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THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

INTERMOLECULAR INTERACTIONS OF ALCOHOLS: METHANOL, 2,2,2-TRIFLUOROETHANOL, AND 1,1,1,3,3,3-HEXAFLUORO-2-PROPANOL

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

SUTTON BURNS FARNHAM

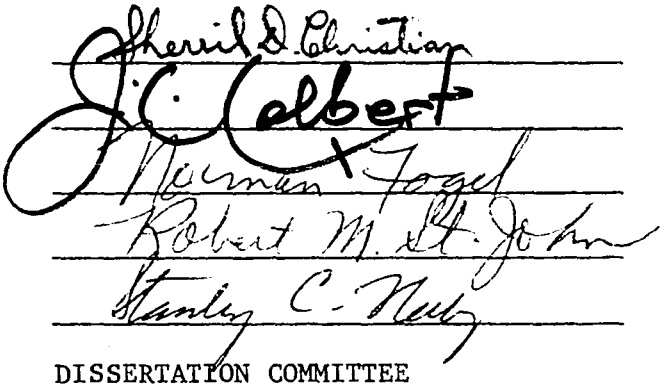
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APPROVED BY



DISSERTATION COMMITTEE

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DEDICATION

I would like to dedicate this work to my family.

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INTERMOLECULAR INTERACTIONS OF ALCOHOLS: METHANOL, 2,2,2-TRIFLUOROETHANOL, AND 1,1,1,3,3,3-HEXAFLUORO-2-PROPANOL

CHAPTER I

INTRODUCTION

Since the concept of the hydrogen bond was proposed,[1] much effort has been expended to evaluate its energetics and to determine its importance.[2,3] The existence of hydrogen bonds has been established for a wide variety of compounds in the vapor, liquid, and solid phases. Hydrogen bonds present in these systems have exhibited a broad range of both bond strengths and degrees of association. In alcohols such bonds generally fall in the intermediate range of both categories. Indeed, alcohols, particularly those of low molecular weight, have been extensively investigated, yet the nature of their association remains open to question. In the belief that new and precise data might prove instructive, a study of several alcohol systems was undertaken.

The alcohols chosen for this study were methanol, 2,2,2-trifluoroethanol (TFE), and 1,1,1,3,3,3-hexafluoro-2-propanol (HFP). Some physical properties of these fluoroalcohols have been previously investigated; dielectric constant, density, viscosity, partial molar volume, and other properties have been reported for various systems by Mukherjee and Grunwald[4]

and by Murto, Kivinen and colleagues,[5-11] and information about internal rotation and conformational stability has been given by Oki and Iwamura,[12] Krueger and Mattee,[13] and Murto and Kivinen.[14] The three alcohols possess important structural differences which can sterically affect their association, but their dominant dissimilarity is the variation in relative acidities of the alcoholic hydrogens. The acidities of the fluoroalcohol analogs, 2-propanol and ethanol, and methanol range from much less than to approximately equal to that of water. The substitution of the highly electronegative fluorine atoms in the alpha position relative to the alcohol functional group greatly decreases the strength by which the hydrogen is bound to the oxygen: the pK_a of TFE is 12.5[4] and that of HFP is 9.3[15] which is comparable to the value for phenol, 9.9. This weakening of the O-H bond is a manifestation of the modification of the charge density of the molecules by the electron withdrawing fluorine atoms. This change doubly affects the ability of the functional group to form hydrogen bonds. The ability to act as a proton donor is indeed enhanced by the weakening of the O-H bond. However, the shifting of the electron density away from the oxygen toward the fluorine atoms markedly decreases the effectiveness of the oxygen to act as a proton acceptor. The substitution of fluorine for the carbon hydrogens results in an increase in hetero-association when an acceptor is supplied[4] and a decrease in self-association in the pure liquid, indicating that the latter effect apparently dominates.[16]

The reactivity of the environment in which the association reactions of the alcohols were examined was also varied. Judging the reactivity of the solvents by their ability to dissolve water, diphenylmethane[17] is considerably less nearly inert than n-hexadecane.[18] Viewed as the third

solvent, the vapor is the most nearly inert medium, a medium which is completely free of competitive solvation effects. Of interest for comparison purposes is the relative reactivity of carbon tetrachloride. This solvent, which is frequently employed in spectroscopic studies, falls between n-hexadecane and diphenylmethane in reactivity.[19]

A brief review of the literature follows. The results of several methanol, TFE, and HFP studies are presented, and, because the hydrogen bonding properties of the fluoroalcohols have not been extensively investigated, studies of their hydrocarbon analogs are included.

Alcohol Association in the Vapor

Alcohols exhibit properties in the vapor phase which cannot be explained by the same rationale used to describe the behavior of most gases. The compressibility data reported by Lambert, Roberts, Rowlinson, and Wilkinson[20] were interpreted to support the classification of organic vapors into two groups of different behavior. The first class included those vapors for which the observed second virial coefficient corresponded to that calculated from critical data by the Berthelot equation; the second class displayed a marked difference in the observed and calculated second virial coefficients. Both methanol and ethanol[21] fall into this second class. Lambert and colleagues[20] attributed this discrepancy in the second virial coefficients to the formation of dimeric species. The difference between the observed second virial coefficient and that calculated for the monomer was taken as the "dimerization second virial coefficient" or -RT/K, where K is the association constant. Over the temperature range studied, van't Hoff plots for the dimerization of

methanol showed a pronounced curvature and only the limiting values of the enthalpy could be inferred. Lambert, Staines, and Woods[22] concluded that this curvature of the van't Hoff plots indicated that the second virial coefficient of dimerization or, more correctly, the monomer-dimer model was too simplistic to describe adequately the system. From thermal conductivity data, Lambert and colleagues[22] suggested that the existence of polymeric species larger than the dimer must be assumed to explain the behavior of methanol vapor. The pressure dependence of the thermal conductivity for several alcohols was also studied by Foz, Banda, and Masia.[23] Their data for ethanol, the propanols, and butanols supported the monomer-dimer equilibrium model. However, this model was not adequate for correlating data for the methanol system and the presence of trimers was proposed.

The monomer-dimer-tetramer model for the association of methanol vapor was proposed by Weltner and Pitzer.[24] Previous heat capacity measurements by DeVries and Collins[25] had illustrated the anomalous behavior of methanol vapor; these investigators suggested that monomers, dimers, and possibly trimers could best describe their data. Noting that the pressure dependence of the heat capacity resembled that of the highly polymeric hydrogen fluoride, Weltner and Pitzer assumed that a higher-order polymer must be included with the dimer to explain the data. Using their limited heat capacity data with the PVT data of Eucken and Meyer,[26] five constants were evaluated: the enthalpy and the entropy of formation for the dimer, the number of monomer units in the polymer, and the enthalpy and the entropy of formation of the polymer. The result was the postulate that methanol vapor exists as an equilibrium mixture of monomer, dimer, and tetramer.

Although Weltner and Pitzer pointed out that their data did not distinguish between the formation of tetramers and the formation of appropriate mixtures of other polymers, the monomer-dimer-tetramer association model has been widely applied to various vapor phase alcohol systems. Barrow,[27] using heat capacity data and vapor densities calculated from vapor pressures and heats of vaporization, concluded that this model adequately described the ethanol system. Similar conclusions for 2-propanol were reached by Hales, Cox, and Lees[28] and Berman, Larkam, and McKetta[29] from their heat capacity data augmented by PVT data from the literature. The precision of Kretschmer and Wiebe's[30] vapor density data for methanol, ethanol, and 2-propanol did not permit a clear choice between the trimer and tetramer as the higher polymer; their data combined with heat capacity data of DeVries and Collins[25] and Sinke and DeVries[31] did indicate that the monomer-dimer-tetramer model was preferable. Using mass spectrometry to investigate the association of methanol vapor, Beckey[32] observed, in addition to high intensities of monomer and dimer, a markedly greater intensity for the peak attributed to the tetramer compared to that for the trimer. The Weltner and Pitzer model was found to be consistent with the ultrasonic dispersion data for methanol vapor of Ener, Basala, and Hubbard.[33] Inskeep, Kelliher, McMahon, and Somers[34] reported infrared (IR) spectroscopic studies of methanol vapor. Similar studies using deuterated methanol were reported by Inskeep, Dickson, and McKuskie.[35] For both systems agreement with the Weltner and Pitzer postulate was concluded. Finally, Berman[36] reviewed the application of the monomer-dimer-tetramer model to calorimetric data for six alcohols and ascribed the success of the model to the particular stability of the tetrameric polymer.

This is not to imply a unanimity of opinion in the interpretation of vapor phase alcohol data. Dunken and Winde[37] reported the association constants and the thermodynamic parameters for the dimerization of methanol vapor inferred from IR spectroscopic data. Clague, Govil, and Bernstein[38] using nuclear magnetic resonance (NMR) chose to neglect higher polymers and reported the enthalpy of formation of the methanol dimer. Johnson[39b] has interpreted PVT data for methanol and other alcohols in terms of monomer-dimer equilibria. Kudchadker[40] reported association constants and enthalpies of formation for the dimer, trimer, and tetramer calculated from compressibility data for methanol. Although McKetta and colleagues[29] reported that their heat capacity data for 2-propanol was best described by the Weltner and Pitzer model, Moreland, McKetta, and Silberberg[41] interpreted their compressibility data for the same system in terms of a monomer-dimer-trimer model. Cox[42] recognized that for selected temperature and pressure regions, the terms reflecting the existence of tetramers, the fourth virial coefficients, determined by Kretschmer and Wiebe[30] are of the same order as their experimental error; in reporting the compressibilities of propanols and butanols, Cox concluded that no terms higher than the second virial coefficient were necessary to explain the data.

Vapor phase studies of fluoroalcohols have not been numerous. Reece and Werner[43] qualitatively observed the self-association of TFE spectroscopically. The spectrum of HFP was studied by Murto and Kivinen[14] in their investigation of intramolecular hydrogen bonding. Johnson and Millen[39a] have studied the IR spectra of both TFE and HFP; in further studies, PVT data for both these fluoroalcohols have been interpreted by

Johnson[39b] in terms of monomer-dimer equilibria. Of interest, because of the similarity of acidic strength to HFP, is the association of phenol vapor reported by Opel.[44] Determined by vapor density techniques, the enthalpy of formation for the dimer was reported as -4.03 kcal/mole.

The results taken from the literature of the studies of several vapor phase alcohol systems are presented in Table 1. The enthalpies of formation for the associated species which were concluded to be present are given with the experimental methods employed in the investigations.

Table 1

Enthalpies of Formation (ΔH) of Associated Species for Alcohol Vapor

Alcohol	$-\Delta H$ dimer (kcal/mole)	$-\Delta H$ trimer (kcal/mole)	$-\Delta H$ tetramer (kcal/mole)	Method	Ref.
Methanol	3.2-7.3			compressibility	20
	7.1			thermal conductivity	23
	3.22		24.2	heat capacity, PVT	24
	4.0		22.1	vapor density, heat capacity	30
	3.5±0.2		18±5	spectrophotometric	34
	10.1[a]			PVT	39[b]
	15.2±2.8			spectrophotometric	37
	4.2±0.5			NMR	38
	4.3	15.1	26.0	compressibility	40
Ethanol	7.0			thermal conductivity	23
	3.4		24.8	heat capacity, vapor density	27
	4.0		20.1	vapor density, heat capacity	30
2,2,2-Trifluoroethanol	3.6[a]			PVT	39[b]
2-Propanol	7.4			thermal conductivity	23
	4.0		22.6	vapor density, heat capacity	30
	5.3		22.3	heat capacity, PVT	29
	4.5		22.9	heat capacity, PVT	28
	4.3[a]			compressibility	42

Table 1 - continued

Alcohol	-ΔH dimer (kcal/mole)	-ΔH trimer (kcal/mole)	-ΔH tetramer (kcal/mole)	Method	Ref.
1,1,1,3,3,3-Hexafluoro-2-propanol	6.9[a]			PVT	39[b]

[a]Values calculated from data in referenced material.

The hetero-association of alcohols with other volatile compounds has been studied by spectrophotometric,[43,45-51] NMR,[38] and classical techniques.[18,39] Arnold and Millen[45] reported a complex band in the near IR spectrum of the methanol-hydrogen fluoride system. Inskeep, Dickson, and Killiher[46] calculated an enthalpy of formation of -(4.7±0.7) kcal./mole for the methanol-diethyl ether complex from the temperature dependence of the complex peak in the IR spectrum. Millen and Zabicky[47,48] studied the near IR spectra of methanol with several amines and evaluated the force constant for the hydrogen bond formed between methanol and triethylamine. Ginn and Wood[49] and Carlson, Wilkowski, and Fateley[50] have investigated the same system in the far IR region. Clague, Govil, and Bernstein[38] used NMR to calculate an enthalpy of formation of -(5.8±0.7) kcal./mole for the methanol-trimethylamine complex. The energy of formation of the methanol-triethylamine complex inferred from spectral measurements was reported as -7.6 kcal./mole by Hirano and Kozina.[51] Vapor density experiments of Tucker[18] yielded a value of -(7.31±0.02) kcal./mole for the enthalpy of formation of the dimeric complex of methanol and diethylamine.

Spectroscopic studies of several alcohols with a variety of acceptors have been made by Reece and Werner.[43] They attempted to correlate

the frequency shifts in the vapor and in carbon tetrachloride which accompany the formation of complexes of methanol, ethanol, 1-butanol, TFE, and 2,2,3,3-tetrafluoro-1-propanol with several oxygen and nitrogen acceptors. Empirical relationships were developed but equilibrium constants and thermodynamic parameters could not be inferred from the data.

Johnson and Millen[39] have examined the spectral and PVT properties of several methanol and TFE two component systems. In interpreting their PVT data, the only intercomponent complexes considered were the dimers. With methanol, trimethylamine and tetrahydrofuran gave enthalpies of formation of -10.6 and -11.0 kcal./mole, respectively. With the same proton acceptors, TFE gave values of -10.0 and -7.8 kcal./mole, respectively. The system of two alcohol components was also studied, and the value obtained for the enthalpy of formation of the methanol-TFE dimer was -7.9 kcal./mole.

The importance of adsorption as a significant problem in the evaluation by classical methods of the behavior of polar gases has generally not been acknowledged.[20,21,26,39,42] However, when the amount of adsorbed vapor is comparable in pressure to that of any important associated species, appropriate corrections must be applied if an accurate interpretation of the association is to be made. This is not to reprehend previous investigators; rather it is probable that the accuracy of previous experiments did not permit observation of the effects of adsorption.

Two important points concerning the adsorption of alcohols on glass have been clearly demonstrated. First, the amount of vapor adsorbed on the walls of the reaction vessel is not always negligible when compared with the accuracy necessary for precise evaluation of vapor phase non-ideal

behavior, and second, adsorption is not a rapid process. Cheam,[52] from adsorption balance studies of water and methanol, has concluded that above approximately 0.6 activity at 25°C the amount of vapor adsorbed becomes an important source of error in vapor pressure measurements. Indeed, Razouk and Salem[53] have reported that for water the number of monolayers which are adsorbed under moderate conditions is quite large. The adsorption of water, methanol, and several other organic compounds has been investigated by Bottomley, Coopes, Nyberg, and Spurling[54] by trapping and measuring the adsorbed layers. Their results indicated that the adsorption is a significant source of error in classical vapor pressure studies; for methanol over a moderate temperature and pressure range, the adsorbed vapor corresponds to a pressure of several hundredths torr in a vapor pressure apparatus of reasonable dimensions. The observable rate of adsorption is dependent upon the activity of the vapor; for activities at which adsorption is significant, Cheam[52] has observed that several hours are required for equilibrium to be achieved between the adsorbed and free vapor. Folman and Yates[55] reported from spectral and interferometric studies that equilibrium for the water and methanol systems is established after approximately an hour.

Association of Alcohols in Solution

The description of the association reactions of alcohols in solution has generally paralleled that in the vapor phase. Although the IR and NMR spectra are perhaps superficially simple,[18,56,57] spectroscopic studies have most often been interpreted to support the view that alcohols in solution exist as the monomer and low (two or three monomer units) and

high (greater than three monomer units) polymers, however, even this general interpretation is not universally accepted.[56] As the existence of both linear and cyclic associated species were suggested in the vapor,[24,36] similar structures in solution are generally considered. Liddel and Becker[58] examined the IR spectra of methanol and ethanol in carbon tetrachloride (CCl_4) and concluded from the large enthalpies of formation that the dimeric species were cyclic. That the structures of the dimer and the higher polymers were different was inferred from the NMR spectrum of ethanol in CCl_4 by Becker, Liddel, and Shoolery.[59] Employing similar methods and interpretation, Chandler and Dinius[60] reported an enthalpy of formation of -5.04 kcal./mole for the dimer of ethanol in cyclohexane. Spectral evidence combined with dielectric constant and density data led Ibbitson and Moore[61] to conclude that for methanol and ethanol in CCl_4 and cyclohexane the lower polymers were linear and the higher polymers were cyclic. The opposite conclusion--double bonded dimers and linear polymers--was reached by Van Ness, Van Winkle, and Richtol[62] from spectral and heats of mixing studies of ethanol in n-heptane and toluene; a value of -5.2 kcal./mole was reported for the enthalpy of formation of the dimer. Davis, Pitzer, and Rao[63] reported the enthalpies of formation of the dimers of methanol, ethanol and 2-propanol in CCl_4 and ethanol in benzene as -9.4, -7.6, -7.3, and -5.1 kcal./mole, respectively. These values and the presence of both linear and cyclic dimers were inferred from NMR data. The apparent decreasing order of the absolute values of the enthalpies displayed by these alcohols has been interpreted as indicating a decreasing importance of the cyclic or double bonded dimer in the association.[58] However, the validity of such inferences of structure remain questionable.[64]

The stoichiometry of the higher polymers has also been disputed. Coburn and Grunwald[65] and Saunders and Hyne[66] have concluded from IR and NMR spectra of ethanol and methanol in CCl_4 that the tetramer is the dominant higher polymer. Fletcher and Heller[67] argued that the IR spectra show that the tetramers--both cyclic and linear--are the only important associated species present in the methanol system. Yet, the inability to differentiate between models of combinations of species in describing IR data for 2-propanol and other alcohols in CCl_4 prompted Dunken and Fritzsche[68] to propose a model of dimers and a general aggregation of polymers.

Perhaps the most radical model for the association of alcohols in solution is the monomer-trimer-octamer proposed by Tucker.[18] Extended to include dimeric species in reactive solvents, this model best describes the classical vapor pressure data for methanol in n-hexadecane, diphenylmethane, and benzyl ether. Further credence in this model comes from its satisfactory application to both NMR and IR spectral data. For methanol in n-hexadecane Tucker reported values of -(11.27±0.09) and -(41.23±0.08) kcal./mole for the enthalpies of formation of the trimer and octamer, respectively; in diphenylmethane, -(3.40±0.33), -(5.33±0.10), and -(23.45±0.14) kcal./mole were reported for the dimer, trimer, and octamer, respectively.

The association of TFE has been investigated by NMR[69] and IR[4,70] techniques. From a comparison of the IR spectra of TFE and ethanol in CCl_4, Mukherjee and Grunwald[4] suggested that TFE existed as the monomer and higher polymers. That the degree of association of TFE in benzene was less than that of ethanol was inferred from NMR data by Rao, Venkateswarlu,

and Murthy.[69] Quantitative measurements of the association of TFE in CCl_4 have been made by Kivinen and Murto[70] from studies of the O-H stretching frequencies in the fundamental and first overtone regions. They reported an association constant of 0.65 M^{-1} at 25°C and, for comparison with the unsubstituted analog, a constant of 0.89 M^{-1} for ethanol; -5.33 kcal./mole was the value reported for the enthalpy of formation of the TFE dimer.

Purcell, Stikeleather, and Brunk[71] reported that NMR spectra indicate that HFP is less associated than TFE in CCl_4. Indeed, the IR studies of HFP by Kivinen and Murto[70] quantify this difference: the association constant of 0.126 M^{-1} at 25°C is significantly less than that for TFE. A further comparison with the association constant of 2-propanol, 0.82 M^{-1}, demonstrates the relative effectiveness of the electron-withdrawing fluorine atoms on the hydrogen bonding propensity of the alcoholic hydrogen and oxygen. The enthalpy of formation of HFP dimer was reported as -5.53 kcal./mole.

IR studies of alcohols with several proton acceptors in CCl_4 have been conducted by Becker[72] and Motoyama and Jarboe.[73] Association constants and enthalpies of formation for the 1:1 complexes were reported. Considering the magnitude of the association constants for the series of branched alcohols derived from methanol, it is apparent that the decrease reflects a decreasing acidity and emphasizes the importance of the proton donating ability in hetero-association reactions in contrast to the dominant influence of the proton accepting ability in self-association reactions.[72]

The spectroscopic representations of the interactions of TFE and HFP with a variety of proton acceptors in CCl_4 have been scrutinized for possible interdependences. Purcell and Wilson[74] inferred correlations

of chemical and IR frequency shifts; Purcell and colleagues[71] attempted to correlate spectral shifts with calorimetric data; and Reece and Werner[43] discussed the relevance of IR frequency shifts in different phases.

A more direct measure of these interactions was supplied by Kivinen, Murto, and Kilpi.[75,76] Employing IR spectral techniques, association constants and thermodynamic parameters for the 1:1 complexes with ketones, ethers, and sulfur-containing bases were calculated. Part of these results combined in Table 2 with those of other investigators provide an interesting comparison of the relative magnitudes of the association constants and enthalpies of formation for several pertinent alcohols. Although the

Table 2

Association Constants (K) and Enthalpies of Formation (ΔH) for 1:1 Alcohol Complexes with 2-Propyl Ether

	K (M^{-1})	$-\Delta H$ (kcal/mole)	Reference
Methanol	1.62[a]	4.31	73
Ethanol	1.07[a]	4.19	73
2-Propanol	2.41	2.1	64
TFE	6.40	5.07	75
HFP	36.4	6.92	75

[a]Association constant evaluated at 21.7°C, others at 25°C.

constant for 2-propanol appears to be large, the enthalpies are in agreement with the order of absolute bond energies reported by Balasurbramanian and Rao:[77] TFE > methanol > ethanol > 2-propanol. Evidence for the 2:1 complexes with several bifunctional

acceptors was also given by Kivinen and colleagues.[10,75,76] Association constants for these complexes were reported to be approximately 35 and 15 times greater than the corresponding 1:1 constants for HFP and TFE, respectively.

CHAPTER II

OBJECTIVES AND APPROACH

The objective of this research was to describe and quantify the intermolecular interactions of several alcohols (methanol, 2,2,2-trifluoroethanol, and 1,1,1,3,3,3-hexafluoro-2-propanol) in media of varied reactivities (the vapor, n-hexadecane, and diphenylmethane). All deviations from ideality were assumed to be attributable to the formation of specific hydrogen bonded complexes. In the vapor phase, the dominant species and the corresponding association constants would be determined from a statistical analysis of precise pressure-volume-temperature (PVT) data. In solution the modes of association and the constants would be inferred from a similar treatment of vapor pressure measurements--measurements of the total solute pressure above a solution of known formal concentration. The standard PVT and vapor pressure techniques would be employed; where the experimental conditions warranted, modifications of these methods would be developed.

