863
35	1-1	(0.020 ± 0.001) Torr^{-1}	.0454
	1-2	(0.00100 ± 0.00005) Torr^{-2}	.0510
	2-1	(0.0046 ± 0.0002) Torr^{-2}	.0478
	2-2	(0.00032 ± 0.00002) Torr^{-3}	.0478
	1-3	(0.000065 ± 0.000006) Torr^{-3}	.0810
44	1-1	(0.0147 ± 0.0004) Torr^{-1}	.0340
	1-2	(0.00065 ± 0.00003) Torr^{-2}	.0576
	2-1	(0.00266 ± 0.00007) Torr^{-2}	.0330
	2-2	(0.000163 ± 0.000007) Torr^{-3}	.0525
	1-3	(0.000038 ± 0.000003) Torr^{-3}	.0910

than diethylamine because of the additional ethyl group. We thought it might be interesting to compare these two amines by their self- and hetero-association with water. Most probably the force holding the two molecules of triethylamine together is of the van der Waals type. The enthalpy change determined here is -1.88 Kcal/mole, which agrees very well with that calculated from the 2nd virial coefficient equation obtained by Lambert and Strong[36] (-1.89 Kcal/mole). The corresponding internal energy change is then $-\Delta E \sim 1.3$ Kcal/mole. Recall that the benzene$\cdot I_2$ complex is thought to be held together almost entirely by van der Waals forces;[67] the $-\Delta E$ value in this case was determined to be also 1.3 Kcal/mole (see Ref. 67, Table I). For diethylamine, $-\Delta E$ was determined to be 3.2 Kcal/mole;[127] the force stabilizing the dimers must be a combination of van der Waals and hydrogen-bonding.

The cross-association of triethylamine and water is best described by an equilibrium of monomers and dimers. Most likely the cross-dimers are held together by one hydrogen of water bonded to the nitrogen of the amine: Et_3N---$HOH\cdot\Delta H_{1-1}$ is determined to be -8.4 Kcal/mole, a value somewhat high compared to that obtained by Tucker[127] for the complex diethylamine$\cdot$water (-6.6 Kcal/mole). As already mentioned, at 25° a mixture ($X_A = 0.887$) was also added volumetrically; an unexpected problem came up: the calculated hetero-constant K_{1-1} was very sensitive to the chosen value of the self-association constant (K_2) of the amine (Fig. 8). (Such a problem does not arise in the method where only one component is added quantitatively.) Actually, it was only after realizing that the K_{1-1} value was unreasonably high (12 x 10^{-4} Torr^{-1} when K_2 was neglected) that we decided to determine the self-association constants of the amine for use in treating data obtained with the mixture technique. Adding a mixture
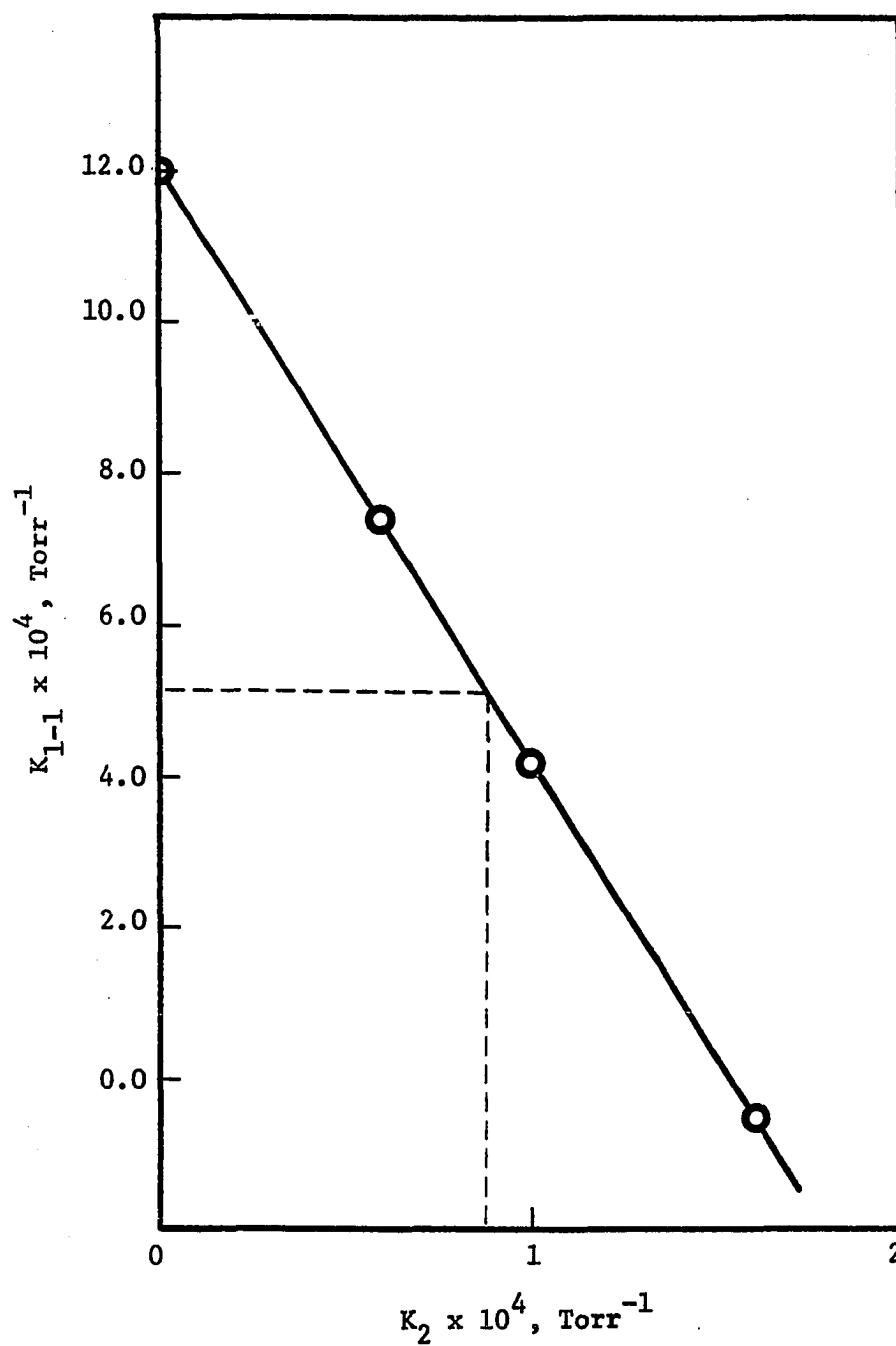
Figure 8. Dependence of Cross-association Constant on
Self-association Constant Values at 25° (for
TEA-W Mixture Added Volumetrically)

has the advantage that the equilibrium is reached almost instantaneously. However, if the virial coefficients of each component are determined independently by the volumetric addition technique, then adding a mixture of those components volumetrically is an excellent method for obtaining cross-virial coefficients.

Kollman and Allen[112] used a quantum-mechanical method to calculate the formation energy of cross dimer ammonia·water; they obtained a value which is probably somewhat high, $\Delta E_{1-1} \simeq -10 Kcal/mole$, compared to those obtained experimentally for the systems discussed above: -7.8 Kcal/mole for triethylamine·water and -6.0 Kcal/mole for diethylamine·water complexes. It seemed to us therefore appropriate to investigate this system, NH_3-water, experimentally to see if the reported ΔE value is of reasonable order of magnitude.

It wasn't necessary for us to determine the self-association constant for NH_3 since its partial pressures were relatively low in any case, and as mentioned above adding water to pure NH_3 does not present special problems as in the mixture experiments. The virial coefficient of NH_3 was obtained by extrapolating the values reported by Lambert and Strong[36] and converted to proper units at 35°. The value calculated was $K_2 = 2.455$ x 10^{-6} Torr^{-1}, a very small constant which could have been ignored completely without influencing the final results. The 1-1 equilibrium constant between NH_3 and water (7.5 x 10^{-5} Torr^{-1} at 35° vs. 31 x 10^{-5} Torr^{-1} for the triethylamine·water complex) is also small; and although this doesn't directly indicate the strength of the hydrogen bridge N-----H it does make it unlikely that the value $\Delta E_{1-1} \simeq -10$ Kcal/mole calculated by Kollman and Allen[112] is correct. These authors now think (private communication) that ΔE_{1-1} is of the order of -5 Kcal, a reasonable value indeed.

