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I. ISOTOPE EFFECTS ON GAS PHASE HYDROGEN-BONDED COMPLEXES OF ACETONE. II. THE DETERMINATION OF THE NUMBER OF CHEMICAL SPECIES USING LINEAR DEPENDENCE TESTS.

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GRADUATE COLLEGE

I. ISOTOPE EFFECTS ON GAS PHASE HYDROGEN-BONDED COMPLEXES OF ACETONE

II. THE DETERMINATION OF THE NUMBER OF CHEMICAL SPECIES USING LINEAR DEPENDENCE TESTS

A DISSERTATION

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in partial fulfillment of the requirements for the

degree of

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BY

EDWIN HAROLD LANE

Norman, Oklahoma

1977

I. ISOTOPE EFFECTS ON GAS PHASE HYDROGEN-BONDED COMPLEXES OF ACETONE

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I. ISOTOPE EFFECTS ON GAS PHASE HYDROGEN-BONDED COMPLEXES OF ACETONE

CHAPTER I

INTRODUCTION

Many areas of physical chemistry (e.g., thermodynamics, kinetics, and molecular structure determination) are concerned with manifestations of bonding; thus, the nature of the chemical bond itself is of great importance. Pauling provides the following definition of a bond:[1] "There is a chemical bond between two atoms or groups of atoms in the case that the forces acting between them are such as to lead to the formation of an aggregate with sufficient stability to make it convenient for the chemist to consider it as an independent molecular species." All such aggregates of atoms can be brought to a low enough temperature for condensation to take place; this liquefaction is an indication of additional interactions among the molecules. However, these intermolecular attractive forces are much weaker than normal chemical bonds.

Between these extremes there are interactions of intermediate energy which give rise to clusters of molecular aggregates. The attractive forces holding together these clusters can be defined as chemical bonds, since the clusters or "complexes" conform in many ways to the criteria identifying molecules. However, in order to classify these complexes more precisely, their formation is called "association."

The situation in which hydrogen is bonded to two other atoms is just such a type of molecular interaction. The concept of this "hydrogen bond" has been traced[2] from early work on the association of liquids through Werner's idea of complex structure[3] to the well-known article by Latimer and Rodebush.[4] These two authors recognized the cause of the association of water molecules and the reason for its unique chemical and physical properties. Their contribution in 1920 was the first definitive study of hydrogen bonding.

From these modest and relatively recent beginnings sprang a rising interest in hydrogen bonding. As the wide occurrence and the great importance of these molecular associations became apparent, the number of investigations in this field increased tremendously. The famous monograph by Pimentel and McClellan,[2] published in 1960, contains references to over 2000 articles on hydrogen bonding. A recent review by Joesten and Schaad[5] covers the literature from 1960 through 1973 and includes more than 3000 references. A number of other books[6-9] and review articles[10-12] have also appeared.

Hydrogen bonding can be more precisely defined as an interaction between a proton donor (A-H) or acid and a proton acceptor (B) or base. Typical proton donor groups include hydrogen bonded covalently to electronegative atoms such as oxygen, nitrogen, sulfur, and the halogens. Since B will lose electrons to the acid in forming the hydrogen-bonded complex, the base can also be regarded as an electron donor and the acid as an electron acceptor.

The importance of the hydrogen bond can hardly be overemphasized.

Besides playing a significant role in many organic and inorganic compounds, it is intimately involved in all biological processes. In commenting on an "extraordinarily stimulating proposal" by Watson and Crick for hydrogen bonding in protein molecules, Pauling proved to be an accurate prophet.[13] In 1957 he foresaw that "the hydrogen bond will continue to play an important role in the field of molecular biology." Indeed, any good study of hydrogen-bond energetics or structure is likely to make a significant, although perhaps indirect, contribution to our understanding of life processes.

The present study deals with isotope effects on hydrogen bonding in the vapor phase. In particular, the interactions of acetone with HCl, DCl, CF_3CH_2OH, and CF_3CH_2OD have been investigated. The importance of good vapor phase thermodynamic data to the study of hydrogen bonding has been emphasized by Pimentel and McClellan.[2,12] They bemoan the lack of such studies and stress their importance to the theoreticians who attempt to gain a deeper understanding of hydrogen bonding in the absence of solvent effects. Similarly, substitution of deuterium for hydrogen in a complex should provide fundamental information concerning hydrogen-bonding interactions.

Isotope Effects on Hydrogen Bonding

Several physical and chemical properties of a hydrogen-bonded complex are affected by substitution of deuterium for hydrogen. The basic cause of the differences in properties of isotopic molecules at moderate temperatures appears to be the differences in zero-point vibrational energy. For the sake of simplicity, consider a diatomic molecule containing hydrogen. In the harmonic oscillator approximation, the vibrational energy levels are given by

$$\varepsilon_v = h\nu\ (v + 1/2)$$

where v is the vibrational quantum number and $\nu = (1/2\pi)(k/\mu)^{1/2}$. A molecule containing deuterium has a larger reduced mass (μ) and therefore less zero-point energy,

$$\varepsilon_{v=0} = h\nu/2$$

Thus, in the case of the isotopes of hydrogen, the ground state of a molecule containing deuterium must lie lower in the potential well than the ground state of a molecule with protium (hereafter referred to as hydrogen).

It should be obvious that changes in the vibrational energy levels will be reflected in variations of bond lengths. And since changes in the hydrogen-bond lengths will be related closely to differences in hydrogen-bond strengths, it is not surprising that many investigations of isotope effects have centered on changes in structural features of the hydrogen-bonding compounds.

The potential function for a hydrogen-bonded complex may be assumed to resemble one of the curves shown in figure I-1. (Of course, these are one-dimensional representations of a very complex situation.) Substitution of deuterium for hydrogen may then affect the bond length in different ways; the changes will depend on the shape of the potential curve as well as on the relative distribution of the vibrational energy levels for hydrogen and deuterium.

Many of the early conclusions regarding isotope effects on hydrogen bonding were based on changes observed in the lattice constants of self-associating compounds.[14,15] The assumption was made that the

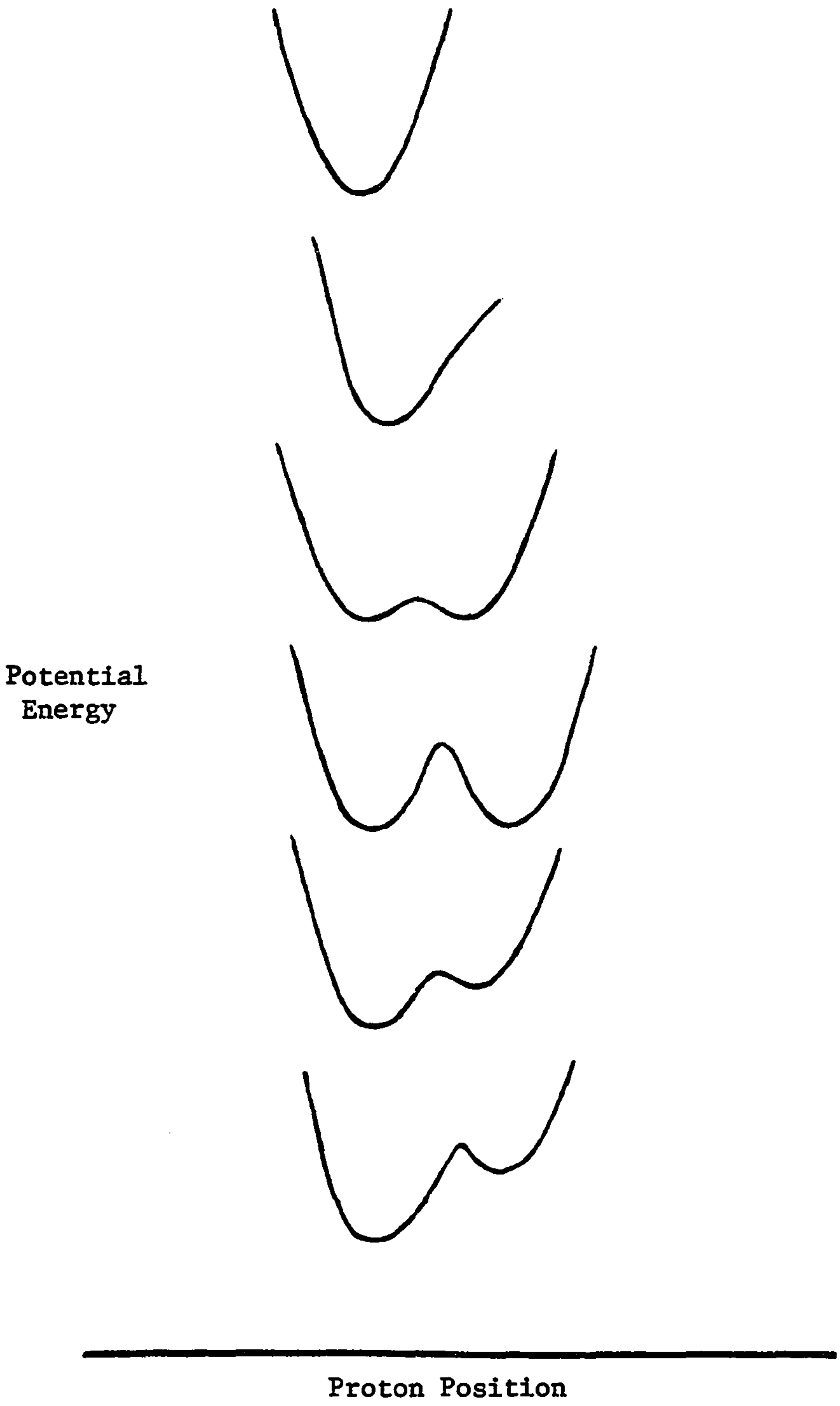
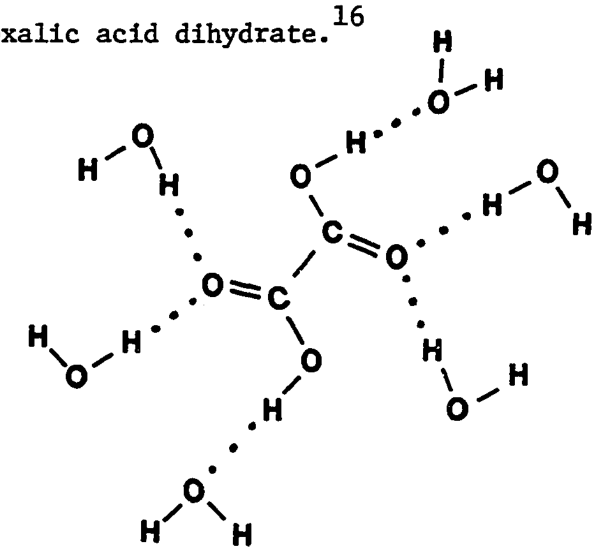


Figure I-1. Possible Potential Functions for a Proton in a Hydrogen Bond effects of deuteration were confined to the bond of interest. From a knowledge of the orientation of the bond with respect to the unit cell axes and of the changes in the unit cell constants, the difference in hydrogen and deuterium bond lengths could supposedly be obtained. This procedure seemed justifiable in simple systems containing only one hydrogen bond per unit cell, but it was often employed for more complicated molecules such as oxalic acid dihydrate.[16]



Recently, the complete structural determinations of the normal and deuterated forms of this compound demonstrated that the above procedure did not give accurate results.[17] Hamilton and Ibers[18] discuss these early structural studies in some detail.

Olovsson and Jönsson summarize data from complete single crystal X-ray diffraction studies made in recent years for both normal and deuterated compounds.[19] They find an expansion of 0.01 - 0.02 Å upon deuteration in O-H•••O hydrogen bonds of length 2.5 - 2.6 Å. This isotope effect seems to decrease with decreasing hydrogen-bond distance until contractions upon deuteration are observed for very short symmetrical hydrogen bonds. However, the authors warn that the amount of data presently available is "clearly insufficient to permit any more definitive statements to be made at this stage."

Nevertheless, the isotope effects that have been studied carefully do seem to be in agreement with qualitative predictions based on older, less reliable data.[14,15,20] These predictions have been given a somewhat more solid base by theoretical calculations carried out for the A-H•••A system by Singh and Wood.[21,22] These authors adopted the potential function of Ibers,[23]

$$2V = k_s \mu_s Q_s^{\ 2} + k_a \mu_a Q_a^{\ 2} + \alpha Q_a^{\ 4} + \beta Q_s Q_a^{\ 2}$$

Q_s is the normal coordinate for the symmetric stretch and is proportional to the change in the A•••A distance. Q_a is the normal coordinate for the antisymmetric stretch and is proportional to the deviation of hydrogen from the center of the bond. The last term in the equation is quite important and is related to coupling between the symmetric and antisymmetric modes.

The predicted isotope effects are most easily considered in three separate cases. Singh and Wood have examined these effects using force constants derived from spectral studies of the bifluoride ion (FHF^-). Their predictions should be valid, to some degree, for other hydrogen-bonded systems.

The case of a symmetric single-minimum potential function is examined first, and the potential is calculated as a function of Q_s and Q_a. It can be shown (see figure 1 of reference 21) that for any given deviation of the proton from the center of the bond, the bond length must be longer for hydrogen than for deuterium. This contraction upon deuteration arises because of the lower zero-point energy for deuterium and because of the coupling between vibrational modes.

The effect of isotopic substitution is also examined in the case of an asymmetric single-minimum potential function. As anharmonicity is introduced, the ratio of deuterium bond length to hydrogen bond length goes through a minimum, then increases until finally an expansion upon deuteration is observed. The change in sign of the isotope effect on the bond length corresponds to the point at which the potential begins to exhibit double-minimum characteristics.

If the potential function is symmetric and has a double minimum, two effects reinforce to give an expansion upon deuteration. The first was explained qualitatively by Rundle.[24] The vibrational ground state is higher for hydrogen and thus is closer to the top of the barrier separating the two minima. As the height of the barrier is decreased, the difference in "tunneling" by hydrogen and deuterium becomes marked. The hydrogen will have considerably more probability density than deuterium in the center of the double well; this increased density in the center of the bond will lead to a shorter bond for hydrogen than for deuterium.[19] As the height of the barrier increases, the wavefunctions of both systems become localized, and the tunneling effect is unimportant. This isotope effect also rapidly disappears as asymmetry is introduced.[21]

The second effect for double-minimum systems is similar but it is common to both symmetric and asymmetric systems; it can be explained with the use of figure I-2. Even if tunneling is unimportant, the fact that the hydrogen-containing complex lies higher in the potential well than one with deuterium means that, due to anharmonicity, the hydrogen wavefunction is concentrated more toward the center of the bond. Thus,

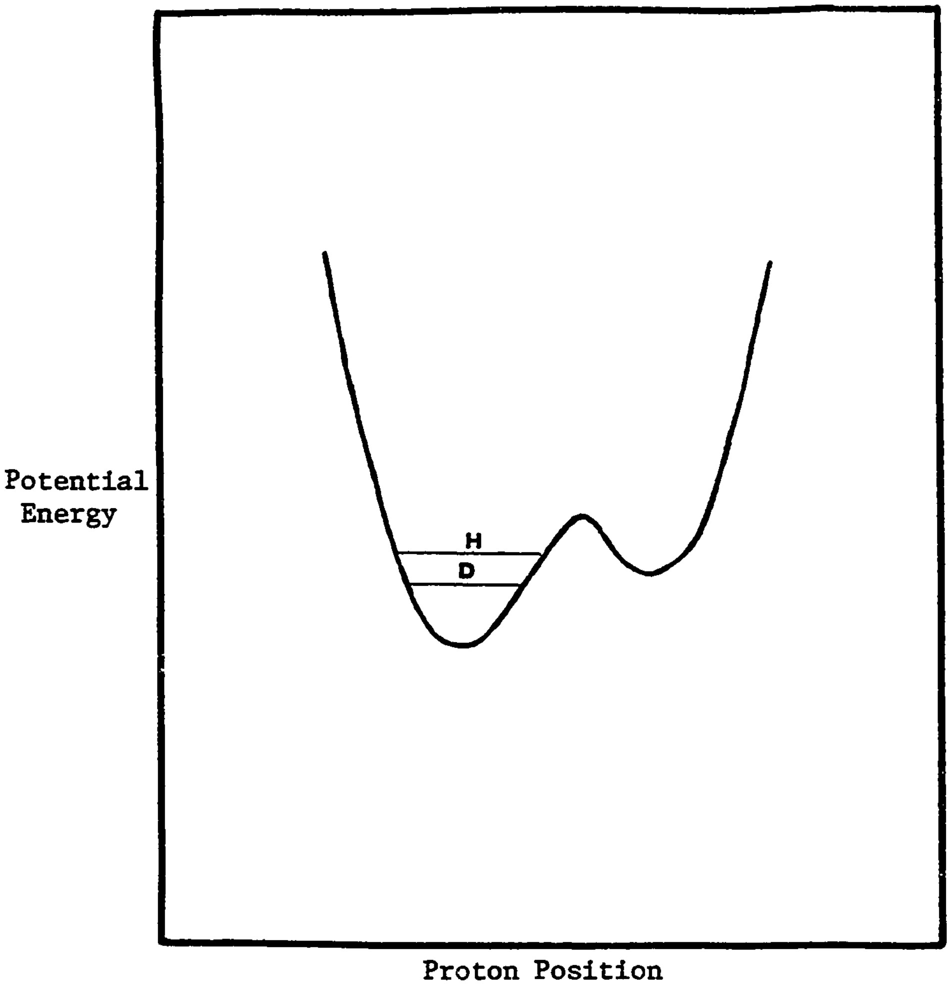


Figure I-2. Asymmetric Double-Minimum Potential Well for a Hydrogen Bond an expansion upon deuteration is again predicted. As the hydrogen bond becomes long and weak, isotope effects will, of course, be expected to disappear.