CHAPTER III

EXPERIMENTAL

Chemicals: Alcohols and Solvents

Methanol (analytical reagent grade, Mallinckrodt Chemical Company) was treated for the removal of traces of water[78] and fractionally distilled on a 30-plate Oldershaw column. 2,2,2-Trifluoroethanol (White Label, Distillation Products Industries, Eastman Organic Chemicals), after storage over a drying agent (Linde 4A sieves) and 1,1,1,3,3,3-hexafluoro-2-propanol (purity: 99.98%, Freon Products Division, E. I. du Pont de Nemours and Company) were each fractionally distilled on a 12-plate Oldershaw column. The center fractions of each of these alcohols exhibited no impurity peaks when analyzed by gas chromatography. Each alcohol was stored at reduced humidity in vapor contact with anhydrous calcium sulfate (Drierite); methanol was used shortly after preparation.

n-Hexadecane (practical grade, Matheson, Coleman and Bell Chemical Company) was treated for the removal of aromatics.[78] After treatment, this solvent and diphenylmethane (practical grade, Matheson, Colman and Bell Chemical Company) were each fractionally distilled at a reduced pressure on a 12-plate Oldershaw column.

General: Temperature and Pressure

Control of the temperature at which the systems were investigated was achieved by submersing the apparatus in a constant temperature bath. Vigorously circulated water was used as the heat exchange medium. Auxillary heating and cooling elements were used when required. Fine temperature control for the vapor pressure studies was maintained by two opaquely enveloped incandescent bulbs which served as heat sources activated by a mercury contact thermoregulator-electronic relay circuit (Model T-260, Precision Thermometer and Instrument Company; Model E2, Lux Scientific, Inc.); for the PVT studies, heat sources were controlled by a thermistor activated proportional power circuit (Model ST Thermonitor, E. H. Sargent and Company). Constancy of temperature was maintained to within ±0.01 and ±0.005°C respectively.

Pressures were measured with a precision pressure gauge (Models 140 with high resolution and 141 with micron resolution, Bourdon Tube Capsules 11C and 14, Texas Instruments, Inc.) united with the system via a 1mm ID capillary with a 10/30 mercury sealed joint with Teflon sleeve at the apparatus and a flareless tubing connector with Teflon ferule at the gauge. Reference pressures below 10^{-4} torr were maintained by continuous pumping and were invariant within the precision of detectability. Minimum reproducibility of the gauge used in the PVT and two component vapor pressure studies was 0.001 torr; for the single component vapor pressure studies, the gauge reproducibility was 0.003 torr.

Temperature of the system within the pressure gauge was 45°C; temperature of the connecting capillary uniting the submerged apparatus with the gauge was >45°C.

Apparatus, Procedure, and Data Refinement

PVT

The apparatus employed in the PVT studies was of modified Burnett[79] design. The system consisted of two spherical glass chambers of unequal volume joined through a high vacuum valve (Model 4172G4Y, Hoke, Inc.); pressures were monitored at the smaller chamber. The smaller chamber supported an evacuation port and entrance ports (Model 795-005 glass valves, Fischer and Porter Company) through which vapor was introduced into the system from previously degassed liquid samples.

The necessary apparatus dimension, the ratio of the volume of the larger chamber to the total or system volume (R_v^o), was evaluated by gas expansion of dry nitrogen corrected for non-specific interactions.[80]

To quantify deviations from ideality of vapor systems using a twin-chamber apparatus, three pressures in addition to chamber dimensions and constancy of temperature are required: the initial pressures of the larger (PL1) and smaller chambers (PS1) and the final system pressure (P2). For an apparatus which has a single pressure sensor at the smaller chamber, these pressures are generally determined in the following manner: The pressure of the larger chamber is obtained by measuring an initial system pressure. When the central valve is closed and the smaller chamber partially evacuated to obtain PS1, the larger chamber remains at the original higher pressure, PL1. The final system pressure, P2, is the pressure observed upon opening the central valve.

This procedure represents a departure in both method and analysis from that generally followed in Burnett experiments.[79] The Burnett

procedure involves the expansion of a gas of known pressure in a larger chamber (P_o) into a smaller evacuated chamber; the initial pressure in this chamber is generally not measured but is negligible. The resulting pressure after the expansion is measured (P_1), and the procedure repeated with P_1 being the pressure in the larger chamber and the final pressure being designated P_2. The sequence is repeated n times to give a series of related pressures, P_0, P_1, P_2, . . ., P_n, of decreasing magnitudes. An experimental advantage of the procedure used in this study is realized here: by measuring each pressure, the necessity of evacuating one chamber to a near-zero pressure is removed. Indeed, the time required to accomplish such an evacuation might complicate any attempt to correct the pressure for adsorption of the gas on the walls of the chambers.

A brief outline of the analysis of data from a Burnett experiment reveals several minor weaknesses of the method. For each successive pair of pressure measurements, P_r and P_{r-1}, the expressions

$$P_r V_L = z_r nRT \tag{1}$$

and

$$P_{r-1}(V_L+V_S) = z_{r-1} nRT \tag{2}$$

can be written, where V_L and V_S are the volumes of the larger and smaller chambers, respectively, the z's are the compressibility factors, and the symbols in the term nRT retain the individual meanings generally used in the perfect gas law. For the r^{th} expansion, these reduce to the ratio

$$\frac{P_{r-1}}{P_r} = N \frac{z_{r-1}}{z_r} \tag{3}$$

where N is defined as the volume ratio, $V_L/(V_L+V_S)$, and is evaluated at $P_r=0$ by extrapolation of P_{r-1}/P_r versus P_r. The ratios (equation 3) for each expansion are multiplied together to give the fundamental Burnett equation:

$$P_r N^r = (P_0/z_0)\ z_r \tag{4}$$

The reference term, P_0/z_0, is evaluated at zero pressure from a plot of $P_r N^r$ versus P_r, and the compressibility factors for each pressure are calculated from equation 4':

$$z_r = P_r N^r (z_0/P_0) \tag{4'}$$

Virial coefficients and association constants can then be determined.

The accuracy of each calculation of a compressiblity factor is dependent upon the accuracy of both N and P_0/z_0. Note that N is not simply related to z_r, but rather is raised to the r^{th} power, thus similarly increasing the effect of any error in N upon the calculated values of z_r. In the method and analysis (vide infra) used in this study, neither extrapolated quantity has such an influence upon the calculated results. The reference term, P_0/z_0, is not required and the volume ratio, N (or R_V^o), which is evaluated directly, enters into the calculations to the first power.

Returning to the experimental procedure used in this investigation, a concentration observable is necessary in the two component systems in addition to the pressures, PL1, PS1, and P2. That which was most convenient, a ratio of the formal pressures of the components (R_π), was obtained directly from quantitative sample introduction into the apparatus.

The determination of the pressure observables for vapor systems of polar and weakly acidic compounds was complicated by physical adsorption. This adsorption was indirectly observed as a decrease in pressure; the rate of this decrease was sufficiently small as to be beyond detection by techniques incapable of continuously monitoring pressures with micron precision, but large enough to introduce non-negligible errors into high precision PVT studies.[52,54] For analysis of the data to be valid, mass balance for the free vapor represented by the initial pressures and the final pressure must be maintained. If it is not, the vapor which has been removed from the gas phase by adsorption is characterized as associated species, giving erroneous results. Because this experimental method permitted a precise and continuous measure of pressure, changes in pressures--the effect of adsorption--were easily followed. The adsorption problem was therefore circumvented by employing an adsorption-time extrapolation technique whereby, in the closed system and at the specific, though hypothetical, time at which PL1, PS1, and P2 were measured, the quantity of adsorbed vapor in both initial chambers equalled that of the final system.

The adsorption-time extrapolation technique may be divided into three segments. After the introduction of the vapor into the system, the system pressure was observed as a function of time (segment I). Following the closing of the central valve, which isolated the larger chamber, and the partial evacuation of the smaller chamber, the pressure in the smaller chamber was observed as a function of time (segment II). Finally, after opening the central valve, the system pressure was again observed with time (segment III). For each segment, the pressure was

monitored for sufficient time to establish graphically the well defined rate curve: a 15:10:10 minute cycle for segments I, II, and III was found to be adequate. The pressure-time data, generally totaling more than 50 observations for the three segments, were plotted (Calcomp Plotter, IBM 1130 Computing Systems), and the rate curves for each segment extrapolated to a specific time t, 25 minutes after initiation of the run. A schematic representation of these curves is given in Figure 1.

Figure 1 may be interpreted in terms of adsorption and desorption. Concurrent with introduction of vapor into the apparatus, adsorption occurs in both chambers. This adsorption is not directly related to the determination of the observable pressure; it does place the resulting pressure curves of segment I on the over-all adsorption isotherm. Segment I and the extrapolation IA correspond to the effect upon pressure of adsorption on the surfaces of both chambers. The extrapolated pressure at time t is the pressure of the systems which would be expected assuming that the adsorption proceeds as defined in segment I. That which is desired, however, is the pressure exerted by the free vapor at time t in the larger chamber only. Assuming that the adsorption is directly proportional to the geometric area of the container, a secondary correction reflecting the unequal surface areas of the two chambers was applied to obtain the necessary observable, PL1. Segment II illustrates the desorption process. After the reduction of pressure in the smaller chamber to below the equilibrium pressure corresponding to the amount of vapor adsorbed during the filling and segment I manipulations, the sorption process is shifted toward the free vapors. Extrapolation of the pressure curve gives the pressure exerted by the free vapor in the smaller chamber at time t, PS1.

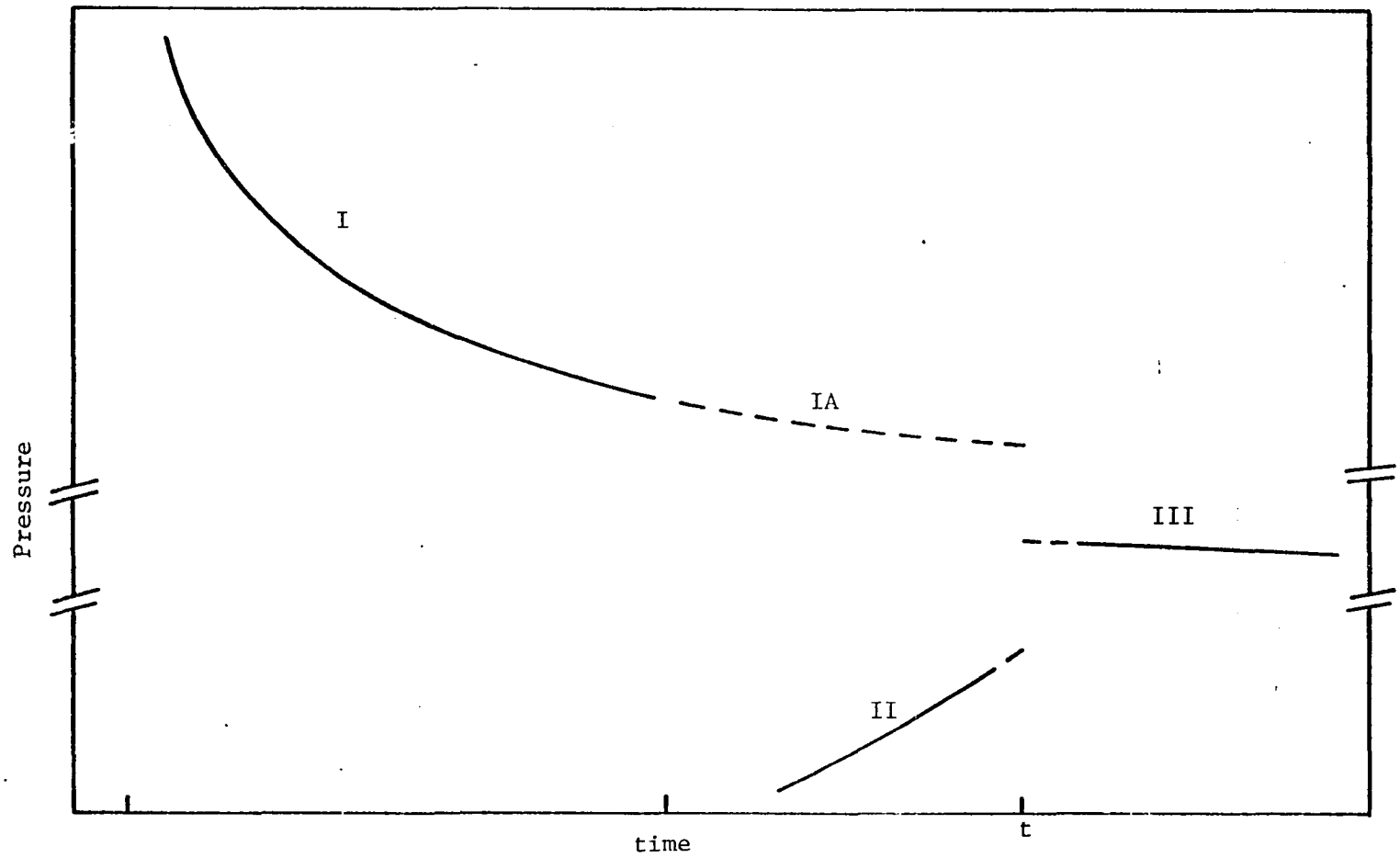


Figure I. Schematic representation of dependence of pressure upon time for a polar vapor. Labels I, IA, II, and III designate the experimental steps of adsorption-time extrapolation technique and are defined in the text.

The final segment, III, reflects the simultaneous occurrence of the two sorption processes: desorption in the larger chamber and adsorption in the smaller chamber. These processes occur because the system pressure is less than the initial pressure of the larger chamber and greater than the initial pressure of the smaller chamber, thus reversing the sorption reactions initiated in the preceding segments. Extrapolation of the pressure curve to time t yields the desired system pressure, P2.

The magnitudes of the pressure changes illustrated in Figure 1 are primarily dependent upon the total pressure of the alcohols. Since each alcohol was studied over a pressure range up to 95% of its saturation pressure, the relative magnitudes of the adsorption effects parallel the vapor pressures: HFP > methanol > TFE. Under the experimental conditions which favored adsorption, segments I with IA and II corresponded to changes in pressure of about 200 and 75 microns, respectively. Changes in segment III were generally less because the opposite effects of the competitive sorption processes partially cancelled.

All data for the single component systems were taken using the adsorption-time extrapolation techniques. Each datum point, PL1, PS1, and P2, results from a single experimental operation and is therefore independent of every other point. The only exceptions are several data points for the HFP systems at 25°C which were taken in sequences of two or three points.

Restricted in pressure range because of azeotrope formation (Appendix II), the investigation of the two component systems was limited to maximum pressures at which adsorption effects were negligible. The vapor mixtures of both components were manipulated as a single component, and the pressures PL1, PS1, and P2 were observed directly.

Evaluation of the concentration observable required for the two component systems followed directly from the method of sample introduction into the system. A known pressure of the second component was bled from the higher pressure smaller chamber into the larger chamber which contained a known pressure of the first component. Using the self-association constants for each component and R_V^o, R_π for the vapor mixture was calculated.

PVT data for both the single and two-component systems are presented in Appendix I.

Vapor Pressure

Different apparatus were used for the single and two component vapor pressure studies. Because of the mechanical difficulty of accomplishing accurate multiple liquid sample additions of the fluoroalcohols, an apparatus designed for vapor additions was used in the single component studies. For the two component systems, where sequential methanol rather than fluoroalcohol additions were made, the more conventional vapor pressure apparatus was used.

The apparatus for the single component studies consisted of two spherical glass chambers connected by a high vacuum valve (Model 4172G4Y, Hoke, Inc.). The smaller chamber or solution flask was detachable from the system (24/40 ☤ Mercury sealed joint, Teflon sleeve); solution agitation was provided by a Teflon sealed stirring bar actuated by an extramural rotating magnet (Model MS-7, Tri-R Instruments, Inc.). The larger or buret chamber supported the several ports and the pressure gauge connection similar to the smaller chamber of the PVT apparatus.

Apparatus dimensions, the volumes of the solution flask and the buret chamber, were determined individually from the differences in the mass of the empty and water filled chambers.

To analyze the vapor pressure data for the single component systems, the total volatile component present and the equilibrium pressure corresponding to its distribution between the solution and vapor phases must be known. More conveniently, this information can be expressed as the formal solution concentration (f_A) and the monomer concentration in the vapor phase (C_A^v). Employing the apparatus designed for vapor additions, three pressure measurements are necessary to obtain this information: an initial and final buret pressure, the difference being a measure of the addition of the volatile component to the system, and a final system pressure which reflects vapor-solution phase equilibrium. In addition, the volume of the solution and the usual temperature and apparatus dimensions must be known.

The following experimental procedure was used and repeated sequentially to give a series of data points over a selected concentration range. With pressure equilibrium established, the central valve was closed isolating the solution flask and the initial pressure of the buret chamber determined. This pressure reflects only the small vapor pressure of the non-volatile solvent for the first data point of each series; for each data point thereafter, it measures the initial vapor concentration of the volatile component in the buret chamber. With the central valve closed, the volatile component was added to the buret chamber by vapor addition from a degassed liquid sample, and the pressure determined. The central valve was opened and, after pressure equilibrium between the vapor and the solution had been achieved, the final system pressure measured.

The monomer concentrations in the vapor, C_A^v, and the formal solution concentrations, f_A, were calculated from the observed pressures for each point. Corrections for vapor association were applied; monomer and formal pressures were calculated. Application of the ideal gas law to the final formal pressure and the sum of the difference between buret formal pressures gave the number of moles of the volatile component in the vapor and in the system, respectively. From their difference and the solution volume, f_A was obtained. C_A^v was calculated from the vapor volume and final pressure of the monomer.

The standard vapor pressure apparatus used for the two component studies has been described previously.[81] Modified to facilitate removal of the solution flask (24/40 ₸ mercury sealed joint; Teflon sleeve) and to permit union with the pressure gauge, the apparatus retained the integrated mercury sealed sintered-glass disc for liquid sample addition. The mechanics of solution agitation were similar to that of the previously described vapor pressure apparatus.

The single apparatus dimension, the total volume of the system, was determined from the difference in mass of the empty and filled apparatus using water as the calibrating liquid.

For vapor pressure systems of two volatile components distributed between the vapor and non-volatile solvent, the total number of moles of each component present in the system (NAT, NBT) and the equilibrium pressure (P) are the necessary observables. Using a liquid sample addition method, the quantities of each component are determined volumetrically; the pressure is measured directly. As in the previous studies, temperature, apparatus dimension, and solution volume are also required.

The conventional experimental procedure was used for the two component systems.[81] To an evacuated system containing a stirred solvent, a measured amount of a fluoroalcohol was volumetrically added by buret (Model S-3200, Roger Gilmont Industries) through the mercury-sealed sintered-glass disc. Using literature values of the density,[4,5,16,82] NBT was calculated. When the system neared equilibrium, methanol was similarly added and NAT calculated.[83] After equlibrium between the two phases had been achieved by the two volatile components, the pressure, P, was measured. Within the pressure restrictions dictated by azeotrope formation (Appendix II), the methanol additions and pressure measurements were repeated to give a series of points of various methanol concentrations in solution for a constant system concentration of fluoroalcohol.

The precision burets used for all liquid sample additions were stored at 25°C in vapor contact with a desiccant (Drierite).

The volumes of the solutions used were approximately 100 to 200 cc. Solvents were weighed in the solution flasks, and the volumes calculated from their masses and the appropriate density values taken from the literature.[83,84,85] Volume corrections to account for the increase in volume of the solution with increasing solute concentration were made based on the assumption that the volumes of the solvent and the alcohols were additive over the concentration ranges studied.

The same solvent samples were often used for several experimental sequences. Pumping on the system for several hours was sufficient to remove the volatile components. The low vapor pressure of the solvents permitted continuous pumping at temperatures of about 20°C without indication by water solubility tests of loss of solvent trapped at acetone-dry ice temperatures.

All data for the vapor pressure systems are presented in Appendix I.

CHAPTER IV

DATA TREATMENT

PVT

Two fundamental pressure relationships can be used to characterize the non-ideal behavior exhibited by the alcohols in the single component PVT systems. If all deviations from ideality are attributed to the formation of specific complexes, Dalton's Law defines the total pressure, P, as

$$P = P_A + P_{A_2} + P_{A_3} + \ldots + P_{A_n} \tag{1}$$

where P_A is the pressure of the monomer and P_{A_2}, P_{A_3}, . . ., P_{A_n} are the partial pressures of the aggregates of 2, 3, . . ., n monomer units, respectively. Assuming that each species behaves ideally, the formal pressure, π, is given by

$$\pi = P_A + 2P_{A_2} + 3P_{A_3} + \ldots + nP_{A_n} \tag{2}$$

Defining all association constants from the monomer and in the same form as that of the dimer,

$$K_{A_2} = \frac{P_{A_2}}{(P_A)^2} \quad , \tag{3}$$

equations 1 and 2 reduce to more convenient forms as functions of the monomer pressure:

$$P = P_A + K_{A_2} P_A^2 + K_{A_3} P_A^3 + \ldots + K_{An}\, P_A^n \tag{4}$$

and

$$\pi = P_A + 2K_{A_2} P_A^2 + 3K_{A_3} P_A^3 + \ldots + nK_{An} P_A^n \tag{5}$$

Because the ideality of each species is assumed to hold, the mass balance relationship

$$(\pi \times \text{Volume})_{\text{initial}} = (\pi \times \text{Volume})_{\text{final}} \tag{6}$$

is assumed to be applicable. Expressed in terms of the observables rendered by this experimental method, this relationship becomes

$$\pi L1 \times R_V^o = \pi 2 - \pi S1\ (1-R_V^o) \tag{7}$$

where R_V^o is the volume ratio and $\pi L1$ and $\pi S1$ are the initial formal pressures of the larger and smaller chambers, respectively, and $\pi 2$ is the final formal pressure of the system.

The total and formal pressure equations apply to each sub-system represented by the three experimentally determined pressures of a single data point, PL1, PS1, and P2. For a given set of assumed species--monomer and any one or two associated species--and assumed values for the corresponding association constants, a final system pressure was calculated. The initial total pressures, PL1 and PS1, were each used in equation 4 to obtain monomer pressures which were then used in equation 5 to calculate the corresponding formal pressures, $\pi L1$ and $\pi S1$. These formal pressures

and the volume ratio were used in equation 7 to calculate the final formal pressure, $\pi 2$. With this formal pressure, equation 5 was solved for the monomer pressure and equation 4 for the total pressure for the final system, P2(calcd.)

The unknowns in this analysis are the values of the association constants. Non-linear least squares evaluation of these constants was accomplished by numerical optimum-seeking techniques[86,87] which minimized the root mean square deviation, RMSD. The RMSD is defined for this set of calculations as

$$\text{RMSD} = \left[\sum_{i=1}^{n} \left[P2_i - P2(\text{calculated})_i \right]^2 / (n - p) \right]^{1/2} \qquad (8)$$

where $P2_i$ and $P2(\text{calculated})_i$ are, respectively, the observed and calculated comparison quantities for the i^{th} data point; n is the total number of points, and p the number of adjustable parameters. The adjustable parameters for a specific fit--the constants for the associated species which were assumed to be present--were systematically varied to affect a minimum of the RMSD for a given data set. The standard errors in the association constants at minimum RMSD were taken as the uncertainties in these parameters at one standard deviation.[87]

All combinations of association constants of the form K_{An} and K_{Am} where $2 \leq n \leq 8$ and $0 \leq m \leq 8$, $m \neq n$, were tested; those which gave plausible results are given in Tables 3, 4, and 5. Presented in these tables are the assumed sets of association constants and the corresponding RMSD's for the methanol, 2,2,2-trifluoroethanol, and 1,1,1,3,3,3-hexafluoro-2-propanol systems at 15, 25, and 35°C.