There has been considerable recent interest in the pyridine-water system, as is indicated by some of the numerous papers on this subject.[101b,121,121b,122,156-164] The approaches vary from spectroscopy (IR, NMR, Raman, UV) to diffusion, partition-solute isopiestic-water titration and even theoretical prediction. Most research, however, pertains to condensed phase and only two authors[121,121b] have reported limited data for the gas phase. Johnson, Kilpatrick, Christian, and Affsprung[101b] studied the hydration of pyridine in organic solvents cyclohexane, CCl_4, toluene, benzene, and 1,2-dichloroethane at 25°, using UV (251 mμ) and partition-solute isopiestic-water titration method. These authors obtained values for the 1-1 complex formation constants in these solvents, which in turn allow them to calculate α (=0.71) by using appropriate distribution constants relative to cyclohexane. Had they determined K_{1-1} value in vapor phase, they could have used vapor state as reference phase. There seemed a clear need for the studies of the pyridine-water system in gas.

To our knowledge, the only reported research on the pyridine-water system in the gas phase resulted in an unreasonably large value of K_{1-1}; Yarym-Agaev, et al.[121b] gave the value K_{1-1} = 0.00900 Torr^{-1} at 40°C. A differential equation for the dependence of pressure of saturated vapor on the composition was derived for a binary mixture where the components interact to form a 1-1 complex in the vapor phase. The composition of both liquid and vapor phases was determined at 40°, and the value of the formation constant, K_{1-1}, was calculated. Hussein, et al.[121] reported a hydrogen bonded O-H stretching frequency at 3480 cm^{-1}, which results in a value of $\Delta\nu_{O-H}$ in the neighborhood of 220 cm^{-1}.

Stevens[99] developed a lattice model of group interaction energies,

which allowed him to calculate the transfer energies of the species pyridine, water, and pyridine·water from vapor to solvents. These energies were then used to calculate α according to its definition by Christian, et al.[101] ($\alpha = 0.75$, in excellent agreement with 0.71 determined by Johnson, et al.[101b]) With all these results, coupled with the $\Delta E - \Delta G$ correlation proposed by Christian, et al.,[165] we should be able to predict the formation energies of the 1-1 complex in vapor phase. We thought it would be worthwhile to investigate this system using our vapor density technique, so that the comparison between the observed and predicted value of this constant could be readily made.

The following equation was derived by Johnson, et al.[101b] where each K_D is the distribution constant for an individual species between

$$\frac{K_{PW}^{(s)}}{K_{PW}^{(v)}} = \frac{K_{D,PW}}{K_{D,P} \, K_{D,W}} = (K_{D,P} \, K_{D,W})^{\alpha-1}$$

vapor (v) and solvent (s), and the subscript PW refers to complex pyridine· water. Assume CCl_4 to be the solvent; then at 25°

$K_{D,W} \simeq 0.0087/0.00128$ where 0.0087 is the solubility of water in CCl_4 and 0.00128 is approximately equal to the formal concentration of water in vapor state ($= P_W^o/RT$)

$= 6.797$

$K_{D,P}$ is calculated from the free energy of transfer, which in turn can be obtained from the $\Delta E - \Delta G$ correlation:[165] $\Delta G_{v \to s}^o = 0.64 \, \Delta E_{v \to s}^o + 300$ cal.

Since $\Delta E_P^{s \to v}$ is equal to 9.1 Kcal (Reference 165), then $\Delta G_{D,P}^{o}{}^{s \to v}$ = 0.64 (-9100) + 300 = -5524 cal. = -RT ln $K_{D,P}$, and $K_{D,P}$ can be calculated.

$$K_{D,P} = 1.1185 \times 10^4.$$

The ratio of the 1-1 constants is now

$$\frac{K_{PW}^{(s)}}{K_{PW}^{(v)}} = (11,185 \times 6.797)^{\alpha-1}$$

If we omit the subscript, PW, and take the logarithm of both sides, we have

$$\log K^V/K^S = 4.881 \ (1-\alpha)$$

With different values of α, the ratio of the constants can be calculated. These values are listed below.

| α	K^V/K^S	$K^V_{(predicted)}$, 1/mole
0.8	9.467	27.2
0.84	6.039	17.3
0.85	5.397	15.5
0.86	4.823	13.8
0.87	4.310	12.4
0.88	3.852	11.1
0.9	3.082	8.8

Johnson, et al.[101b] reported values of $K_{PW}^{(s)}$ (2.87 1/mole), $K_{P_2W}^{(s)}$ and $K_{PW_3}^{(s)}$ for the pyridine-water reaction in CCl_4 at 25°. From this $K_{PW}^{(s)}$ (or K^S) value reported, we can predict K^V values, which are listed above in the 3rd column. Comparing these with the observed constant,

$K^V = 14.1 \pm 0.4$ l/mole, it is seen that α must be equal to 0.86 ± 0.02 in order to have the predicted and observed values of K^V within reasonable range of agreement (within about 20%). The value of $\alpha = 0.85$ is a bit higher than that calculated by Stevens (0.75). This discrepancy can probably be explained by the additional interaction energy between the large value of the dimer dipole moment and the solvent CCl_4, which Stevens didn't take into account in his lattice model treatment. Similar complex dipole-solvent interaction effects have been observed with $TMA \cdot SO_2$ and aliphatic amine$\cdot H_2O$ complexes.[7]

Several authors[122,157,158] have reported spectral evidence for 2-1 complexes where both water hydrogens are involved in complexing, as pictured below. If such a structure exists, then the water oxygen must
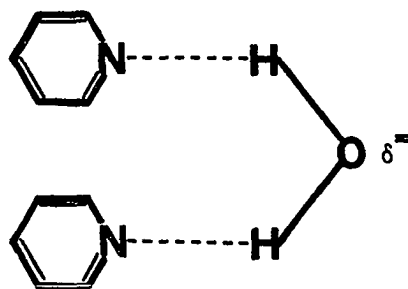
be so basic by virtue of inductive effects that another water molecule should readily attach to it through hydrogen bonding so that the 2-2 complex, if it exists, might look like
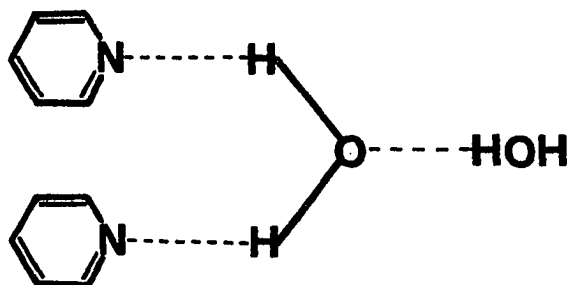
Although the 2-1 and 2-2 fits (K_{A_2W} = 3.3 x 10^{-5} Torr^{-2}, $K_{A_2W_2}$ = 2.55 x 10^{-6} Torr^{-3}) are comparable to that of the 1-1 case, it is unlikely that the two species are physically favored over the dimers at these low pressures, which are well below saturation. We therefore suggest that the 1-1 complexes are the major cross-associated species at these pressures, although possibly higher polymers also exist to a small extent.

Table 32 (pyridine-water data) is appended with data taken generally at higher activities of pyridine and higher total pressures; these data were taken some time after the first set of data was analyzed. Since the saturation curve at 25° is not well defined, these higher pressures data were not used as the primary set. When combining these with the original set, different fits seem to indicate that higher polymers like 3-3, may become important at high pressures (K_{3-3} = 1.58 x 10^{-8} Torr^{-1}). This is not too surprising, since it is generally expected that as the saturation line is approached, higher species become more important, and cyclization probably occurs so that a limiting degree of polymerization is reached.