If one were able to know the type of potential function which exists for a given hydrogen-bonding system, then predictions regarding isotope effects might be forthcoming. Unfortunately, theoretical studies of hydrogen-bonding systems have not advanced to the point at which reliable potential energy surfaces can be calculated for anything but very small molecules.[10]

There have been infrequent attempts to apply statistical thermodynamic methods to the isotope effect on hydrogen bonding.[25-27] In order to point out the shortcomings of these attempts, it will be necessary to derive an expression relating the equilibrium constants for the association reactions.

If the equilibrium constants for the following two reactions,

$$\text{A-H} + \text{B} \rightleftharpoons \text{A-H}\cdots\text{B}$$

$$\text{A-D} + \text{B} \rightleftharpoons \text{A-D}\cdots\text{B}$$

are K_H and K_D, respectively, then the equilibrium constant for the exchange reaction

$$\text{A-H} + \text{A-D}\cdots\text{B} \rightleftharpoons \text{A-D} + \text{A-H}\cdots\text{B}$$

is $K_{ex} = K_H/K_D$. K_{ex} can be expressed in terms of the total partition functions of the individual species as

$$K_{ex} = \frac{q_{AD}\, q_{AHB}}{q_{AH}\, q_{ADB}}$$

where the minima of the potential energy curves have been taken as energy zero.

The vibrational partition function for a single mode is given by

$$q_{vib} = \sum_{v=0}^{\infty} \exp [-h\nu (v + 1/2)/kT]$$

A common assumption[26,27] is that all levels above the ground state can be ignored so that

$$q_{vib} = e^{-h\nu/2kT}$$

Another assumption is that all parts of the partition functions will cancel except for vibrations affected by deuteration. It follows that

$$K_{ex} = \exp [-h(\Sigma\nu_{AD} + \Sigma\nu_{AHB} - \Sigma\nu_{AH} - \Sigma\nu_{ADB})/2kT]$$

or $$\frac{K_H}{K_D} = K_{ex} = \exp [-h (\Sigma\Delta\nu_{AHB} - \Sigma\Delta\nu_{AH})/2kT]$$

where the summations are over all vibrational states affected by deuteration, and Δ indicates the shift upon deuteration.

It should be evident that such an expression may bear little resemblance to the actual ratio of equilibrium constants. Even if it is reasonable to expect other parts of the partition functions to cancel, it may not be justifiable to ignore excited vibrational states. (There have even been disagreements over the importance of bending modes in calculations of this type.[28]) The assumption with the least validity may well be the use of harmonic oscillator approximations for the vibrational modes. This procedure is probably not tenable in view of the importance of anharmonicity and vibrational coupling in hydrogen-bonding systems.[21,29-32]

Since structural and theoretical studies of the isotope effects on hydrogen bonding have not proved satisfactory, one would hope that thermodynamic studies could help to clear the confusion. Unfortunately, this has not been the case. Equilibrium constants and enthalpy changes for cases of self-association, intermolecular complexation, and intramolecular association have been used to support both hydrogen bonding and deuterium bonding as the stronger. Some of these thermodynamic results are summarized in the following paragraphs.

The earliest studies of self-associating compounds containing deuterium were concerned with measurements of quantities such as vapor pressures, heats of vaporization and fusion, and densities.[33-36] All of the results were interpreted as being consistent with a stronger deuterium bond. Since then, many other investigators have reached the same conclusion. Plourde[37] studied the shift of the -OH stretch for phenol complexes in CCl_4. Using ethylacetate, tetrahydrofuran, and n-butylether as bases, he found that -ΔH° of hydrogen bonding with phenol-d was about 300 cal/mole larger than for phenol. Glasoe et al.[38] followed the dimerization of benzoic acid in CCl_4 with infrared techniques. At 25° they found K_{assoc} = 4850 ℓ/mole for ϕCO_2H and 6590 ℓ/mole for ϕCO_2D. The enthalpy change for the normal acid was -5.9 ± 0.5 kcal/mole-bond and for the deuterated acid was -7.9 ± 0.7 kcal/mole-bond, so that at higher temperatures (>40°) the deuterated acid became less associated.

Potter et al.[27] measured vapor densities for CH_3CO_2H and CD_3CO_2D. Assuming dimerization and trimerization, they found a dimerization constant which was ∿25% greater for the deuterated compound at 80°. Creswell and Allred[39] used fluorine magnetic resonance techniques to study the association of fluoroform and tetrahydrofuran in cyclohexane. This weak hydrogen bond (ΔH° = -2.6 kcal/mole) showed a 140 cal/mole increase in -ΔH° upon deuteration. Wolff et al.[40,41] made extensive measurements on vapor pressures of normal and deuterated alcohols and amines in n-hexane. Their results suggest "that the association energy and the association degree are somewhat greater for the OD, ND, and ND_2 compounds than for their OH, NH, and NH_2 analogues."

Heat of mixing studies have also been employed to support the same point of view. Benjamin and Benson[42] investigated the CH_3OH-H_2O and CH_3OD-D_2O systems. The mixing of acetone with normal and deuterated chloroform was examined by Morcom and Travers[43] as well as by Duer and Bertrand.[44] The latter pair also reprocessed others' data for chloroform with tetrahydrofuran, pyridine, and p-dioxane. In each case it was concluded that substitution of deuterium for hydrogen led to a very slight increase in the strength of the bond.

On the other hand, there have been several studies which have led to opposite conclusions. Taylor and Templeman[45] studied the vapor pressures of CF_3CO_2H and CF_3CO_2D. They found that the association constant was ∿7% larger for CF_3CO_2H at 75°. The heat of dimerization was also somewhat larger for the hydrogen bond. Grimison[46] investigated the freezing point depression of naphthalene by imidazole and imidazole-d_1. He discovered that the deuterated form of the compound was associated to a smaller degree.

Similar conclusions have been reached in studies employing infrared techniques. Walling and Heaton[47] followed the -OH stretch of t-butyl hydroperoxide in CCl_4 and concluded that the heat of dimerization was about 1 kcal/mole greater for the hydrogen bond. Lin and Fishman[48] investigated the intramolecular bonding of orthohalophenols in the vapor phase; they found that deuterium formed a weaker bond (600 cal/mole less in o-chlorophenol). Singh and Rao[25] used the hydroxyl stretch of phenol in CCl_4 to study its dimerization as well as its complexation with triethylamine, acetone, pyridine, and acetonitrile. They found heats of complexation which were as much as eight times greater for hydrogen than for deuterium. (Their results have been questioned by Boettcher and Drago.[49])

Solvent Effects on Hydrogen Bonding

The importance of obtaining thermodynamic data for vapor-phase hydrogen-bonding reactions has already been stressed. Such data are of immense value in theoretical studies of hydrogen bonding. Moreover, these investigations can also lead to the elucidation of solvent effects on hydrogen bond formation. Because of the relative paucity of gas phase results, solvent effects on complex formation are not well understood.

Christian and Lane have recently reviewed much of the theory and data concerned with solvent effects on molecular complex formation.[50] Two main schools of thought seem to have emerged on this subject. The arguments of their proponents will be summarized in the following paragraphs.

Drago and coworkers have claimed that if thermodynamic studies are carried out in poorly-solvating media ("inert" or "innocent" solvents), the results can be expected to approximate those in the gas phase.[51] Furthermore, they claim to have developed an "elimination of solvation procedure" which has the "potential of extracting gas phase data from studies in polar solvents."[52-54] Their favorite scheme for predicting complex formation enthalpies is embodied in the following four-parameter equation:

$$-\Delta H = E_A E_B + C_A C_B \tag{I-1}$$

The subscripts A and B refer to acid and base, respectively.[55]

Drago has used experimental enthalpies to calculate and tabulate values of the E and C parameters.[51] The E terms are reportedly related to the propensity of the acid and base to undergo electrostatic interactions, and the C terms are related to the compounds' tendencies to form covalent bonds. C/E ratios are related to the "hardness" and "softness" of the acids and bases.

The validity of Drago's argument can be considered with the aid of the following thermodynamic cycle:

$$\begin{tikzcd}
AH\ (g) \arrow[d, "\Delta E^\circ_{AH}"] & + & B\ (g) \arrow[d, "\Delta E^\circ_{B}"] \arrow[r, "\Delta E^\circ(g)"] & AH\cdots B\ (g) \arrow[d, "\Delta E^\circ_{AHB}"] \\
AH\ (s) & + & B\ (s) \arrow[r, "\Delta E^\circ(s)"] & AH\cdots B\ (s)
\end{tikzcd}$$

The energy change measured in the gas phase, $\Delta E^\circ(g)$, can be represented as

$$\Delta E^\circ(g) = \Delta E^\circ(s) + \Delta E^\circ_{AH} + \Delta E^\circ_{B} - \Delta E^\circ_{AHB} \tag{I-2}$$

$\Delta E^\circ(s)$ is the energy change in solution; the other terms represent energies of solvation for acid, base, and complex. (Energies are employed instead of enthalpies so that the ΔPV term in the gas phase does not complicate matters.) The available gas-phase thermodynamic data seem to indicate that $\Delta E^\circ(g) \neq \Delta E^\circ(s)$ even for relatively inert solvents.[5,50] Nevertheless, some authors insist that the data are not conclusive and the near cancellation of the transfer energies should be assumed.[56]

In contrast to Drago's assumptions, Christian and coworkers have attempted to develop methods to correlate and predict solvent effects.

They believe that thermodynamic constants are dependent upon the medium in which the reaction occurs, and that no solvent is truly inert in comparison to the gas phase.[57-59] They have emphasized the importance of obtaining thermodynamic data for the transfer reactions, so that quantities such as the following can be calculated:

$$\alpha = \frac{\Delta E^\circ_{AHB}}{\Delta E^\circ_{AH} + \Delta E^\circ_{B}} \tag{I-3}$$

This constant represents the fraction of the energy of solvation of the acid plus base that is retained by the complex. Christian et al. claim that it has proved to be useful in characterizing solvent effects. In general, α for hydrogen-bonded complexes is expected to be less than unity.[50] The effect of squeezing out solvent molecules from around the acid and base as the complex forms is evidently not completely compensated by increased interactions between the complex and the solvent.

From the preceding review it should be obvious that there is confusion over the nature of isotope and solvent effects on hydrogen bonding. Theoretical and thermodynamic studies have so far failed to resolve the disagreements in these areas. It was hoped that a careful vapor phase study would be helpful in determining whether there are significant isotope and solvent effects on hydrogen bonding and in which direction they lie.

CHAPTER II

EXPERIMENTAL

Chemicals

The acetone used in these studies was purified in two separate distillations. The first portion (reagent grade from Mallinckrodt) was stored over anhydrous calcium sulfate (Drierite) to remove traces of water; it was then fractionally distilled on a 30-plate column while in vapor contact with additional Drierite. The second portion (reagent grade from J.T. Baker Co.) was distilled in a similar manner from P_2O_5 on a 20-plate column. The center fractions were used in the vapor density experiments and were stored in a desiccator in vapor contact with Drierite.

The hydrogen chloride gas used in the work at 25° and in a portion of the work at 15° was taken from a lecture bottle (Matheson, electronic grade, 99.99% minimum). In the other studies HCl was vaporized from a concentrated aqueous solution (Dupont, reagent grade hydrochloric acid, ∿38% HCl by weight) by a process described later in this chapter. Deuterium chloride was also obtained from solution (Merck, 38% w/w DCl in D_2O, 99 atom % D minimum).

2,2,2-trifluoroethanol (hereafter referred to as TFE) was obtained from Aldrich (Gold Label grade) and was dried by passing the vapor through a column containing 4 Å molecular sieve which had been previously heated and evacuated. The hydroxyl proton in TFE was deuterated by refluxing the alcohol with an excess of D_2O (Merck, minimum 99.7% deuterium) followed by distillation through a 10-plate column. The process was repeated until the hydroxyl singlet in the pmr spectrum of the compound had diminished to the level of the ^{13}C satellites from the methylene quartet. It is possible that the electron-withdrawing ability of the trifluoromethyl group causes the methylene protons in TFE to be acidic enough to undergo some isotope exchange. However, this exchange should occur to a small enough extent that the hydrogen-bonding properties of TFE-d will not be significantly affected. (There was no measurable exchange between the methylene protons and the hydroxyl deuterium after the distillation and over the course of the experiment.) TFE-d was dried in the same manner as TFE.

Temperature Control

Temperature control was achieved by immersing the apparatus in a water-filled 70-liter aquarium. The water was vigorously circulated with submersible pumps from Little Giant Pump Co. Cooling, when needed, was provided by cold water which was pumped through copper coils from a separate refrigerated bath. 200 W light bulbs, either covered with aluminum foil or painted, served as heat sources. During earlier studies a mercury-contact differential thermoregulator (Precision Scientific) with an electronic relay (Emil Greener Co.) activated the heaters. Later in the work, a thermistor-actuated, direct-dialing "thermonitor" (Sargent-Welch) was employed; the latter provides proportional voltage control of the heaters and is a much more precise controller. In all studies temperature constancy was maintained to ±0.01° or better.

At 15°, 25°, and 35° one-degree thermometers having 1/100 degree divisions were used (with the following exceptions). The 35° (fixed temperature) studies on HCl-acetone were carried out while using an inaccurate thermometer which read 35.00° at a temperature of 34.91° (the latter was checked with several other precise thermometers). The DCl-acetone studies were done at this same temperature in order to make comparisons easier. A portion of the HCl-acetone work at 15° was done with an imprecise thermometer. Subsequent acquisition of a 15° one-degree thermometer showed that this initial work was carried out at 14.85°. In order to correct for this imprecision, pressures measured at 14.85° were scaled to 15.00° by use of a factor involving the ratio of the two temperatures (288.15/288.00). This correction should not significantly affect the thermodynamic constants derived from the study; an examination of the contribution of each data set to the calculated constants confirmed this presumption.

At 45° temperatures were measured using a 34-46° thermometer with 1/100 degree divisions. It was calibrated against a one-degree thermometer at 44° and shown to be accurate. In the variable temperature studies a 19-35° thermometer with 1/100 degree divisions was used at 20.0°, 22.5°, 27.5°, 30.0°, and 32.5°. At 12.5°, 17.5°, and 47.5°, a 0-50° thermometer with 1/10 degree divisions was employed. Both of these thermometers were calibrated against the available one-degree thermometers. All of the thermometers used in this work were from Brooklyn Thermometer Co.

Pressure Measurement

Pressures were measured with a precision pressure gauge (Model 141, Texas Instruments Corp.). The gauge employs a fused quartz Bourdon tube, enclosed in an all-glass capsule, to provide highly precise pressure measurements (0.003 torr resolution). The instrument uses photoelectric nulling of a light beam reflected from a mirror attached to the Bourdon tube. The reference side of the capsule is continuously evacuated so that pressures are measured in the absolute mode.

The ports on the capsule were glass so that the capsule was permanently connected to the vapor density apparatus. Most of the connecting line was made with 1 mm i.d. capillary tubing, which was wrapped in heating tape and maintained at a temperature above that of the capsule (∿43°). The capsule was protected against mechanical shock by using short spirals of 2 mm i.d. thin-walled glass tubing to attach the sample and reference ports to the capillary tubing and vacuum line, respectively. These spirals were heated by enclosing them and the top of the gauge in a box made of heavy paper and by forcing in warm air. In this way, the spirals could be maintained at ∿40°.

The pressure gauge was calibrated with the use of another gauge (from Mensor Corp.) which had been recently calibrated by its manufacturer. Simultaneous readings of the same pressure were recorded from both gauges. True pressures were calculated from the calibration curve of the Mensor gauge and then used to establish a calibration curve for the TI gauge used in these studies.

Apparatus

The basic vapor density apparatus has been described previously.[60-63] Figure I-3 shows the system which was used in these studies. It consisted of a 1 liter Pyrex flask (total volume of the system was ∿1100 cc) which was attached directly to the pressure gauge. A mercury-covered sintered glass disc of fine porosity was attached to the system by a 24/40 female ground glass joint seated on a male joint in a mercury cup. A Teflon sleeve was used on the joint to prevent its freezing. The system was evacuated through a Teflon Fischer-Porter needle valve (4 mm bore) and a Kontes quick-opening valve. A 10/30 male joint in a mercury cup was provided for attaching liquid and gas reservoirs to the system.