TABLE 3

RMSD's for Several Fits of Methanol Vapor at Three Temperatures

fit	15° RMSD,(torr)	25° RMSD,(torr)	35° RMSD,(torr)
1-2	0.0550	0.0946	0.2175
1-3	0.0298	0.0360	0.0627
1-4	0.0157	0.0230	0.0693
1-2-3	0.0170[a]	0.0224[a]	0.0336[a]
1-2-4	0.0163[a]	0.0149	0.0178
1-3-4	0.0163[b]	0.0166	0.0234
1-3-8	0.0168	0.0097	0.0121

[a]Dimer constant produced by these fits was negative;

[b]for this fit, the trimer constant was negative.

TABLE 4

RMSD's for Several Fits of 2,2,2-Trifluoroethanol Vapor at Three Temperatures

fit	15° RMSD,(torr)	25° RMSD,(torr)	35° RMSD,(torr)
1-2	0.0153	0.0188	0.0184
1-3	0.0138	0.0111	0.0235
1-4	0.0134	0.0115	0.0462
1-2-3	0.0139[a]	0.0109[a]	0.0137
1-2-4	0.0140[a]	0.0106	0.0135
1-3-4	0.0140[b]	0.0107	0.0152[c]
1-3-8	0.0141[e]	0.0107	0.0191[d]

[a]Dimer constant produced by these fits was negative; [b]for this fit, the trimer constant was negative; [c]for this fit, the tetramer constant was negative; [d]for this fit, the octamer constant was negative; [e]error in the octamer constant for this fit was greater than the value of the constant.

TABLE 5

RMSD's for Several Fits of 1,1,1,3,3,3-Hexafluoro-2-Propanol Vapor at Three Temperatures

fits	15° RMSD,(torr)	25° RMSD,(torr)	35° RMSD,(torr)
1-2	0.0193	0.0264	0.0933
1-3	0.0093	0.0263	0.0498
1-4	0.0198	0.0539	0.1464
1-2-3	0.0096[c]	0.0176	0.0237
1-2-4	0.0099	0.0185	0.0238
1-3-4	0.0095[a]	0.0164[a]	0.0271[a]
1-3-8	0.0097[b]	0.0180[b]	0.0349[b]

[a]Tetramer constant produced by these fits was negative; [b]for these fits, the octamer constant was negative; [c]error in dimer constant for this fit was greater than the value of the constant.

The total and formal pressure expressions which applied to the single component PVT systems can be extended to include a second component for the two component systems. Because of the relatively low pressure ranges used in the two component experiments, the self-association in the data analysis was limited to the major associated species (vide infra) of each component. For the same reason, the hetero-association included only the dimer and the two trimers. With these simplifications, the total pressure equation for a system of components A and B becomes

$$P = P_A + P_{A_3} + P_B + P_{B_3} + P_{AB} + P_{A_2B} + P_{AB_2} \quad . \tag{9}$$

P_A and P_{A_3} are the monomer and trimer pressures of component A; P_B and P_{B_3} represent the same for component B; P_{AB} is the pressure of the hetero-dimer; and P_{A_2B} and P_{AB_2} are the pressures of the hetero-trimers of 2:1 and 1:2 stoichiometry, respectively. The formal pressure equations for components A and B are

$$\pi A = P_A + 3P_{A_3} + P_{AB} + 2P_{A_2B} + P_{AB_2} \tag{10}$$

$$\pi B = P_B + 3P_{B_3} + P_{AB} + P_{A_2B} + 2P_{AB_2} \tag{11}$$

As for the self-association, the hetero-association constants are defined from the monomer pressures:

$$K_{AB} = \frac{P_{AB}}{P_A P_B} \quad , \quad K_{A_2B} = \frac{P_{A_2B}}{(P_A)^2 P_B} \quad , \quad K_{AB_2} = \frac{P_{AB_2}}{P_A (P_B)^2} \tag{12}$$

In terms of monomer pressures of the two components, equations 9, 10, and 11 become:

$$P = P_A + K_{A_3} P_A^3 + P_B + K_{B_3} P_B^3 + K_{AB} P_A P_B + K_{A_2B} P_A^2 P_B + K_{AB_2} P_A P_B^2 \quad (13)$$

$$\pi A = P_A + 3K_{A_3} P_A^3 + K_{AB} P_A P_B + 2K_{A_2B} P_A^2 P_B + K_{AB_2} P_A P_B^2 \quad (14)$$

$$\pi B = P_B + 3K_{B_3} P_B^3 + K_{AB} P_A P_B + K_{A_2B} P_A^2 P_B + 2K_{AB_2} P_A P_B^2 \quad (15)$$

The concentration observable which is invariant for a given vapor mixture is defined as

$$R_\pi = \pi_B / \pi_A \quad (16)$$

The calculations for the two component systems paralleled those for the single component systems. For the selected hetero-associated species and the assumed values of the corresponding association constants, the calculation of the final system pressures followed from the solutions of the pertinent equations. For the two initial total pressures, PL1 and PS1, equations 13 and 16 were solved simultaneously by iteration and the resulting sets of monomer pressures were used in equations 14 and 15 to obtain the corresponding formal pressures. These initial formal pressures for each component and the volume ratio were used in equation 7 to calculate the final formal pressures of both components. The expressions for these quantities (equations 14 and 15) were then solved simultaneously for the final monomer pressures of both components, and from equation 13 the final total pressure, P2(calcd.), was calculated.

The hetero-association constants were evaluated by the same non-linear least squares analysis as was used for the self-association constants. Again the final system pressures, P2 and P2(calcd.), were the comparison quantities on which the RMSD's were based. All one and

two parameter fits which represented the existence of the mixed component dimer and trimers were tested. A comparison of the RMSD's for several of these fits is given for the methanol-2,2,2-trifluoroethanol and methanol-1,1,1,3,3,3-hexafluoro-2-propanol systems at 15, 25, and 35°C in Tables 6 and 7.

Vapor Pressure

The formal concentration in solution of a solute which associates can be expressed as

$$f_A = C_A + 2C_{A_2} + 3C_{A_3} + \ldots + nC_{A_n} \tag{17}$$

where C_A, C_{A_2}, C_{A_3}, . . . , C_{A_n} are the concentrations of monomer and aggregates of 2, 3, . . ., n monomer units, respectively. Introducing the association constants defined from the monomers,

$$K_{An} = \frac{C_{A_n}}{C_A{}^n} \quad , \tag{18}$$

and the distribution constant defined in terms of monomer concentrations in the vapor, C_A^v, and in solution,

$$K_{DA} = \frac{C_A}{C_A{}^v} \quad , \tag{19}$$

equation 17 becomes

$$f_A = K_{DA}C_A{}^v + 2K_{A_2}(K_{DA}\,C_A{}^v)^2 + 3K_{A_3}(K_{DA}C_A{}^v)^3 + \ldots + nK_{An}(K_{DA}C_A{}^v)^n \tag{20}$$

This single equation, a function of the observables f_A and $C_A{}^v$, describes the single component vapor pressure systems.

Linear least squares analysis was used to evaluate the distribution and association constants and their standard errors.[88] The RMSD's were

TABLE 6

RMSD's for Several Fits of the Methanol-2,2,2-Trifluoroethanol Vapor System at Three Temperatures

fits[a]	15° RMSD,(torr)	25° RMSD,(torr)	35° RMSD,(torr)
AB	0.0163	0.0168	0.0206
AB_2	0.0152	0.0190	0.0169
A_2B	0.0131	0.0182	0.0223
AB,AB_2	0.0158[b]	0.0174[c]	0.0166
AB,A_2B	0.0135[b]	0.0163	0.0154

[a]The stoichiometry of the species is indicated--methanol is represented by A and TFE by B; [b]hetero-dimer constant produced by these fits was negative; [c]for this fit, the hetero-trimer constant was negative.

TABLE 7

RMSD's for Several Fits of the Methanol-1,1,1,3,3,3-Hexafluoro-2-Propanol Vapor System at Three Temperatures

fits[a]	15° RMSD,(torr)	25° RMSD,(torr)	35° RMSD,(torr)
AB	0.0183	0.0192	0.0398
AB_2	0.0293	0.0440	0.0706
A_2B	0.0329	0.0414	0.0591
AB,AB_2	0.0159	0.0177	0.0148
AB,A_2B	0.0187[b]	0.0170	0.0374

[a]The stoichiometry of the species is indicated--methanol is represented by A and HFP by B; [b]error in hetero-trimer constant for this fit was greater than the value of the constant.

calculated from the formal concentrations of the alcohols. Most reasonable one through four parameter fits were examined; the RMSD's for several combinations of assumed species are presented in Tables 8-12. The results are given for 2,2,2-trifluoroethanol and 1,1,1,3,3,3-hexafluoro-2-propanol in n-hexadecane and diphenylmethane and methanol in diphenylmethane at three temperatures.

The introduction of a second volatile component in a vapor pressure system greatly increases the complexity of its mathematical representation. Although the actual data analysis included additional associated species, for simplicity in this description, self-association is limited to trimers and hetero-association in the vapor is represented by dimers and in solution by both dimers and trimers. Within these limitations, the total number of moles of components A and B in the system may be expressed as the sums of the moles of each species:

$$NAT = N_A^S + 3N_{A_3}^S + N_{AB}^S + 2N_{A_2B}^S + N_{AB_2}^S + N_A^V + 3N_{A_3}^V + N_{AB}^V \quad (21)$$

$$NBT = N_B^S + 3N_{B_3}^S + N_{AB}^S + N_{A_2B}^S + 2N_{AB_2}^S + N_B^V + 3N_{B_3}^V + N_{AB}^V \quad (22)$$

where the superscripts s and v indicate the solution and vapor phases, respectively, and the subscripts indicate the species: A and B denote the monomers, A_3 and B_3 the self-associated trimers, and AB, A_2B, and AB_2 the hetero-associated dimer and trimers. Those terms representing the vapor can be reduced to functions of the monomer pressures of both components by application of the assumption that all species behave ideally and the introduction of the vapor phase association constants. The solution terms

TABLE 8

RMSD's for Several Fits of 2,2,2-Trifluoroethanol in n-Hexadecane at Three Temperatures

fit	20° RMSD, ($Mx10^4$)	25° RMSD, ($Mx10^4$)	35° RMSD, ($Mx10^4$)
1-0	5.85	9.11	19.62
1-2	1.03	2.68	3.80
1-3	0.75	2.41	1.44
1-4	1.10	2.69	2.20
1-2-3	0.76	2.45[b]	1.41[a]
1-2-4	0.74	2.43	1.25
1-2-5	0.73	2.41	1.22
1-2-6	0.74	2.41	1.27
1-2-7	0.74	2.41	1.36
1-3-4	0.76[a]	2.45[a]	1.35
1-3-5	0.77[a]	2.45[a]	1.32
1-3-8	0.77[a]	2.46	1.28

[a]An association constant produced by these fits was negative; [b]error in an association constant for this fit was greater than the value of the constant.

TABLE 9

RMSD's for Several Fits of 1,1,1,3,3,3-Hexafluoro-2-Propanol in n-Hexadecane at Three Temperatures

fit	20° RMSD, ($Mx10^4$)	25° RMSD, ($Mx10^4$)	35° RMSD, ($Mx10^4$)
1-0	10.94	20.32	34.37
1-2	1.36	2.48	3.65
1-3	1.05	2.09	2.63
1-4	2.25	3.97	6.49
1-2-3	0.73	1.59	1.37
1-2-4	0.70	1.53	1.25
1-2-5	0.69	1.51	1.23
1-2-6	0.70	1.52	1.28
1-2-7	0.71	1.53	1.35
1-3-4	0.82[a]	1.75[a]	1.74[a]
1-3-5	0.86[a]	1.81[a]	1.88[a]
1-3-8	0.94[a]	1.91[a]	2.16[a]

[a]An association constant produced by these fits was negative.

TABLE 10

RMSD's for Several Fits of 2,2,2-Trifluoroethanol in Diphenylmethane at Three Temperatures

fit	25° RMSD, ($Mx10^4$)	30° RMSD, ($Mx10^4$)	35° RMSD, ($Mx10^4$)
1-0	54.00	56.00	85.0
1-2	3.60	4.22	7.37
1-3	5.13	5.55	6.62
1-4	11.38	12.10	16.88
1-2-3	0.49	1.66	0.94
1-2-4	0.23	1.63	0.67
1-2-5	0.44	1.73	1.14
1-2-6	0.72	1.86	1.67
1-3-4	1.89[a]	2.46[a]	2.57[a]
1-3-5	2.32[a]	2.83[a]	3.12[a]
1-2-3-4	0.23[b]	1.65[b]	0.65

[a]An association constant produced by these fits was negative; [b]error in an association constant for these fits was greater than the value of the constant.

TABLE 11

RMSD's for Several Fits of 1,1,1,3,3,3-Hexafluoro-2-Propanol in Diphenylmethane at Three Temperatures

fit	25° RMSD, ($Mx10^4$)	30° RMSD, ($Mx10^4$)	35° RMSD, ($Mx10^4$)
1-0	143.00	341.00	479.00
1-2	11.26	40.66	67.02
1-3	12.32	14.21	13.15
1-4	29.46	51.59	60.54
1-2-3	1.42	6.07	11.28
1-2-4	0.80	1.44	3.74
1-2-5	1.58	2.88	3.36
1-2-6	2.45	6.02	8.30
1-3-4	4.69[a]	9.38[a]	12.83[a]
1-3-5	5.74[a]	10.34[a]	13.16[a]
1-2-3-4	0.78	0.93[a]	2.18[a]

[a]An association constant produced by these fits was negative.

TABLE 12

RMSD's for Several Fits of Methanol in Diphenylmethane at Three Temperatures

fit	25° RMSD, ($Mx10^4$)	30° RMSD, ($Mx10^4$)	35° RMSD, ($Mx10^4$)
1-0	109.00	144.00	212.00
1-2	19.23	25.48	42.73
1-3	4.34	5.96	12.80
1-4	13.05	15.09	15.13
1-2-3	4.41	5.82[a]	9.51[a]
1-2-4	2.70	3.00	4.65
1-2-5	2.35	1.56	1.95
1-2-6	3.09	2.58	3.76
1-3-4	4.22	5.17	6.77
1-3-5	4.11	4.87	5.74
1-3-8	3.83	4.20	3.77
1-2-3-5	2.34	1.60[a]	2.00
1-2-3-8	2.45	1.96	2.07

[a]An association constant produced by these fits was negative.

can be similarly reduced by conversion to species concentrations and introducing the appropriate association and distribution constants. The self-association constants for both phases, the hetero-association constant for the vapor, and the distribution constants for both components are defined as before. The hetero-association constants in solution are defined by

$$K^S_{A_nB_m} = \frac{C^S_{A_nB_m}}{(C^S_A)^n (C^S_B)^m} \tag{23}$$

where C^s_A and C^s_B are the monomer concentrations and $C^s_{A_nB_m}$ is the concentration of the aggregate composed of n monomer units of component A and m of component B. Accomplishing these transformations, equations 21 and 22 become

$$\begin{aligned} NAT = {} & V^s\left(\frac{K_{DA}}{RT}\right) P_A + 3K^s_{A_3} V^s \left(\frac{K_{DA}}{RT}\right)^3 PA^3 \\ & + K^s_{AB} V^s \frac{K_{DA}K_{DB}}{(RT)^2} P_A P_B + 2K^s_{A_2B} V^s \frac{K_{DA}^2 K_{DB}}{(RT)^3} P_A^2 P_B \\ & + K^s_{AB_2} V^s \frac{K_{DA}K_{DB}^2}{(RT)^3} P_A P_B^2 + \frac{V^v}{RT} P_A + 3K^v_{A_3} \frac{V^v}{RT} P_A^3 \\ & + K^v_{AB} \frac{V^v}{RT} P_A P_B \end{aligned} \tag{24}$$

$$NBT = V^s\left(\frac{K_{DB}}{RT}\right) P_B + 3K^s_{B_3} V^s\left(\frac{K_{DB}}{RT}\right)^3 P_B^3$$

$$+ K^s_{AB} V^s \frac{K_{DB}K_{DA}}{(RT)^2} P_BP_A + K^s_{A_2B} V^s \frac{K_{DB}K_{DA}^2}{(RT)^3} P_BP_A^2$$

$$+ 2K^s_{AB_2} V^s \frac{K_{DB}^2K_{DA}}{(RT)^3} P_B^2P_A + \frac{V^v}{RT} P_B + 3K^v_{B_3} \frac{V^v}{RT} P_B^3$$

$$+ K^v_{AB} \frac{V^v}{RT} P_BP_A \qquad (25)$$

As a result of these transformations, the temperature, T, the gas constant, R, and solution and vapor volumes, V^s and V^v, are functionally introduced into these expressions. Equation 24 and 25 plus the total pressure equation, reduced to a functional dependence upon the monomer pressures,

$$P = P_A + K^v_{A_3} P_A^3 + P_B + K^v_{B_3} P_B^3 + K^v_{AB} P_A P_B \qquad (26)$$

describe the two component vapor pressure systems.

The evaluation of the hetero-association constants was accomplished by the non-linear least squares techniques described previously for the PVT data analysis. With the known values of NBT and P and assumed values

of the association constants, equations 25 and 26 were solved simultaneously for the monomer pressures of both components. Using these monomer pressures and the assumed association constants in equation 24, the calculated total moles of component A, NAT(calcd.), was obtained This value was compared with the observed value, NAT, and the RMSD calculated. The hetero-associated species which were assumed to be present included the dimer through all stoichiometrically possible tetramers; most reasonable choices of one through three species fits were tested. A comparison of the relative merit of several fits can be inferred from Tables 13-16 for the methanol-2,2,2-trifluoroethanol and methanol-1,1,1, 3,3,3-hexafluoro-2-propanol systems in n-hexadecane and diphenylmethane.

Thermodynamic Parameters

For systems where a choice of species was possible from an evaluation of the statistical treatment of the data, the changes in enthalpy (ΔH^{o}_{An}) and entropy (ΔS^{o}_{An}) and their errors for the association reactions were calculated from the free energy (ΔG^{o}_{An}) relationship,

$$-RT \ln K_{An} = \Delta G^{o}_{An} = \Delta H^{o}_{An} - T\Delta S^{o}_{An} \qquad (27)$$

by linear least squares analysis. When the linearity of the logarithm of the association constants (K_{An}) with the reciprocal of temperature (1/T) was strictly maintained within the error limits of the constants, the least squares treatment was applied to a set of constants at each temperature which were generated in such a manner that their distribution approximated the error function.[89] These constants resulted from the incrementation of K_{An} by the product of the error in K_{An} and a set of randomly selected normal deviations.[88]

TABLE 13

RMSD's for Several Fits of the Methanol-2,2,2-Trifluoroethanol System in n-Hexadecane at Two Temperatures

fits[a]	25° RMSD, (moles x 10^4)	35° RMSD, (moles x 10^4)
AB	2.40	2.94
A_2B	1.21	1.23
A_3B	2.90	3.24
AB_2	3.69	4.38
AB, A_2B	0.91	0.96
AB, A_3B	0.82	0.70
AB, A_4B	0.90	0.78
AB_2, AB	2.24[b]	2.61[b]
AB_2, A_2B	0.70	0.84
AB_2, A_3B	0.32	0.29
AB_2, A_4B	1.54	0.65
AB, AB_2, A_2B	0.60[c]	0.81[c]
AB, AB_2, A_3B	0.32[c]	0.30[c]
AB, AB_2, A_4B	0.54	0.57

[a]The stoichiometry of the species is indicated--methanol is represented by A and TFE by B; [b]trimer constant produced by these fits was negative; [c]for these fits, the dimer constant was negative.

TABLE 14

RMSD's for Several Fits of the Methanol-1,1,1,3,3,3-Hexafluoro-2-Propanol System in n-Hexadecane at 25°C

fit[a]	RMSD, (moles x 10^4)
AB	2.54
A_2B	2.15
A_3B	5.23
AB_2	4.30
AB, A_2B	0.52
AB, A_3B	0.39
AB, A_4B	0.68
AB_2, AB	1.93[b]
AB_2, A_2B	0.26
AB_2, A_3B	0.82
AB_2, A_4B	1.40
AB, AB_2, A_2B	0.26[c]
AB, AB_2, A_3B	0.38
AB, AB_2, A_4B	0.65[b]

[a]The stoichiometry of the species is indicated--methanol is represented by A and HFP by B; [b]trimer constant produced by these fits was negative; [c]for this fit, the dimer constant was negative.

TABLE 15

RMSD's for Several Fits of the Methanol-2,2,2-Trifluoroethanol System in Diphenylmethane at Two Temperatures

fits[a]	25° RMSD,(moles x 10^4)	35° RMSD,(moles x 10^4)
AB	14.29	19.19
A_2B	4.60	6.01
A_3B	11.22	15.01
AB_2	19.97	27.12
AB,A_2B	4.49	5.83
AB,A_3B	1.87	2.21
AB,A_4B	0.86	1.30
AB_2,A_2B	4.37	5.69
AB_2,A_3B	1.30	1.61
AB_2,A_4B	2.77	3.91
AB,AB_2,A_2B	4.25[b]	3.10[b]
AB,AB_2,A_3B	1.30[b]	1.65[b]
AB,AB_2,A_4B	0.78[b]	0.95[b]

[a]The stoichiometry of the species is indicated--methanol is represented by A and TFE by B; [b]an association constant produced by these fits was negative.

TABLE 16

RMSD's for Several Fits of the Methanol-1,1,1,3,3,3-Hexafluoro-2-Propanol System in Diphenylmethane at 25°C

fits[a]	RMSD,(moles x 10^4)
AB	15.92
A_2B	7.16
A_3B	18.39
AB,A_2B	4.18
AB,A_3B	0.75
AB,A_4B	2.43
AB_2,A_2B	2.80
AB_2,A_3B	4.69
AB_2,A_4B	8.22
AB,AB_2,A_2B	2.50[b]
AB,AB_2,A_3B	0.75[b]
AB,AB_2,A_4B	1.50[b]

[a]The stoichiometry of the species is indicated--methanol is represented by A and HFP by B; [b]an association constant produced by these fits was negative.

The energies (E_D^o) accompanying the vaporization of the alcohols from solution were calculated by a similar treatment of the temperature dependence of the distribution constants.

Isoplectic Enthalpies

One weakness in the methods which have been used to infer thermodynamic constants from spectral or classical data on associating systems is that when several types of aggregates are present, it is usually not possible to calculate accurate parameters for any of the individual complex-formation reactions. It seemed reasonable to attempt to circumvent this problem by employing a rationale similar to that used to obtain adsorption enthalpies for gases distributed between the free vapor and an adsorbed surface layer. Such an approach developed by Freundlich[90] is based upon the variation of pressure with temperature for a constant amount of adsorbed material. Termed isosteric enthalpy, the heat accompanying adsorption is determined from the temperature dependence of the pressures of adsorbing gas in equilibrium with that adsorbed, the total amount adsorbed being the same over the temperature range. By analogy, if a measure were available of the total concentration of associated species in either vapor or solution studies, it should be possible to apply the Clapeyron equation to deduce an enthalpy for the gross process of dissociation of the polymeric species. The term isoplectic* enthalpy is applied to the heats of dissociation calculated by such a procedure.

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*The author is indebted to Professor Michael H. Dunn of the Classics Department, The University of Oklahoma, who suggested the name, isoplectic. The term is derived from the Greek prefix ισο, meaning equal, and the verb πλεκω, meaning to combine or intertwine.