We thought it might be of interest to compare the acidity of methanol with that of water by studying the similar system pyridine-methanol. And for curiosity we also made an investigation on the hetero-association reaction between pyridine and 2,2,2-trifluoroethanol (TFE). The cross-association constants for the systems pyridine-methanol and pyridine-TFE at 25° appear to be the first ones reported. The 1-1 fits in both cases are sufficiently good to account for the nonideality of the mixtures. Reece and Werner[123] reported the hydroxyl frequency shifts for both systems: Δv(Pyr-M) = 210 cm^{-1} and Δv(Pyr-TFE) = 370 cm^{-1}. The

value K_{1-1} = 9.3 x 10^{-4} $Torr^{-1}$ for pyridine-methanol system is in the

order of magnitude of the 1-1 constant for TFE-MeOH system reported by

Farnham[13] (10.9 x 10^{-4} $Torr^{-1}$). Methanol in this respect behaves simi-

larly to water, as a proton donor or acceptor.

Since $K_{Pyr-TFE}$ = 7.7 x 10^{-3} $Torr^{-1}$ is ~ $7K_{MeOH-TFE}$, it is tempting

to say that pyridine is considerably more basic than methanol in terms of

proton acceptor ability. Recall that K_{Pyr-W} is equal 7.6 x 10^{-4} $Torr^{-1}$

at 25°; this is somewhat less than $K_{Pyr-MeOH}$ = 9.3 x 10^{-4} $Torr^{-1}$. Tucker[127]

also observed the same trend with diethylamine associating with water and

methanol. It appears then that in spite of the electron donating ability

of the methyl group methanol is a better proton donor than water in terms

of K and also ΔH in gas. Methanol also seems to be a better proton ac-

ceptor than water: K_{TFE-W} ~ 4 x 10^{-4} and K_{TFE-M} = 10.9 x 10^{-4} at 25°

(Ref. 13). However, the relative strength of proton-donating ability of

water and methanol seems to be reversed in solutions.[127]

Summary and Suggested Extension of this Research

Stoichiometry of molecular complexes and thermodynamic constants

for their formation have been reported for several vapor phase systems

of polar substances. The present results for methanol vapor at 25° (up

to 70 or possibly 85% of the saturation pressure) are well explained by

using the monomer-trimer model, which is the simplest of the models

commonly used in accounting for the association of alcohols. For the

methanol-water system, it is demonstrated that higher-order hetero-polymers

(such as the 3-3 complex) are the predominant associated species at 25°,

and in the range of mixtures studied: Y_{MeOH} = 0.7 - 0.9, P = 65 - 85% of

saturation. Even though such aggregates are apparently not as important

at 35 and 45°, it is clear that the cross-polymers larger than dimers do exist; e.g., M_3W_2 at 35°, and M_2W at 45°. At the lower temperatures, where the measured range of pressures extended nearly to the saturation pressure, higher aggregates become more important through the cooperative inductive effects. Raising the temperature leads to extensive dissociation of the strongest complexes, and in the pressure ranges studied, leads to formation of relatively large fractions of the lower-molecular weight aggregates.

Thermodynamic constants have also been obtained for the following systems: pyridine-water; pyridine-methanol; pyridine-TFE; triethylamine, triethylamine-water, ammonia-water; TFA, TFA-water; TMA-SO$_2$. The 1:1 mixed dimers in these systems are found to be sufficient to account for the observed non-ideality. Finally it appears that in the vapor phase, methanol is better than water both as a proton donor and acceptor.

The techniques developed here should be applicable in studies of a wide range of molecular complex systems. It would be desirable to extend measurements over wide ranges of temperature and pressure for some of the systems reported here (e.g. pyridine-water, TFA-W). If each component of a mixture can be added accurately through the disk and virial coefficients are determined for each, then adding a mixture volumetrically should be a very good method to use in obtaining accurate stoichiometries for molecular complexes. Deviations due to adsorption can be taken care of quite satisfactorily (see Appendix I). Selective adsorption (by one or the other component) is not considered in this research but the techniques used here could be modified to study the specific adsorption of the molecules of interest. Spectral studies

should be undertaken in conjunction with the PVT and vapor density experiments.

Condensed phases studies of those systems investigated in the gas phase would be very useful in elucidating solvation effects. In this connection, values of the energy and free energy of transfer of donor, acceptor and complex molecules into solvents of interest are badly needed.

APPENDIX I

ADSORPTION STUDIES

Even though many authors have neglected adsorption effects on
their virial coefficient measurements, a few others[13,166-168] have at-
tempted to determine the amount of the vapor of interest adsorbed on
the apparatus surface in contact with the vapor. Bottomley and co-
workers[166,167] determined the amounts of several vapors adsorbed on
glass surfaces which were trapped by an ascending mercury surface and
released later after the mercury was withdrawn. It is questionable
that this method works very well when the vapors react or adsorb on
Hg surface, as was specifically observed by these authors in the CCl_4
vapor case.

Farnham[13] developed an elaborate "adsorption-time extrapolation"
technique to obtain necessary corrections for his PVT experiments on
alcohol vapors. It is clear from the work of Razouk and Salem[168] that
the amount of a vapor adsorbed on a surface varies widely as experi-
mental conditions are modified; in the case of water vapor the thickness
of the adsorbed film near saturation ranges from a few monolayers to
several hundred layers. Apparently one of the main problems is that the
actual surface area can be many times larger than the geometric area,
depending on how the cleaning is done. Essentially, the studies reported

here can do away with the necessity of knowing absolute values of actual

areas, so long as the surfaces are clean.

Adsorption Microbalance

Basically the balance was constructed the same way as the one

used for buoyancy experiments, except that the closed bulb was not

attached (see below). Details of experimentation are essentially the

Pointer, R

Cathetometer ⟶

Counterweight
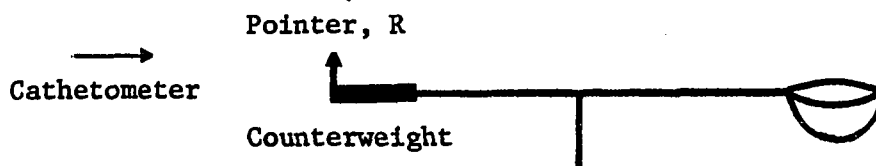
same as explained in Chapter III, but a closed-end mercury manometer was

used instead of the TI Gage. The cathetometer, read to within 0.025 mm,

detected the change of pointer readings, ΔR.

The open bulb, B, was cleaned with distilled acetone and dried

in the $110^\circ C$ oven overnight the same way as the bulbs used in the buoyancy

experiments. The geometric area of the bulb B was estimated to be ~ 70 cm^2,

and the sensitivity of the balance > 10 mm/1 mg. Although the actual area

of the bulb is not known, an estimation of the number of monolayers at

a certain pressure might give us a rough but informative, indication of

the approximate magnitude of the amount of vapor adsorbed. Data for

water adsorption experiment at 25° are given in Table 39 and plotted in

Figure 9.