Additions of liquid acetone through the mercury-covered disc were made using an Ultraprecision Micrometer Buret with a 0.25 ml capacity (Roger Gilmont Instruments). The buret is built around a Swiss-made micrometer and can be read to 0.00001 ml. Ethylene-propylene O-rings were used in the buret because the usual Viton O-rings are not suitable for use with acetone. The acetone-filled buret was stored in a cylindrical desiccator containing Drierite and was maintained at 25° by suspending the desiccator in a thermostatted temperature bath. (The temperature of the auxiliary bath was controlled in the same manner as described above for the main bath.)

Vapor Density - Isothermal Volumetric Addition Method

Vapor pressures and vapor density studies involving accurate volumetric additions of liquids to a system with a microburet have often

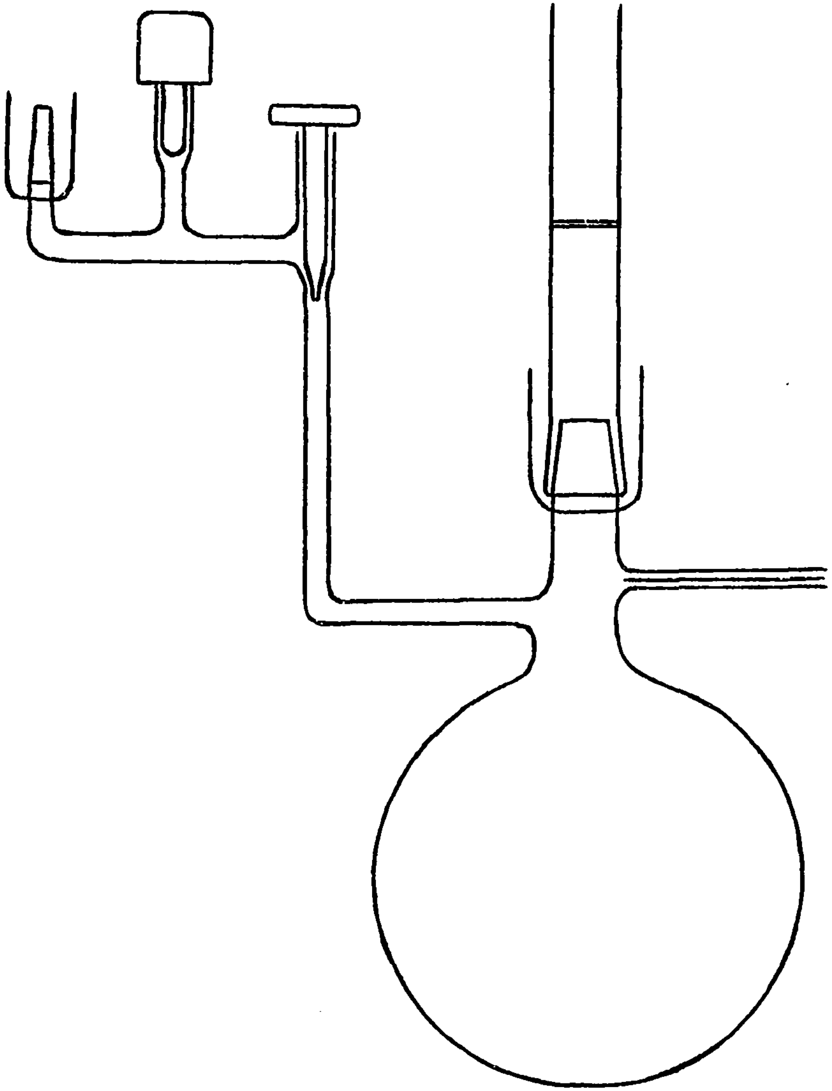


Figure I-3. Vapor Density Apparatus

been employed in this laboratory.[64-67] These techniques provide a convenient and direct method for acquiring information about molecular association in the gas phase and in solution. In the present studies the hydrogen bonding of acetone with HCl, DCl, CF_3CH_2OH, and CF_3CH_2OD was investigated in the vapor phase.

Before acetone and the hydrogen donors were mixed, calibration runs using acetone alone were required. Increments of liquid acetone (0.01 - 0.03 ml) were delivered to the previously evacuated system through the mercury-covered disc with the micrometer buret. The liquid evaporated through the disc very quickly, but a period of 10-15 minutes was allowed to elapse before the pressure was recorded. In this way, the system should be essentially at equilibrium (with respect to acetone self-association and adsorption). The addition process was repeated seven to ten times.

Data from several of these calibration runs were processed simultaneously. The measured pressure was fit as a quadratic function of liquid volume added. The resulting curve could then be used to predict acetone pressure when a known volume of liquid acetone was added. Such a calibration curve together with an assumed dimerization constant (see Chapter III) made it unnecessary to know the exact system volume or to accurately calibrate the microburet. Furthermore, this procedure should minimize errors due to acetone adsorption in isothermal experiments. The amount of air dissolved in the acetone should be of negligible significance. Calculations using Ostwald coefficients[68] indicate that the acetone contains less than 0.5 moles of air per thousand moles of acetone.

In order to study the intermolecular hydrogen bonding of acetone, increments were added, in a procedure exactly as described above, to the system in which a known pressure of hydrogen donor was present. The donors were introduced in several different ways.

TFE and TFE-d were placed in a reservoir outside the thermostatted bath and were introduced into the system, after degassing, through a 10/30 ground glass joint (see Figure I-3). The alcohol pressure which could be used varied with temperature because of azeotrope formation with acetone. The composition of the azeotrope was approximately 0.25 mole fraction acetone, and it occurred at a total pressure of $\sim$32 torr at 15°, $\sim$58 torr at 25°, and $\sim$100 torr at 35°. In the vapor density studies, regions of composition and pressure were chosen in which azeotrope formation was avoided.

It had been hoped that studies at 15° could be done with the alcohol-acetone systems, so that the work by Tucker and Christian[69] on TFE-acetone could be extended to lower temperatures. Unfortunately, the limit on pressures caused by azeotrope formation proved to be severe, and not enough hydrogen-bonded complex was formed at 15° to permit a precise determination of equilibrium constants. Thus, measurements were made on the TFE-acetone and TFE-d-acetone systems at 25°, 35°, and 45°.

In the initial work with HCl, a lecture bottle of electronic grade HCl, fitted with a Monel needle valve, was used as the source of the acid. HCl was bubbled into the system through the mercury-covered disc using Tygon tubing and a disposable pipet. The needle valve required frequent cleaning because of corrosion by the HCl. Eventually, the tank-top valve corroded, and the use of HCl from this source was discontinued. HCl from the lecture bottle was employed in all of the 25° work and in portions of the 15° studies (indicated by formal HCl pressures of ∿200 torr).

In all other studies involving HCl and DCl, the source of the acid was a concentrated (∿38% by weight) aqueous solution. Approximately 10 ml of the solution was placed in a reservoir and degassed thoroughly. (Freezing had to be done carefully because of expansion by the solution.) The contents of this first reservoir were held at about -23° with a Dry Ice-CCl_4 bath and connected (through a stainless steel Cajon Ultra-torr tube fitting) to a second reservoir, which was evacuated and held at -196° with liquid nitrogen. Stopcocks between the two reservoirs were opened for 15-20 minutes, and the vapor passing into the second was frozen.

The material collected in this second reservoir (which should be enriched in acid) was then warmed to approximately -55° using a bath containing cold $CHCl_3$. This reservoir was the same as that used for TFE and was connected to the system through a ground glass joint sealed with mercury. Upon opening the reservoir to the system, acid pressures of up to ∿100 torr were obtained. Frequently, the above procedure had to be repeated in order to get sufficient acid in the system. The vapor pressure of ice at -55° is ∿15μ, so that very little water vapor should have been mixed with the HCl or DCl. Pressure measurements of acetone complexing with HCl and DCl were made at 15°, 25°, and 34.91°.

Vapor Density - Variable Temperature Studies

In addition to the isothermal studies described above, a somewhat different type of study was also carried out for the same hydrogen-bonding systems. Instead of measuring pressure as the amounts of material were varied, the amount of material was kept constant, and pressure was measured as a function of temperature. The experimental runs began at a fixed temperature (usually 25°) at which a known pressure of hydrogen donor was introduced. Then a measured volume of acetone was added with the micrometer buret.

For the HCl-acetone and DCl-acetone systems the following procedure was generally followed. The system was cooled to 12.5° or lower and equilibration was allowed to occur for 1-2 hours. Then the temperature was raised from 12.5° to 35.0° in 2.5° increments, with the light bulbs in the bath being augmented by a 500 W heating coil. The length of time necessary to effect these 2.5° changes depended on the rate at which the bath was cooled by the chilled water and/or the surroundings. The changes normally took 10-15 minutes, after which 15-20 minutes was allowed for equilibration; thus, readings were taken about every thirty minutes.

There was apparently a slow irreversible reaction between the acid and the acetone which may have had a slight effect on the precision of this work. When acetone, HCl, or DCl was in the system separately at constant temperature, the pressure remained constant once the adsorption process had come to equilibrium. However, the mixed systems showed a slow but continuous decrease in pressure of $\sim$0.002 torr per hour. Such small changes should not seriously affect the results of these studies, since their duration was normally less than 10 hours. (The isothermal experiments would have been affected even less because of the shorter length of those studies.)

Azeotrope formation restricted the pressures which could be used with the TFE-acetone and TFE-d-acetone systems. The temperature range studied was 25.0°-47.5°, so that the total pressure was limited to approximately 60 torr. The hydrogen donor and acceptor were introduced at 25°, and temperature increments of 2.5° were begun once the system had reached equilibrium (after 1-2 hours). Temperature and pressure measurements were made in the same manner as described above for the HCl and DCl systems. There was no evidence of a reaction between the components.

CHAPTER III

DATA TREATMENT AND RESULTS

Isothermal Studies

When acetone vapor is the only component present in the system, its nonideality is accounted for by assuming dimerization of the acetone molecules. Thus, the acetone pressure predicted for a given volume of acetone added to the system ($P_{B,pred}$) is estimated from the calibration curve described in the preceding chapter and is used in the following manner:

$$P_{B,pred} = P_B^{\S} + P_{B_2}^{\S}$$

$P_B^{\S}$ and $P_{B_2}^{\S}$ are the pressures of acetone monomer and dimer in the absence of hydrogen donors. (Unmarked symbols will be used later to indicate monomer and dimer pressures in mixed systems.) It follows that

$$P_{B,pred} = P_B^{\S} + K_2(P_B^{\S})^2 \qquad \text{(I-4)}$$

where K_2 is the vapor phase dimerization constant for acetone, defined as

$$K_2 = \frac{P_{B_2}^{\S}}{(P_B^{\S})^2} = \frac{P_{B_2}}{(P_B)^2}$$

If K_2 is known, equation I-4 can be solved for $P_B^{\S}$, which is used to calculate the formal or ideal gas pressure of acetone (π_B),

$$\pi_B = P_B^{\S} + 2P_{B_2}^{\S}$$

or $$\pi_B = P_B^{\S} + 2K_2(P_B^{\S})^2 \qquad (\text{I-5})$$

The dimerization constants employed in this work are derived from studies by Lambert et al.[70] and are listed here.

$K_2 = 1.20 \times 10^{-4}$ torr^{-1} at 15°

$K_2 = 1.05 \times 10^{-4}$ torr^{-1} at 25°

$K_2 = 0.93 \times 10^{-4}$ torr^{-1} at 35°

$K_2 = 0.83 \times 10^{-4}$ torr^{-1} at 45°

The correction for dimerization proves to be quite small. For example, the maximum amount of acetone dimer present in any of the studies is estimated to be ∿0.3 torr. This particular dimer pressure corresponds to a formal acetone pressure of 51.5 torr and, therefore, to less than a 1% deviation between ideal behavior and observed behavior. Furthermore, it is found that the calculated 1:1 hydrogen donor - acetone association constants for the systems studied are relatively insensitive to changes in the dimerization constants. For this reason, the data from Lambert et al. are judged to be adequate. (For other virial coefficient studies on acetone, see the compilation of data by Dymond and Smith.[71])

HCl vapor and TFE vapor are assumed to be ideal gases over the temperature and pressure ranges involved in this study. Estimates using the van der Waals' constant for HCl[72] and previous work in this laboratory on TFE[73] show that maximum deviations from ideality will be less than 0.2%. The effect of this nonideality on the final 1:1 association constant is insignificant.

The formal pressure of acetone in a mixture with a hydrogen donor is expressed as

$$\pi_B = P_B + 2P_{B_2} + P_{AB}$$

where P_{AB} is the pressure of the acid-base complex. Expressing π_B in terms of the association constants gives

$$\pi_B = P_B + 2K_2P_B^2 + KP_AP_B \qquad \text{(I-6)}$$

P_A is the pressure of uncomplexed acid; K is the acetone - hydrogen donor association constant, defined as

$$K = \frac{P_{AB}}{P_A\,P_B}$$

π_B is estimated from equation I-5 for a given volume of acetone added. Then, equation I-6 can be used to calculate P_B if all of the other quantities are known. Unfortunately, it is not possible to do this directly, since the value of P_A is linked to that of P_B,

$$P_A = \frac{\pi_A}{1 + KP_B} \qquad \text{(I-7)}$$

π_A, the formal acid pressure, is given by

$$\pi_A = P_A + P_{AB}$$

π_A is taken to be the initial acid pressure (before any acetone is added); any self-association of the acid is ignored. Therefore, an iterative procedure must be used to calculate P_A and P_B for given values of π_A, π_B, K, and K_2.

The total pressure of the mixed system is given by

$$P_{tot} = P_A + P_B + P_{B_2} + P_{AB}$$

or

$$P_{tot} = P_A + P_B + K_2 P_B^2 + K P_A P_B \qquad \text{(I-8)}$$

A K value is needed which will minimize deviations between the measured pressures and P_{tot} values calculated from equation I-8. An initial estimate of K is used to calculate P_B and P_A from equations I-6 and I-7. These values are then used to calculate P_{tot} in equation I-8. Further optimization is carried out with the Enwall modification of a nonlinear least squares routine by Marquardt.[74] The root-mean-square deviation in P_{tot} is minimized,

$$\text{RMSD} = \left\{ \frac{\Sigma(P_{tot} - P_{tot}^{calc})^2}{N - 1} \right\}^{\frac{1}{2}}$$

where N is the number of data points.

There appear to be no systematic variations in the residuals $(P_{tot} - P_{tot}^{calc})$ which would indicate the presence of significant quantities of 2:1 acid-acetone complex. Attempts to calculate 2:1 equilibrium constants lead to results which are not physically or statistically meaningful.

The enthalpy and entropy changes for the association reactions are determined from the following expression:

$$- RT \ln K = \Delta G° = \Delta H° - T \Delta S°$$

or

$$R \ln K = - \frac{\Delta H°}{T} + \Delta S°$$

where K, the equilibrium constant, is in units of torr^{-1}. We assume that the error introduced by replacing activities with pressures in the expression for K is negligible and that ΔH° and ΔS° are invariant over the temperature ranges involved. A weighted linear least squares program is used to calculate -ΔH° and ΔS° as the slope and intercept of the R ℓn K vs. 1/T line. Plots of these lines for the systems studied are shown in Figures I-4 and I-5.