Vapor Phase

If Σ and P_A are defined as the summed total of the formal pressures of all associated species and the pressure of the monomer, respectively, the equilibrium between the idealized pressure of the associated vapor and the monomer pressure can be expressed as:

$$\frac{\Sigma}{n^2} \rightleftarrows P_A \tag{28}$$

where n reflects the number of monomer units per aggregate. The isoplectic enthalpy of association ($-\Delta H_{iso}$) can then be determined from the temperature dependence of the monomer pressure at a constant value of Σ.

The PVT data obtained in this study for the single component systems can be effectively reduced to the form of equation 28 by the following manipulations. The volume ratio, defined as the quotient of the volumes of the larger chamber and the total system, can be expressed as a function of formal pressures,

$$R_V^o = \frac{\pi 2 - \pi S1}{\pi L1 - \pi S1} \quad ; \tag{29}$$

note that the formal pressures, π, are defined as before to account for all species, including the monomer, whereas Σ represents only the associated species. A similar expression can also be written for total pressures:

$$R_V = \frac{P2 - PS1}{PL1 - PS1} \tag{30}$$

where R_V is not a constant. It is convenient to define a new function, σ, which may be expressed in terms of the observables:

$$\sigma = (PL1 - PS1)\ (R_V - R_V^o) \tag{31}$$

At low pressures the equivalence of total pressure and formal pressure is approached, and the difference, after rearranging, between equations 29 and 30 can be written as

$$\sigma = R_V^o\ (\pi L1 - PL1) - (\pi 2 - P2) \tag{32}$$

Because the degree of association is very small, the monomer pressure approximates the total pressure, and the terms in parentheses in equation 32 take the general form

$$\pi - P \simeq (n - 1)\ K_{An}\ P^n \tag{33}$$

where K_{An} is the association constant. Combining these latter two equations and replacing P2 by the product $(PL1 \times R_V^o)$, it can be seen that within the limits of the approximations, σ is a function of the formal pressure of the associated species in the larger chamber, $\Sigma L1$, and a constant which is dependent only upon the apparatus dimensions and aggregate size:

$$\sigma = \Sigma L1\ \{(1 - (R_V^o)^{n-1})(R_V^o)\ (n - 1) / n\} \tag{34}$$

A graphical representation of the variance of σ with PL1 should display a set of similar curves for different temperatures and this variation of PL1 with temperature for a constant value of σ should yield the enthalpy change for the reaction defined in equation 28. The constancy of n with temperature should be reflected by the linearity of the Clapeyron relationships. Any variation of n with different values of σ should result in different values of ΔH_{iso} corresponding to the varied influence of different association reactions upon the over-all heat of association. In the limit as σ approaches zero, $-\Delta H_{iso}$ should correspond to the formation of the smallest associated species present.

σ's were calculated for each PL1 from the defining relationship, and these two variables plotted for each temperature; the form of such a representation is seen in Figure 2 which is typical of the vapor systems. The values of ΔH_{iso} were determined graphically from the Clapeyron equation. A linear dependence of P_A with the reciprocal of temperature as well as a trend toward increasing ΔH_{iso} with increasing σ was observed for each alcohol, although the data supported only the evaluation of the limiting values of ΔH_{iso}. The isoplectic enthalpies reported are the limiting values.

Solution

From analysis of the single component vapor pressure data, isoplectic enthalpies of association can be determined for the solution equilibrium described in terms of the monomer concentration, C_A, and the total formal concentration of associated species, Φ:

$$\frac{\Phi}{n^2} \quad \rightleftarrows \quad C_A \quad , \tag{35}$$

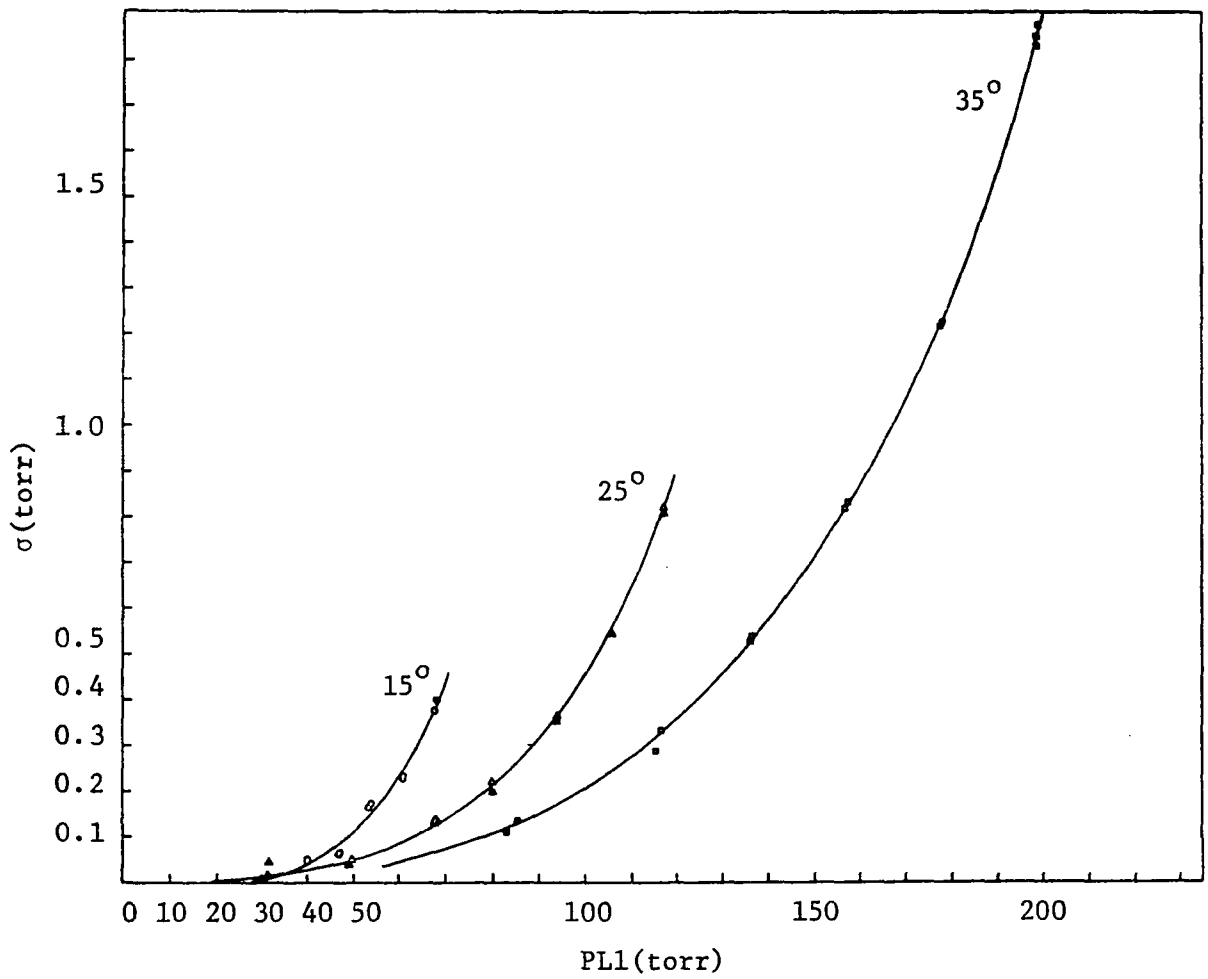


Figure 2: The product of the formal pressure of associated species and a constant (σ) vs. the total pressure (PL1) for methanol vapor at three temperatures.

If only a single associated species is present, n is the number of monomer units of which it is composed, otherwise n represents the number of monomer units in an average polymer. Graphical representation of C_A versus Φ at different temperatures should give sets of similar curves, and van't Hoff plots of C_A for different temperatures at constant Φ should give the enthalpy change, ΔH_{iso}.

The isoplectic treatment of vapor pressure data depends upon the determination of the monomer concentrations in solution; therefore, values of the distribution constants must be known. Because these constants are relatively insensitive to the choice of species in the standard treatment of vapor pressure data, the values thus determined were used with the assumption that this indirect dependence upon species did not prejudice the isoplectic treatment.

With these values of the distribution constants, C_A was calculated from the corresponding vapor concentration, and Φ, the difference between the formal concentration of the alcohol, f_A, and C_A, determined for each point. A typical plot of these data for an alcohol in solution of a relatively inert solvent is presented in Figure 3. From such plots, the values of C_A and the corresponding temperatures were taken for a given Φ and the limiting values of ΔH_{iso}, which reflect the formation of the smallest associated species, were evaluated for each alcohol from van't Hoff plots.

Isoplectic analysis permits the determination of enthalpies of association without requiring knowledge of the individual species which are present. For solutions of alcohols where species from the monomer through very large aggregates are believed to exist, this model-less

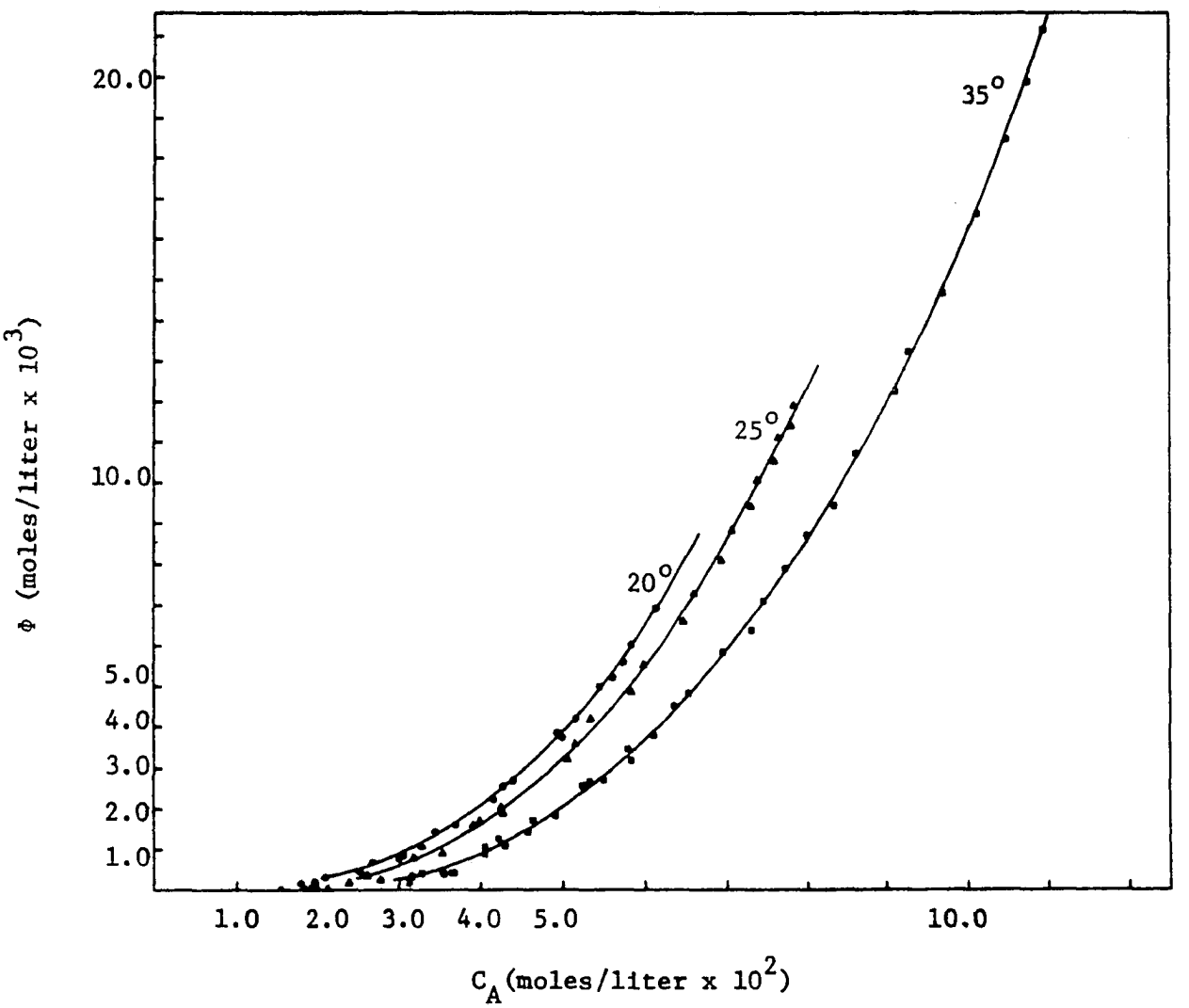


Figure 3. Formal concentration of associated species (Φ) vs. concentration of the monomer (C_A) for 1,1,1,3,3,3-Hexafluoro-2-Propanol in n-hexadecane at three temperatures.

approach offers an interesting check upon the choice of species which other methods have indicated to be present in dominant concentrations. To relate the ΔH_{iso} to the thermodynamic parameters and species concentrations for a specific model, consider the following. If only one associated species is present, the formal concentration of that species of n monomer units is

$$\Phi = n K_{A_n} C_A^n \tag{36}$$

where K_{A_n} is the association constant for the corresponding reaction. Assuming Φ is constant with temperatures, differentiation of equation 36 with respect to temperature yields

$$0 = \frac{d\Phi}{dT} = n C_A^n \frac{dK_{A_n}}{dT} + K_{A_n} n C_A^{n-1} \frac{dC_A}{dT} \tag{37}$$

But

$$\frac{d \ln K_{A_n}}{dT} = \frac{\Delta H_{A_n}}{RT^2} \tag{38}$$

and

$$\frac{d \ln C_A}{dT} = \frac{\Delta H_{iso}}{RT^2} \quad . \tag{39}$$

Therefore, the isoplectic enthalpy is related to the enthalpy change, ΔH_{A_n}, for the reaction

$$A \longrightarrow \frac{1}{n} A_n \tag{40}$$

by the equality

$$\Delta H_{iso} = - \frac{\Delta H_{A_n}}{n} \tag{41}$$

If two associated species, A_n and A_m, are present, the formal concentration of associated species is

$$\Phi = mK_{A_m} C_A^m + nK_{A_n} C_A^n \quad , \tag{42}$$

where all terms are defined as before. Differentiating with respect to temperature, setting equal to zero, and introducing equations 38 and 39, equation 42 becomes

$$0 = \frac{m^2 K_{A_m} C_A^m}{RT^2} \left[\frac{\Delta H_{A_m}}{m} + \Delta H_{iso} \right] + \frac{n^2 K_{A_n} C_A^n}{RT^2} \left[\frac{\Delta H_{A_n}}{n} + \Delta H_{iso} \right]. \tag{43}$$

Introducting the defining expressions for the formal concentrations of species A_n and A_m and equation 43 reduces to

$$\Delta H_{iso} = \frac{\Delta H_{A_m} f_{A_m} + \Delta H_{A_n} f_{A_n}}{m f_{A_m} + n f_{A_n}} \tag{44}$$

Not limited to two species, equation 44 can be extended to equate ΔH_{iso} with similar functions of ΔH and f for any number of specific associated species.

The vapor pressure data reported by Tucker[18] which support the monomer-trimer-octamer and monomer-dimer-trimer-octamer models for methanol in n-hexadecane and diphenylmethane were tested. The results are summarized in Figures 4 and 5 and reflect the dependence of changes

Figure 4. Isoplectic enthalpy change (ΔH_{iso}) as a function of formal concentration of associated species (Φ) for methanol in n-hexadecane. Line is standard ΔH_{iso}; points are calculated on basis of monomer-trimer-octamer model at 25(●), 35(□), and 45°(Δ). - H_{An}/n indicates value of ΔH_{iso} assuming only species of n monomer units were present. Vapor pressure data taken from ref. 18.

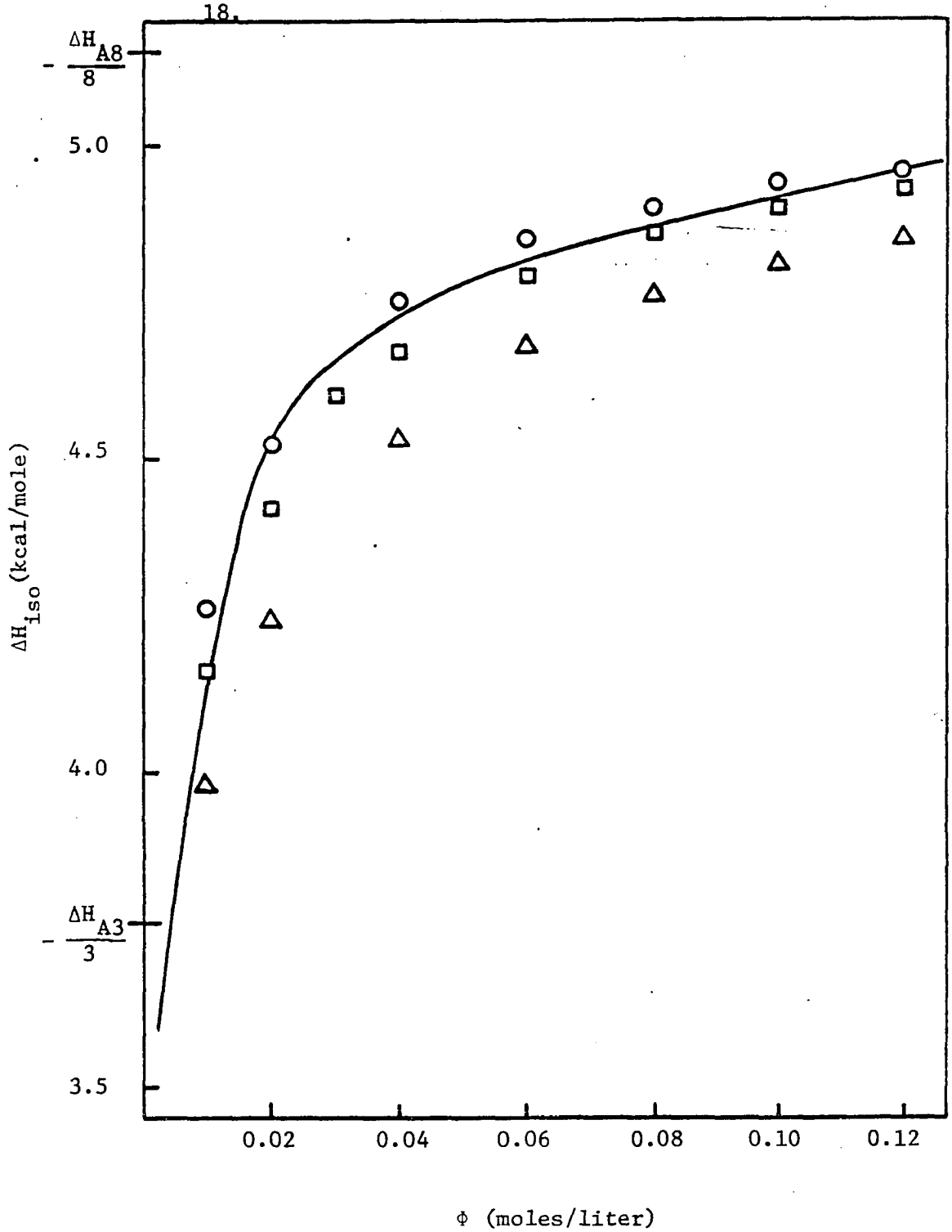
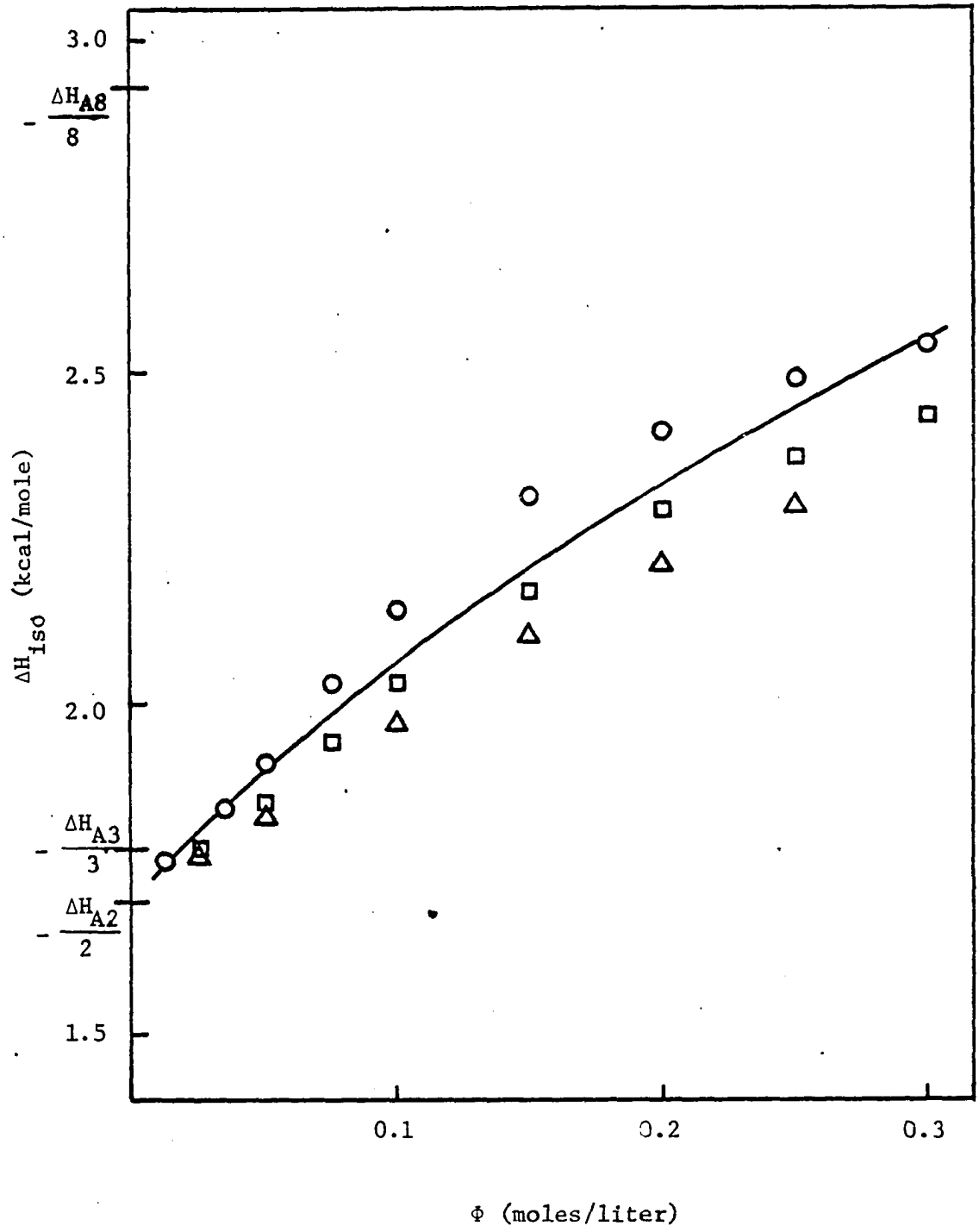


Figure 5. Isoplectic enthalpy change (ΔH_{iso}) as a function of formal concentration of associated species (Φ) for methanol in diphenylmethane. Line is standard ΔH_{iso}; points are calculated on basis of monomer-dimer-trimer-octamer model at 25(o), 35(□), and 45°(Δ). $-\Delta Hn/n$ indicates value of ΔH_{iso} assuming only species of n monomer units were present. Vapor pressure data taken from reference 18.



of enthalpy upon the formal concentration of associated species and therefore, of aggregate size upon concentration. The lines represent isoplectic enthalpies of association calculated directly from the vapor pressure data; the points are the enthalpies calculated from equation 44 and the ΔH's and K's of the appropriate model.