At 15 Torr of water, ΔR is about 0.15 mm. Then the weight of

water adsorbed on the bulb B is (1 mg) (0.15)/10 mm $=$ 0.015 mg. One

monolayer of water on 70 cm^2 weighs roughly

$$\frac{70 \times 10^{16} \times 18}{6 \times 10^{23} \times 10A^2} = 0.002 \text{ mg/monolayer}$$

TABLE 39

ADSORPTION OF WATER VAPOR ON PYREX BULB AT 25°

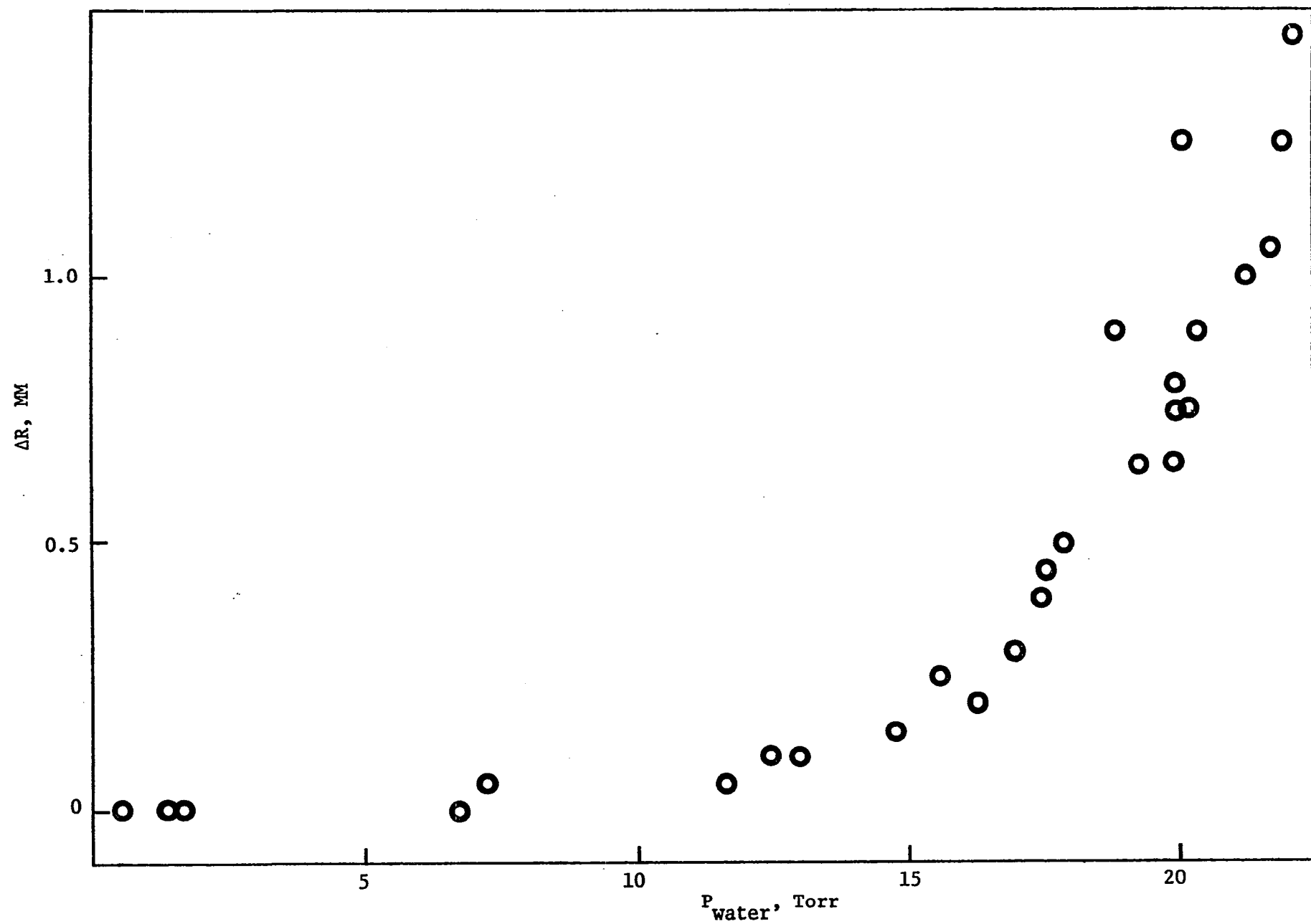| P_W, MM	$\frac{\Delta R}{MM}$'
0.45	0
1.35	0
1.65	0
6.75	0
7.25	0.05
11.65	0.05
12.50	0.10
13.45	0.10
14.80	0.15
15.60	0.25
16.30	0.20
17.00	0.30
17.55	0.45
17.90	0.50
18.85	0.90
19.40	0.65
19.45	0.65
19.95	0.80
19.95	0.80
20.10	1.25
20.00	0.75
20.10	0.70
20.25	1.10
20.40	0.90
21.25	1.00
21.70	1.05
21.95	1.25
22.10	1.45

Figure 9.

Then the number of monolayers is 0.015/0.002 = 7.5. (Since the actual area is expected to be larger than 70 cm^2, 2-3 times or possibly more,[168] the number of monolayers probably is less than 7.) Roughly then, at pressures 15-16 Torr of water at 25°, the effective number of monolayers is ∿5-10. Then at water activities 20-22 Torr, the number of monolayers would be around 50, and go up very fast just below saturation.

It might be interesting to compare this estimation of the number of monolayers to that obtained from adsorption bulb experiment (see the next section). At pressures 15-16 Torr of water, the amount of water adsorbed on the adsorbent corresponds to roughly 0.11 Torr pressure in the total system volume ($V_L + V_{Sa}$), see Table 41. This corresponds to the weight of 0.337 mgm. One monolayer would weigh

$$\frac{(3500 \times 10^{16}) \; 18}{6 \times 10^{23} \times 10A^2} = 10.5 \times 10^{-5} \; gm/monolayer$$

Then the number of monolayers on the adsorbent is about 3.3. To this number should be added 1 or 2 monolayers that "stick" well on the adsorbent (see next section); however, with the microbalance there is no need to add these extra layers since they already contribute to changes of the readings of the pointer. The fact that the adsorbent was not cleaned and dried as the bulbs on the microbalance were, might cause the adsorbent to adsorb less than the bulbs do. In any case, the two experiments lead to adsorption results which agree reasonably well: at pressures 15-16 Torr of water at 25° the number of monolayers is smaller than 10, probably in the neighborhood of 5.

These observations basically agree with those of McHaffie and Lenher[169] who concluded that only very slight adsorption of water occurs

below 60% activity, but that the thickness of layers sharply increases
thereafter, to ∿ 200 monolayers just below saturation. So in PVT
studies at 25°, adsorption of water could be neglected at activities
in the vicinity of 50-60% or less.

Methanol adsorption experiments were also performed with the
microbalance apparatus. These observations were useful in determining
the region of pressure where adsorption is not important (Table 40 and
Figure 10). As this Figure shows, adsorption of methanol vapor at 25°
begins at around 100 Torr total pressure. Slight adsorption could have
occurred before reaching 100 Torr; however, since in the buoyancy experi-
ment the open bulb serves as a counterbalance for the adsorption effect
the error in observed densities due to adsorption should be extremely
small. Therefore the choice of 90 Torr as the limit of non-adsorption
is justified. Besides, the buoyancy results for methanol appear to indi-
cate that adsorption is balanced out up to around 110 Torr (see dis-
cussions in Chapter V)

Adsorption Bulb

The adsorption bulb, S_a, (refer to Fig. 1b) is very small com-
pared to the large bulb, L; in this case the ratio of volumes V_L/V_{Sa} ∿ 60;
this ratio could be made conveniently bigger than 60 so that when expand-
ing a gas or a mixture of gases from S_a to L, one does not need to worry
about the excess of pressure due to dissociation of gases; then the excess
in pressure at equilibrium is set equal to desorption processes. Note
that in most of this research where the amount associated is very small
compared to that of the monomers, this excess in pressure is then just