Since standard energy changes are useful in studying solvent effects on complex formation, ΔE° values have also been calculated. These values can be derived by expressing the equilibrium constants in concentration units and calculating the following derivative:

$$\Delta E^\circ = -R \left(\frac{\partial \ln K_c}{\partial (1/T)} \right)$$

The derived equilibrium constants, their standard errors, and the RMSD's for the fits are given in Tables I-1 to I-4. Standard energy, enthalpy, and entropy changes are included. Experimental data for these systems are given in Tables I-5 through I-16 (all pressures are in torr). The values for the pressure of the 1:1 complex are calculated using the optimum K values,

$$P_{AB} = K P_A P_B$$

TABLE I-1

Summary of Results for the HCl-Acetone System

15° $K = (4.83 \pm 0.02) \times 10^{-4}\ \mathrm{torr}^{-1}$ RMSD = 88 μ

25° $K = (3.50 \pm 0.03) \times 10^{-4}\ \mathrm{torr}^{-1}$ RMSD = 92 μ

34.91° $K = (2.58 \pm 0.04) \times 10^{-4}\ \mathrm{torr}^{-1}$ RMSD = 57 μ

$-\Delta H^\circ = 5.55 \pm 0.03$ kcal/mole

$-\Delta S^\circ = 34.4 \pm 0.1$ eu/mole

$-\Delta E^\circ = 4.96 \pm 0.03$ kcal/mole

TABLE I-2

Summary of Results for the DCl-Acetone System

15° $K = (5.08 \pm 0.05) \times 10^{-4}\ \mathrm{torr}^{-1}$ RMSD = 61 μ

25° $K = (3.81 \pm 0.03) \times 10^{-4}\ \mathrm{torr}^{-1}$ RMSD = 52 μ

34.91° $K = (2.69 \pm 0.03) \times 10^{-4}\ \mathrm{torr}^{-1}$ RMSD = 55 μ

$-\Delta H^\circ = 5.52 \pm 0.48$ kcal/mole

$-\Delta S^\circ = 34.2 \pm 1.6$ eu/mole

$-\Delta E^\circ = 4.93 \pm 0.48$ kcal/mole

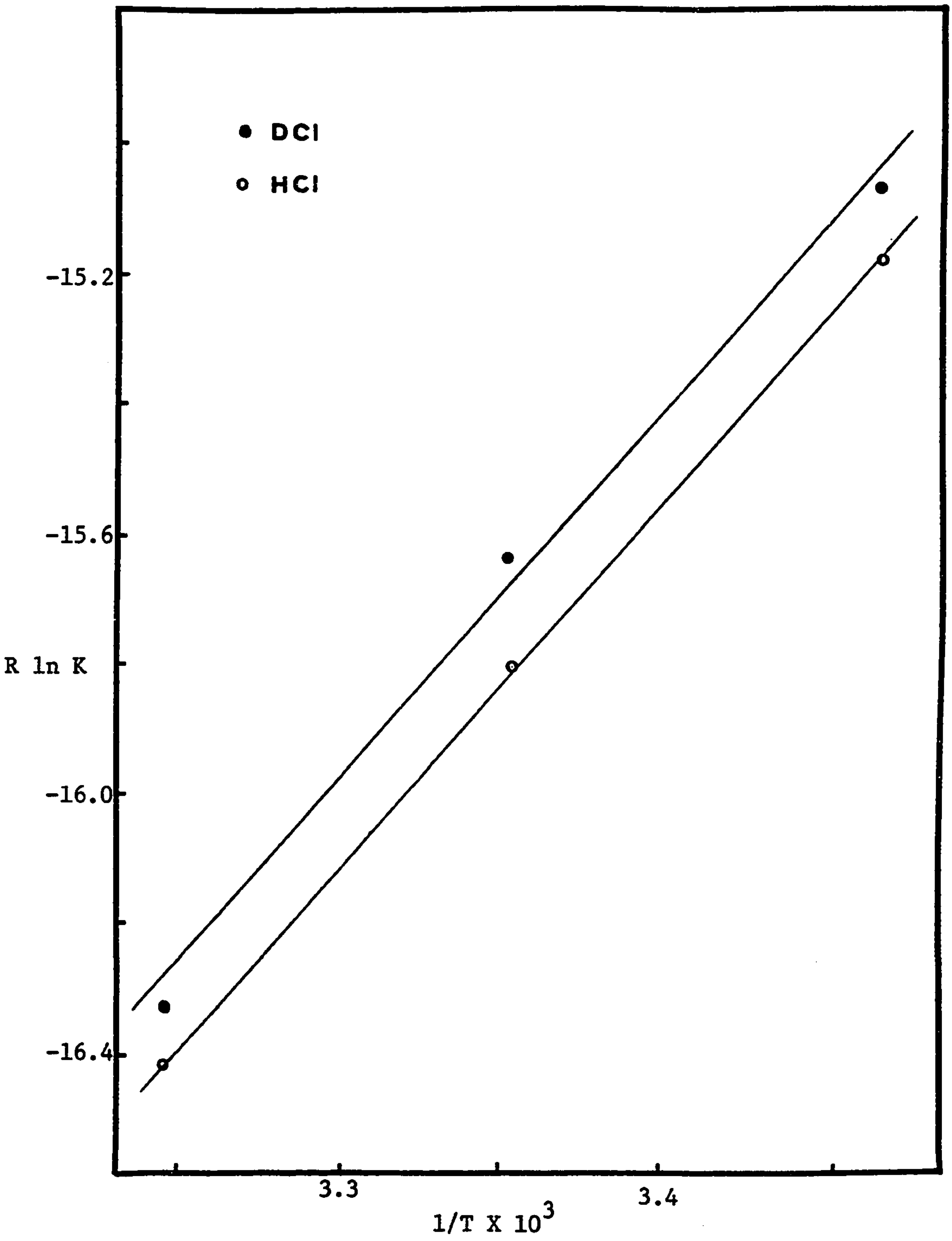


Figure I-4. Van't Hoff Plots for the Vapor Phase Association of Acetone with HCl and DCl

TABLE I-3

Summary of Results for the TFE - Acetone System

25° $K = (2.56 \pm 0.02) \times 10^{-3}$ torr^{-1} RMSD = 67 μ

35° $K = (1.78 \pm 0.01) \times 10^{-3}$ torr^{-1} RMSD = 65 μ

45° $K = (1.25 \pm 0.01) \times 10^{-3}$ torr^{-1} RMSD = 73 μ

$-\Delta H^\circ = 6.77 \pm 0.08$ kcal/mole

$-\Delta S^\circ = 34.6 \pm 0.3$ eu/mole

$-\Delta E^\circ = 6.16 \pm 0.07$ kcal/mole

TABLE I-4

Summary of Results for the TFE-d - Acetone System

25° $K = (2.57 \pm 0.02) \times 10^{-3}$ torr^{-1} RMSD = 59 μ

35° $K = (1.888 \pm 0.005) \times 10^{-3}$ torr^{-1} RMSD = 38 μ

45° $K = (1.352 \pm 0.005) \times 10^{-3}$ torr^{-1} RMSD = 39 μ

$-\Delta H^\circ = 6.28 \pm 0.31$ kcal/mole

$-\Delta S^\circ = 32.9 \pm 1.0$ eu/mole

$-\Delta E^\circ = 5.67 \pm 0.30$ kcal/mole

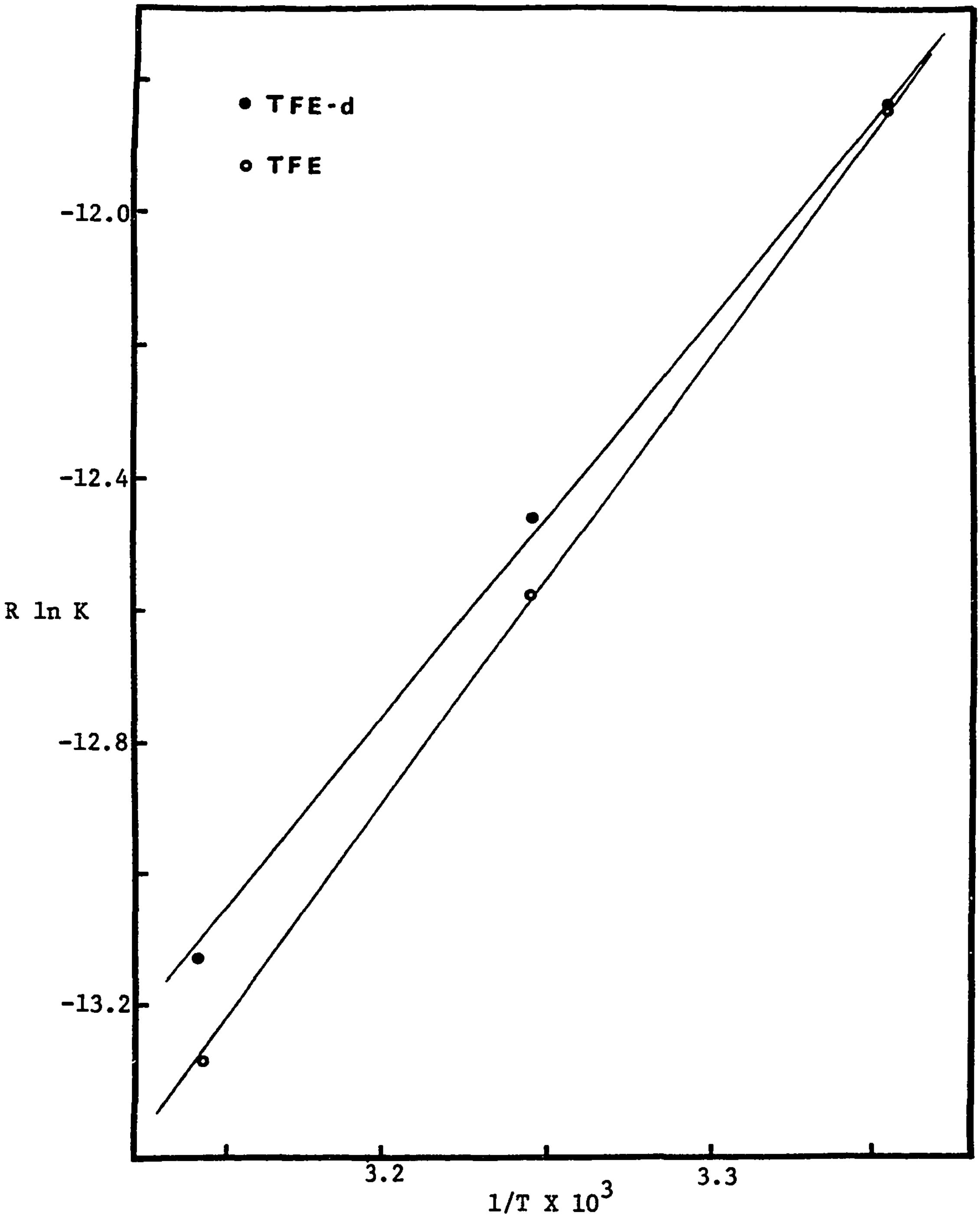


Figure I-5. Van't Hoff Plots for the Vapor Phase Association of Acetone with TFE and TFE-d

TABLE I-5

Vapor Density Data for HCl - Acetone at 15°

π_B	π_A	P_{tot}	P^{calc}_{tot}	P_{AB}
7.377	193.408	200.225	200.152	0.628
14.818	193.408	207.072	206.948	1.256
22.296	193.408	213.857	213.773	1.881
29.724	193.408	220.545	220.547	2.496
36.805	193.408	226.923	227.000	3.078
44.454	193.408	233.799	233.965	3.701
51.513	193.408	240.195	240.388	4.271
7.083	196.650	203.215	203.116	0.612
13.952	196.650	209.521	209.383	1.201
21.092	196.650	216.046	215.891	1.808
28.130	196.650	222.404	222.301	2.401
35.286	196.650	228.856	228.814	2.999
42.429	196.650	235.273	235.311	3.591
49.695	196.650	241.804	241.914	4.188
7.257	193.923	200.645	200.556	0.619
14.210	193.923	207.039	206.906	1.207
21.149	193.923	213.355	213.238	1.790
28.207	193.923	219.757	219.674	2.377
35.165	193.923	226.053	226.015	2.951
42.102	193.923	232.299	232.331	3.519
49.182	193.923	238.614	238.773	4.093
7.021	183.578	190.081	190.025	0.570
14.116	183.578	196.585	196.533	1.141
21.083	183.578	202.968	202.920	1.696
28.211	183.578	209.501	209.449	2.260
35.387	183.578	216.050	216.016	2.823
42.620	183.578	222.603	222.632	3.386
49.932	183.578	229.227	229.313	3.949
6.960	196.505	202.912	202.859	0.601
14.223	196.505	209.631	209.485	1.223
21.035	196.505	215.826	215.694	1.802
28.008	196.505	222.125	222.046	2.389
34.849	196.505	228.305	228.273	2.961
41.682	196.505	234.440	234.489	3.527
49.026	196.505	241.044	241.164	4.131
6.749	186.757	192.992	192.945	0.556
14.029	186.757	199.692	199.614	1.152
21.175	186.757	206.274	206.156	1.731
28.430	186.757	212.940	212.793	2.314
35.650	186.757	219.507	219.391	2.889
42.845	186.757	226.019	225.962	3.457
49.627	186.757	232.132	232.151	3.989
6.670	187.337	193.501	193.451	0.552
13.489	187.337	199.767	199.697	1.111

TABLE I-5 (continued)

π_B	π_A	P_{tot}	P^{calc}_{tot}	P_{AB}
20.582	187.337	206.292	206.189	1.688
27.615	187.337	212.728	212.622	2.255
34.487	187.337	218.952	218.901	2.805
41.616	187.337	225.416	225.411	3.370
48.366	187.337	231.497	231.570	3.901
6.681	190.662	196.847	196.777	0.561
13.487	190.662	203.089	203.002	1.129
20.495	190.662	209.509	209.406	1.708
27.324	190.662	215.737	215.643	2.268
34.296	190.662	222.046	222.006	2.835
41.267	190.662	228.327	228.363	3.397
48.133	190.662	234.481	234.619	3.946
7.155	189.962	196.596	196.513	0.599
14.077	189.962	202.942	202.846	1.174
20.825	189.962	209.085	209.015	1.729
27.703	189.962	215.329	215.298	2.291
34.750	189.962	221.709	221.731	2.863
41.590	189.962	227.876	227.969	3.412
48.447	189.962	234.020	234.219	3.958
7.272	190.434	197.170	197.090	0.610
14.405	190.434	203.718	203.614	1.204
21.652	190.434	210.357	210.238	1.801
28.748	190.434	216.818	216.718	2.382
35.894	190.434	223.261	223.238	2.961
43.027	190.434	229.696	229.743	3.534
49.825	190.434	235.799	235.937	4.077
6.899	83.243	89.888	89.872	0.266
13.730	83.243	96.457	96.426	0.526
20.615	83.243	103.085	103.025	0.787
27.458	83.243	109.615	109.575	1.043
34.281	83.243	116.132	116.099	1.296
41.146	83.243	122.636	122.656	1.549
48.005	83.243	129.130	129.199	1.799
6.716	98.858	105.328	105.264	0.305
13.494	98.858	111.801	111.722	0.610
20.339	98.858	118.352	118.237	0.915
27.175	98.858	124.836	124.736	1.218
34.004	98.858	131.279	131.221	1.517
40.812	98.858	137.673	137.679	1.813
47.688	98.858	144.123	114.194	2.109
6.945	77.011	83.756	83.702	0.248
13.771	77.011	90.314	90.271	0.490
20.549	77.011	96.823	96.786	0.727
27.350	77.011	103.348	103.315	0.964
34.182	77.011	109.877	109.865	1.199
41.049	77.011	116.434	116.442	1.434

TABLE I-6

Vapor Density Data for HCl - Acetone at 25°

π_B	π_A	P_{tot}	P^{calc}_{tot}	P_{AB}
6.794	102.649	109.266	109.203	0.235
13.605	102.649	115.857	115.767	0.468
21.130	102.649	123.123	123.011	0.725
28.554	102.649	130.275	130.148	0.976
36.232	102.649	137.623	137.521	1.233
44.309	102.649	145.303	145.267	1.502
52.411	102.649	153.010	153.027	1.769
6.783	103.311	109.929	109.854	0.236
13.748	103.311	116.677	116.565	0.476
20.563	103.311	123.246	123.123	0.710
27.809	103.311	130.248	130.089	0.956
35.763	103.311	137.845	137.726	1.225
43.235	103.311	144.972	144.890	1.475
51.088	103.311	152.441	152.412	1.736
6.785	103.657	110.269	110.201	0.237
13.981	103.657	117.245	117.133	0.486
20.790	103.657	123.805	123.685	0.720
27.597	103.657	130.361	130.228	0.952
34.504	103.657	136.951	136.860	1.186
41.529	103.657	143.648	143.596	1.423
48.795	103.657	150.536	150.557	1.666
7.061	123.054	129.911	129.820	0.290
14.144	123.054	136.737	136.600	0.580
21.262	123.054	143.510	143.405	0.868
28.409	123.054	150.314	150.230	1.156
35.716	123.054	157.245	157.200	1.448
42.860	123.054	163.999	164.008	1.731
7.258	112.738	119.751	119.716	0.274
14.557	112.738	126.831	126.726	0.548
21.861	112.738	133.862	133.733	0.820
29.239	112.738	140.899	140.802	1.093
36.494	112.738	147.803	147.745	1.359
43.803	112.738	154.761	154.731	1.626
51.212	112.738	161.746	161.806	1.894
6.583	205.798	212.223	212.188	0.459
13.911	205.798	218.812	218.763	0.928
20.778	205.798	225.189	225.155	1.382
27.695	205.798	231.578	231.588	1.836
34.709	205.798	238.023	238.105	2.293
41.727	205.798	244.423	244.620	2.747
7.124	190.240	196.946	196.916	0.443
14.493	190.240	203.870	203.816	0.898
22.134	190.240	210.976	210.962	1.367

TABLE I-6 (continued)

π_B	π_A	P_{tot}	P_{tot}^{calc}	P_{AB}
29.480	190.240	217.774	217.827	1.814
36.859	190.240	224.608	224.715	2.260
44.410	190.240	231.569	231.757	2.713
7.140	202.469	209.183	209.133	0.471
14.378	202.469	215.958	215.883	0.945
21.625	202.469	222.673	222.636	1.416
28.893	202.469	229.387	229.401	1.885
36.153	202.469	236.063	236.153	2.351
43.396	202.469	242.697	242.883	2.812
7.061	205.651	212.278	212.235	0.472
14.496	205.651	219.254	219.162	0.966
21.798	205.651	226.068	225.958	1.448
29.082	205.651	232.787	232.732	1.925
36.438	205.651	239.570	239.565	2.404
43.882	205.651	246.430	246.476	2.884
51.214	205.651	253.145	253.274	3.355