CHAPTER V

CONCLUSIONS AND DISCUSSION

Vapor Association

Over the temperature and pressure range studied, methanol vapor appears to be best described as consisting of monomers, trimers, and octamers. With this and the other systems investigated, the conclusions concerning which are the dominant associated species were based on a comparison of the root mean square deviations (RMSD) and consideration of the association constants which resulted from the systematic application of various association models to the data. In judging the relative capabilities of the several models to describe the data, primary emphasis was placed on the superiority of the minimum RMSD with the restriction that the resulting constants were chemically significant. Of secondary importance was the condition that the results be consistent over the narrow temperature range at which each system was investigated.

The application of these criteria to the methanol results readily eliminated most fits; the RMSD's for several combinations of species which merit discussion are presented in Table 3. The inability of any one parameter fit to describe the data at the higher temperatures is apparent. The introduction of the second associated species representing the monomer-dimer-trimer and -tetramer and

monomer-trimer-tetramer equilibria produced for the three temperatures one or more negative constants each, a mathematically satisfactory but physically meaningless representation of the vapor behavior. The RMSD's clearly reflect the superiority of the 1-3-8 fit at the higher temperatures. At 15°C, this fit is quite adequate, but, because of the low vapor pressure at this temperature, the concentration of both monomer and aggregates are small, and the data treatment is relatively insensitive to various reasonable choices of species. Both the trimer and octamer constants display an excellent temperature dependence. The association constants are presented in Table 17; the thermodynamic parameters and their standard errors for both species and the limiting value of the isoplectic enthalpy are presented in Table 18.

It is difficult to reconcile the 1-3-8 model with generally held view of the association of methanol vapor. In fact, almost any association model which includes specific aggregates other than the dimer, either in solution or the vapor, is apt to be questioned. Therefore, a comment about what is actually demonstrated by statistical treatments of data similar to those employed in this study is appropriate. Even at the low concentrations of the vapor phase, it is reasonable to assume the existence of numerous associated species including large polymeric aggregates. Models which include a limited number of species attempt only to determine which species are primarily responsible for the functional form displayed by the observable parameters and are therefore necessary for an adequate description of the association data. For the methanol system, all that is inferred from the data treatment is that concentrations of the trimer and octamer are present in dominant amounts, amounts which are sufficient to effectively control the pattern of the PVT data.

TABLE 17

Association Constants for Methanol Vapor

T, °C	K_3, torr^{-2}	K_8, torr^{-7}
15	$(1.20\pm0.11) \times 10^{-6}$	$(7.6\pm1.5) \times 10^{-17}$
25	$(5.71\pm0.12) \times 10^{-7}$	$(1.49\pm0.11) \times 10^{-18}$
35	$(2.89\pm0.03) \times 10^{-7}$	$(3.44\pm0.19) \times 10^{-20}$

TABLE 18

Thermodynamic Parameters for the Vapor Phase Association of Methanol

$\Delta H_3^o = -12.53\pm0.12$ kcal/mole $\quad\quad \Delta S_3^o = -44.2\pm0.4$ eu

$\Delta H_8^o = -67.84\pm0.28$ kcal/mole $\quad\quad \Delta S_8^o = -216.9\pm0.9$ eu

$\Delta H_{iso} = 4.6$ kcal/mole

Standard state: 1 atmosphere

Both 2,2,2-trifluoroethanol (TFE) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) probably associate primarily as trimers; however, at the higher temperatures and pressures, it is apparent that associated species other than the trimer tend toward increased importance. Tables 4 and 5 afford a comparison of the more reasonable fits for each alcohol. The reasons for the elimination of most of these fits is clear from the information given in the tables, however for several fits, a further explanation is necessary. For HFP, the apparently superior 1-2-3 and 1-2-4 fits were eliminated because of the extremely poor temperature dependence of the dimer constants. In both, the constants at 25°C were much greater than those at 15°C; in addition, the error in the dimer constant at 15°C was greater than the constant itself for the 1-2-3 fit. Examination of the RMSD's of the remaining single parameter possibilities underscores the advantage of the 1-3 fit. Obscured by the small extent of association, the choice for TFE between the one parameter fits is less clear. At 15 and 25°C the 1-3 fits are equivalent with the best, and at 35°C, the 1-3 fit is still acceptable. However, at the higher temperatures and correspondingly higher pressures, the significant decrease in the RMSD's for both systems with the introduction of a second parameter suggests an increased importance of other than trimeric species. Tables 19 and 20 summarize the parameters for HFP and TFE association.

Dimer and tetramer constants of approximately 1×10^{-4} mm^{-1} and 1.5×10^{-9} mm^{-3}, respectively, generally describe the vapor association of low molecular weight alcohols at room temperature. When the association is described by the formation of the dimer only, the magnitude

TABLE 19

Association Constants for 2,2,2-Trifluoroethanol and 1,1,1,3,3,3-Hexafluoro-2-Propanol Vapor

T, °C	K_3, $torr^{-2}$
2,2,2-Trifluoroethanol	
15	$(1.62\pm0.19) \times 10^{-6}$
25	$(7.46\pm0.27) \times 10^{-7}$
35	$(3.46\pm0.10) \times 10^{-7}$
1,1,1,3,3,3-Hexafluoro-2-propanol	
15	$(6.22\pm0.13) \times 10^{-7}$
25	$(2.86\pm0.06) \times 10^{-7}$
35	$(1.31\pm0.22) \times 10^{-7}$

TABLE 20

Thermodynamic Parameters for the Vapor Phase Association of 2,2,2-Trifluoroethanol and 1,1,1,3,3,3-Hexafluoro-2-Propanol

2,2,2-Trifluoroethanol

$\Delta H_3^\circ = -13.62\pm0.15$ kcal/mole $\quad \Delta S_3^\circ = -47.4\pm0.5$ eu

$\Delta H_{iso} = 3.8$ kcal/mole

1,1,1,3,3,3-Hexafluoro-2-Propanol

$\Delta H_3^\circ = -13.97\pm0.21$ kcal/mole $\quad \Delta S_3^\circ = -50.5\pm0.7$ eu

$\Delta H_{iso} = 3.4$ kcal/mole

Standard state: 1atmosphere

of the reported constants is about 2.5×10^{-4} mm^{-1} or approximately twice that of an exclusively dipole-dipole interaction such as acetone[91] (Appendix II). The constants reported in this study fall in the appropriate ranges. The trimer constants for the fluoroalcohols reflect the expected relative magnitudes; however, compared with methanol they are apparently somewhat large. This is probably a result of ascribing all association of the fluoroalcohols exclusively to the trimer even though the presence of other associated species is indicated. The effect of adding a second species, as was done for methanol, is generally to lower the value of a single constant which describes all association. This would also explain the relative order of the absolute values of the enthalpy of formation of the trimer. The isoplectic enthalpies follow the reverse order: methanol > TFE > HFP, an order which is generally observed for association of similar alcohols and, perhaps erroneously, explained in terms of the decreasing influence of the double bonded dimer. If higher polymers become increasingly important with higher pressures as suggested, the effect upon the enthalpy of formation of the trimer would be to exhibit a falsely large negative value. This result is observed and is believed to reflect the influence of other polymerization reactions rather than the true relative bond strengths of the alcohols.

In contrast to the generally held belief that the dimer is the most important of the associated species in alcohol vapor,[36] this study indicates that the trimer is of greater importance. A reason for the dominance of the trimer is probably the cooperative effect proposed by Frank and Wen[92] for water and extended to alcohol systems by Franks

and Ives.[93] Additional evidence for the importance of the trimer in methanol vapor is provided by the vapor density studies of Cheam.[52] Using extremely sensitive buoyancy balances, this investigation confirmed the superiority for methanol vapor of the 1-3-n model where n is 8 or 9, but more importantly, it determined an upper limit for the value of the dimer constant--the maximum value of this constant at 25°C is only 0.5×10^{-4} $torr^{-1}$. From this value of the dimer constant and the corresponding trimer constant, it is readily apparent that a significantly greater amount of methanol vapor exists as the trimer than as the dimer throughout most of the accessible pressure range.

For the alcohols the degree of association is quite small. At pressures corresponding to 0.9 activity or about 90% of the saturation vapor pressures, methanol is about 1.9, 2.5, and 3.5% associated at 15, 25, and 35°C, respectively. At similar activities at 25°C, TFE is about 1.0% and HFP 1.7% associated. Conforming with the concept that increasing temperatures favor the smaller associated species, the percent methanol in the octamer form decreases accordingly. For the same activities the total association of each alcohol increases with temperature, the result of mass action being more important in promoting bond formation than temperature in bond breaking. The same effect was observed with adsorption. Although the determination of the total amount of vapor adsorbed was not made in this study, the pressure-time data indicated a far greater adsorption at higher temperatures for equal activities. A relative increase in adsorption with the increasing proton donor capability of the alcohols was also indicated. Under conditions of temperature and pressure which favored both association and adsorption, rates of

several microns per minute were generally encountered in the experimental procedure. However, the segment of the adsorption isotherm under study determines the rate of adsorption calculated: it should be emphasized that measurements were not made during the period in which the greatest adsorption probably occurred but rather at a somewhat later time--several minutes after the initial introduction of the samples into the apparatus. Two points are clear concerning adsorption. It does play a determinable role in a Burnett-type experiment--the varied effects of the sorption processes in the different experimental steps have been demonstrated. More importantly, the magnitude of the partial pressures of the associated species are comparable in size to the necessary corrections for adsorption. This study clearly illustrates the need to account quantitatively for sorption in treating PVT data for alcohols.

The RMSD's for the fits applied to the methanol-TFE and methanol-HFP systems are shown in Tables 6 and 7. The existence of a single hetero-association species, the 1:1 complex, adequately describes the methanol-TFE data. For the methanol-HFP system, the inclusion of a second species, a trimer consisting of one methanol and two HFP monomer units, reduced the RMSD enough to suggest the presence of significant amounts of both the 1:1 and the 1:2 complexes. It is interesting to note that the constant which reflects only the addition of the second HFP molecule to the existing methanol-HFP dimer approximately equals that for the formation of the hetero-dimer itself, and is greater than that expected for a self-associated HFP dimer. If the dimer were formed by the interaction of the HFP hydrogen with the methanol oxygen

and the trimer by the addition of the second HFP molecule to the free oxygen of that dimer, then one might conclude that the effect of the formation of the hetero-dimer bond was to transform the HFP oxygen from its original condition of electron deficiency into a proton acceptor as effective as that of free methanol. The association constants and thermodynamic parameters for the methanol-TFE and methanol-HFP systems are presented in Tables 21 and 22.

The values of these association constants are in good agreement with those for similar systems. For the methanol-TFE system, the hetero-dimer constants determined in this study are slightly larger than the 8.20 and 5.00 x 10^{-4} mm^{-1} values calculated by Johnson[39b] at 25 and 35°C, respectively. The proposition that methanol is a slightly more effective base than water is supported by a comparison of the hetero-dimer constants for methanol and water with the fluoroalcohols; the values for water with TFE and HFP at 25°C are 3.7 and 5.96 x 10^{-4} $torr^{-1}$, respectively (Appendix II). The interaction between the fluoroalcohols is described by a hetero-dimer constant of 7.34 x 10^{-4} $torr^{-1}$ at 35°C (Appendix II).

The relative values of the vapor association constants reflect the preference of the alcohols to form mixed component complexes rather than self-associated species. For methanol with TFE, the degree of association is greater than that of either single component, and with the better proton donor, HFP, the tendency toward intercomponent complex formation is even more pronounced. It is because of this greater tendency for hetero-complexation that the influence of the trimer in this latter system was observed. Such mixed-component species have generally not been previously considered in vapor phase studies--even in the single component systems where a much higher total pressure range is

TABLE 21

Association Constants[a] for the Methanol-2,2,2-Trifluoroethanol and Methanol-1,1,1,3,3,3-Hexafluoro-2-Propanol Vapor Systems

T, °C	K_{AB}, torr^{-1}	K_{AB_2}, torr^{-2}
Methanol-2,2,2-Trifluoroethanol		
15	$(1.85\pm0.27) \times 10^{-3}$	
25	$(1.09\pm0.08) \times 10^{-3}$	
35	$(8.03\pm0.37) \times 10^{-4}$	
Methanol-1,1,1,3,3,3-Hexafluoro-2-Propanol		
15	$(8.1\pm1.4) \times 10^{-3}$	$(4.6\pm1.7) \times 10^{-5}$
25	$(4.13\pm0.62) \times 10^{-3}$	$(1.57\pm0.48) \times 10^{-5}$
35	$(2.45\pm0.12) \times 10^{-3}$	$(8.26\pm0.67) \times 10^{-6}$

[a]Stoichiometry is indicated--A represents methanol and B the fluoroalcohol.

TABLE 22

Thermodynamic Parameters[a] for the Vapor Phase Association of the Methanol-2,2,2-Trifluoroethanol and Methanol-1,1,1,3,3,3-Hexafluoro-2-Propanol Systems

Methanol-2,2,2-Trifluoroethanol

$\Delta H^{o}_{AB} = -7.30\pm0.21$ kcal/mole $\quad \Delta S^{o}_{AB} = -24.7\pm0.7$ eu

Methanol-1,1,1,3,3,3-Hexafluoro-2-Propanol

$\Delta H^{o}_{AB} = -10.45\pm0.28$ kcal/mole $\quad \Delta S^{o}_{AB} = -32.7\pm0.9$ eu

$\Delta H^{o}_{AB_2} = -14.15\pm0.69$ kcal/mole $\quad \Delta S^{o}_{AB_2} = -43\pm2$ eu

[a]Stoichiometry is indicated--A represents methanol and B the fluoroalcohol.

Standard state: 1 atmosphere

experimentally accessible, few studies have reported evidence of the existence of the trimer. Because of the relatively low total pressures at which the hetero-association was studied, the partial pressures of the hetero-dimers represent the major contribution of association to the total pressures in both the methanol-TFE and methanol-HFP systems. Yet the 1:2 complex must be considered important in the methanol-HFP system. While the partial pressure of this trimer is less than that of the hetero-dimer, it far exceeds the partial pressures of the self-associated trimers of either component.

Association in Solution

The same criteria which were used to evaluate the statistical fits of the PVT data were likewise applied to the results of the vapor pressure data. A comparison of the adequacy of several choices of assumed species in describing the interactions of the alcohols in solution can be made from the information presented in Tables 8-12.

In n-hexadecane, the most important associated species of HFP and TFE are probably the trimers. For HFP the fit which includes only monomers and trimers is superior to any other fit of one associated species. In terms of RMSD, the 1-2-n series of fits appear better, but for each such fit the temperature dependence of the dimer constant was unacceptable. As in the vapor phase, the study of the TFE system was plagued by the problems of low concentrations and small degree of association which made the resolution of the question of dominant species somewhat problematical. The best single associated species fit is that for the trimer. Several fits in the 1-2-n series have slightly

lower RMSD's, but again, these constants did not generally display a good temperature dependence. For both systems, all other fits were eliminated by the straightforward application of the evaluation criteria. The association and distribution constants for the alcohols are given in Table 23 and the thermodynamic parameters in Table 24.

A comparison of the RMSD's indicates that in diphenylmethane, both TFE and HFP exist primarily as monomers, dimers, and tetramers, while methanol can best be described by a monomer-dimer-pentamer equilibrium. The association and distribution constants for these systems are presented in Table 25. Although the logarithm of these constants do display linearity with the reciprocal of temperature, the range of temperatures is not sufficiently broad for this to be interpreted as much support for the conclusions regarding the choices of specific species. Some support does come, however, from a multi-parameter linear least squares[94] fit of the data. Rather than being limited to four associated species, this fitting technique permitted the simultaneous evaluation of the coefficients which corresponded to the association constants for all reasonable species. The results are interesting only in that the coefficients not directly related to the dimer and tetramer constants for HFP and TFE and the dimer and pentamer constants for methanol were generally determined to be either relatively small or negative. Because of the narrow temperature range, the thermodynamic parameters given in Table 26 should be accepted as only approximate values, even though the reported errors in the parameters, which reflect the high degree of precision of the data, are quite small. Further, it is recognized that the magnitudes of the tetramer constants for HFP are so small that they probably do not accurately reflect true species concentrations.

TABLE 23

Association and Distribution Constants for 2,2,2-Trifluoroethanol and 1,1,1,3,3,3-Hexafluoro-2-Propanol in n-Hexadecane

T, °C	K_D	K_3, M^{-2}
2,2,2-Trifluoroethanol		
20	11.96±0.03	60.8±1.1
25	10.83±0.06	44.0±1.4
35	9.02±0.02	25.67±0.16
1,1,1,3,3,3-Hexafluoro-2-Propanol		
20	12.96±0.02	10.11±0.14
25	11.58±0.02	8.18±0.09
35	9.49±0.01	5.39±0.04

TABLE 24

Thermodynamic Parameters for the Association and Distribution of 2,2,2-Trifluoroethanol and 1,1,1,3,3,3-Hexafluoro-2-Propanol in n-Hexadecane

2,2,2-Trifluoroethanol

ΔE_D^o = -3.38±0.01 kcal/mole $\quad \Delta S_D^o$ = -8.58±0.01 eu

ΔH_3^o = -10.24±0.06 kcal/mole $\quad \Delta S_3^o$ =-26.8±0.2 eu

ΔH_{iso} = 3.0 kcal/mole

1,1,1,3,3,3-Hexafluoro-2-Propanol

ΔE_D^o = -3.72±0.01 kcal/mole $\quad \Delta S_D^o$ = -9.60±0.02 eu

ΔH_3^o = -7.54±0.03 kcal/mole $\quad \Delta S_3^o$ = -21.1±0.1 eu

ΔH_{iso} = 2.2 kcal/mole

Standard state: 1 mole/liter

TABLE 25

Association and Distribution Constants for Methanol, 2,2,2-Trifluoroethanol, and 1,1,1,3,3,3-Hexafluoro-2-Propanol in Diphenylmethane

T, °C	K_D	K_2, M^{-1}	K_4, M^{-3}	K_5, M^{-4}
Methanol				
25	48.88±0.15	0.999±0.012		46.34±0.28
30	41.57±0.08	0.972±0.006		34.22±0.05
35	36.85±0.09	0.831±0.006		22.42±0.07
2,2,2-Trifluoroethanol				
25	106.97±0.05	0.572±0.003	1.60±0.03	
30	89.72±0.18	0.481±0.013	1.35±0.11	
35	75.42±0.06	0.456±0.004	1.13±0.03	
1,1,1,3,3,3-Hexafluoro-2-Propanol				
25	113.62±0.08	0.406±0.003	0.45±0.01	
30	93.56±0.10	0.385±0.002	0.43±0.01	
35	77.39±0.19	0.352±0.003	0.41±0.01	

TABLE 26

Thermodynamic Parameters for the Association and Distribution of Methanol, 2,2,2-Trifluoroethanol, and 1,1,1,3,3,3-Hexafluoro-2-Propanol in Diphenylmethane

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Methanol

ΔE_D^o = -5.16±0.03 kcal/mole ΔS_D^o = -11.60±0.11 eu

ΔH_2^o = -3.34±0.12 kcal/mole ΔS_2^o = -11.2±0.4 eu

ΔH_5^o = -13.24±0.11 kcal/mole ΔS_5^o = -36.7±0.4 eu

ΔH_{iso} = 2.0 kcal/mole

2,2,2-Trifluoroethanol

ΔE_D^o = -6.38±0.01 kcal/mole ΔS_D^o = -14.11±0.02 eu

ΔH_2^o = -2.65±0.07 kcal/mole ΔS_2^o = -10.2±0.2 eu

ΔH_4^o = -6.43±0.1 kcal/mole ΔS_4^o = -20.6±0.6 eu

ΔH_{iso} = 1.45 kcal/mole

1,1,1,3,3,3-Hexafluoro-2-Propanol

ΔE_D^o = -7.01±0.01 kcal/mole ΔS_D^o = -16.12±0.02 eu

ΔH_2^o = -2.58±0.04 kcal/mole ΔS_2^o = -10.5±0.1 eu

ΔH_{iso} = 0.95 kcal/mole

Standard state: 1 mole/liter

In this study, where the trimer has been consistently found to be more important than the dimer in describing both PVT and vapor pressure data for various systems, the elevation of the dimeric species to prominence in diphenylmethane deserves comment. If an increased stabilization of the polar alcohol dimer is induced by interactions with this proton-accepting solvent, then the importance of this dimer in diphenylmethane can be reconciled with the dominance of the trimers in the relatively inert media--the vapor and n-hexadecane. Such a specific solvent interaction has been proposed by Bellamy, Morgan, and Pace[95] to explain solvent effects upon hydrogen bonded systems of alcohols and phenols; the same concept has been applied by Tucker[18] to several methanol systems. Bellamy and colleagues[95] concluded that the differences in the spectral shifts for various systems in different solvents was, in part, due to specific associations of the solvent with the existing solute dimer. It is suggested, therefore, that in diphenylmethane, the dimers of the alcohols are stabilized by a specific interaction with the solvent to form a pseudo-trimer--the importance of such an interaction is greatly diminished in solvents which are less capable of interacting with the solute, that is, less capable of acting as a proton donor or acceptor. Of course, vapor pressure data do not give direct evidence of such an interaction, however, the results for methanol and the fluoro-alcohols in this aromatic solvent are consistent with this interpretation, and the importance of the dimer and trimer in the different media can be thus correlated.

Agreement with the results of other studies is mixed. Kivinen and Murto[70] investigated the association of TFE and HFP in carbon

tetrachloride by spectral techniques. The results of their study as well as this appear to be consistent within themselves--that is, in each solvent the relative magnitudes of the association constants for the alcohols display the same order as expected from the vapor results: methanol > TFE > HFP. However, the correlation between the two studies based on the relative reactivities of the media is not as illuminating. Different associated species were reported in the two studies; however, the dimer constants for the fluoroalcohols in carbon tetrachloride and diphenylmethane can be compared. One would expect the magnitude of the association constants in carbon tetrachloride to be greater than those in diphenylmethane since carbon tetrachloride is more nearly like the non-polar n-hexadecane than the aromatic diphenylmethane. For TFE at 25°C in carbon tetrachloride the dimer constant of 0.69 M^{-1} calculated by Kivinen and Murto[70] is larger than that reported here for TFE in diphenylmethane, but not as large as might be expected in view of the reactivities of the solvents. Furthermore, the values of the dimer constants for HFP in both solvents display the reverse order of that expected: the value of the constant in diphenylmethane is greater than that in carbon tetrachloride. Tucker[18] studied the association of methanol in hexadecane, diphenylmethane, and benzyl ether and used the 1-3-8 and 1-2-3-8 association models to correlate his vapor pressure data for the three systems. Again, different species are reported for the common system but a comparison of the constants of methanol in diphenylmethane can be made. The distribution constants evaluated by Tucker[18] agree to within a few percent with those reported here; however, the dimer constants calculated in the two studies differ

by considerably more. This is, in part, due to the different association models used in fitting the data. If the data from both studies are fit according to the same model, the values of the distribution and dimer constants agree quite well. In fact, the conclusions reached in the two studies that different specific higher polymers predominate in this system are not necessarily contradictory. For a system in which multiple equilibria between the monomer and a series of polymers most probably exist, total concentration necessarily exercised an effect upon the relative concentrations of the higher polymers. The maximum concentrations of methanol in the two studies differed by several fold, enough to alter the relative importance of the different higher polymers. However, this difference is relatively unimportant. What is significant is the agreement of these two studies upon the major importance of the trimer in alcohol association: over moderate concentration ranges of methanol, TFE, and HFP, the trimer appears to dominate the association in a variety of media.