TABLE 40

ADSORPTION OF METHANOL VAPOR ON PYREX BULB AT 25°C

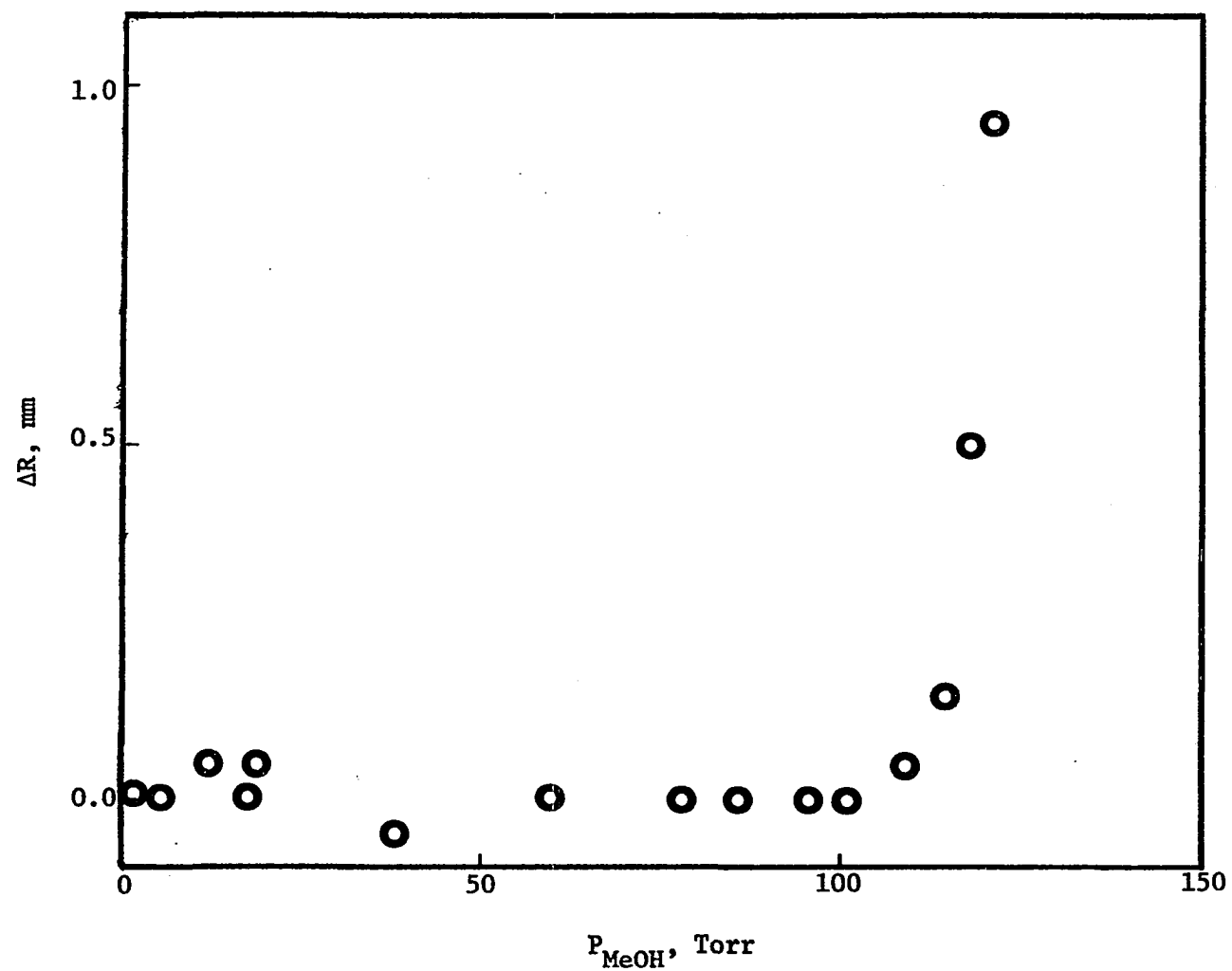| P_{MeOH}, Torr	ΔR, MM
0.45	0
4.80	0
11.55	0.05
17.20	0
17.80	0.05
37.90	-0.05
59.25	0
77.90	0
85.70	0
95.50	0
101.20	0
108.80	0.05
114.45	0.15
118.60	0.50
120.70	0.95

Figure 10. Change of Pointer Reading as a Function of Pressure of Methanol at 25°

set equal to the amount desorbed. In strong interaction cases, the dissociation can be taken into account, of course.

To obtain the Pyrex adsorbent, about 40-50 bulbs of (150 50) cc were blown from Pyrex tubes drawn into convenient sizes easy to handle. The total area inside and outside the bulbs were estimated to be 3 or 4 times that of L. The bulbs were then broken into small pieces of about 2 mm on a side, and then transferred into S_a, which was then carefully connected to L by Mr. Ronald Stermer, the University glassblower. A Fisher and Porter stopcock, C_2, cat. no. 795-005-0004, was used to separate or connect the two chambers S_a and L. This quick opening type stopcock is preferred over the needle type because the equilibrium of pressures is reached faster and manipulation of vapor samples is easier.

Now water stored at $25^\circ C$ is added quantitatively into L through the disk up to 15 or 16 Torr at $25^\circ C$ using the micropipette, 53100A. Any deviation from ideality is assumed to be due to adsorption on L and dimerization of water. It was considered prudent to restrict measurements to pressures less than about 16 Torr to avoid the possibility that larger aggregates of water molecules might be present. The dimerization constant of water at $25^\circ C$ was obtained by extrapolating the results at high temperature given by Kell, et al.[53] Their second virial coefficients—obtained from latent heat and vapor pressure data ($100-200^\circ C$)—were used along with their covolume $b_o = 22.1$ cc/mole to get corresponding K_p's. The extrapolated value to $25^\circ C$ was $K_p = 6.7 \times 10^{-5}$ Torr^{-1}. The latter value allows us to calculate the pressure deficit due to dimerization of water vapor; this pressure must be subtracted from the total pressure deficit, ΔP. This difference is the pressure adsorbed on L, δ_a^L. If we

now know the adsorption pressure on S_a, δ_a^{Sa}, we can get the ratio δ_a^{Sa}/δ_a^L, which is equal to the ratio of the two corresponding areas.

It is not difficult to obtain δ_a^{Sa}. Water is added quickly to a desired pressure in both bulbs L and S_a. Note that this pressure, P_{Sa}, should be in the range where we obtained δ_a^L above. Next the stopcock is closed and L is pumped down to a convenient low pressure, P_L. The pumping is stopped, the stopcock is opened, and the pressure is allowed to reach an equilibrium value P_F. The difference $P_F - (X_L P_L + X_{Sa} P_{Sa})$ is set equal to pressure change due to desorption of S_a. Note here that some dissociation occurs in this process $S_a \rightarrow L$; however, the excess pressure due to dissociation is equal to only about $(.0155 \text{ Torr}) (.01747) = 2.7 \times 10^{-4}$ Torr = .0001 gu which is certainly negligible, as mentioned above. The value 0.0155 Torr is the pressure due to dimer of water at 15 Torr, and $X_{Sa} = 0.01747$. We thus obtained δ_a^{Sa}; in the apparatus used, $\delta_a^{Sa}/\delta_a^L = 2.99 \approx 3$, which agrees well with the estimation by geometry to be 3-4 times. Table 41 gives the necessary data that led to obtaining the ratio equal to 3.

The pressure deficiency due to adsorption in L can in this way be determined; it will be added to the observed equilibrium pressure, and the sum is called P, as reported in Chapter IV. Note that δ_a^{Sa} was determined during about the same time period required for a corresponding density run.

Note that at 15-16 Torr of water at 25°C, if Eucken[52] were correct in that there are higher polymers than dimers, the ratio A_{Sa}/A_L might actually be somewhat higher than 3, because P_X would be higher. On the other hand, if there were no association at all in this pressure range,

TABLE 41

DATA FOR THE DETERMINATION OF RELATIVE AREAS BETWEEN

THE BULBS L AND Sa

P, Torr	P_X^+, Torr	P_X^+, gu	$\Delta P^{\ddagger}$, gu	δ_a^{L**}, gu	δ_a^{Sa}, gu	$\delta_a^{Sa}/\delta_a^{L*}$
16.10	0.0174	0.0065	0.0208	0.0143	0.0415	2.90
15.61	0.0163	0.0061	0.0143	0.0082	0.0350	4.27
15.52	0.0161	0.0060	0.0201	0.0141	0.0340	2.41
15.77	0.0167	0.0062	0.0182	0.0120	0.0380	3.17
16.02	0.0172	0.0064	0.0248	0.0184	0.0413	2.24
15.89	0.0169	0.0063	0.0194	0.0131	0.0385	2.94

average ratio = 2.99

≃ 3

[+] P_X is obtained using the extrapolated value to 25°C of water data by Kell et al.;[66] then the unit Torr of P_X values was changed to unit "Gage Unit," gu, through the usual calibrated Bourdon gage formula, P(Torr) = 2.679 (gu) + 0.000242 $(gu)^2$ − 0.00000077 $(gu)^3$.

[‡] $\Delta P = P_{ideal} - P_{observed}$, where P_{ideal} is the value expected from the calibration of pipette.