TABLE I-7

Vapor Density Data for HCl - Acetone at 34.91°

π_B	π_A	P_{tot}	P_{tot}^{calc}	P_{AB}
7.218	76.008	83.064	83.083	0.138
14.422	76.008	90.096	90.136	0.275
21.688	76.008	97.191	97.241	0.413
28.890	76.008	104.232	104.276	0.548
36.206	76.008	111.385	111.413	0.685
43.437	76.008	118.430	118.459	0.819
50.866	76.008	125.604	125.690	0.956
7.035	77.091	84.050	83.985	0.137
14.209	77.091	91.076	91.007	0.275
21.301	77.091	97.993	97.940	0.411
28.582	77.091	105.074	105.051	0.550
35.717	77.091	112.056	112.009	0.685
42.789	77.091	118.971	118.900	0.818
49.881	77.091	125.820	125.810	0.951
7.347	78.210	85.348	85.407	0.145
14.640	78.210	92.422	92.544	0.287
22.114	78.210	99.771	99.849	0.433
29.414	78.210	106.900	106.974	0.574
36.667	78.210	113.983	114.045	0.713
44.113	78.210	121.267	121.296	0.855
51.387	78.210	128.299	128.372	0.993
7.421	84.808	92.036	92.067	0.158
14.736	84.808	99.238	99.212	0.313
21.983	84.808	106.331	106.283	0.466
29.266	84.808	113.423	113.381	0.618
36.446	84.808	120.426	120.370	0.767
43.776	84.808	127.582	127.497	0.919
51.052	84.808	134.644	134.564	1.068
7.059	87.228	94.140	94.128	0.155
14.289	87.228	101.207	101.186	0.312
21.650	87.228	108.429	108.365	0.471
29.024	87.228	115.608	115.548	0.630
36.446	87.228	122.770	122.768	0.787
43.734	87.228	129.846	129.850	0.944
50.968	87.228	136.819	136.871	1.096

TABLE I-8

Vapor Density Data for DCl - Acetone at 15°

π_B	π_A	P_{tot}	P_{tot}^{calc}	P_{AB}
6.875	92.010	98.576	98.574	0.306
13.992	92.010	105.434	105.361	0.619
20.961	92.010	112.105	112.000	0.923
27.830	92.010	118.652	118.537	1.220
34.715	92.010	125.171	125.081	1.514
41.651	92.010	131.705	131.666	1.809
48.577	92.010	138.206	138.234	2.100
6.766	72.469	74.046	78.991	0.239
13.668	72.469	85.690	85.636	0.481
20.468	72.469	92.222	92.174	0.717
27.276	72.469	98.773	98.712	0.950
34.215	72.469	105.448	105.368	1.187
41.027	72.469	111.972	111.895	1.416
47.864	72.469	118.501	118.438	1.645
6.941	83.666	90.341	90.320	0.282
13.764	83.666	96.859	96.854	0.556
20.560	83.666	103.343	103.354	0.827
27.545	83.666	109.984	110.027	1.102
34.417	83.666	116.524	116.584	1.371
41.243	83.666	123.002	123.089	1.635
48.089	83.666	129.458	129.607	1.898
6.790	87.291	93.798	93.789	0.287
13.631	87.291	100.355	100.328	0.573
20.451	87.291	106.858	106.840	0.856
27.249	87.291	113.311	113.323	1.136
34.123	87.291	119.851	119.871	1.416
41.247	87.291	126.608	126.651	1.703
48.146	87.291	133.120	133.208	1.979
6.585	83.448	89.744	89.761	0.267
13.183	83.448	96.075	96.080	0.531
19.786	83.448	102.420	102.397	0.794
26.399	83.448	108.756	108.716	1.054
33.019	83.448	115.066	115.035	1.313
39.652	83.448	121.344	121.359	1.570
46.278	83.448	127.594	127.670	1.824

TABLE I-9

Vapor Density Data for DCl - Acetone at 25°

π_B	π_A	P_{tot}	P^{calc}_{tot}	P_{AB}
6.991	102.469	109.229	109.193	0.262
14.060	102.469	116.056	115.986	0.524
21.092	102.469	122.790	122.734	0.784
28.236	102.469	129.644	129.583	1.045
35.429	102.469	136.530	136.471	1.306
42.423	102.469	143.165	143.161	1.558
49.494	102.469	149.861	149.917	1.811
6.844	108.297	114.896	114.866	0.270
13.714	108.297	121.531	121.453	0.540
20.590	108.297	128.121	128.039	0.807
27.484	108.297	134.702	134.635	1.073
34.365	108.297	141.216	141.212	1.337
41.251	108.297	147.741	147.785	1.599
48.148	108.297	154.289	154.364	1.860
6.850	95.577	102.172	102.183	0.240
13.689	95.577	108.790	108.770	0.477
20.556	95.577	115.408	115.377	0.714
27.422	95.577	122.006	121.977	0.949
34.299	95.577	128.576	128.579	1.183
41.175	95.577	135.118	135.173	1.415
48.073	95.577	141.660	141.781	1.646
6.812	87.577	94.174	94.165	0.219
13.646	87.577	100.796	100.767	0.437
20.497	87.577	107.405	107.378	0.655
27.357	87.577	114.025	113.990	0.870
34.217	87.577	120.658	120.596	1.085
41.104	87.577	127.282	127.220	1.298
47.998	87.577	133.860	133.842	1.510
6.839	91.298	97.876	97.904	0.229
13.693	91.298	104.503	104.516	0.457
20.565	91.298	111.142	111.138	0.684
27.425	91.298	117.775	117.741	0.908
34.306	91.298	124.381	124.358	1.132
41.184	91.298	130.946	130.965	1.354
48.103	91.298	137.498	137.602	1.576

TABLE I-10

Vapor Density Data for DCl - Acetone at 34.91°

π_B	π_A	P_{tot}	P_{tot}^{calc}	P_{AB}
7.515	82.194	89.551	89.541	0.162
14.668	82.194	96.555	96.527	0.316
21.978	82.194	103.716	103.658	0.471
29.254	82.194	110.808	110.746	0.626
36.643	82.194	118.025	117.937	0.781
44.044	82.194	125.215	125.131	0.936
51.336	82.194	132.243	132.210	1.087
7.176	73.526	80.597	80.558	0.139
14.434	73.526	87.680	87.662	0.278
21.767	73.526	94.841	94.832	0.419
28.900	73.526	101.815	101.797	0.554
36.015	73.526	108.788	108.738	9.688
43.376	73.526	115.950	115.909	0.827
50.652	73.526	122.995	122.989	0.962
7.201	110.328	117.389	117.318	0.207
14.328	110.328	124.307	124.228	0.411
21.559	110.328	131.283	131.230	0.616
28.749	110.328	138.205	138.186	0.819
36.133	110.328	145.331	145.321	1.027
43.618	110.328	152.506	152.546	1.236
50.913	110.328	159.439	159.579	1.438
7.248	88.495	95.601	95.570	0.168
14.427	88.495	102.622	102.570	0.334
21.474	88.495	109.476	109.433	0.495
28.747	88.495	116.495	116.506	0.661
35.924	88.495	123.433	123.482	0.823
43.192	88.495	130.500	130.537	0.987
50.314	88.495	137.355	137.442	1.146
7.187	122.818	129.816	129.771	0.229
14.506	122.818	136.921	136.844	0.462
21.760	122.818	143.880	143.847	0.690
29.036	122.818	150.870	150.862	0.918
36.307	122.818	157.882	157.866	1.145
43.675	122.818	164.947	164.955	1.373
50.862	122.818	171.761	171.863	1.594

TABLE I-11

Vapor Density Data for TFE - Acetone at 25°

π_B	π_A	P_{tot}	P_{tot}^{calc}	P_{AB}
4.306	25.559	35.110	35.189	0.316
8.549	25.559	39.036	39.123	0.620
12.742	25.559	42.919	43.012	0.916
17.092	25.559	46.952	47.050	1.216
21.330	25.559	50.904	50.986	1.503
25.628	25.559	54.878	54.981	1.788
30.013	25.559	58.911	59.059	2.074
4.276	30.123	34.086	34.094	0.303
8.613	30.123	38.148	38.124	0.605
12.921	30.123	42.177	42.131	0.898
17.271	30.123	46.200	46.179	1.189
21.557	30.123	50.197	50.169	1.469
25.846	30.123	54.161	54.164	1.744
30.106	30.123	58.113	58.135	2.012
4.508	25.678	29.928	29.909	0.275
9.180	25.678	34.276	34.296	0.554
13.727	25.678	38.588	38.568	0.820
18.177	25.678	42.765	42.750	1.075
22.740	25.678	47.030	47.040	1.330
27.257	25.678	51.273	51.288	1.578
31.892	25.678	55.580	55.650	1.827
4.660	30.370	34.727	34.695	0.333
9.058	30.370	38.877	38.780	0.640
13.432	30.370	42.964	42.846	0.940
17.819	30.370	47.065	46.926	1.234
22.186	30.370	51.140	50.990	1.521
26.307	30.370	54.932	54.827	1.787
30.558	30.370	58.833	58.788	2.056
4.639	32.924	37.206	37.204	0.357
8.894	32.924	41.183	41.133	0.678
13.248	32.924	45.228	45.156	1.000
17.916	32.924	49.496	49.474	1.338
22.634	32.924	53.848	53.840	1.672
27.345	32.924	58.133	58.204	1.998
6.992	30.923	37.422	37.406	0.505
10.533	30.923	40.716	40.692	0.755
14.018	30.923	43.955	43.927	0.996
17.532	30.923	47.219	47.192	1.236
21.159	30.923	50.591	50.563	1.479
24.708	30.923	53.867	53.862	1.713
28.236	30.923	57.112	57.145	1.942

TABLE I-12

Vapor Density Data for TFE - Acetone at 35°

π_B	π_A	P_{tot}	P_{tot}^{calc}	P_{AB}
6.992	41.882	48.431	48.391	0.479
14.081	41.882	55.028	54.993	0.954
21.173	41.882	61.597	61.601	1.418
28.247	41.882	68.151	68.195	1.870
35.368	41.882	74.780	74.836	2.314
42.420	41.882	81.386	81.413	2.744
49.605	41.882	88.025	88.117	3.172
7.069	46.600	53.182	53.130	0.535
14.184	46.600	59.798	59.707	1.061
21.297	46.600	66.373	66.286	1.575
28.430	46.600	72.976	72.887	2.078
35.446	46.600	79.459	79.384	2.562
42.589	46.600	86.057	86.001	3.044
49.723	46.600	92.626	92.613	3.514
7.206	37.235	44.054	43.994	0.442
14.391	37.235	50.829	50.736	0.873
21.474	37.235	57.487	57.384	1.287
28.754	37.235	64.259	64.219	1.703
35.939	37.235	70.951	70.966	2.103
43.150	37.235	77.734	77.738	2.495
50.350	37.235	84.479	84.501	2.878
7.008	40.948	47.538	47.482	0.471
14.060	40.948	54.154	54.059	0.933
21.105	40.948	60.735	60.633	1.384
28.195	40.948	67.292	67.252	1.827
35.183	40.948	73.767	73.776	2.254
42.257	40.948	80.343	80.385	2.677
49.375	40.948	86.918	87.034	3.092
7.203	44.237	50.989	50.917	0.519
14.337	44.237	57.631	57.536	1.022
21.753	44.237	64.487	64.422	1.532
29.048	44.237	71.233	71.197	2.021
36.209	44.237	77.873	77.852	2.490
43.378	44.237	84.533	84.516	2.949
50.580	44.237	91.153	91.214	3.400
7.152	40.539	47.291	47.211	0.476
14.447	40.539	54.126	54.020	0.949
21.528	40.539	60.708	60.632	1.397
28.618	40.539	67.286	67.254	1.836
35.678	40.539	73.845	73.852	2.263
42.810	40.539	80.494	80.517	2.684
49.972	40.539	87.185	87.212	3.097
7.194	46.492	53.201	53.138	0.543

TABLE I-12 (continued)

π_B	π_A	P_{tot}	P_{tot}^{calc}	P_{AB}
14.309	46.492	59.788	59.716	1.068
21.455	46.492	66.338	66.327	1.583
28.672	46.492	72.976	73.008	2.091
35.904	46.492	79.665	79.706	2.588
43.005	46.492	86.192	86.285	3.065
50.298	46.492	92.914	93.046	3.544

TABLE I-13

Vapor Density Data for TFE - Acetone at 45°

π_B	π_A	P_{tot}	P_{tot}^{calc}	P_{AB}
7.287	49.844	56.748	56.703	0.424
14.671	49.844	63.645	63.654	0.845
22.129	49.844	70.615	70.674	1.263
29.511	49.844	77.556	77.621	1.670
36.912	49.844	84.555	84.587	2.070
44.360	49.844	91.550	91.595	2.465
51.839	49.844	98.549	98.631	2.855
7.233	47.539	54.385	54.366	0.402
14.498	47.539	61.206	61.223	0.799
21.807	47.539	68.035	68.120	1.191
29.114	47.539	74.925	75.014	1.576
36.406	47.539	81.821	81.894	1.953
43.805	47.539	88.782	88.874	2.329
51.138	47.539	95.643	95.790	2.695
7.389	56.314	63.237	63.217	0.482
14.886	56.314	70.248	70.222	0.962
22.270	56.314	77.163	77.122	1.426
29.783	56.314	84.268	84.143	1.890
37.397	56.314	91.426	91.258	2.351
44.876	56.314	98.339	98.247	2.797
52.320	56.314	105.267	105.204	3.232
7.547	52.063	59.147	59.149	0.457
15.051	52.063	66.212	66.194	0.903
22.511	52.063	73.229	73.198	1.338
29.876	52.063	80.168	80.113	1.760
37.297	52.063	87.174	87.080	2.178
44.747	52.063	94.168	94.073	2.590
52.167	52.063	101.126	101.038	2.993
7.316	47.890	54.750	54.792	0.410
14.732	47.890	61.723	61.789	0.817
22.068	47.890	68.644	68.709	1.213
29.386	47.890	75.585	75.612	1.601
36.790	47.890	82.609	82.594	1.986
44.126	47.890	89.519	89.511	2.362
51.540	47.890	96.393	96.500	2.734

TABLE I-14

Vapor Density Data for TFE-d - Acetone at 25°

π_B	π_A	P_{tot}	P^{calc}_{tot}	P_{AB}
4.145	33.264	37.065	37.084	0.324
8.268	33.264	40.890	40.886	0.640
12.304	33.264	44.637	44.611	0.943
16.308	33.264	48.339	48.310	1.238
20.417	33.264	52.090	52.107	1.536
24.455	33.264	55.868	55.931	1.830
28.345	33.264	59.333	59.443	2.095
4.397	30.761	34.852	34.837	0.319
8.892	30.761	39.073	39.007	0.639
13.368	30.761	43.228	43.163	0.950
17.828	30.761	47.407	47.306	1.254
21.909	30.761	51.213	51.100	1.527
25.771	30.761	54.783	54.691	1.781
29.793	30.761	58.472	58.434	2.040
4.040	32.906	36.625	36.633	0.313
8.193	32.906	40.465	40.466	0.628
12.456	32.906	44.440	44.404	0.945
16.479	32.906	48.162	48.122	1.238
20.587	32.906	51.906	51.923	1.533
24.682	32.906	55.624	55.714	1.821
28.804	32.906	59.396	59.531	2.105
4.118	32.017	35.842	35.823	0.310
8.213	32.071	39.647	39.611	0.613
12.208	32.017	43.321	43.309	0.903
16.268	32.017	47.089	47.069	1.192
20.442	32.017	50.950	50.937	1.484
24.678	32.017	54.868	54.866	1.775
29.411	32.017	59.168	59.258	2.092
4.210	31.185	35.131	35.084	0.310
8.427	31.185	39.060	38.992	0.614
12.658	31.185	42.979	42.916	0.913
16.953	31.185	46.950	46.902	1.211
21.268	31.185	50.959	50.909	1.504
25.537	31.185	54.883	54.875	1.788
29.752	31.185	58.731	58.794	2.064

TABLE I-15

Vapor Density Data for TFE-d - Acetone at 35°

π_B	π_A	P_{tot}	P_{tot}^{calc}	P_{AB}
6.947	46.130	52.530	52.523	0.550
14.135	46.130	59.152	59.144	1.105
21.175	46.130	65.630	65.634	1.635
28.209	46.130	72.117	72.124	2.153
35.272	46.130	78.655	78.644	2.660
42.377	46.130	85.221	85.207	3.158
49.532	46.130	91.810	91.821	3.648
7.086	49.129	55.603	55.617	0.594
14.274	49.129	62.214	62.205	1.182
21.372	49.129	68.723	68.717	1.749
28.456	49.129	75.244	75.221	2.301
35.514	49.129	81.740	81.707	2.838
42.619	49.129	88.286	88.240	3.366
49.734	49.129	94.762	94.788	3.883
7.109	44.178	50.798	50.743	0.540
14.180	44.178	57.347	57.277	1.065
21.300	44.178	63.908	63.862	1.580
28.345	44.178	70.395	70.382	2.077
35.457	44.178	76.941	76.968	2.568
42.497	44.178	83.468	83.490	3.042
49.589	44.178	90.034	90.064	3.508
7.083	51.180	57.666	57.643	0.616
14.186	51.180	64.145	64.131	1.220
21.262	51.180	70.581	70.601	1.807
28.336	51.180	77.038	77.074	2.380
35.408	51.180	83.518	83.552	2.939
42.490	51.180	89.994	90.044	3.486
49.598	51.180	96.502	96.565	4.023
7.051	46.645	53.156	53.128	0.564
14.262	46.645	59.836	59.764	1.126
21.337	46.645	66.355	66.282	1.664
28.390	46.645	72.848	72.783	2.188
35.486	46.645	79.388	79.328	2.703
42.614	46.645	85.950	85.909	3.208
49.772	46.645	92.503	92.520	3.703
7.107	49.928	56.452	56.427	0.605
14.212	49.928	62.960	62.930	1.195
21.307	49.928	69.444	69.430	1.770
28.392	49.928	75.951	75.928	2.330
35.497	49.928	82.472	82.448	2.879
42.610	49.928	88.964	88.981	3.416
49.730	49.928	95.435	95.525	3.941