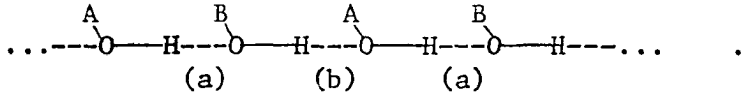
The two studies by Tucker[18] and Kivinen and Murto[70] also permit a comparison of the heats which accompany the several reactions. The energy of solution of -3.40 kcal/mole[18] and enthalpy of formation of the dimer of -5.26 kcal/mole[18] agree to better than a tenth of a kilocalorie within error limits with those reported here for methanol in diphenylmethane. In n-hexadecane, the values of solvation energy, -2.90 kcal./mole,[18] and enthalpy for the trimer, -11.27 kcal./mole,[18] correspond well in relative magnitude with those of the fluoroalcohols. However, the values of -5.3 and -5.5 kcal./mole[70] for the formation of the dimers of TFE and HFP, respectively, in carbon tetrachloride show an order which is the reverse of that consistently observed in this study.

The complexity of the mixed alcohol systems greatly impaired the evaluation of the importance of specific hetero-association species. However, based on the values of the RMSD's and requiring chemically acceptable constants, the results of the data treatments presented in Tables 13-16 clearly indicate that these systems generally follow the patterns set by self-association in the two solvents. In n-hexadecane over the concentration range studied, methanol with HFP and TFE apparently interact to form primarily the trimer of one methanol and two fluoroalcohol molecules and another polymer. For TFE, the other polymer is probably the tetramer while for HFP it is the trimer, these polymers having 3:1 and 2:1 methanol-fluoroalcohol stoichiometry, respectively. What is significant is that the presence of the hetero-dimer need not be assumed to describe the data. Indeed, when the dimer was incorporated into fits of the two other associated species, the resulting RMSD's did not represent a significant improvement over the original two parameter fits.

The dominance of the hetero-trimer corresponds well with the self-association results in n-hexadecane, yet the absence of a need to assume the presence of the hetero-dimer to adequately describe the data is surprising. Hence, a different approach to the analysis of the data--one which would give some indication of the importance of the effect of an adjacent bond upon a central bond--was attempted. Johnson, Christian, and Affsprung[96] have explained the dominance of the trimeric species in the self-association and hydration of phenol in several organic solvents by employing a method of analysis in which the association constants were reduced to the specific contributions of each bond. Applying this

concept, each bond was represented by a stability factor which is related to the formation of that specific isolated bond: in aggregates larger than the dimer, additional terms were introduced which measure the effect of an adjacent bond upon a specific bond. Several different mathematical representations of this general form were tried and each gave the same quantitative result. One formulation in which the effect of an adjacent bond upon a central bond is represented by the product of the stability factors of both bonds is described here.

The influence of each bond upon the association constants was assessed in the following manner. Stability factors (f_a and f_b) were assigned to the two possible types of bonds (a and b) between two different alcohol molecules (A-OH and B-OH) in a hetero-polymer:



The contribution of each bond to the hetero-association constant was of the form $f_b(1.0 + \alpha f_a)^2$ shown here for the bond b, where α is an enhancement parameter measuring the effect of the adjacent bonds upon the central bond. If a is the terminal bond in the polymer, then the contribution of this bond was $f_a(1.0 + \alpha f_b)$. For a dimer, the contribution was just the bond stability factor, f_a or f_b. The association constant for a polymer of specific stoichiometry and arrangement of monomer units was taken as the product of the individual bond contributions. The association constants for polymers of a specific stoichiometry equalled these products summed over all possible ways of forming that polymer of given stoichiometry. Factors for bonds between like molecules

were evaluated from the self-association trimer constants following a similar rationale. The equations resulting from the substitution of the expressions for the polymer association constants into the equations for the total moles of both components were solved by non-linear least squares analysis for the two bond factors, f_a and f_b, and the enhancement parameter, α.

The results did indicate that the enhancement effect is very large. This effect is reflected in the terms of the association constants which contain α and is broadly defined as the contribution made by the adjacent bonds to that portion of the association constant attributed to a specific bond. In both the methanol-TFE and methanol-HFP systems, the enhancement contribution composed the significant part of the total contribution of an affected bond to the association constant--that is, the product of the αf term and the factor for the central bond approximated the factor which by itself describes an isolated bond as in the dimer. This supports the initial data analysis in the conclusion that the dimer is relatively unimportant, that the amounts of the alcohol in the hetero-dimer form are relatively small when compared with the higher polymers.

The results for the hetero-association in diphenylmethane also parallel the self-association. For both the methanol-TFE and methanol-HFP systems, it was necessary to assume the existence of the dimer in describing the data. In addition, the inclusion of a single higher polymer, probably the 4:1 methanol complex with TFE and the 3:1 complex with HFP was also necessary. No three parameter fits tried bettered these two parameter fits. As with the self-association, the existence

of the dimer is explained by the increase in stability caused by specific interactions with the solvent to form an alcohol-solvent trimer.

The association constants for the two component systems are given in Tables 27 and 28.

Association constants for other systems afford a background against which these results can be judged. Mukherjee and Grunwald[4] reported a constant of 6.4 ± 1.6 M^{-1} for the ethanol-TFE dimer in carbon tetrachloride at 25°C. The hetero-association of several compounds with TFE and HFP in carbon tetrachloride and at 25°C were studied by Kivinen, Murto, and colleagues.[10,75,76] Although interactions with other alcohols were not studied, mean values of the dimer constants with several oxygen-containing acceptors were reported:[75] with diisopropyl ether, TFE and HFP gave constants of 6.40 and 36.4 M^{-1}, respectively, and with tetrahydrofuran, the alcohols gave constants of 10.04 and 77.7 M^{-1}, respectively. Association constants for HFP were inferred from the data reported by Purcell and colleagues.[71] The data for most systems were generally not very consistent, but a mean value of about 21.5 M^{-1} was calculated for diethyl ether in carbon tetrachloride. Higher polymers of the fluoroalcohols with other compounds have generally been neglected or unobserved,[74] but Kivinen and Murto[76] have reported constants for the 2:1 alcohol-base complex with several bifunctional proton acceptors. From the relative magnitudes of the association constants for the 1:1 and 2:1 complexes, they suggested that the higher complex does not have the two alcohol molecules bonded to different acceptor sites. Rather, they reported that the more probable structure is that in which the first alcohol is bonded to

TABLE 27

Association Constants[a] for the Methanol-2,2,2-Trifluoroethanol and Methanol-1,1,1,3,3,3-Hexafluoro-2-Propanol Systems in n-Hexadecane

T, °C	K_{AB_2}, M^{-2}	K_{A_2B}, M^{-2}	K_{A_3B}, M^{-3}
Methanol-2,2,2-Trifluoroethanol			
25	$(1.31\pm0.04)\times10^{3}$		$(3.02\pm0.05)\times10^{4}$
35	$(8.10\pm0.20)\times10^{2}$		$(1.12\pm0.02)\times10^{4}$
Methanol-1,1,1,3,3,3-Hexafluoro-2-Propanol			
25	$(6.57\pm0.22)\times10^{3}$	$(5.63\pm0.05)\times10^{3}$	

[a]Stoichiometry is indicated--A represents methanol and B the fluoroalcohol.

TABLE 28

Association Constants[a] for the Methanol-2,2,2-Trifluoroethanol and Methanol-1,1,1,3,3,3-Hexafluoro-2-Propanol Systems in Diphenylmethane

T, °C	K_{AB}, M^{-1}	K_{A_3B}, M^{-3}	K_{A_4B}, M^{-4}
Methanol-2,2,2-Trifluoroethanol			
25	6.1±0.06		706±6
35	4.88±0.07		342±4
Methanol-1,1,1,3,3,3-Hexafluoro-2-Propanol			
25	21.7±0.2	1134±9	

[a]Stoichiometry is indicated--A represents methanol and B the fluoroalcohol.

the acceptor and the second alcohol bonded to the first in a linear fashion.

General

Throughout this study, various trends with respect to the different media are apparent in the associations, distributions and heats of reactions. Within each medium, the relative extent of self-association decreases in the order methanol > TFE > HFP. For a given alcohol, association similarly decreases in the different media: vapor > n-hexadecane > diphenylmethane. The first effect reflects the corresponding decrease in the proton acceptor ability of the alcoholic oxygen of each compound and the dominant role it plays in self-association, while the second effect mirrors the decreasing inertness of the media. The reactivity of the solvents is also evidenced by the distribution constants for the alcohols: a comparison of the magnitude of these constants for each alcohol illustrates their preference for the more reactive solvents. The greater preference, relative to the vapor, of the more polar alcohols for a given solvent follows the order of their dipole moments:[10,97] HFP > TFE > methanol.

It is the ability to reach higher concentrations in the more reactive media which makes it possible to investigate systems in which there is a relatively small degree of association. Because of the reactivity of the solvent, a set of competitive reactions exist between self-association and solute interaction. This competition is translated into the energies of solution as well as the enthalpies of association. The energy required to free an alcohol from a given solvent to the vapor increases with the polarity of the alcohol. Similarly, for a given

alcohol, the energy necessary for the same process increases with the reactivity of the solvents. If the heat required to disrupt the solvent interactions of two monomer units is lost from that gained in the formation of the dimer and the resulting solvent interactions with that dimer, then the enthalpies of association should generally be expected to decrease progressively from the vapor to increasingly more reactive media. The isoplectic enthalpies display this order. Solvent interactions are expected to be greater for the more polar solutes; this is reflected in the decreasing order of the isoplectic enthalpies of the alcohols in a given medium: methanol > TFE > HFP.

Throughout this study trimeric species have been found to dominate the association of a variety of systems. This raises the question of why the association of alcohols tends to show a greater propensity for continued association after the formation of the initial dimer bond. The answer to this question is probably not forthcoming from classical PVT and vapor pressure studies, but the results of this study do offer supportive evidence for some interesting conjecture. The answer most probably lies in the "cooperative effect" proposed by Frank and Wen[92] and extended by Franks and Ives.[93] Simply stated, it is that the formation of a single hydrogen bond sufficiently alters the initial charge densities to make the resulting double molecule both a better proton donor and acceptor than the parent monomers. Perhaps the most direct evidence on this subject has come from spectral investigations. The relationships between the stability of a bond and the frequency shifts from the monomer peak--shifts which are much greater for the peaks assigned to the polymer than those to the dimer--have been considered for some time,[98] but of greater interest here is the evidence

that after association the terminal hydrogen and oxygen atoms show an increased acid and base strength relative to the isolated monomers.[95,99] This is interpreted to support the evidence that polymers are formed in preference to the dimer and that polymeric bonds, whether in cyclic or linear aggregates, are stronger than dimer bonds. That increased acidity of the proton donor is reflected in an increased bond strength and extent of association is illustrated in the vapor results for the methanol-TFE and methanol-HFP systems. Furthermore, that bond formation increases the proton-accepting capability of terminal oxygen is indicated by magnitudes of the constants for the methanol-HFP vapor complexation. The isoplectic treatment of methanol data (Figures 4 and 5) clearly shows the diminishing influence of the dimer in the enthalpy of association over the concentration range; this is most evident in n-hexadecane where solvent stabilization of the dimer is negligible. Indeed, the increasing importance of higher polymers with concentration follows closely the particular species models by which the data are best described. In two component vapor pressure systems, the great enhancement effect which this study has shown emphasizes the importance of the higher polymers. When that portion of an association constant which results from the effect of adjacent bonds is of the same magnitude as that for an isolated bond, the importance of any species which does not benefit from this enhancement is necessarily diminished.

A point which has been implied throughout deserves explication at this time. Rather simple models of association--simple in a chemical sense but often complicated and difficult in their application--have

been used to describe the PVT and vapor pressure data in this study; in fact, these models have described the systems to a high degree of precision, generally to within the precision of the experimental measurements. Furthermore, it is suggested that this approach has been highly successful and accurate in the determination and evaluation of the dominant associated forms which exercise a controlling influence upon the systems. However, this does not imply an acceptance of the idea that these systems are simple; rather it is recognized that the systems studied are extremely complex. Consequently, simplistic models were employed because they were the most profitable way to infer useful information about the properties of these systems, but this is not to suggest that such models reflect the true complexity of the real systems.

Summary

The intermolecular interactions of methanol, 2,2,2-trifluoroethanol (TFE), and 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) in the vapor, n-hexadecane, and diphenylmethane were investigated by classical methods. The data were interpreted in terms of models of specific associated species; those species which predominate were determined and their association constants evaluated. The thermodynamic parameters for the alcohol distributions between phases and for most important association reactions are reported.

The importance of the trimer in alcohol association was demonstrated. In the vapor and in n-hexadecane, the trimer was determined to be the dominant self-associated species. In diphenylmethane, an assumed equilibrium between the monomer, dimer, and a higher polymer best correlated the data; the apparent importance of the dimer was

interpreted in terms of solvent stabilization of this species. Although the intercomponent dimers are primarily responsible for the hetero-association in both the methanol-TFE and methanol-HFP vapor systems, the influence of the trimer, the 2:1 HFP-methanol complex, is significant. In solution, the hetero-association in the methanol-TFE and methanol-HFP systems parallels the self-association: large aggregates are definitely present, but the single associated species in each solvent which must be assumed to exist in order to adequately describe the data is the hetero-dimer in diphenylmethane and the hetero-trimer, the 2:1 fluoroalcohol-methanol complex, in n-hexadecane. That the assumption of the existence of the dimer was not necessary to describe the n-hexadecane data is significant. Further analysis of the data for these systems suggested that the effect of adjacent bonds upon a central bond is to greatly enhance its hydrogen-bonding capabiltiy relative to an isolated bond. This enhancement effect is reflected in the dominance of the trimer with respect to the dimer in alcohol association.

Several experimental and data treatment methods were modified or developed for application in this investigation. Classical vapor pressure techniques were satisfactorily applied to systems of two volatile components which formed a variety of intercomponent aggregates as well as self-associated species in both phases. The Burnett procedure was modified to facilitate the taking of data and to afford a more direct method of analyzing the data for the association parameters. It was established that adsorption effects can cause non-negligible errors in accurate PVT studies of alcohol vapor. And a technique for the determination of the heat of association from classical

and spectral data for systems in which association may produce many different species was developed; such heats are termed isoplectic enthalpies.

APPENDIX I

PRIMARY DATA FOR THE PVT AND VAPOR PRESSURE SYSTEMS

The data described in Chapter III and analyzed in Chapter IV are presented in this section. All symbols are described in the text. Calculated values presented here, P2(calcd.), f_A(calcd.), and NAT(calcd.), are based on the models discussed in Chapter V which best described the data for that particular system. For the single component systems, A in the symbols C_A^V and f_A refers to the solute alcohol, either methanol, 2,2,2-trifluoroethanol, or 1,1,1,3,3,3-hexafluoro-2-propanol; for the two component systems, A refers to methanol and B to the fluoroalcohols in the symbols NAT and NBT and for the evaluation of R_π. Pressures are in units of torr and concentrations are in units of moles per liter. The volume ratio of the apparatus used in the PVT studies was 0.659549±0.000033; the only exception is several data points for the 1,1,1,3,3,3-hexafluoro-2-propanol system at 25°C for which the volume ratio was 0.716982±0.000020--the calculated final pressures for these points in Table 36 are designated by asterisks (*). In the studies of the hetero-association in solution, the total volume of the vapor pressure apparatus was 792.31 cc and the volumes of the solvent are tabulated under the heading V.

TABLE 29

PVT Data for the Methanol System at 15°

PL1	PS1	P2	P2(calcd.)
28.902	4.840	20.713	20.727
28.989	5.085	20.855	20.868
39.809	4.749	27.923	27.923
39.974	5.223	28.189	28.192
46.756	5.638	32.822	32.841
46.965	5.481	32.908	32.926
53.448	5.384	37.249	37.222
53.821	4.442	37.183	37.154
61.183	4.318	42.056	42.065
61.237	4.864	42.273	42.285
67.773	5.225	46.854	46.855
68.299	4.447	46.960	46.956

TABLE 30

PVT Data for the Methanol System at 25°

PL1	PS1	P2	P2(calcd.)
31.600	4.438	22.372	22.364
31.635	4.694	22.479	22.474
48.888	4.583	33.844	33.848
49.694	3.318	33.955	33.953
67.909	4.973	46.616	46.604
67.963	4.657	46.552	46.533
79.770	1.347	53.292	53.287
79.795	4.429	54.334	54.343
93.930	4.722	63.924	63.915
94.036	2.102	63.092	63.107
105.730	4.201	71.708	71.715
105.764	4.783	71.930	71.932
116.830	4.964	79.554	79.556
116.916	5.138	79.681	79.673

TABLE 31

PVT Data for the Methanol System at 35°

PL1	PS1	P2	P2(calcd.)
82.729	5.685	56.609	56.610
85.197	5.164	58.086	58.071
115.257	4.598	77.870	77.893
116.445	5.453	78.990	78.974
136.034	3.999	91.610	91.603
136.385	3.910	91.822	91.809
156.786	4.815	105.863	105.859
157.341	3.456	105.780	105.780
177.863	5.267	120.317	120.334
178.102	6.155	120.786	120.792
198.426	4.971	134.389	134.387
198.656	4.637	134.445	134.436
198.820	1.412	133.482	133.486

TABLE 32

PVT Data for the 2,2,2-Trifluoroethanol System at 15°

PL1	PS1	P2	P2(calcd.)
16.251	5.008	12.398	12.426
16.254	4.750	12.313	12.341
21.920	3.884	15.796	15.789
22.017	4.815	16.181	16.170
25.851	3.986	18.412	18.423
26.072	4.927	18.887	18.889
29.523	6.046	21.559	21.553
29.981	4.712	21.402	21.404
33.794	4.323	23.785	23.799
33.904	2.662	23.315	23.309
36.831	4.047	25.715	25.721
37.763	3.868	26.291	26.280
37.801	4.150	26.402	26.400

TABLE 33

PVT Data for the 2,2,2-Trifluoroethanol System at 25°

PL1	PS1	P2	P2(calcd.)
28.259	4.543	20.204	20.195
29.885	4.508	21.257	21.257
39.885	4.509	27.861	27.871
40.770	4.624	28.487	28.496
47.659	4.320	32.945	32.957
47.694	4.731	33.108	33.119
55.015	3.708	37.644	37.631
55.142	4.227	37.897	37.891
61.686	4.840	42.429	42.448
61.869	5.398	42.756	42.758
67.306	2.906	45.539	45.538
67.413	4.350	46.112	46.096

TABLE 34

PVT Data for the 2,2,2-Trifluoroethanol System at 35°

PL1	PS1	P2	P2(calcd.)
49.923	4.689	34.554	34.551
50.041	4.000	34.401	34.395
66.615	5.037	45.747	45.719
68.512	6.316	47.447	47.410
68.918	4.435	47.083	47.042
80.417	4.777	54.815	54.788
81.067	5.503	55.505	55.465
93.506	4.391	63.363	63.361
93.694	4.833	63.642	63.636
105.525	1.841	70.516	70.515
105.557	4.476	71.418	71.424
106.136	4.572	71.823	71.843
118.277	5.165	80.139	80.159
118.315	4.633	79.996	80.005

TABLE 35

PVT Data for the 1,1,1,3,3,3-Hexafluoro-2-propanol System at 15°

PL1	PS1	P2	P2(calcd.)
34.773	4.367	24.421	24.438
35.198	4.897	24.898	24.899
48.013	6.233	33.850	33.832
48.083	5.021	33.466	33.467
56.774	4.750	39.145	39.137
57.136	4.398	39.259	39.258
65.341	4.681	44.809	44.805
65.813	3.947	44.879	44.871
74.287	3.994	50.524	50.529
74.337	5.383	51.018	51.030
82.750	3.545	56.031	56.026
82.907	4.488	56.446	56.448

TABLE 36

PVT Data for the 1,1,1,3,3,3-Hexafluoro-2-propanol System at 25°

PL1	PS1	P2	P2(calcd.)
18.770	4.538	14.744	14.743*
18.805	4.537	14.775	14.768*
18.855	4.616	14.827	14.826*
24.165	5.406	18.852	18.857*
24.253	5.018	18.805	18.811*
24.267	4.832	18.765	18.769*
31.754	4.962	24.165	24.176*
31.834	5.068	24.252	24.263*
31.886	4.985	24.267	24.278*
42.388	4.777	31.756	31.756*
42.459	4.912	31.833	31.845*
42.541	4.842	31.886	31.884*
57.110	5.037	42.396	42.405*
57.221	4.959	42.455	42.463*
57.385	4.885	42.545	42.560*
63.339	4.609	43.447	43.393
63.717	2.830	43.095	43.039
77.557	5.072	57.132	57.127*
77.621	5.257	57.240	57.224*
77.780	5.467	57.402	57.398*
85.479	4.443	58.057	58.013
85.908	4.844	58.474	58.434
100.019	4.678	67.802	67.757
100.915	3.569	68.020	67.979
106.017	5.048	77.681	77.659*
106.096	4.601	77.602	77.591*
106.183	5.205	77.831	77.823*
116.898	5.048	79.169	79.133
116.990	4.403	79.015	78.977
132.676	4.495	89.483	89.498
133.005	3.885	89.494	89.513
147.005	4.852	99.203	99.232
147.570	3.830	99.217	99.270

TABLE 37

PVT Data for the 1,1,1,3,3,3-Hexafluoro-2-propanol System at 35°

PL1	PS1	P2	P2(calcd.)
106.781	4.237	72.018	71.982
107.287	5.169	72.678	72.633
145.681	5.053	98.144	98.089
147.050	5.123	99.074	99.023
172.518	5.066	116.054	115.981
173.793	4.955	116.868	116.795
199.405	4.106	133.688	133.646
199.522	5.655	134.282	134.244
225.627	5.255	151.631	151.646
226.032	5.639	152.024	152.046
252.479	6.949	170.341	170.327
252.641	7.472	170.572	170.611
252.872	4.708	169.779	169.846

TABLE 38

PVT Data for the Methanol-2,2,2-Trifluoroethanol System at 15°

R_π	PL1	PS1	P2	P2(calcd.)
0.64587	13.237	1.522	9.233	9.262
0.55600	14.273	0.992	9.747	9.769
0.59945	14.304	1.196	9.834	9.859
0.94836	14.915	0.728	10.103	10.106
0.94101	15.215	0.957	10.387	10.383
0.98041	15.393	3.689	11.434	11.423
0.64587	18.622	2.701	13.236	13.228
0.59945	19.626	3.890	14.304	14.293
0.55600	19.914	3.257	14.272	14.271
0.98041	20.774	4.921	15.393	15.403
0.94836	21.813	1.461	14.914	14.928
0.94101	21.849	2.286	15.215	15.229
0.64587	26.368	3.475	18.622	18.628
0.59945	27.222	4.684	19.626	19.601
0.55600	28.026	3.969	19.913	19.894