[**] $\delta_a^L = \Delta P - P_X$ = net pressure change due to adsorption on L.

[*] The ratio is assumed to be equal to that of corresponding areas A_{Sa}/A_L = 3; then the adsorption on L is equal that on Sa divided by 3.

the ratio would be lower than 3, and 2 would be nearer the correct value. Even with this uncertainty, we feel our way of treating this "sticky" problem is the best one so far proposed for correcting gas phase density results. The results of previous work, where adsorption was not taken care of could easily be off by 10-20% in the observed deviations from ideal behavior.

In the expansion process, $S_a \rightarrow L$, one might ask what happened to the molecules, or layers, that "stick" tightly to the Pyrex surface. It was observed that indeed under the conditions of the present studies about 1/5-1/4 of the amount initially adsorbed does not descrb readily and that many hours are required to attain nearly complete desorption. But this does not detract from the utility of the adsorption studies described, which provide information about the numbers of molecules that desorb and adsorb readily within the time it takes to carry out each run. After the first 2-3 runs, the "sticky" layers are established, so that the following runs become more consistent.

With the Burnett-type experiments, the area of the small bulb S_b was estimated relative to that of the large bulb. Recall that the expansions were made from $L \rightarrow S_b$; in essence we had a built-in balancing adsorption (on S_b) - desorption (on L) apparatus. Calculations which took all these processes into account at 25° did show that adsorption corrections can be altogether neglected for the TEA system. In the systems studied before the adsorption bulb had been devised (such as the MeOH-water system) adsorption-time curves were plotted for each component and the sum of individual curves was set equal to the value of the mixture.

We believe that our way of solving adsorption corrections in vapor phase experiments is one of the best yet proposed to handle this situation.

APPENDIX II

SOME SHORTHAND AND NOTATIONS USED IN THIS DISSERTATION

M	Methanol, methanol monomer, MeOH
W	Water, water monomer
TFA	Trifluoroacetic Acid
TFE	2,2,2-trifluoroethanol
HFP	1,1,1,3,3,3-hexafluoro-2-propanol
TMA	Trimethylamine
TEA	Triethylamine
Pyr	Pyridine, Pyridine monomer
x	Mole fraction in solution
y	Mole fraction in vapor
X	Volume ratio; $X_L = V_L/V_{total}$
P	Total pressure
π	Formal pressure or that pressure a gas would exert if it behaved ideally.
	= (Formal concentration) (RT)
RMSD(P)	Standard deviation in P
Torr	mm of Hg which has been corrected to $0^{\circ}C$ to std. gravity 980.665 cm/sec.^{2} At $25^{\circ}C$, (P,mm)(0.9955) = P,torr
K_p	Equilibrium constant for association process, standard state 1 Torr or 1 atmosphere.

Note that K_p (association) $= 1/K_p$ (dissociation)

K_c Equilibrium constant, standard state 1 mole/liter

$K_p \times RT$ $= K_c$ for dimerization; K_p $(2 \times 10^4) \simeq K_c$ at Rm T°.

K_x Mole fraction equilibrium constant.

     $= K_c/\overline{V}_s$ for a solution where solvent molar volume is $\overline{V}_s$;

     for CCl_4 $\overline{V}_s \simeq 0.1$ liter $\rightarrow K_x \simeq 10K_c$ for CCl_4 as solvent;

     $K_x \simeq 7K_c$ for heptane

K(cc/mole) $= b-B$ where B is 2nd virial coefficient, b covolume (Ref. 34)

     $= 2/3\pi d_o^3 - B$ where d_o is approximately the kinetic theory diameter[37]