TABLE I-16

Vapor Density Data for TFE-d - Acetone at 45°

π_B	π_A	P_{tot}	P_{tot}^{calc}	P_{AB}
7.401	49.157	56.103	56.097	0.457
14.773	49.157	63.041	63.011	0.903
22.131	49.157	69.906	69.912	1.340
29.513	49.157	76.803	76.837	1.770
36.968	49.157	83.827	83.830	2.196
44.369	49.157	90.808	90.773	2.610
51.690	49.157	97.672	97.640	3.013
7.428	55.327	62.198	62.239	0.512
14.810	55.327	69.067	69.110	1.011
22.214	55.327	75.936	76.003	1.502
29.562	55.327	82.798	82.846	1.981
36.910	55.327	89.641	89.689	2.450
44.270	55.327	96.466	96.545	2.911
51.649	55.327	103.355	103.420	3.366
7.382	51.357	58.262	58.260	0.475
14.764	51.357	65.129	65.164	0.940
22.131	51.357	72.065	72.056	1.396
29.545	51.357	79.039	78.992	1.846
37.102	51.357	86.100	86.063	2.296
44.511	51.357	93.000	92.995	2.729
51.882	51.357	99.892	99.894	3.151
7.409	57.238	64.115	64.115	0.527
14.790	57.238	70.938	70.970	1.042
22.289	57.238	77.953	77.936	1.556
29.669	57.238	84.858	84.792	2.052
37.051	57.238	91.734	91.652	2.538
44.423	57.238	98.547	98.504	3.015
51.800	57.238	105.390	105.362	3.484
7.396	51.081	58.002	58.000	0.473
14.773	51.081	64.848	64.902	0.936
22.168	51.081	71.797	71.821	1.391
29.479	51.081	78.680	78.664	1.833
36.803	51.081	85.549	85.518	2.267
44.170	51.081	92.418	92.414	2.695
51.522	51.081	99.279	99.296	3.115

Variable Temperature Studies

The hydrogen donors in the systems studied are assumed to show negligible self-association. Therefore, the formal pressure of an acid at any temperature can be calculated from its pressure at any other temperature. For example, if π_A is measured at 25°C, then the formal pressure at absolute temperature T is given by

$$\pi_{A,T} = \pi_{A,25°C} \left(\frac{T}{298.15}\right)$$

Estimating the formal pressures of acetone at the various temperatures is more difficult because the effects of adsorption and dimerization must be taken into account. Since the calibration curves for acetone addition used in the isothermal studies should include at least some of the effects of adsorption, they are also of use in these experiments. The acetone pressures measured in the calibration runs are fit as a function of temperature and volume of liquid acetone added. It was found that the following function provided a satisfactory fit of the calibration data:

$$P_{B,pred} = a\,v\,T + b\,v^2\,T + c\,v\,T^2$$

$P_{B,pred}$ is the predicted acetone pressure in the absence of hydrogen donor; a, b, and c are fitting parameters; v is the volume of liquid acetone used; and T is the absolute temperature. Using a temperature-dependent dimerization constant from Lambert et al.[70] allows the calculation of π_B from $P_{B,pred}$ at the experimental temperatures; the procedure described at the beginning of this chapter is employed.

Initial estimates of ΔH° and ΔS° for the complexation reaction provide estimates of K as a function of temperature,

$$K_T = \exp\left(-\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}\right)$$

Monomer pressures at each temperature are then calculated via equations I-6 and I-7 with an iterative process. Finally, a nonlinear least squares routine to minimize deviations in P_{tot} (see equation I-8) produces optimum ΔH° and ΔS° values.

Tables I-17 and I-18 give values of ΔH° and ΔS° derived in this manner. Tables I-19 through I-22 list the experimental data (all pressures are in torr).

TABLE I-17

Results of P-T Studies on HCl - Acetone and DCl - Acetone Systems

HCl $-\Delta H^\circ = 5.27 \pm 0.10$ kcal/mole
$-\Delta S^\circ = 33.4 \pm 0.3$ eu/mole
RMSD = 44 μ

DCl $-\Delta H^\circ = 5.01 \pm 0.08$ kcal/mole
$-\Delta S^\circ = 32.4 \pm 0.3$ eu/mole
RMSD = 40 μ

TABLE I-18

Results of P-T studies on TFE - Acetone and TFE-d - Acetone Systems

TFE $-\Delta H^\circ = 6.17 \pm 0.10$ kcal/mole
$-\Delta S^\circ = 32.7 \pm 0.3$ eu/mole
RMSD = 31 μ

TFE-d $-\Delta H^\circ = 6.44 \pm 0.16$ kcal/mole
$-\Delta S^\circ = 33.6 \pm 0.5$ eu/mole
RMSD = 50 μ

TABLE I-19

P-T Data for HCl - Acetone

T(°C)	π_B	P_{tot}	P_{tot}^{calc}	P_{AB}
$\pi_{A,25°}$ = 107.778 for following 10 points				
12.5	51.498	151.808	151.800	2.669
15.0	51.961	153.356	153.318	2.520
17.5	52.425	154.867	154.827	2.381
20.0	52.889	156.353	156.327	2.252
22.5	53.354	157.876	157.818	2.131
25.0	53.820	159.340	159.302	2.019
27.5	54.286	160.846	160.779	1.914
30.0	54.752	162.294	162.250	1.816
32.5	55.219	163.775	163.714	1.724
35.0	55.687	165.214	164.174	1.639
$\pi_{A,25°}$ = 99.459 for following 10 points				
12.5	50.886	143.427	143.447	2.444
15.0	51.344	144.841	144.879	2.307
17.5	51.802	146.274	146.301	2.179
20.0	52.261	147.662	147.716	2.060
22.5	52.720	149.111	149.122	1.950
25.0	53.180	150.485	150.522	1.847
27.5	53.641	151.929	151.915	1.750
30.0	54.102	153.281	153.302	1.661
32.5	54.564	154.677	154.684	1.577
35.0	55.026	156.029	156.061	1.498
$\pi_{A,25°}$ = 96.793 for following 10 points				
12.5	51.132	141.224	141.188	2.392
15.0	51.593	142.657	142.596	2.258
17.5	52.053	144.020	143.996	2.133
20.0	52.514	145.417	145.388	2.017
22.5	52.976	146.789	146.772	1.908
25.0	53.438	148.160	148.150	1.807
27.5	53.901	149.555	149.521	1.713
30.0	54.364	150.910	150.886	1.625
32.5	54.828	152.280	152.246	1.543
35.0	55.292	153.603	153.601	1.466

TABLE I-19 (continued)

T(°C)	π_B	P_{tot}	P_{tot}^{calc}	P_{AB}
	$\pi_{A,25°}$ = 85.193 for following 10 points			
12.5	51.648	130.807	130.835	2.138
15.0	52.113	132.073	132.138	2.017
17.5	52.578	133.404	133.432	1.905
20.0	53.044	134.656	134.720	1.800
22.5	53.510	135.950	136.000	1.703
25.0	53.977	137.219	137.275	1.613
27.5	54.445	138.475	138.544	1.528
30.0	54.912	139.761	139.807	1.449
32.5	55.381	140.987	141.066	1.376
35.0	55.850	142.250	142.321	1.307

TABLE I-20

P-T Data for DCl - Acetone

T(°C)	π_B	P_{tot}	P_{tot}^{calc}	P_{AB}
	$\pi_{A,25°}$ = 107.526 for following 10 points			
12.5°	50.101	150.140	150.150	2.697
15.0	50.552	151.668	151.645	2.556
17.5	51.003	153.130	153.132	2.425
20.0	51.455	154.610	154.611	2.302
22.5	51.908	156.079	156.082	2.187
25.0	52.361	157.549	157.547	2.079
27.5	52.815	159.007	159.005	1.979
30.0	53.269	160.465	160.457	1.884
32.5	53.723	161.918	161.904	1.796
35.0	54.178	163.350	163.346	1.712
	$\pi_{A, 25°}$ = 107.334 for following 10 points			
12.5	51.826	151.551	151.587	2.782
15.0	52.292	153.058	153.100	2.637
17.5	52.758	154.577	154.605	2.501
20.0	53.226	156.051	156.102	2.374
22.5	53.694	157.553	157.590	2.256
25.0	54.162	159.021	159.072	2.145
27.5	54.631	160.513	160.547	2.041
30.0	55.100	161.982	162.017	1.944
32.5	55.570	163.422	163.480	1.853
35.0	56.041	164.907	164.939	1.767
	$\pi_{A,25°}$ = 86.602 for following 10 points			
12.5	50.514	130.982	130.992	2.212
15.0	50.969	132.257	132.292	2.095
17.5	51.424	133.585	133.585	1.986
20.0	51.880	134.823	134.871	1.885
22.5	52.336	136.133	136.151	1.790
25.0	52.792	137.403	137.425	1.701
27.5	53.250	138.662	138.694	1.618
30.0	53.707	139.949	139.958	1.540
32.5	54.166	141.171	141.218	1.467
35.0	54.624	142.449	142.474	1.399

TABLE I-20 (continued)

T(°C)	π_B	P_{tot}	P_{tot}^{calc}	P_{AB}
	$\pi_{A,25°}$ = 104.621 for following 10 points			
12.5	52.232	149.485	149.435	2.735
15.0	52.702	150.971	150.927	2.593
17.5	53.172	152.480	152.411	2.459
20.0	53.643	153.932	153.886	2.335
22.5	54.115	155.428	155.354	2.218
25.0	54.587	156.867	156.815	2.109
27.5	55.059	158.347	158.270	2.007
30.0	55.533	159.764	159.718	1.911
32.5	56.006	161.234	161.161	1.821
35.0	56.480	162.644	162.599	1.737

TABLE I-21

P-T Data for TFE - Acetone

T(°C)	π_B	P_{tot}	P_{tot}^{calc}	P_{AB}
	$\pi_{A,25°}$ = 30.662 for following 10 points			
25.0	30.691	59.257	59.285	1.982
27.5	30.974	59.967	59.940	1.867
30.0	31.256	60.630	60.588	1.760
32.5	31.540	61.257	61.229	1.659
35.0	31.824	61.882	61.864	1.566
37.5	32.108	62.534	62.493	1.478
40.0	32.393	63.167	63.116	1.397
42.5	32.678	63.777	63.736	1.321
45.0	32.964	64.358	64.350	1.250
47.5	33.250	64.926	64.960	1.183
	$\pi_{A,25°}$ = 30.639 for following 10 points			
25.0	30.625	59.164	59.203	1.977
27.5	30.907	59.872	59.856	1.862
30.0	31.189	60.536	60.503	1.755
32.5	31.472	61.160	61.143	1.655
35.0	31.755	61.782	61.777	1.562
37.5	32.039	62.423	62.405	1.474
40.0	32.323	63.065	63.028	1.393
42.5	32.608	63.675	63.646	1.317
45.0	32.893	64.257	64.259	1.246
47.5	33.179	64.820	64.868	1.180
	$\pi_{A,25°}$ = 30.812 for following 10 points			
25.0	30.385	59.080	59.141	1.973
27.5	30.665	59.785	59.794	1.858
30.0	30.945	60.448	60.439	1.751
32.5	31.225	61.080	61.078	1.651
35.0	31.506	61.694	61.711	1.558
37.5	31.788	62.328	62.338	1.471
40.0	32.070	62.972	62.960	1.390
42.5	32.352	63.584	63.577	1.314
45.0	32.635	63.168	64.190	1.244
47.5	32.919	64.730	63.798	1.177

TABLE I-21 (continued)

T(°C)	π_B	P_{tot}	P_{tot}^{calc}	P_{AB}
	$\pi_{A,25°}$ = 30.930 for following 10 points			
25.0	30.532	59.342	59.389	1.989
27.5	30.813	60.046	60.045	1.873
30.0	31.095	60.704	60.694	1.766
32.5	31.377	61.335	61.336	1.665
35.0	31.659	61.961	61.972	1.571
37.5	31.942	62.613	62.602	1.484
40.0	32.225	63.243	63.227	1.402
42.5	32.509	63.852	63.847	1.325
45.0	32.793	64.435	64.463	1.254
47.5	33.078	65.006	65.074	1.187

TABLE I-22

P-T Data for TFE-d - Acetone

T(°C)	π_B	P_{tot}	P_{tot}^{calc}	P_{AB}
$\pi_{A,25°}$ = 30.606 for following 10 points				
25.0	30.498	59.010	59.058	1.962
27.5	30.779	59.721	59.716	1.842
30.0	31.060	60.395	60.366	1.730
32.5	31.342	61.044	61.008	1.626
35.0	31.624	61.669	61.644	1.529
37.5	31.906	62.307	62.274	1.439
40.0	32.189	62.950	62.898	1.355
42.5	32.473	63.561	63.516	1.277
45.0	32.757	64.154	64.130	1.204
47.5	33.041	64.711	64.740	1.136
$\pi_{A,25°}$ = 30.579 for following 10 points				
25.0	30.508	59.011	59.041	1.961
27.5	30.788	59.717	59.698	1.841
30.0	31.069	60.392	60.348	1.729
32.5	31.351	61.020	60.990	1.625
35.0	31.633	61.628	61.626	1.528
37.5	31.916	62.263	62.255	1.438
40.0	32.199	62.901	62.879	1.354
42.5	32.482	63.509	63.498	1.276
45.0	32.767	64.098	64.111	1.204
47.5	33.051	64.656	64.720	1.136
$\pi_{A,25°}$ = 30.958 for following 10 points				
25.0	29.655	58.578	58.602	1.932
27.5	29.928	59.268	59.253	1.813
30.0	30.202	59.946	59.896	1.703
32.5	30.475	60.601	60.532	1.601
35.0	30.750	61.221	61.162	1.505
37.5	31.024	61.834	61.785	1.416
40.0	31.300	62.464	62.403	1.334
42.5	31.575	63.081	63.016	1.257
45.0	31.852	63.677	63.623	1.185
47.5	32.128	64.246	64.227	1.118

TABLE I-22 (continued)

T(°C)	π_B	P_{tot}	P_{tot}^{calc}	P_{AB}
	$\pi_{A,25°}$ = 30.625 for following 10 points			
25.0	30.730	59.218	59.292	1.977
27.5	31.012	59.923	59.953	1.856
30.0	31.296	60.580	60.605	1.743
32.5	31.579	61.213	61.251	1.638
35.0	31.863	61.828	61.890	1.541
37.5	32.148	62.472	62.522	1.450
40.0	32.433	63.106	63.149	1.366
42.5	32.719	63.715	63.771	1.287
45.0	33.005	64.294	64.387	1.214
47.5	33.292	64.855	64.999	1.145

CHAPTER IV

DISCUSSION

Isotope Effects on Hydrogen Bonding

Isotope effects on hydrogen bonding can be examined most easily by considering the exchange reaction between the normal hydrogen-bonded complex and the deuterated complex. The equilibrium constant for this reaction,

$$\text{A-H} + \text{A-D}\cdots\text{B} \xrightleftharpoons{K_{ex}} \text{A-D} + \text{A-H}\cdots\text{B}$$

can be expressed in terms of the association constants for the separate complexation reactions,

$$\text{A-H} + \text{B} \xrightleftharpoons{K_H} \text{A-H}\cdots\text{B}$$

$$\text{A-D} + \text{B} \xrightleftharpoons{K_D} \text{A-D}\cdots\text{B}$$

as $$K_{ex} = \frac{K_H}{K_D}$$

Similarly, the enthalpy change for the exchange reaction is related to the separate enthalpy changes,

$$\Delta H^\circ_{ex} = \Delta H^\circ_H - \Delta H^\circ_D$$

where ΔH°_H and ΔH°_D are standard enthalpy changes for the formation of normal and deuterated complexes, respectively.

It would be convenient if the results from the present studies could be compared with reliable literature data on isotope effects. Unfortunately, previous studies in the field seem to share only their disagreement over the direction and magnitude of isotope effects on hydrogen bonding. Part of the reason for this discordance must lie with the tendency of these studies to concentrate on self-associating systems or on systems in which one of the components is polymerized to a significant extent. Thus, the value of their numerical results must depend on the accuracy of the models chosen to represent these systems. Similarly, the common infrared investigations of isotope effects must be regarded as inherently less reliable than other types of studies in which measurements can be made more precisely (e.g., calorimetric experiments, vapor density measurements, nmr studies, PVT experiments).