TABLE 39

PVT Data for the Methanol-2,2,2-Trifluoroethanol System at 25°

R_π	PL1	PS1	P2	P2(calcd.)
0.62148	23.721	2.215	16.441	16.427
0.63400	24.246	3.693	17.300	17.274
0.61750	24.348	3.665	17.358	17.332
1.02979	25.264	3.459	17.861	17.870
0.95822	26.397	2.658	18.339	18.350
0.99874	26.576	4.689	19.162	19.155
0.62148	33.488	4.669	23.721	23.727
0.63400	33.970	5.300	24.245	24.259
0.61750	34.339	4.913	24.348	24.374
0.99874	37.773	4.740	26.578	26.596
1.02979	37.780	0.786	25.264	25.272
0.95822	37.927	3.880	26.397	26.409
0.61750	48.915	5.690	34.339	34.314
0.62148	48.945	3.161	33.488	33.487
0.63400	49.233	4.004	33.970	33.961

TABLE 40

PVT Data for the Methanol-2,2,2-Trifluoroethanol System at 35°

R_{π}	PL1	PS1	P2	P2(calcd.)
0.76061	35.113	2.764	24.116	24.147
0.78664	36.431	5.177	25.834	25.835
0.74334	36.573	4.165	25.584	25.587
1.27833	39.511	2.627	26.992	27.016
1.26112	41.132	2.724	28.102	28.123
1.17264	42.220	3.536	29.124	29.119
0.76061	50.557	4.920	35.112	35.115
0.78664	52.529	5.020	36.431	36.458
0.74334	53.311	3.865	36.572	36.588
1.27833	58.831	1.731	39.511	39.540
1.26112	59.894	4.321	41.133	41.115
1.17264	62.023	3.430	42.220	42.233
0.76061	73.740	5.009	50.556	50.558
0.78664	77.263	3.801	52.529	52.501
0.74334	77.865	4.936	53.311	53.281

TABLE 41

PVT Data for the Methanol-1,1,1,3,3,3-Hexafluoro-2-propanol System at 15°

R_π	PL1	PS1	P2	P2(calcd.)
1.72637	12.839	3.125	9.558	9.570
0.37144	13.939	2.920	10.223	10.233
0.37771	14.009	3.012	10.301	10.311
1.58514	14.210	3.213	10.519	10.517
1.72637	17.139	4.351	12.837	12.851
1.84106	18.460	4.272	13.725	13.708
0.37144	18.799	4.286	13.939	13.938
1.58514	18.920	4.801	14.210	14.195
0.36114	18.970	3.412	13.756	13.764
0.37771	19.467	3.159	14.009	14.017
0.36758	19.857	4.619	14.729	14.757
0.79681	24.965	4.312	18.141	18.125
0.37144	25.906	4.584	18.799	18.820
0.36114	26.286	4.296	18.969	18.981
0.37771	26.384	5.547	19.467	19.457
0.36758	27.302	4.794	19.856	19.831

TABLE 42

PVT Data for the Methanol-1,1,1,3,3,3-Hexafluoro-2-propanol System at 25°

R_π	PL1	PS1	P2	P2(calcd.)
0.38949	22.437	3.772	16.151	16.153
0.36869	23.151	3.185	16.437	16.433
0.35096	26.804	4.855	19.436	19.427
0.39929	30.208	4.256	21.495	21.514
0.38949	31.667	4.108	22.437	22.443
0.27322	32.191	5.027	23.059	23.074
0.38304	32.445	2.966	22.589	22.589
0.36869	32.610	4.347	23.151	23.151
0.59039	32.774	3.361	22.984	22.963
0.69965	33.100	2.423	22.902	22.882
0.75495	39.108	2.524	26.984	26.977
0.45905	41.927	4.058	29.367	29.355
0.32194	42.531	4.479	29.833	29.860
0.39929	42.930	4.743	30.207	30.242
0.38949	44.901	4.997	31.667	31.655
0.38304	46.161	4.805	32.445	32.444
0.36869	46.474	4.704	32.610	32.618
0.59039	46.638	4.577	32.774	32.739

TABLE 43

PVT Data for the Methanol-1,1,1,3,3,3-Hexafluoro-2-propanol System at 35°

R_π	PL1	PS1	P2	P2(calcd.)
0.82381	38.718	2.596	26.612	26.619
0.75770	38.785	2.875	26.747	26.756
0.77700	38.894	3.669	27.081	27.091
0.79031	38.895	2.906	26.831	26.840
0.41424	46.593	3.400	32.129	32.144
0.39020	48.792	4.449	33.937	33.962
0.38983	49.034	5.925	34.594	34.611
0.49544	49.916	5.201	34.975	34.986
0.50199	50.696	0.741	34.048	34.053
0.82381	55.536	4.913	38.719	38.704
0.75770	55.649	4.901	38.785	38.776
0.79031	55.812	4.894	38.895	38.884
0.77700	56.132	4.207	38.894	38.878
0.41424	67.159	5.135	46.593	46.597
0.38983	70.636	5.444	49.034	49.045
0.39020	70.817	4.341	48.792	48.812
0.50199	73.349	4.681	50.696	50.692
0.49544	74.174	0.426	49.917	49.891

TABLE 44

Vapor Pressure Data for the 2,2,2-Trifluoroethanol System in n-Hexadecane at 20°

c_A^V	f_A	f_A(calcd.)
0.000397	0.00467	0.00477
0.000983	0.01202	0.01205
0.001401	0.01761	0.01761
0.001688	0.02166	0.02169
0.001896	0.02478	0.02480
0.002060	0.02732	0.02737
0.002193	0.02946	0.02951
0.000694	0.00846	0.00840
0.001193	0.01495	0.01480
0.001557	0.01994	0.01980
0.001809	0.02360	0.02348
0.002005	0.02660	0.02650
0.002139	0.02875	0.02864
0.000694	0.00836	0.00840
0.000947	0.01161	0.01159
0.001277	0.01596	0.01592
0.001587	0.02026	0.02023
0.001835	0.02387	0.02387
0.002019	0.02669	0.02671
0.002157	0.02889	0.02893
0.000726	0.00873	0.00880
0.001232	0.01527	0.01532
0.001593	0.02024	0.02031
0.001852	0.02402	0.02413
0.000647	0.00775	0.00782
0.001165	0.01440	0.01442
0.001533	0.01942	0.01945
0.001804	0.02335	0.02341

TABLE 45

Vapor Pressure Data for the 2,2,2-Trifluoroethanol System in n-Hexadecane at 25°

C_A^V	f_A	f_A(calcd.)
0.001000	0.01095	0.01099
0.001664	0.01877	0.01880
0.002119	0.02445	0.02454
0.002454	0.02888	0.02906
0.002692	0.03219	0.03242
0.002866	0.03470	0.03498
0.003007	0.03682	0.03713
0.003119	0.03855	0.03886
0.000438	0.00453	0.00475
0.000875	0.00935	0.00958
0.001290	0.01407	0.01433
0.001735	0.01937	0.01966
0.002220	0.02554	0.02588
0.002552	0.03006	0.03043
0.002796	0.03360	0.03395
0.000645	0.00710	0.00704
0.001458	0.01653	0.01631
0.002008	0.02338	0.02311
0.002384	0.02838	0.02810
0.002692	0.03270	0.03243
0.002920	0.03608	0.03581
0.001001	0.01111	0.01101
0.001452	0.01646	0.01624
0.002006	0.02332	0.02308
0.002323	0.02753	0.02726
0.002631	0.03180	0.03156
0.002861	0.03518	0.03482
0.003007	0.03741	0.03712
0.003153	0.03972	0.03941
0.000433	0.00460	0.00470
0.000935	0.01024	0.01026
0.001498	0.01686	0.01679
0.002058	0.02381	0.02375
0.002459	0.02915	0.02914
0.002771	0.03351	0.03357

TABLE 46

Vapor Pressure Data for the 2,2,2-Trifluoroethanol System in n-Hexadecane at 35°

C_A^V	f_A	f_A(calcd.)
0.001983	0.01835	0.01832
0.003232	0.03113	0.03105
0.004078	0.04058	0.04059
0.004653	0.04756	0.04763
0.005057	0.05282	0.05289
0.005354	0.05689	0.05692
0.005592	0.06028	0.06028
0.005766	0.06282	0.06281
0.005910	0.06494	0.06494
0.001099	0.01004	0.00998
0.002650	0.02512	0.02494
0.003662	0.03595	0.03579
0.004371	0.04419	0.04412
0.004867	0.05043	0.05039
0.005221	0.05517	0.05511
0.005471	0.05869	0.05857
0.005657	0.06142	0.06122
0.005818	0.06380	0.06357
0.005952	0.06577	0.06557
0.000491	0.00435	0.00443
0.001040	0.00936	0.00944
0.001688	0.01548	0.01548
0.002602	0.02450	0.02445
0.003617	0.03525	0.03527
0.004347	0.04366	0.04382
0.004863	0.05005	0.05032
0.005221	0.05474	0.05510
0.005482	0.05834	0.05871
0.001312	0.01196	0.01195
0.002712	0.02572	0.02558
0.003724	0.03654	0.03649
0.004382	0.04422	0.04425
0.004837	0.04994	0.04999
0.005171	0.05441	0.05442
0.005412	0.05776	0.05774

TABLE 47

Vapor Pressure Data for the 1,1,1,3,3,3-Hexafluoro-2-propanol System in n-Hexadecane at 20°

C_A^V	f_A	f_A(calcd.)
0.000197	0.00252	0.00255
0.000536	0.00686	0.00695
0.000985	0.01273	0.01282
0.001503	0.01968	0.01969
0.002058	0.02733	0.02724
0.002665	0.03595	0.03578
0.003295	0.04523	0.04506
0.003809	0.05313	0.05300
0.004205	0.05946	0.05940
0.004499	0.06431	0.06431
0.004725	0.06813	0.06818
0.000609	0.00773	0.00790
0.001413	0.01835	0.01849
0.002355	0.03136	0.03138
0.003216	0.04390	0.04387
0.003845	0.05356	0.05357
0.004330	0.06131	0.06145
0.001538	0.01994	0.02016
0.002308	0.03068	0.03072
0.002850	0.03852	0.03846
0.003395	0.04668	0.04658
0.003988	0.05586	0.05586
0.004416	0.06280	0.06290
0.000182	0.00229	0.00235
0.000376	0.00477	0.00488
0.000567	0.00725	0.00736
0.000772	0.00992	0.01003
0.000978	0.01264	0.01272
0.001174	0.01527	0.01532
0.001373	0.01795	0.01796
0.001608	0.02115	0.02111

TABLE 48

Vapor Pressure Data for the 1,1,1,3,3,3-Hexafluoro-2-propanol System in n-Hexadecane at 25°

C_A^V	f_A	f_A(calcd.)
0.000841	0.00937	0.00976
0.001635	0.01871	0.01910
0.002389	0.02792	0.02819
0.003049	0.03623	0.03639
0.003689	0.04459	0.04464
0.004373	0.05383	0.05383
0.005028	0.06306	0.06307
0.005583	0.07123	0.07130
0.005992	0.07445	0.07760
0.006307	0.08243	0.08262
0.006556	0.08643	0.08669
0.006740	0.08943	0.08974
0.002051	0.02392	0.02408
0.003452	0.04164	0.04155
0.004443	0.05501	0.05480
0.005163	0.06529	0.06505
0.005692	0.07316	0.07296
0.006099	0.07941	0.07929
0.006368	0.08378	0.08360
0.006599	0.08750	0.08740
0.006766	0.09024	0.09019
0.000144	0.00163	0.00166
0.000430	0.00489	0.00498
0.000805	0.00922	0.00934
0.001199	0.01386	0.01395
0.001673	0.01951	0.01955
0.002172	0.02561	0.02555
0.002835	0.03391	0.03371
0.003677	0.04484	0.04449
0.004612	0.05758	0.05716
0.000208	0.00227	0.00241
0.000568	0.00634	0.00659
0.000811	0.00915	0.00941
0.001155	0.01317	0.01343
0.001481	0.01706	0.01728
0.001832	0.02128	0.02145
0.002247	0.02638	0.02646
0.002742	0.03255	0.03255
0.003377	0.04069	0.04058

TABLE 49

Vapor Pressure Data for the 1,1,1,3,3,3-Hexafluoro-2-propanol System in n-Hexadecane at 35°

C_A^V	f_A	f_A(calcd.)
0.000455	0.00414	0.00432
0.001242	0.01152	0.01181
0.002240	0.02114	0.02140
0.003333	0.03197	0.03213
0.004443	0.04338	0.04336
0.005628	0.05605	0.05586
0.006878	0.07007	0.06975
0.008148	0.08515	0.08477
0.009088	0.09689	0.09660
0.009789	0.10604	0.10583
0.003746	0.03593	0.03626
0.006142	0.06142	0.06147
0.007707	0.07946	0.07945
0.008805	0.09294	0.09296
0.009618	0.10344	0.10354
0.010225	0.11163	0.11178
0.010663	0.11773	0.11791
0.011044	0.12320	0.12339
0.011321	0.12724	0.12745
0.011553	0.13071	0.13091
0.003851	0.03694	0.03732
0.004530	0.04405	0.04426
0.005180	0.05097	0.05106
0.005800	0.05773	0.05773
0.006433	0.06480	0.06471
0.001178	0.01036	0.01062
0.002331	0.02202	0.02229
0.003458	0.03322	0.03338
0.004278	0.04165	0.04166
0.004894	0.04815	0.04805
0.005514	0.05486	0.05463
0.006104	0.06134	0.06106
0.006696	0.06801	0.06767
0.007328	0.07534	0.07497
0.007849	0.08154	0.08115
0.008432	0.08867	0.08828
0.000480	0.00433	0.00455
0.000956	0.00874	0.00907
0.001430	0.01322	0.01360

TABLE 49 - continued

0.001902	0.01774	0.01814
0.002346	0.02205	0.02243
0.002806	0.02656	0.02692
0.003298	0.03146	0.03178
0.003717	0.03569	0.03597
0.004283	0.04151	0.04171
0.004839	0.04732	0.04747

TABLE 50

Vapor Pressure Data for the Methanol System

in Diphenylmethane at 25°

c_A^V	f_A	f_A(calcd.)
0.000299	0.01490	0.01506
0.000538	0.02764	0.02770
0.000849	0.04474	0.04499
0.001179	0.06413	0.06443
0.001523	0.08566	0.08603
0.001831	0.10649	0.10686
0.002104	0.12624	0.12660
0.002339	0.14464	0.14500
0.002545	0.16178	0.16223
0.000215	0.01080	0.01071
0.000523	0.02705	0.02686
0.000933	0.05001	0.04980
0.001340	0.07448	0.07436
0.001694	0.09742	0.09741
0.001992	0.11841	0.11831
0.002259	0.13877	0.13863
0.002495	0.15809	0.15793
0.002704	0.17651	0.17644
0.002889	0.19397	0.19404
0.003046	0.20998	0.21013
0.003192	0.22593	0.22614
0.000205	0.01034	0.01021
0.000531	0.02758	0.02731
0.000974	0.05247	0.05220
0.001370	0.07633	0.07622
0.001720	0.09928	0.09918
0.002020	0.12059	0.12038
0.002283	0.14075	0.14049
0.002513	0.15974	0.15949
0.002717	0.17789	0.17762
0.002898	0.19522	0.19501
0.003060	0.21179	0.21166
0.003199	0.22689	0.22685
0.003329	0.24207	0.24207

TABLE 51

Vapor Pressure Data for the Methanol System

in Diphenylmethane at 30°

c_A^V	f_A	f_A(calcd.)
0.000622	0.02740	0.02716
0.001262	0.05810	0.05787
0.001800	0.08636	0.08611
0.002285	0.11404	0.11387
0.002693	0.13947	0.13936
0.003028	0.16228	0.16213
0.003332	0.18451	0.18452
0.003599	0.20598	0.20598
0.003820	0.22507	0.22514
0.004015	0.24306	0.24324
0.004196	0.26110	0.26127
0.000674	0.02943	0.02953
0.001308	0.06002	0.06022
0.001839	0.08820	0.08825
0.002292	0.11423	0.11428
0.002665	0.13748	0.13753
0.002992	0.15945	0.15955
0.003278	0.18057	0.18044
0.000293	0.01234	0.01247
0.000789	0.03474	0.03487
0.001405	0.06518	0.06517
0.001942	0.09376	0.09397
0.002396	0.12048	0.12059
0.002782	0.14514	0.14518
0.003122	0.16870	0.16882
0.003405	0.19018	0.19026
0.003648	0.21041	0.21006
0.003872	0.22991	0.22986
0.004064	0.24803	0.24797
0.004242	0.26596	0.26600
0.004398	0.28292	0.28278

TABLE 52

Vapor Pressure Data for the Methanol System

in Diphenylmethane at 35°

C_A^V	f_A	f_A(calcd.)
0.000403	0.01529	0.01520
0.001147	0.04542	0.04527
0.002045	0.08518	0.08509
0.002784	0.12141	0.12135
0.003378	0.15375	0.15358
0.003892	0.18473	0.18443
0.004329	0.21360	0.21343
0.004694	0.24047	0.24011
0.005017	0.26612	0.26590
0.005296	0.29013	0.29020
0.005537	0.31265	0.31289
0.005755	0.33483	0.33493
0.005948	0.35609	0.35578
0.000560	0.02136	0.02133
0.001526	0.06145	0.06154
0.002358	0.09978	0.09998
0.003052	0.13524	0.13549
0.003629	0.16803	0.16827
0.004114	0.19863	0.19881
0.004507	0.22601	0.22609
0.004845	0.25185	0.25190
0.005149	0.27709	0.27720
0.005408	0.30037	0.30053
0.005628	0.32182	0.32192
0.005838	0.34376	0.34375

TABLE 53

Vapor Pressure Data for the 2,2,2-Trifluoroethanol System in Diphenylmethane at 25°

C_A^V	f_A	f_A(calcd.)
0.000099	0.01066	0.01067
0.000253	0.02784	0.02784
0.000395	0.04415	0.04415
0.000528	0.05992	0.05992
0.000651	0.07488	0.07488
0.000766	0.08927	0.08927
0.000875	0.10328	0.10327
0.000975	0.11653	0.11652
0.001072	0.12962	0.12962
0.001162	0.14212	0.14214
0.001247	0.15415	0.15420
0.001326	0.16564	0.16563
0.001400	0.17662	0.17661
0.001472	0.18752	0.18749
0.001540	0.19806	0.19805
0.001603	0.20800	0.20802
0.001662	0.21748	0.21748

TABLE 54

Vapor Pressure Data for the 2,2,2-Trifluoroethanol System in Diphenylmethane at 30°

C_A^V	f_A	f_A(calcd.)
0.000233	0.02139	0.02129
0.000455	0.04248	0.04244
0.000652	0.06205	0.06189
0.000838	0.08101	0.08082
0.001010	0.09911	0.09891
0.001176	0.11691	0.11691
0.001321	0.13338	0.13314
0.001463	0.14957	0.14943
0.001590	0.16473	0.16451
0.001710	0.17935	0.17902
0.001822	0.19306	0.19305
0.001925	0.20628	0.20625
0.002029	0.22006	0.21984
0.000129	0.01164	0.01173
0.000364	0.03343	0.03365
0.000571	0.05359	0.05378
0.000762	0.07278	0.07300
0.000941	0.09141	0.09159
0.001103	0.10876	0.10893
0.001257	0.12576	0.12593
0.001401	0.14214	0.14229
0.001533	0.15752	0.15769
0.001657	0.17242	0.17261
0.001772	0.18660	0.18670
0.001877	0.19999	0.20007
0.001981	0.21343	0.21350
0.002072	0.22556	0.22563
0.002167	0.23845	0.23852
0.000253	0.02340	0.02321
0.000484	0.04545	0.04531
0.000699	0.06660	0.06654
0.000893	0.08659	0.08651
0.001074	0.10574	0.10574
0.001242	0.12413	0.12419
0.001389	0.14084	0.14091

TABLE 55

Vapor Pressure Data for the 2,2,2-Trifluoroethanol System in Diphenylmethane at 35°

C_A^V	f_A	f_A(calcd.)
0.000180	0.01378	0.01376
0.000534	0.04175	0.04175
0.000856	0.06849	0.06847
0.001149	0.09376	0.09378
0.001415	0.11769	0.11769
0.001661	0.14064	0.14064
0.001886	0.16253	0.16255
0.002095	0.18355	0.18359
0.002282	0.20310	0.20310
0.002458	0.22203	0.22203
0.002621	0.24027	0.24024
0.002775	0.25768	0.25782
0.002900	0.27246	0.27260
0.003020	0.28718	0.28723
0.003133	0.30124	0.30122
0.000376	0.02915	0.02908
0.000716	0.05669	0.05666
0.001013	0.08182	0.08183
0.001149	0.09376	0.09375
0.001413	0.11747	0.11747
0.001653	0.13992	0.13996
0.001864	0.16033	0.16035
0.002058	0.17973	0.17978
0.002237	0.19826	0.19829
0.002403	0.21615	0.21607
0.002554	0.23274	0.23266
0.002697	0.24901	0.24887
0.002835	0.26503	0.26491

TABLE 56

Vapor Pressure Data for the 1,1,1,3,3,3-Hexafluoro-2-propanol System in Diphenylmethane at 25°

C_A^V	f_A	f_A(calcd.)
0.000312	0.03637	0.03641
0.000606	0.07271	0.07273
0.000876	0.10768	0.10773
0.001124	0.14138	0.14143
0.001351	0.17363	0.17367
0.001562	0.20479	0.20487
0.001757	0.23479	0.23488
0.001937	0.26350	0.26356
0.002106	0.29141	0.29155
0.002261	0.31818	0.31824
0.002405	0.34384	0.34385
0.002546	0.36972	0.36975
0.002679	0.39482	0.39488
0.002797	0.41802	0.41808
0.002915	0.44164	0.44168
0.000323	0.03785	0.03780
0.000612	0.07361	0.07350
0.000883	0.10882	0.10874
0.001132	0.14262	0.14258
0.001356	0.17443	0.17436
0.001565	0.20523	0.20521
0.001760	0.23529	0.23526
0.001940	0.26418	0.26411
0.002109	0.29209	0.29205
0.002266	0.31926	0.31920
0.002413	0.34548	0.34534
0.002552	0.37103	0.37092
0.002684	0.39601	0.39591

TABLE 57

Vapor Pressure Data for the 1,1,1,3,3,3-Hexafluoro-2-propanol System in Diphenylmethane at 30°

C_A^V	f_A	f_A(calcd.)
0.000504	0.04869	0.04887
0.000941	0.09399	0.09414
0.001339	0.13767	0.13776
0.001693	0.17871	0.17875
0.002011	0.21756	0.21753
0.002305	0.25526	0.25517
0.002571	0.29103	0.29086
0.002822	0.32615	0.32608
0.003047	0.35922	0.35918
0.003254	0.39073	0.39073
0.003451	0.42214	0.42200
0.003631	0.45181	0.45177
0.003801	0.48074	0.48087
0.003957	0.50854	0.50850
0.004109	0.53619	0.53620
0.004252	0.56308	0.56334
0.004385	0.58903	0.58925
0.004509	0.61412	0.61414
0.004631	0.63923	0.63931
0.004746	0.66363	0.66358
0.004857	0.68793	0.68765

TABLE 58

Vapor Pressure Data for the 1,1,1,3,3,3-Hexafluoro-2-propanol System in Diphenylmethane at 35°

C_A^V	f_A	f_A(calcd.)
0.000334	0.02620	0.02633
0.001052	0.08579	0.08618
0.001681	0.14209	0.01424
0.002233	0.19504	0.19532
0.002727	0.24549	0.24564
0.003162	0.29294	0.29277
0.003553	0.33797	0.33763
0.003903	0.38057	0.38015
0.004227	0.42186	0.42148
0.004526	0.46192	0.46160
0.004798	0.50021	0.50000
0.005047	0.53675	0.53670
0.005278	0.57200	0.57212
0.005490	0.60598	0.60617
0.005688	0.63877	0.63898
0.005874	0.67066	0.67107
0.006046	0.70131	0.70167
0.006210	0.73138	0.73192
0.006362	0.76047	0.76068
0.006508	0.78924	0.78931
0.006644	0.81668	0.81651
0.006773	0.84409	0.84321