$T^\circ K$ $= t^\circ C + 273.16$

RT $= 62.3656(T)$ 1 Torr/deg mole

$RT(25^\circ C)$ $= 18,594.93$ 1 Torr/mole $\simeq 2 \times 10^4$ 1 Torr/mole

CT   Charge-transfer

BIBLIOGRAPHY

1. W. M. Latimer and W. H. Rodebush, J. Am. Chem. Soc., $\underline{42}$, 1419 (1920).

2. T. S. Moore and T. F. Winmill, J. Chem. Soc., $\underline{101}$, 1635 (1912).

3. P. Pfeiffer, Ann., 137 (1913).

4. G. C. Pimentel and A. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, 1960.

5. D. Hadzi, "Hydrogen Bonding," Pergamon Press, Inc., New York, 1959.

6. H. E. Whipple, "Forms of Water in Biologic Systems," Ann. New York Acad. Sci., $\underline{125(2)}$, 249 (1965).

7. S. D. Christian, A. A. Taha, and B. W. Gash, Quart. Rev., $\underline{26}$, 20 (1970).

8. F. Franks and D. J. G. Ives, Quart. Rev., $\underline{20}$, 1 (1966).

9. A. N. Fletcher and C. A. Heller, J. Phys. Chem., $\underline{71}$, 3742 (1967); Ibid., $\underline{72}$, 1839 (1968).

10. E. E. Tucker, S. B. Farnham, and S. D. Christian, J. Phys. Chem., $\underline{73}$, 3820 (1969).

11. S. D. Christian and E. E. Tucker, J. Phys. Chem., $\underline{74}$, 214 (1970).

12. V. Cheam, S. B. Farnham, and S. D. Christian, J. Phys. Chem., $\underline{74}$, 4157 (1970).

13. S. B. Farnham, Ph.D. Dissertation (1970), the University of Oklahoma at Norman, Oklahoma.

14. U. Liddel and E. D. Becker, Spectrochim. Acta, $\underline{10}$, 70 (1957).

15. E. D. Becker, U. Liddel, and J. N. Shoolery, J. Mol. Spectroscopy, $\underline{2}$, 1 (1958).

16. J. C. Davis, K. S. Pitzer, C. N. R. Rao, J. Phys. Chem., $\underline{64}$, 1744 (1960).

17. A. P. Kudchadker, Ph.D. Dissertation (1968), Texas A&M University at College Station, Texas.

18. H. W. Woolley, J. Chem. Phys., 21, 236 (1953).

19. A. P. Kudchadker and P. T. Eubank, J. Chem. Eng. Data, 15, 7 (1970).

20. C. B. Kretschmer and R. Wiebe, J. Am. Chem. Soc., 76, 2579 (1954).

21. J. Russel and O. Maass, Can. J. Research, 5, 436 (1931).

22. G. S. Kell and G. E. McLaurin, J. Chem. Phys., 51, 4345 (1969).

23. G. A. Bottomley and T. H. Spurling, Aust. J. Chem., 20, 1789 (1967).

24. G. A. Bottomley and T. H. Spurling, Aust. J. Chem., 17, 501 (1964).

25. G. A. Bottomley, C. R. Reeves, and R. Whytlaw-Gray, Proc. Roy. Soc. A, 246, 504 (1958).

26. O. R. Foz Gazulla, J. F. G. Banda, and A. P. Masiá, Z. Electrochem., 56, 569 (1952).

27. O. R. Foz Gazulla, J. Morcillo, A. P. Masiá, and A. Méndez, An. R. Soc. esp. Fis. Quim, 50, 23 (1954).

28. R. L. Scott and R. D. Dunlap, J. Phys. Chem., 66, 639 (1962).

29. M. P. Moreland, J. J. McKetta, and F. H. Silberberg, J. Chem. Eng. Data, 12, 329 (1967).

30. T. DeVries and B. T. Collins, J. Am. Chem. Soc., 63, 1343 (1941).

31. G. C. Sinke and T. DeVries, J. Am. Chem. Soc., 75, 1815 (1953).

32. J. D. Lambert, E. N. Staines, and S. D. Woods, Proc. Roy. Soc. (London), 200A, 262 (1950).

33. J. D. Lambert, Disc. Faraday Soc., 15, 226 (1953).

34. W. Weltner, Jr. and K. S. Pitzer, J. Am. Chem. Soc., 73, 2606 (1951).

35. J. D. Lambert, G. A. H. Roberts, J. S. Rowlinson, and V. J. Wilkinson, Proc. Roy. Soc. (London), 196A, 113 (1949).

36. J. D. Lambert and E. D. T. Strong, Proc. Roy. Soc. (London), 200A, 566 (1950).

37. O. K. Rice, "Statistical Mechanics, Thermodynamics and Kinetics," W. H. Freeman and Co., San Francisco, 1967.

38. A. D. H. Clague, G. Govil, and H. J. Bernstein, Can. J. Chem., 47, 625 (1969).

39. C. F. Curtiss and J. O. Hirschfelder, J. Chem. Phys., 10, 491 (1942).

40. H. Dunken and H. Winde, Z. Chem., 7, 37 (1966).

41. A. Eucken and L. Meyer, Z. Physik. Chem., 5B, 452 (1929).

42. J. D. Ingle and H. P. Cady, J. Phys. Chem., 42, 397 (1938).

43. D. H. Knoebel and W. C. Edmister, J. Chem. Eng. Data, 13, 312 (1968).

44. A. N. Fletcher, J. Phys. Chem., 75, 1808 (1971).

45. N. S. Berman, Am. Inst. Chem. Eng. J., 14, 497 (1968).

46. G. M. Barrow, J. Chem. Phys., 20, 1739 (1952).

47. H. D. Beckey, Naturwissenschaften, 45, 259 (1958).

48. N. S. Berman, C. W. Larkam, and J. J. McKetta, J. Chem. Eng. Data, 9, 218 (1964).

49. C. Ener, A. Busala, and J. C. Hubbard, J. Chem. Phys., 23, 155 (1955).

50. J. L. Hales, J. D. Cox, and E. B. Lees, Trans. Faraday Soc., 59, 1544 (1963).

51. (a) R. G. Inskeep, J. M. Kelliher, P. E. McMahon, and B. C. Somers, J. Chem. Phys., 28, 1033 (1958);
    (b) R. G. Inskeep, F. E. Dickson, and H. McKuskie Olson, J. Mol. Spectroscopy, 5, 284 (1960).

52. A. Eucken, Z. Electrochem., 53, 102 (1949); 52, 255 (1948).

53. G. S. Kell, G. E. McLaurin, and E. Whalley, J. Chem. Phys., 48, 3805 (1968).

54. W. A. P. Luck and W. Ditter, Ber. Bunsengesellschaft Phys. Chem., 70, 1113 (1966).

55. P. Kebarle, S. K. Searles, A. Zolla, J. Scarborough, and M. Arshadi, J. Am. Chem. Soc., 89, 6393 (1967).

56. J. S. Rowlinson, Trans. Faraday Soc., 45, 974 (1949); 47, 120 (1951).

57. M. Van Thiel, E. D. Becker, and G. C. Pimentel, J. Chem. Phys., 27, 486 (1957).

58. A. B. Burg, J. Am. Chem. Soc., 65, 1629 (1943).

59. S. D. Christian and J. Grundnes, Nature, 214, 1111 (1967).

60. J. Grundnes and S. D. Christian, J. Am. Chem. Soc., 90, 2239 (1968).

61. J. Grundnes, S. D. Christian, and V. Cheam, Acta Chem. Scand., 24, 1836 (1970).

62. J. Grundnes, S. D. Christian, V. Cheam, and S. B. Farnham, J. Am. Chem. Soc., 93, 20 (1971).

63. J. Grundnes and S. D. Christian, Acta Chem. Scand., 23, 3583 (1969).

64. J. Childs, Ph.D. Dissertation (1971), The University of Oklahoma at Norman, Oklahoma.

65. D. van der Helm, J. D. Childs, and S. D. Christian, Chem. Comm., 887 (1969).

66. S. D. Christian and J. Grundnes, J. Am. Chem. Soc., in press.

67. O. K. Rice, Int. J. Quant. Chem., IIs, 219-224 (1968).

68. M. Tamres and S. N. Bhat, J. Phys. Chem., 75, 1057 (1971).

69. D. Atack and O. K. Rice, J. Phys. Chem., 58, 1017 (1954).

70. F. T. Lang and R. L. Strong, J. Am. Chem. Soc., 87, 2345 (1965).

71. J. N. Goodenow and M. Tamres, J. Chem. Phys., 43, 3393 (1965); M. Tamres and J. M. Goodenow, J. Phys. Chem., 71, 1982 (1967).

72. W. K. Duerksen and M. Tamres, J. Am. Chem. Soc., 90, 1379 (1968).

73. M. Kroll, J. Am. Chem. Soc., 90, 1097 (1968).

74. J. Prochorow, J. Chem. Phys., 43, 3394 (1965); J. Prochorow and A. Tramer, Ibid., 44, 4545 (1966).

75. J. A. Moede and C. Curran, J. Am. Chem. Soc., 71, 852 (1949).

76. A. S. Coolidge, J. Am. Chem. Soc., 50, 2166 (1928).

77. F. H. MacDougall, J. Am. Chem. Soc., 58, 2585 (1936).

78. H. L. Ritter and J. H. Simons, Ibid., 67, 757 (1945).

79. E. W. Johnson and L. K. Nash, Ibid., 72, 547 (1950).

80. M. D. Taylor, Ibid., 73, 315 (1951).

81. M. D. Taylor and J. Bruton, Ibid., 74, 4151 (1952).

82. R. E. Lundin, F. E. Harris, and L. K. Nash, Ibid., 74, 743 (1952).

83. R. E. Lundin, F. E. Harris, and L. K. Nash, Ibid., 74, 4654 (1952).

84. M. D. Taylor and M. Templeman, Ibid., 78, 2950 (1956).

85. J. Karle and L. O. Brockway, Ibid., 66, 574 (1944).

86. I. E. Coop, N. R. Davidson, and L. E. Sutton, J. Chem. Phys., 6, 905 (1938).

87. R. C. Badger, Ibid., 5, 605 (1937).

88. R. C. Herman, Ibid., 8, 252 (1940).

89. R. E. Kagarise, Ibid., 27, 519 (1957).

90. L. G. Bonner and J. S. Kirby-Smith, Physics Review, 57, 1078 (1940).

91. N. Fuson, M.-L. Josien, E. A. Jones, and J. R. Lawson, J. Chem. Phys., 20, 1627 (1952).

92. A. D. H. Clague and H. J. Bernstein, Spectrochim. Acta, 25A, 593 (1969).

93. D. M. Mathews and R. W. Sheets, J. Chem. Soc. A, 2203 (1969).

94. A. A. Maryott, M. E. Hobbs, and P. M. Gross, J. Am. Chem. Soc., 71, 1673 (1949).

95. H. E. Affsprung and C. Lin, unpublished work.

96. S. D. Christian, H. E. Affsprung, and C. Ling, J. Chem. Soc., 2378 (1965).

97. C. Ling, S. D. Christian, H. E. Affsprung, and R. W. Gray, J. Chem. Soc. A, 293 (1966).

98. C. Ling, S. D. Christian, and H. E. Affsprung, J. Chem. Phys., 70, 901 (1966).

99. T. L. Stevens, Ph.D. Dissertation (1968), The University of Oklahoma at Norman, Oklahoma.

99b. J. R. Goates, R. L. Snow, and J. B. Ott, J. Phys. Chem., 66, 1301 (1962).

100. H. Dunken and G. Marx, Abhandl. Deut. Akad. Wiss. Berlin, Kl. Math. Phy. Tech., 6, 101 (1964).

101. S. D. Christian, J. R. Johnson, H. E. Affsprung and P. J. Kilpatrick, J. Phys. Chem., 70, 3376 (1966).

101b. J. R. Johnson, P. J. Kilpatrick, S. D. Christian, and H. E. Affsprung, J. Phys. Chem., 72, 3223 (1968).