A compendium of the results from a majority of past investigations demonstrates that isotope effects on hydrogen bonding may be quite small and that understated (or unstated) error limits on experimental results may well mask these diminutive effects. This conclusion is supported by the calorimetric studies of isotope effects,[42-44,49] in which enthalpy changes are measured most directly. They indicate an isotope effect of 150 cal/mole or less, a change which most methods would be unable to detect.

Furthermore, if isotope effects on ΔH are small, changes in equilibrium constants might be expected to be difficult to discover. Pimentel and McClellan[2] point out and document the following relation: A higher value of $-\Delta H$ implies stronger bonding with a more restricted configuration in the complex. Hence, $-\Delta S$ must also be greater. These two effects tend to work against each other in ΔG, so that the association constant will not be particularly sensitive to changes in ΔH of hydrogen bond formation. (However, one must remember that, in general, ΔG can be measured much more accurately than ΔH.)

Because of the confusing record of past investigations and the difficulties which are apparently present in various attempts to characterize isotope effects, it was hoped that the precision available in vapor density measurements would be sufficient to overcome these problems and to lead to acceptable results. In the following two sections, results from the two types of vapor density studies are discussed.

Isothermal Experiments

Data from Tables I-1 through I-4 were combined to give the thermodynamic quantities in Table I-23, which describe the isotope exchange reaction. For the association of acetone with HCl and DCl, no significant isotope effect is found on ΔH° of complexation. However, in the temperature range studied, the association constant for the formation of the deuterium bond averages about 6% higher than the constant for the hydrogen bond. When TFE and TFE-d are used as proton donors, there does appear to be an isotope effect on the enthalpy change. -ΔH° is 0.5 kcal/mole greater for hydrogen bonding than for deuterium bonding. Unfortunately, this change in -ΔH° is only slightly larger than its standard error, making the isotope effect marginally significant. The van't Hoff plots for the acetone-alcohol association cross just outside the temperature range studied, so that K_H/K_D will be larger than unity at temperatures below ∿20°C and smaller at higher temperatures.

TABLE I-23

Thermodynamic Results for the Isotopic Exchange Reaction
(from Isothermal Experiments)

T (°C)	$K_{ex} = K_H/K_D$	ΔH°_{ex} (kcal/mole)
Acetone with HCl and DCl:		
15°	0.95 ± 0.01	
25°	0.92 ± 0.01	-0.03 ± 0.48
34.91°	0.96 ± 0.02	
Acetone with TFE and TFE-d:		
25°	1.00 ± 0.01	
35°	0.94 ± 0.01	-0.49 ± 0.32
45°	0.92 ± 0.01	

Because of the lack of reliable theoretical and experimental studies in this area, it is difficult to predict the direction and magnitude of isotope effects. However, the bulk of spectral and structural evidence presently available indicates that the H (or D) atom is localized near the donor molecule in the majority of hydrogen-bonding systems, even when the hydrogen is bonded between two similar atoms.[8,9] In this type of situation, the potential function must have an asymmetric double-minimum form, with the lower of the two minima located nearer the donor molecule. If this is the case, then the qualitative arguments presented in the introduction would lead one to anticipate a stronger bond with hydrogen than with deuterium. This prediction seems to be reflected in the results with the alcohols. A smaller isotope effect would be expected for the HCl-DCl system because the bonds are weaker.

Since gas phase hydrogen-bonding data are rather exiguous, it is not surprising that there are few literature data with which to compare the results of the present study. Christian et al.[81] used vapor density techniques to investigate the HCl-acetone complex at 29°. Their association constant of 4.0×10^{-4} torr^{-1} is higher than the K value interpolated from the present results, 3.1×10^{-4} torr^{-1}. Tucker[69] has studied the TFE-acetone complex in the gas phase. A comparison of his results with those from the preceding chapter is given in Table I-24. The association constants at 25° are remarkably close. However, the values diverge as the temperature increases, so that $-\Delta E^\circ$ is smaller in the present study. The experimental procedures in these investigations were all similar; in each case, reasonably good fits of the experimental data were obtained. In view of these differences, a closer examination of possible experimental problems is called for.

The RMSD values given in Tables I-1 through I-4 may provide an incomplete measure of the goodness of these fits. The RMSD values were

TABLE I-24

Comparison of Results on TFE - Acetone in the Gas Phase

	Present Study	Tucker[69]
$K_{25^\circ} \times 10^3$ (torr^{-1})	2.56 ± 0.02	2.55 ± 0.02
$K_{35^\circ} \times 10^3$ (torr^{-1})	1.78 ± 0.01	1.72 ± 0.01
$K_{45^\circ} \times 10^3$ (torr^{-1})	1.25 ± 0.01	1.160 ± 0.005
$-\Delta E^\circ$ (kcal/mole)	6.16 ± 0.07	6.79 ± 0.13

calculated with the assumption that all data provided the fitting program were free from systematic errors. In fact, this cannot be true. For example, the variable being fit by the program (P_{tot}) is a pressure calculated from a reading on the pressure gauge. The conversion of gauge readings to pressures requires the calibration of two gauges and may introduce errors as large as 0.04 torr into this variable alone. Similar errors may be present in π_A values, since the same conversion procedure was employed. Values of π_B are likely to be even less accurate, because additional calculations were involved. π_B was calculated from $P_{B,pred}$ which was estimated by using an equation relating measured pressures to acetone addition volumes.

It should be apparent that, while the precision of this technique is good, errors in calculated quantities may be underestimated somewhat. If acetone self-association is ignored, the association constant can be expressed as

$$K \simeq \frac{\pi_A + \pi_B - P_{tot}}{(P_{tot} - \pi_A)(P_{tot} - \pi_B)}$$

Obviously, errors in the conversion of gauge readings to pressures for these fundamental quantities will affect the precision of K values. This imprecision will, at least to some degree, be in addition to errors caused by experimental techniques, which should be reflected in the RMSD values.

In order to examine further the precision of this method, it is instructive to consider the estimates of hydrogen-bonded complex pressures given in Tables I-5 through I-16. In several instances, the maximum amount of complex formed for a system at a given temperature is quite low (1.1 torr for HCl-acetone at 35°; 1.6 torr for DCl-acetone at 35°; 1.9 torr for DCl-acetone at 25°; 2.1 torr for TFE-acetone and TFE-d-acetone at 25°). It is not difficult to imagine that hidden inaccuracies, such as those described above, could combine to cause problems in systems where the maximum amount of complex formed is as low as 1% of the total pressure.

Despite difficulties such as these, vapor density methods have historically proved to be one of the best and most accurate ways to study complexation in the gas phase. Normally, errors of a few percent in K and 200 cal/mole in $\Delta H°$ are not crucial. However, in studying isotope effects it has become clear that the changes which are occurring may very well be of the same order of magnitude as typical errors in this method. Thus, it may not be possible to characterize clearly isotope effects with any methods currently in use for studying vapor phase hydrogen bonding.

Variable Temperature Studies

In an attempt to focus more directly on changes in $\Delta H°$, a different type of experiment was attempted. Errors associated with additions of liquid acetone should be minimized here, since temperature and not moles of acetone was varied. It is indeed unfortunate, but perhaps not surprising, that in changing the emphasis of the study, an experimental problem which had been of little consequence previously becomes important here.

In describing vapor density experiments on NO_2-N_2O_4 in 1879,

J. Willard Gibbs addressed this same problem. Gibbs made the following remarks about discrepancies in the literature:[75] "It does not seem possible to account for these discrepancies by any causes which would apply to cases of normal or constant density. They are illustrations of the fact that when density varies rapidly with the temperature, determinations of density for the same temperature and pressure by different observers, or different determinations by the same observer, exhibit discordances which are entirely of a different order of magnitude from those which occur with substances of normal or constant densities, or which occur with the same substance at temperatures at which the density approaches a constant value. In some cases, the results may be accounted for by carelessness on the part of the observer, not controlled by a comparison of the result with a value already known. But such an argument is inadequate to explain the general fact, and evidently inadmissable in the present case."

The problem which confounded Gibbs and plagued the present study is adsorption of gases on the walls of the apparatus. The only component in the systems investigated which seemed to adsorb significantly was acetone. In the isothermal experiments acetone adsorption was apparently not a problem because of the use of calibration curves for acetone additions which implicitly included adsorption. Temperature changes evidently brought out the worst of the adsorption problem, causing slow pressure changes which lasted for several hours. These changes could not be completely accounted for because of limitations on the length of the variable temperature studies. In particular, the experiments with HCl and DCl could not be lengthened without the introduction of other errors due to the apparent irreversible reaction between the components.

Because of these experimental problems it became apparent that the precision of the variable temperature studies would not match that of the isothermal experiments. Even though enthalpy changes were determined more directly, their worth may easily be imagined to be less than that of the values determined in the fixed temperature investigations. One should keep these admonitions in mind while examining the results of the variable temperature studies on isotope effects.

Data from Tables I-17 and I-18 have been combined to give the results shown in the following two tables. In Table I-25 values of ΔH° and ΔS° have been employed to calculate association constants at several temperatures. They are compared with the values derived from the isothermal studies. Table I-26 presents results on isotope effects in the form of thermodynamic values for the isotope exchange reaction.

For acetone complexation with HCl and DCl, K values in the isothermal studies are several percent lower than the values obtained from variable temperature experiments. Conversely, in the TFE and TFE-d systems, K values in the isothermal studies were several percent higher. Obviously, some sort of systematic errors are complicating the interpretation of these data. If adsorption were the sole culprit, one would expect values of the association constant to be uniformly higher in the variable temperature studies. Temperatures were increased during the course of the experiments; if desorption is a slow process, then measured pressures would have been lower than expected, leading to greater apparent complexation and higher K values. Such an effect is seen in

TABLE I-25

Association Constants Derived from Variable Temperature and Isothermal Experiments

System	T (°C)	K ($torr^{-1}$)	
		Variable Temperature Study	Isothermal Study
HCl - Acetone	15°	$(5.07 \pm 0.03) \times 10^{-4}$	$(4.83 \pm 0.02) \times 10^{-4}$
	25°	$(3.72 \pm 0.01) \times 10^{-4}$	$(3.50 \pm 0.03) \times 10^{-4}$
	35°	$(2.79 \pm 0.02) \times 10^{-4}$	$(2.58 \pm 0.04) \times 10^{-4}$
DCl - Acetone	15°	$(5.31 \pm 0.03) \times 10^{-4}$	$(5.08 \pm 0.05) \times 10^{-4}$
	25°	$(3.96 \pm 0.01) \times 10^{-4}$	$(3.81 \pm 0.03) \times 10^{-4}$
	35°	$(3.01 \pm 0.02) \times 10^{-4}$	$(2.69 \pm 0.03) \times 10^{-4}$
TFE - Acetone	25°	$(2.42 \pm 0.02) \times 10^{-3}$	$(2.56 \pm 0.02) \times 10^{-3}$
	35°	$(1.73 \pm 0.01) \times 10^{-3}$	$(1.78 \pm 0.01) \times 10^{-3}$
	45°	$(1.26 \pm 0.01) \times 10^{-3}$	$(1.25 \pm 0.01) \times 10^{-3}$
TFE-d - Acetone	25°	$(2.41 \pm 0.02) \times 10^{-3}$	$(2.57 \pm 0.02) \times 10^{-3}$
	35°	$(1.70 \pm 0.01) \times 10^{-3}$	$(1.89 \pm 0.01) \times 10^{-3}$
	45°	$(1.22 \pm 0.01) \times 10^{-3}$	$(1.35 \pm 0.01) \times 10^{-3}$

TABLE I-26

Thermodynamic Results for the Isotopic Exchange Reaction (from Variable Temperature Studies)

T (°C)	$K_{ex} = K_H/K_D$	ΔH°_{ex} (kcal/mole)
Acetone with HCl and DCl:		
15°	0.95 ± 0.01	
25°	0.94 ± 0.01	-0.26 ± 0.13
35°	0.93 ± 0.01	
Acetone with TFE and TFE-d:		
25°	1.00 ± 0.01	
35°	1.02 ± 0.01	0.27 ± 0.19
45°	1.03 ± 0.01	

the HCl and DCl systems, but in the alcohol systems some other effect(s) must be present.

The isotope effects on HCl and DCl complexation with acetone are remarkably similar to those found in the isothermal studies. While all K values are higher in the variable temperature studies, the K_D values are still about 6% greater than the K_H values. Furthermore, $-\Delta H^\circ$ values are lower than in the isothermal studies, but ΔH°_{ex} is -0.26 kcal/mole, an entirely reasonable value in light of the comments in the preceding section. Thus, the hydrogen bond is found to be very slightly stronger than the deuterium bond.

When the complexation of acetone with TFE and TFE-d is studied with the variable temperature method, the results do not follow the pattern established thus far. K_H/K_D ratios are greater than unity and ΔH°_{ex} is positive. The isotope effects found here are opposite in direction from those observed in the other parts of this research and disagree with predictions from theoretical considerations. The results seem to reinforce the earlier conclusion that methods which are adequate for studying simple complexation may not be able to detect accurately small changes in K and ΔH° values. This is especially true in cases where adsorption is an obvious problem.

Many studies of hydrogen bonding (including those concerned with isotope effects) have been carried out in solution. Thus, it is imperative that the complicating effects of the solvent on these association reactions be investigated. Only in this way can the intricacies of hydrogen bonding be fully understood.

Solvent Effects on Hydrogen Bonding

In order to examine solvent effects on hydrogen bonding, thermodynamic data must be available from both vapor phase and solution studies. Normally, the scarcity of vapor phase data hinders these investigations. However, of the four hydrogen-bonding systems studied here in the gas phase, only one (TFE - acetone) has apparently been examined in solution.[76] Thus, remarks about solvent effects must be limited to this one complex.

The thermodynamic cycle introduced in Chapter I is reproduced on the next page with values of ΔE° enumerated. The value of ΔE°(g) is from Table I-3. $\Delta E^\circ(CCl_4)$ is from the work of Sherry and Purcell.[76]

$$\begin{tikzcd}
\text{TFE(g)} \arrow[d, "\Delta E^\circ=-4.76"] & + & \text{Acetone(g)} \arrow[r, "\Delta E^\circ=-6.16"] \arrow[d, "\Delta E^\circ=-6.32"] & \text{TFE-Acetone(g)} \arrow[d, "\Delta E^\circ=-9.97"] \\
\text{TFE}(\text{CCl}_4) & + & \text{Acetone}(\text{CCl}_4) \arrow[r, "\Delta E^\circ=-5.05"] & \text{TFE-Acetone}(\text{CCl}_4)
\end{tikzcd}$$

Transfer energies for acetone and TFE have been calculated from data on vapor pressures,[77,78] heats of solution,[76] and heats of mixing.[79] The transfer energy for the complex has been derived from the other steps in the cycle. Values of the transfer energies may be in error by a few percent; this imprecision will not affect the observations that follow.

It is apparent from the above cycle that transfer energies for the individual components and complex have magnitudes which are comparable to ΔE° for the association reaction in the vapor phase or in solution. Thus, they certainly cannot be ignored on the grounds that their size is insignificant. It should also be clear that ΔE° in the vapor phase and solution are significantly different. The assumption of their equality when an "inert" solvent (such as CCl_4) is used is not supported.

For the same reasons, Drago's E and C parameters,[51] which estimate a $-\Delta H$ value for TFE-acetone of 4.88 ± 0.22 kcal/mole, obviously cannot predict gas phase enthalpies from solution data. Such a set of parameters might be useful if they were based on vapor phase results. However, the paucity of gas phase data prevents such an analysis at the present time. E and C parameters have not been estimated for the other bases employed in this study; therefore, solution results cannot be predicted for the other complexes investigated.

The transfer energy of the complex is 90% of the sum of the transfer energies of the monomers. This value is slightly higher than α values (see equation I-3) found for other non-cyclic hydrogen-bonded complexes.[50] Tucker has used his value of $\Delta E°(g) = -6.8$ kcal/mole to estimate that $\alpha = 0.83$. This value of α is more in line with the values for other complexes and, perhaps, is an indication that the true value of $-\Delta E°(g)$ may be larger than the value found in the present study. In any case, a value of α which is significantly less than unity reemphasizes the fact that vapor phase and solution energies cannot be assumed to be equivalent for hydrogen-bonded complexes.

Summary and Proposals for Future Work

The present research was unable to provide definitive and irrefutable evidence concerning isotope effects. Nevertheless, it has indicated that similar vapor density experiments, with improvements, should be capable of yielding success in this field. Vapor density measurements should be able to deliver very precise data if two major weaknesses are overcome. The first is the matter of liquid additions to the system. The microburet is adequate under many circumstances, especially when a strong complex is being investigated. However, an automated system, such as that proposed by Tucker,[80] with remotely actuated valves, would improve this technique. Such a system could greatly increase the reproducibility of the liquid additions by removing errors due to human imprecision and the limitations of microburets in handling volatile liquids.