TABLE 59

Vapor Pressure Data for the Methanol-2,2,2-Trifluoroethanol System in n-Hexadecane at 25°

V	P	NBT	NAT	NAT(calcd)
121.9	24.72	0.001381	0.001234	0.001218
121.9	35.84	0.001381	0.002462	0.002440
121.9	61.20	0.001381	0.005850	0.005880
121.9	24.74	0.001395	0.001228	0.001210
121.9	35.89	0.001395	0.002455	0.002436
121.9	46.11	0.001395	0.003683	0.003698
121.9	59.25	0.001395	0.005527	0.005572
121.9	24.74	0.001391	0.001228	0.001213
121.9	35.94	0.001391	0.002458	0.002444
121.9	46.18	0.001391	0.003689	0.003710
121.9	55.23	0.001391	0.004921	0.004970
121.9	63.18	0.001391	0.006154	0.006191
121.9	24.79	0.001389	0.001232	0.001220
121.9	35.98	0.001389	0.002465	0.002451
121.9	46.24	0.001389	0.003697	0.003719
121.9	55.32	0.001389	0.004933	0.004983
121.9	63.23	0.001389	0.006167	0.006200
147.1	29.22	0.002353	0.001288	0.001294
147.1	43.48	0.002353	0.003297	0.003285
147.1	57.97	0.002353	0.005765	0.005739
147.1	28.04	0.002778	0.000751	0.000771
147.1	33.45	0.002778	0.001490	0.001530
147.1	40.23	0.002778	0.002472	0.002509
147.1	46.42	0.002778	0.003454	0.003474
147.1	54.70	0.002778	0.004927	0.004911
147.1	61.46	0.002778	0.006290	0.006227
147.1	35.60	0.001951	0.002456	0.002430
147.1	55.09	0.001951	0.005411	0.005406
147.1	65.35	0.001951	0.007375	0.007311

TABLE 60

Vapor Pressure Data for the Methanol-2,2,2-Trifluoroethanol System in n-Hexadecane at 35°

V	P	NBT	NAT	NAT(calcd)
122.9	35.96	0.002079	0.001232	0.001241
122.9	49.11	0.002079	0.002463	0.002468
122.9	61.52	0.002079	0.003692	0.003694
122.9	73.23	0.002079	0.004928	0.004940
122.9	84.06	0.002079	0.006161	0.006186
122.9	94.18	0.002079	0.007394	0.007438
122.9	103.42	0.002079	0.008629	0.008661
122.9	111.83	0.002079	0.009863	0.009837
122.9	35.66	0.002074	0.001228	0.001218
122.9	48.71	0.002074	0.002455	0.002434
122.9	61.17	0.002074	0.003683	0.003662
122.9	72.85	0.002074	0.004910	0.004901
122.9	83.77	0.002074	0.006138	0.006153
122.9	93.87	0.002074	0.007367	0.007402
122.9	103.09	0.002074	0.008597	0.008618
122.9	111.54	0.002074	0.009825	0.009797
148.2	38.56	0.002771	0.001287	0.001273
148.2	50.24	0.002771	0.002554	0.002530
148.2	71.29	0.002771	0.005040	0.004988
148.2	89.83	0.002771	0.007533	0.007486
148.2	44.92	0.003489	0.001320	0.001361
148.2	69.71	0.003489	0.004288	0.004332
148.2	95.43	0.003489	0.007999	0.007980

TABLE 61

Vapor Pressure Data for the Methanol-1,1,1,3,3,3-Hexafluoro-2-Propanol System in n-Hexadecane at 25°

V	P	NBT	NAT	NAT(calcd)
121.9	18.78	0.001146	0.001231	0.001207
121.9	28.34	0.001146	0.002585	0.002604
121.9	36.90	0.001146	0.003813	0.003842
121.9	45.20	0.001146	0.005044	0.005015
121.9	18.79	0.001148	0.001233	0.001207
121.9	27.42	0.001148	0.002463	0.002469
121.9	36.08	0.001148	0.003690	0.003725
121.9	44.48	0.001148	0.004922	0.004915
121.9	18.76	0.001146	0.001235	0.001205
121.9	27.52	0.001146	0.002468	0.002484
121.9	36.20	0.001146	0.003704	0.003741
121.9	46.24	0.001146	0.005181	0.005160
121.9	18.67	0.001146	0.001228	0.001192
121.9	27.26	0.001148	0.002455	0.002446
121.9	35.91	0.001148	0.003689	0.003700
121.9	44.32	0.001148	0.004920	0.004893
121.9	19.62	0.001337	0.001228	0.001205
121.9	27.73	0.001337	0.002455	0.002467
121.9	35.83	0.001337	0.003683	0.003707
121.9	18.73	0.001150	0.001228	0.001198
121.9	27.38	0.001150	0.002455	0.002462
121.9	35.96	0.001150	0.003683	0.003708
121.9	44.28	0.001150	0.004910	0.004889
147.1	20.86	0.001927	0.001266	0.001304
147.1	30.67	0.001927	0.003246	0.003254
147.1	38.25	0.001927	0.004722	0.004684

TABLE 62

Vapor Pressure Data for the Methanol-2,2,2-Trifluoroethanol System in Diphenylmethane at 25°

V	P	NBT	NAT	NAT(calcd)
123.1	13.18	0.006366	0.002455	0.002559
123.1	18.07	0.006366	0.004910	0.005052
123.1	22.80	0.006366	0.007365	0.007516
123.1	27.24	0.006366	0.009820	0.009909
123.1	31.52	0.006366	0.012275	0.012324
123.1	35.54	0.006366	0.014730	0.014712
123.1	39.38	0.006366	0.017186	0.017134
123.1	43.02	0.006366	0.019641	0.019586
123.1	46.43	0.006366	0.022096	0.022047
123.1	49.66	0.006366	0.024551	0.024529
123.1	52.67	0.006366	0.027006	0.027008
123.1	55.53	0.006366	0.029461	0.029510
123.1	58.21	0.006366	0.031920	0.032013
123.1	60.74	0.006366	0.034379	0.034510
123.1	64.02	0.006366	0.037816	0.037977
123.1	68.97	0.006366	0.043708	0.043750
123.1	18.06	0.006370	0.004910	0.005048
123.1	27.20	0.006370	0.009821	0.009889
123.1	35.49	0.006370	0.014733	0.014679
123.1	42.94	0.006370	0.019645	0.019533
123.1	49.60	0.006370	0.024556	0.024479
123.1	56.81	0.006370	0.030697	0.030688
123.1	63.02	0.006370	0.036838	0.036897
123.1	12.31	0.005534	0.002457	0.002537
123.1	22.19	0.005534	0.007367	0.007479
123.1	31.13	0.005534	0.012277	0.012284
123.1	39.18	0.005534	0.017192	0.017095
123.1	46.38	0.005534	0.022102	0.021994
123.1	52.75	0.005534	0.027016	0.026940
123.1	58.37	0.005534	0.031928	0.031906
123.1	63.29	0.005534	0.036839	0.036799
123.1	14.86	0.005535	0.003683	0.003790
123.1	22.19	0.005535	0.007365	0.007480
123.1	29.01	0.005535	0.011060	0.011103
123.1	35.30	0.005535	0.014742	0.014703
123.1	17.37	0.005537	0.004912	0.005037
123.1	29.00	0.005537	0.011053	0.011092
123.1	39.17	0.005537	0.017192	0.017091
123.1	44.66	0.005537	0.020876	0.020761
123.1	49.69	0.005537	0.024559	0.024482
123.1	54.36	0.005537	0.028343	0.028300
123.1	58.50	0.005537	0.032027	0.032034
123.1	62.35	0.005537	0.035811	0.035823
123.1	65.80	0.005537	0.039504	0.039520
123.1	70.85	0.005537	0.045647	0.045515

TABLE 63

Vapor Pressure Data for the Methanol-2,2,2-Trifluoroethanol System in Diphenylmethane at 35°

V	P	NBT	NAT	NAT(calcd)
124.1	26.76	0.007200	0.004916	0.005061
124.1	39.49	0.007200	0.009830	0.009957
124.1	51.22	0.007200	0.014752	0.014754
124.1	61.99	0.007200	0.019662	0.019556
124.1	71.82	0.007200	0.024573	0.024402
124.1	82.89	0.007200	0.030711	0.030564
124.1	92.29	0.007200	0.036604	0.036524
124.1	100.00	0.007200	0.042005	0.042010
124.1	107.46	0.007200	0.047897	0.047910
124.1	114.37	0.007200	0.054034	0.053956
124.1	25.08	0.008289	0.003687	0.003865
124.1	34.60	0.008289	0.007370	0.007582
124.1	43.58	0.008289	0.011052	0.011201
124.1	52.04	0.008289	0.014735	0.014784
124.1	62.49	0.008289	0.019645	0.019561
124.1	72.13	0.008289	0.024555	0.024430
124.1	80.84	0.008289	0.029466	0.029337
124.1	90.31	0.008289	0.035359	0.035329
124.1	98.69	0.008289	0.041252	0.041315
124.1	106.19	0.008289	0.047144	0.047300
124.1	112.84	0.008289	0.053036	0.053155
124.1	21.80	0.008290	0.002455	0.002599
124.1	28.33	0.008290	0.004910	0.005126
124.1	34.63	0.008290	0.007365	0.007595
124.1	40.71	0.008290	0.009820	0.010027
124.1	49.38	0.008290	0.013508	0.013634
124.1	57.49	0.008290	0.017190	0.017216
124.1	65.09	0.008290	0.020873	0.020823
124.1	76.25	0.008290	0.026765	0.026686
124.1	86.22	0.008290	0.032665	0.032647
124.1	95.08	0.008290	0.038560	0.038649

TABLE 64

Vapor Pressure Data for the Methanol-1,1,1,3,3,3-Hexafluoro-2-Propanol System in Diphenylmethane at 25°

V	P	NBT	NAT	NAT(calcd)
129.8	8.25	0.003827	0.002455	0.002513
129.8	12.20	0.003827	0.004910	0.004911
129.8	16.28	0.003827	0.007367	0.007336
129.8	20.32	0.003827	0.009823	0.009768
129.8	28.25	0.003827	0.014736	0.014733
129.8	37.18	0.003827	0.020632	0.020704
122.5	6.91	0.004206	0.001229	0.001230
122.5	8.84	0.004206	0.002458	0.002498
122.5	10.83	0.004206	0.003686	0.003734
122.5	10.59	0.003838	0.003683	0.003686
122.5	16.85	0.003838	0.007365	0.007301
122.5	25.22	0.003838	0.012278	0.012241
122.5	33.20	0.003838	0.017194	0.017231
122.5	42.01	0.003838	0.023089	0.023128
122.5	49.85	0.003838	0.028981	0.028823
122.5	8.64	0.003919	0.002458	0.002495
122.5	12.72	0.003919	0.004913	0.004915
122.5	16.93	0.003919	0.007373	0.007350
122.5	23.23	0.003919	0.011066	0.011071
122.5	14.04	0.003828	0.005665	0.005682
122.5	23.26	0.003828	0.011080	0.011053
122.5	29.40	0.003828	0.014769	0.014809
122.5	36.77	0.003828	0.019440	0.019559
122.5	43.18	0.003828	0.023850	0.023931
122.5	48.08	0.003828	0.027543	0.027477
122.5	8.51	0.003826	0.002455	0.002453
122.5	12.63	0.003826	0.004915	0.004871
122.5	16.84	0.003826	0.007370	0.007289
122.5	23.13	0.003826	0.011056	0.010973
122.5	31.27	0.003826	0.015977	0.015988
122.5	38.82	0.003826	0.020905	0.020930
122.5	45.73	0.003826	0.025828	0.025752
122.5	47.37	0.003826	0.027065	0.026948
129.1	8.34	0.006050	0.001228	0.001206
129.1	11.37	0.006050	0.003683	0.003704
129.1	21.49	0.006050	0.011048	0.010963
129.1	28.42	0.006050	0.015958	0.015996
129.1	36.70	0.006050	0.022096	0.022294
129.1	44.32	0.006050	0.028233	0.028395
129.1	51.18	0.006050	0.034371	0.034224

APPENDIX II

DATA AND RESULTS FOR SEVERAL RELATED SYSTEMS

PVT

Reported in the text are the results of the PVT studies of the water-2,2,2-trifluoroethanol (TFE), and water-1,1,1,3,3,3-hexafluoro-2-propanol (HFP) systems at 25°C and the TFE-HFP system at 35°C. For each system, the data were adequately described by assuming only the 1:1 hetero-associated complex. The association constants and corresponding root mean square deviations (RMSD) for the systems are: water-TFE $(3.7 \pm 2.1) \times 10^{-4}$ $torr^{-1}$ and 0.009 torr; water-HFP, $(5.96 \pm 1.01) \times 10^{-4}$ $torr^{-1}$ and 0.011 torr; and TFE-HFP, $(2.39 \pm 0.44) \times 10^{-4}$ $torr^{-1}$ and 0.013 torr. The data for these systems are presented here in the same form as in Appendix I. The apparatus, experimental procedure, and method of calculation were the same as those for the other hetero-association PVT systems. The symbols used here are also the same. In the evaluation of R_π, water was represented by A and the fluoroalcohols by B, for the TFE-HFP system, A represented HFP and B represented TFE.

TABLE 65

PVT Data for the Water -2,2,2-Trifluoroethanol System at 25°

R_π	PL1	PS1	P2	P2(calcd.)
1.24041	11.585	3.941	8.969	8.984
1.24004	11.779	2.701	8.687	8.690
1.77975	14.078	2.408	10.093	10.108
1.52057	14.339	3.552	10.672	10.669
1.46946	14.533	4.157	11.008	11.003
1.24041	15.221	4.529	11.585	11.583
1.24004	15.810	3.984	11.779	11.787
1.77975	18.916	4.661	14.078	14.066
1.52057	19.754	3.816	14.339	14.332
1.46946	19.890	4.153	14.533	14.537
1.24041	20.984	4.047	15.221	15.224
1.24004	21.413	4.922	15.810	15.805

TABLE 66

PVT Data for the Water-1,1,1,3,3,3-Hexafluoro-2-propanol System at 25°

R_π	PL1	PS1	P2	P2(calcd.)
0.83697	13.039	4.229	10.035	10.042
0.70543	14.534	3.185	10.679	10.674
0.63428	15.092	5.334	11.766	11.773
0.58631	15.206	2.935	11.052	11.033
0.83697	17.945	3.478	13.039	13.026
0.70543	20.191	3.548	14.534	14.534
0.63428	20.345	4.947	15.092	15.111
0.62548	20.813	4.949	15.414	15.420
0.58631	21.410	3.152	15.206	15.204
0.58990	23.431	4.013	16.847	16.833
0.49686	24.627	4.526	17.794	17.796
0.49598	24.831	4.552	17.932	17.940
0.83697	26.251	1.841	17.945	17.960
0.63428	28.195	5.068	20.345	20.339
0.70543	28.289	4.418	20.191	20.181
0.62548	29.265	4.412	20.813	20.823
0.58631	29.829	5.054	21.410	21.414
0.58990	32.788	5.171	23.431	23.410
0.49598	34.815	5.416	24.831	24.833
0.49686	34.826	4.804	24.627	24.633

TABLE 67

PVT Data for the 2,2,2-Trifluoroethanol-1,1,1,3,3,3-Hexafluoro-2-propanol System at 35°

R_{π}	PL1	PS1	P2	P2(calcd.)
1.49376	18.237	3.748	13.327	13.307
1.11378	19.808	3.002	14.096	14.091
1.45475	19.843	3.461	14.276	14.270
1.49376	25.171	4.846	18.237	18.257
1.11378	27.246	5.339	19.808	19.795
1.45475	27.604	4.739	19.843	19.827
1.68975	28.321	3.350	19.832	19.828
1.49376	35.987	4.157	25.171	25.165
1.11378	39.206	4.072	27.245	27.263
1.45475	39.282	4.969	27.604	27.618
1.68975	40.636	4.418	28.321	28.326
1.49376	52.060	4.796	35.986	36.005
1.11378	56.601	5.380	39.206	39.205
1.45475	56.828	5.147	39.282	39.277
1.68975	59.202	4.473	40.636	40.619

The self-association of acetone at 25°C was studied. The data were best fit by assuming the existence of only the dimeric complex. The constant for the formation of the dimer is $(1.31 \pm 0.11) \times 10^{-4}$ mm^{-1}, the corresponding RMSD is 0.086 mm. The experimental method was similar to that described in the text. Temperature control, determination of volumes, and the methods of sample addition and evacuation were the same as before. The basic apparatus consisted of two chambers connected by a vacuum valve. Pressures were determined by means of mercury monometers attached to each chamber; the relative heights of the mercury were measured with a cathetometer which could be read to better than 0.05 mm. The procedure and data analysis were essentially the same as that previously described. The gas was expanded by increments from the higher pressure chamber into the lower pressure chamber through the central valve. The pressures of both chambers were measured before and after the expansion and the volumes of both chambers were corrected for the displacement of the mercury in the manometers. The resulting data consisted of four pressures and volumes for each point: an initial pressure and volume for the right chamber (PR1 and VR1), the same for the left chamber (PL1 and VL1), and similar observables for both chambers after expansion (PR2 and VR2 and PL2 and VL2). The data fitting technique described in Chapter IV was expanded to include the two final sub-systems; volumes rather than a volume ratio was used. The calculated final pressure in the left chamber (PL2(calcd.)) was used as the comparison quantity on which the RMSD was based. The pressure and volume data and the calculated pressures for acetone are presented in Table 68.

TABLE 68

PVT Data for Acetone at 25°

VR1	PR1	VL1	PL1	VR2	PR2	VL2	PL2	PL2(calcd)
536.69	51.34	524.32	63.25	537.20	56.28	523.80	58.08	58.21
536.03	44.98	524.96	69.57	536.69	51.34	524.32	63.25	63.12
535.31	37.76	525.69	76.83	536.03	44.98	524.96	69.57	69.57
534.61	30.84	526.38	83.63	535.31	37.76	525.69	76.83	76.73
539.86	82.14	525.62	85.32	540.03	83.70	525.46	83.71	83.72
539.31	76.85	526.15	90.65	539.86	82.14	525.62	85.32	85.24
533.84	23.20	527.13	91.10	534.61	30.84	526.38	83.63	83.55
539.78	81.27	526.87	97.89	540.59	89.55	526.03	89.59	89.43
533.11	15.88	527.85	98.28	533.84	23.20	527.13	91.10	91.11
538.49	68.56	526.98	98.89	538.86	72.24	526.60	95.11	95.17
532.58	10.68	528.37	103.22	533.11	15.88	527.85	98.28	98.17
537.96	63.44	527.49	103.95	538.49	68.56	526.98	98.89	98.80
538.86	72.44	527.78	106.81	539.78	81.27	526.87	97.89	97.88
537.48	58.76	527.96	108.55	537.96	63.44	527.49	103.95	103.87
537.02	53.98	528.43	113.19	537.48	58.76	527.96	108.55	108.44
531.49	0.0	529.39	113.39	532.58	10.68	528.37	103.22	103.11
537.86	62.49	528.77	116.65	538.86	72.44	527.78	106.81	106.70
536.60	49.95	528.83	117.15	537.02	53.98	528.43	113.19	113.17
536.00	43.92	529.41	122.96	536.60	49.95	528.83	117.15	117.03
535.61	40.09	529.80	126.75	536.00	43.92	529.41	122.96	123.01
534.92	33.18	530.47	133.33	535.61	40.09	529.80	126.75	126.62
534.55	29.42	530.83	137.04	534.92	33.18	530.47	133.33	133.42
535.69	40.92	530.91	137.87	536.71	51.12	529.92	128.00	127.93
534.05	24.47	531.30	141.78	534.55	29.42	530.83	137.04	137.03
533.30	17.00	532.02	148.86	534.05	24.47	531.30	141.78	141.75
534.44	28.47	532.12	149.84	535.69	40.92	530.91	137.87	137.87
534.69	31.00	532.32	151.85	535.20	36.05	531.83	146.95	147.02
534.29	26.98	532.71	155.71	534.69	31.00	532.32	151.85	151.88
533.16	15.81	533.33	161.90	534.44	28.47	532.12	149.84	149.91
531.58	0.0	533.75	165.98	532.89	12.95	532.53	153.83	153.86
533.16	15.76	533.79	166.37	533.82	22.18	533.19	160.44	160.33
532.30	7.08	534.62	174.70	532.75	11.56	534.20	170.49	170.53
531.57	0.07	534.82	176.68	533.16	15.81	533.33	161.90	162.03
531.59	0.20	535.28	181.14	532.30	7.08	534.62	174.70	174.79

Azeotrope Formation

Vapor mixtures of both methanol-TFE and methanol-HFP were observed to form low boiling azeotropes. In studying the hetero-association of these systems, it was necessary to avoid the ranges of composition and pressure in which condensation of the azeotropes occurs. In the PVT studies, the effects of the azeotropes were readily recognized by the pressure changes. Therefore, the information which was needed was the pressure below which the hetero-association in solution could be studied. Experimentally, this was obtained by volumetrically adding the alcohols to an evacuated chamber and measuring the pressures. In the azeotrope region, pressure equilibrium was achieved after several hours. The observables were the total pressure and the gross mole fraction of methanol in both the vapor and condensed phases. The data for the methanol-TFE and methanol-HFP systems at 25 and 35^{o}C are tabulated here.

TABLE 69

Concentration-Pressure Data for Methanol-2,2,2-Trifluoroethanol Azeotrope at 25°

mole fraction of methanol[a]	total pressure
0.00	71.4
0.10	68.0
0.19	67.0
0.24	66.5
0.30	67.0
0.34	67.5
0.39	68.0
0.45	69.0
0.48	70.5
0.60	73.5
0.72	79.5
0.83	93.5
0.93	100.5
1.00	127.1

[a]mole fraction in total system.

TABLE 70

Concentration-Pressure Data for Methanol-2,2,2-Trifluoroethanol Azeotrope at 35°

mole fraction of methanol[a]	total pressure
0.00	125.0
0.09	117.5
0.17	116.5
0.28	116.0
0.39	118,0
0.52	124.0
0.59	128.5
0.74	142.5
0.85	156.5
1.00	208.6

[a]mole fraction in total system

TABLE 71

Concentration-Pressure Data for Methanol-1,1,1,3,3,3-Hexafluoro-2-Propanol at 25°

mole fraction of methanol[a]	total pressure
0.00	156.3
0.11	59.5
0.20	53.0
0.30	48.5
0.34	47.5
0.46	48.0
0.59	48.5
0.67	51.0
0.80	58.0
0.86	63.5
0.93	79.5
0.96	108.5
1.00	127.1

[a]mole fraction in total system

TABLE 72

Concentration-Pressure Data for Methanol-1,1,1,3,3,3-Hexafluoro-2-Propanol at 35°

mole fraction of methanol[a]	total pressure
0.00	266.9
0.06	119.0
0.12	106.0
0.25	85.5
0.35	85.0
0.47	84.0
0.57	84.0
0.64	87.0
0.75	95.0
0.78	102.0
0.83	120.0
0.90	151.5
1.00	208.6

[a]mole fraction in total system

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