102. T. S. S. R. Murty and K. S. Pitzer, Ibid., 73, 1426 (1969).

103. T. S. S. R. Murty, Ibid., 75, 1330 (1971).

104. M. Kirszenbaum, J. Corset, and M.-L. Josien, Ibid., 75, 1327 (1971).

105. C. Lin, Ph.D. Dissertation (1964), the University of Oklahoma at Norman, Oklahoma.

106. J. de Villepin, A. Lautié, and M. L. Josien, Ann. Chim. (Paris) 14, 365 (1966).

107. L. Pauling, "Nature of the Chemical Bond," 2nd ed., Cornell University Press (1940).

108. W. H. Stockmayer, J. Chem. Phys., 9, 398 (1941).

109. J. O. Hirschfelder, F. T. McClure, and I. F. Weeks, J. Chem. Phys., 10, 201 (1942).

110. G. C. Pimentel, M. O. Bulanin, and M. Van Thiel, J. Chem. Phys., 36, 500 (1962).

111. J. E. Lowder, J. Quant. Spectr. Radiat. Transfer, 10, 1085 (1970).

112. P. A. Kollman and L. C. Allen, J. Am. Chem. Soc., 92, 753 (1970).

113. D. L. Hildebrand and W. F. Giauque, J. Am. Chem. Soc., 75, 2811 (1953).

114. R. D. Waldron and D. F. Hornig, J. Am. Chem. Soc., 75, 6079 (1953).

115. D. J. Millen and J. Zabicky, Nature, 196, 889 (1962); J. Chem. Soc., 168, 3080 (1965).

116. E. Hirano and K. Kozima, Bull. Chem. Soc. Japan, 39, 1216 (1966).

117. E. M. Arnett, L. Joris, E. Mitchell, T. S. S. R. Murty, T. M. Gorrie, and P. V. R. Schlever, J. Am. Chem. Soc., 92, 2365 (1970).

118. J. D. Cox and R. J. L. Andon, Trans. Faraday Soc., 54, 1622 (1958).

119. R. J. L. Andon, J. D. Cox, E. F. G. Herington, and J. F. Martin, Trans. Faraday Soc., 53, 1074 (1957).

120. J. P. McCullough, D. R. Douslin, J. F. Messerly, I. A. Hossenlopp, J. C. Kincheloe, and G. Waddington, J. Am. Chem. Soc., 79, 4289 (1957).

121. M. A. Hussein, D. J. Millen, and G. W. Mines, Chem. Communications, 178 (1970).

121b. N. L. Yarym-Agaev, E. A. Kogan, and E. D. Soldatova, Zhur. Fiz. Khim., 36, 1173 (1962).

122. S. C. Mohr, W. D. Wilk, and G. M. Barrow, J. Am. Chem. Soc., 87, 3048 (1965).

123. I. H. Reece and R. L. Werner, Spectr. Acta, 24A, 1271 (1968).

124. M. Fild, M. F. Swiniarski, and R. R. Holmes, inorg. chem., 9, 839 (1970).

125. S. G. W. Ginn and J. L. Wood, Nature, 200, 467 (1963).

126. G. L. Carlson, R. E. Witkowski, and W. G. Fateley, Nature, 211, 1289 (1966).

127. E. E. Tucker, Ph.D. Dissertation (1969), the University of Oklahoma at Norman, Oklahoma.

128. F. Cracco and P. Huyskens, Bull. Soc. Chim. Belg., 69, 255 (1960).

129. R. G. Inskeep, F. E. Dickson, and J. M. Killiher, J. Mol. Spectroscopy, 4, 477 (1960).

130. G. Govil, A. D. H. Clague, and H. J. Bernstein, J. Chem. Phys., 49, 2821 (1968).

131. A. T. Gladishev and Ya. K. Syrkin, Compt. Rend. Acad. Sci., USSR, 20, 145 (1938).

132. L. P. Bilozerska and N. D. Shchepkin, Opt. Spektrosk. (Akad. Nauk USSR, Otd. Fiz. Mat. Nauk), 3, 290 (1968); Opt. Spectrosc. Suppl., 3, 146 (1968).

133. D. J. Millen and O. A. Samsonov, Chem. and Industr., 1694 (1963); J. Chem. Soc., 3085 (1965).

134. J. Arnold, J. E. Bertie, and D. J. Millen, Proc. Chem. Soc. (London), 121 (1961); J. E. Bertie and D. J. Millen, J. Chem. Soc., 497 (1965); Ibid., 514 (1965).

135. J. Arnold and D. J. Millen, J. Chem. Soc., 510 (1965).

136. J. Arnold and D. J. Millen, J. Chem. Soc., 503 (1965).

137. J. D. Lambert, J. S. Clarke, J. F. Duke, C. L. Kicks; S. D. Lawrence, D. M. Morris, and M. G. T. Shane, Proc. Roy. Soc. (London), 249A, 414 (1959).

138. A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, 1963.

139. K. B. Wiberg, "Laboratory Technique in Organic Chemistry," McGraw-Hill, New York, 1960.

140. J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., New York, 1965.

141. J. D. Edwards, J. Ind. Eng. Chem., $\underline{9}$, 790 (1917).

142. S. D. Christian, E. Neparko, and H. E. Affsprung, J. Phys. Chem., $\underline{64}$, 442 (1960).

143. R. S. Bradley, J. Sci. Instrum., $\underline{30}$, 84 (1953).

144. H. Carmichael, Can. J. Phys., $\underline{30}$, 524 (1952).

145. E. S. Burnett, J. Appl. Mech., $\underline{58}$, A-136 (1936).

146. A. A. Taha, Ph.D. Dissertation (1965), The University of Oklahoma at Norman, Oklahoma.

147. A. A. Taha, R. D. Grigsby, J. R. Johnson, S. D. Christian, and H. E. Affsprung, J. Chem. Ed., $\underline{43}$, 432 (1966).

148. J. Timmermans, "The Physico-Chemical Constants of Binary Systems in Concentrated Solutions," Interscience Publishers, Inc., New York, 1960.

149. D. J. Wilde, "Optimum Seeking Methods," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1964.

150. S. D. Christian, J. Chem. Educ., $\underline{42}$, 604 (1965).

151. D. D. McCracken and W. S. Dorn, "Numerical Methods and Fortran Programming," John Wiley and Sons, Inc., New York, 1964.

152. S. Roach and S. D. Christian, unpublished data.

153. H. S. Frank and W. Y. Wen, Disc. Faraday Soc., $\underline{24}$, 133 (1957).

154. L. D. Bellamy and R. J. Pace, Spectrochim. Acta, $\underline{22}$, 525 (1966).

155. C. C. Costain and G. P. Srivastava, J. Chem. Phys., $\underline{41}$, 1620 (1964).

156. P. Saumagne and M. L. Josien, Bull. Soc. Chim. Fr., $\underline{6}$, 813 (1958).

157. A. N. Sidorov, Opt. Spectr. (USSR), $\underline{8}$, 51 (1960).

158. P. Saumagne, Thesis, Bordeaux (1961).

159. G. Mavel, Thesis, Paris (1961).

160. W. K. Thompson, J. Chem. Soc., 4028 (1964).

161. B. Brun, R. Gaufres, J. Rouvière, and J. Salvinien, Compt. Rend. Acad. Sci., 260, 3943 (1965); Ibid., 260, 3636 (1965).

162. B. Brun and J. Salvinien, J. Chim. Phys., 64, 1319 (1967).

163. J. Rouvière and J. Salvinien, Compt. Rend. Acad. Sci. C, 265, 949 (1967).

164. J. M. Sorensen, Ph.D. Dissertation, Case Western Reserve University, 1968.

165. (a) S. D. Christian and J. Grundnes, Acta Chem. Scand., 22, 1702 (1968);
     (b) S. D. Christian, Final Progress Report (Grant No. 14-01-0001-1315) "Solute Properties of Water--Effect of solvents on Molecular Complex Formation," Office of Saline Water, in press.

166. G. A. Bottomley, I. H. Coopes, G. L. Nyberg, and T. H. Spurling, Australian J. Chem., 18, 1105 (1965).

167. G. A. Bottomley and C. G. Reeves, Trans. Farad. Soc., 53, 1455 (1957).

168. R. I. Razouk and A. S. Salem, J. Phys. Chem., 52, 1208 (1948).

169. I. R. McHaffie and S. Lenher, J. Chem. Soc., 127, 1559 (1925).