A second weakness in the vapor density studies is the presence of adsorption. One way to limit the errors caused by this phenomenon is to work at fixed temperatures, so that changes in the amount of material adsorbed are dependent only on changes in pressure (which can be kept small). A second improvement would be to render the walls of the apparatus less reactive toward polar compounds. This can be accomplished with a silanization reagent, such as dimethylsilyldichloride. In this way, compounds normally used in hydrogen-bonding studies should show a lesser tendency to adsorb.

The present research has made several contributions to the knowledge of hydrogen bonding. Thermodynamic results in the vapor phase are intrinsically valuable in demonstrating the existence and magnitude of solvent effects. The study of the TFE-acetone complex provided additional evidence for the nonequivalence of energies of complexation in the gas phase and solution. Results on the other systems may provide an impetus for other investigators to study these complexes in solution.

Although no clear-cut differences in hydrogen and deuterium bonding were discovered, this very fact tends to show that isotope effects are quite small in magnitude. Differences in $\Delta\overline{H}°$ on the order of a few hundred calories or less are quite likely. The preponderance of evidence accumulated here appears to indicate that hydrogen bonds may be slightly stronger than deuterium bonds, but that association constants for deuterium bonding are probably larger at the temperatures employed here.

It should be pointed out that studies which attempt to derive thermodynamic information about hydrogen bonding are inherently of value. Theoretical investigations and calculations can be no better than the experimental data on which they are based. In the words of Pimentel,[12] "The ubiquitous manifestations of the hydrogen bond can be well understood and predicted only when the thermochemistry of the interaction is well known."

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II. THE DETERMINATION OF THE NUMBER OF CHEMICAL SPECIES USING TESTS OF LINEAR DEPENDENCE

CHAPTER I

INTRODUCTION

Absorption spectroscopy has often been used to study solutions in which several chemical species exist simultaneously. If one assumes that Beer's law is obeyed by each species and if one has a model which predicts the components which could be present, it may be possible to deduce the number of species as well as information concerning their interaction. However, in cases where mass-balance relationships are not known, finding even the number of species can be difficult.

Over the past two decades several numerical techniques have been proposed for analyzing spectral data to determine the number of absorbing species in solutions of organic and inorganic complexes, in solutions of organic dyes, and in unknown mixtures. The first method was proposed by Wallace[1] and is based only on the assumption that Beer's law is valid for each of the components at all wavelengths and concentrations. Thus, in a single solution, absorbances are measured at several wavelengths, and they can be expressed in terms of the concentrations of the m components as

$$A_{\lambda} = \sum_{k=1}^{m} \varepsilon_{\lambda,k} C_{k} \qquad \text{(II-1)}$$

A_{λ} is the absorbance per unit path length at wavelength λ, $\varepsilon_{\lambda,k}$ is the absorptivity of the k<u>th</u> component at wavelength λ, and C_k is the concentration of the k<u>th</u> component. If n experiments are performed in which the relative values of the concentrations are caused to change, equation II-1 expands to become a series of n equations of the form

$$A_{\lambda,j} = \sum_{k=1}^{m} \varepsilon_{\lambda,k} C_{k,j} \qquad \text{(II-2)}$$

$A_{\lambda,j}$ is the absorbance per unit path length at wavelength λ in the j<u>th</u> experiment, and $C_{k,j}$ is the concentration of the k<u>th</u> species in the j<u>th</u> experiment.

Equation II-2 follows the rules for matrix multiplication and may be written in the following form:

$$\mathbf{A} = \mathbf{E}\mathbf{C}$$

A is a p x n matrix whose elements are absorbances measured at p wavelengths in n experiments. **E** is a p x m matrix of absorptivities for the m components. **C** is an m x n matrix whose terms are concentrations. The method for determining the number of species hinges upon finding the rank of the above matrices.*

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*For a general matrix **M**, one can form all possible square submatrices. If at least one determinant of order r is nonzero and if all determinants of order r+1 and higher vanish, the matrix **M** has rank r.[2]

The rank of **A** is equal to the smaller of the ranks of **C** and **E**, and the ranks of **C** and **E** can be no larger than m; therefore, the rank of **A** can be no larger than m. The ranks of **C** and **E** will normally be equal to m (if $p \geq m$ and $n \geq m$), so that finding the rank of **A** should be equivalent to finding m, the number of components in the system. The only situations under which problems are likely to arise are (1) when the concentration of one or more of the components can be expressed as a linear combination of the other components in all experiments, or (2) when the spectra of one or more components can be expressed as a linear combination of the spectra of the other components.

One difficulty with this technique is that the elements of **A** are experimental quantities and are subject to error. Therefore, it is quite unlikely that <u>any</u> square submatrix of **A** will be singular in a strict mathematical sense. Statistical criteria are necessary for deciding when the determinant of a submatrix has vanished and thus for finding the rank of the matrix. Wallace[1,3] and Varga[4] discuss propagation of error methods for solving this problem. Ainsworth[5] and Katakis[6] provide similar techniques. In all cases, however, absorbance matrices are manipulated without regard for errors in measured quantities and therefore without proper weighting. The experimental errors are introduced only at a later stage of the calculations at which tests of significance are made.

Graphical methods for determining number of absorbing species have been presented by Coleman et al.[7] and Budesinsky.[8] An advantage claimed for these graphical techniques is that trends in the number of species as a function of wavelength or solution concentration should be evident.[9] These methods rely on the fact that, if m species are present, then all submatrices of rank m+1 should have determinants equal to zero. This condition allows the formulation of linear equations which are easily converted into graphs. It seems that this method could be modified to take into account weights for individual absorbances (although some of the differentiation might be complicated), but the users of the technique have apparently not done so.

In recent years the most popular methods for finding the number of chemical species have been techniques generally referred to as factor analysis.[10,11] These methods have been applied not only to absorption spectra but also to similar types of experimental information such as mass spectral data.[12,13] Typical of the factor analysis methods is an approach in which eigenvalues of a matrix are calculated.* It can be shown that $\mathbf{M} = \mathbf{A}\,\mathbf{A}^T$ has as many nonzero eigenvalues as the

---

*Given a square matrix $\mathbf{M}(n \times n)$, the identity matrix $\mathbf{I}\ (n \times n)$, and a scalar λ,

$$\det(\mathbf{M} - \lambda\mathbf{I}) = 0$$

has n solutions for λ which are called the eigenvalues of $\mathbf{M}$ (λ_i, $i = 1,2,\ldots,n$). The equation $\mathbf{M}\mathbf{x}_j = \lambda_j\mathbf{x}_j$, where $\mathbf{x}_j$ is a column vector, defines the n eigenvectors of matrix $\mathbf{M}$. If a square matrix $\mathbf{X}$ is formed from the eigenvectors $\mathbf{x}_j$,

$$(\mathbf{X})_{ij} = x_{ij} \quad \text{where} \quad \mathbf{x}_j = \begin{pmatrix} x_{1j} \\ x_{2j} \\ \vdots \\ x_{nj} \end{pmatrix}$$

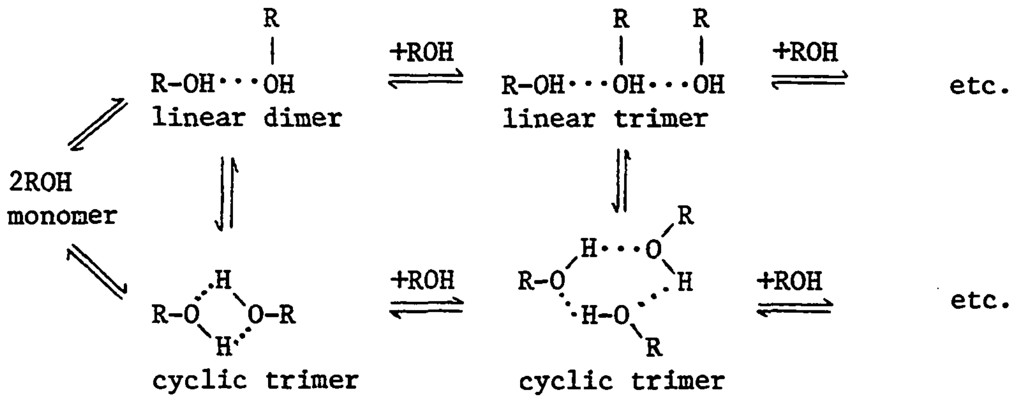
and a diagonal matrix $\mathbf{D}$ is formed from the eigenvalues, $(\mathbf{D})_{ii} = \lambda_i$, then

$$\mathbf{M} = \mathbf{X}\mathbf{D}\mathbf{X}^{-1}$$

rank of the matrix **A**.[14-17] Again, the errors in absorbance create a mathematical problem, and one has to seek statistical criteria for the vanishing of an eigenvalue. The criteria currently in use are summarized by Bulmer and Shurvell.[18] As in the matrix-rank methods, weighting of individual data points is ignored in matrix manipulations, and errors are considered only after eigenvalues have been calculated.

One area of chemistry for which these methods may prove particularly helpful is the study of hydrogen bonding species which contain both donor and acceptor groups. These molecules can self-associate through hydrogen bonds to form complicated cyclic and/or linear polymers. Several reviews on hydrogen bonding discuss experimental evidence and the resulting disagreements concerning the number and identity of the species formed.[19-24]

The study of the self-association of alcohols is typical. The equilibria involved may be generalized as follows:



One approach to this problem has been matrix isolation spectroscopy, in which the alcohol is frozen in an inert matrix at ∿20°K and studied spectrally.[25] Absorption bands observed in the spectra are assigned to various polymers. A different but more common approach is the development of a model which assumes that only a few specific hydrogen-bonded species are present. Then computations from the experimental data determine whether reasonable and consistent values of equilibrium constants can be obtained. The literature on the subject presents a rather confusing picture. Many different models have been proposed for simple alcohols in nonpolar solvents; the following are examples:

Monomer - cyclic trimer[26]

Monomer - linear tetramer - cyclic tetramer[27]

Monomer - linear dimer - cyclic trimer or tetramer[28]

Monomer - linear trimer - cyclic octamer[29]

Monomer - linear trimer - cyclic polymers[30]

Monomer - linear dimer -···- polymers[31]

Monomer - linear dimer - linear trimer - cyclic polymers[32]

Monomer - cyclic dimer -···- polymers[33]

Monomer - cyclic dimer - cyclic trimer - linear polymers[34-35]

Monomer - dimer - trimer -···- polymers (with various assumptions about the equality of the successive equilibrium constants)[36-39]

Clearly, if the number of unique species present in the solution were known, the thermodynamic analysis of the data would be greatly simplified. Thus, it seems that application of a method for determining the number of species to data on alcohol association could be quite helpful.

The following chapters will describe a new method for using linear dependence tests to determine the number of species contributing to physical measurements of various types.[40] Not only spectral data, but also vapor pressure, colligative property, and concentration data may be used, as well as other types of physical data which are linearly dependent on species concentrations. An advantage of this new approach is the convenience of using weighting factors which take into account errors in the individual measurements. Weighting is found to be particularly important when sets of data of varying type and precision are processed simultaneously.

CHAPTER II

THEORY AND PROCEDURE

Assume that absorbances have been measured at m wavelengths for a solution containing m chemical species with distinct spectra. In addition, assume that each species absorbs at at least one of the wavelengths, and that there are no subsets of species for which the absorbances are linearly dependent. If Beer's law is obeyed by all of the species at all wavelengths and concentrations, the absorbances at the m wavelengths may be related to species concentrations in the following manner:

$$\begin{array}{l} A_1 = \varepsilon_{1,1}C_1 + \varepsilon_{2,1}C_2 + \cdots + \varepsilon_{i,1}C_i + \cdots + \varepsilon_{m,1}C_m \\ A_2 = \varepsilon_{1,2}C_1 + \varepsilon_{2,2}C_2 + \cdots + \varepsilon_{i,2}C_i + \cdots + \varepsilon_{m,2}C_m \\ \vdots \\ A_j = \varepsilon_{1,j}C_1 + \varepsilon_{2,j}C_2 + \cdots + \varepsilon_{i,j}C_i + \cdots + \varepsilon_{m,j}C_m \qquad \text{(II-3)} \\ \vdots \\ A_m = \varepsilon_{1,m}C_1 + \varepsilon_{2,m}C_2 + \cdots + \varepsilon_{i,m}C_i + \cdots + \varepsilon_{m,m}C_m \end{array}$$

An A_j value represents the absorbance per unit pathlength measured at wavelength j; $\varepsilon_{i,j}$ is the absorptivity for chemical species i at wavelength j; and C_i is the concentration of species i.

Equations II-3 can be written in matrix notation as

$$\mathbf{a} = \mathbf{E}\mathbf{c}$$

where **a** and **c** are column vectors of length m and **E** is a square (m x m) matrix. If **E** is nonsingular, the equation may be rearranged to give

$$\mathbf{E}^{-1}\mathbf{a} = \mathbf{c}$$

Thus, each of the species concentrations may be expressed in the form

$$C_i = \alpha_i A_1 + \beta_i A_2 + \ . \ . \ . + \mu_i A_m \qquad \text{(II-4)}$$

where the constants α_i, β_i, ..., μ_i are functions only of the $\varepsilon_{i,j}$ values. These linear relations can be used to express the absorbance at any other wavelength (e.g., A_{m+1}) as a function of the absorbances at wavelengths 1 to m. Thus,

$$A_{m+1} = \varepsilon_{1,m+1}C_1 + \varepsilon_{2,m+1}C_2 + \dots + \varepsilon_{m,m+1}C_m$$

which, upon substitution of the expressions for C_1, C_2, ..., C_m from equation II-4, becomes

$$A_{m+1} = rA_1 + sA_2 + \dots + z\ A_m \qquad \text{(II-5)}$$

The constants r,s, ..., z depend only on the absorptivities of the m species at the m+1 wavelengths.

Equation II-5 is an important relation which can be used as the basis for determining the number of species contributing to the observed spectra. It implies that if there are exactly m species, the absorbance at any given wavelength can be represented as a linear combination of absorbances at any m other wavelengths. Weighted least squares analysis can be used to determine whether absorbance data at wavelength m+1 can be fitted adequately in the form of equation II-5. In performing this analysis, separate sets of measured absorbances ($A_1, A_2, \ldots, A_m, A_{m+1}$) are required for at least m+1 mixtures of the m chemical species. Assuming that the observables are subject only to random errors of measurement, statistical tests can be used to ascertain if equation II-5, with fitted values of the parameters (r,s, ..., z), is adequate for representing the entire collection of data. If the number of absorbing species is greater than m, it should not be possible to obtain a satisfactory numerical fit of absorbance data at each wavelength in the form of equation II-5; on the other hand, if the number of species is less than m, there is more than enough information to give a good least squares fit.

It should be emphasized that other types of physical data which depend linearly on species concentrations may be treated simultaneously with or independently of spectral data in tests of linear dependence. For example, the total concentration of a self-associating solute, B, may be expressed as

$$[B] = C_1 + 2C_2 + 3C_3 + \ldots \qquad \text{(II-6)}$$

where C_1, C_2, C_3, ... represent the concentrations of monomeric, dimeric, trimeric, etc., species. Similarly, the vapor pressure of such a solution is related to the species concentrations by

$$P = \frac{RT}{K_{d_1}} C_1 + \frac{RT}{K_{d_2}} C_2 + \frac{RT}{K_{d_3}} C_3 + \ldots \qquad \text{(II-7)}$$

The K_{d_i} values are distribution constants for the various species between solution and the vapor phase.

Equations II-6 and II-7, as well as other functions which are linearly dependent on species concentration, may be treated as typical A_j relations (see equations II-3) in formulating the linear dependency problem. Weighting of the individual data points can be conveniently handled in least squares fitting of data of mixed type via equations II-5; in fact, variable weighting becomes quite important when data of varying precision are employed (see Appendix A).

In fitting data obtained at p wavelengths for q sets of species concentrations ($q \geq p$), the following strategy has been used. Data are first fitted in all of the one-parameter (two-wavelength) forms of equation II-5:

$$A_1 = rA_2;\ A_1 = r'A_3;\ \ldots;\ A_2 = r''A_3;\ \ldots;\ A_{p-1} = r'''A_p$$

Next, sets of data are fitted in all two-parameter linear forms:

$$A_1 = sA_2 + tA_3;\ A_1 = s'A_2 + t'A_4;\ \ldots$$

Continuing in this way, linear expressions are developed and tested for data in all of the three-parameter, four-parameter, ..., and p-1 parameter forms of equation II-5.

In order to illustrate this procedure, hypothetical absorbance data were produced at four wavelengths for fifteen different sets of concentrations of two species. One species absorbed at only wavelengths 1 and 2, while the second species absorbed at all four wavelengths. Random, normally distributed errors were introduced into all absorbance values in order to simulate a set of measured absorbances with errors. Table II-1 displays the results of the above type of analysis on this collection of hypothetical data. For each combination of wavelengths, and thus each least squares fit, a χ^2 value is calculated,

$$\chi^2 = \sum_i \left(\frac{R_i}{\sigma_{R_i}}\right)^2$$

R_i is the residual from the fit of the i<u>th</u> set of absorbances, and σ_{R_i} is the estimated error in the residual. For a normally distributed set of residuals, χ^2 has an average value equal to the number of degrees of freedom (the number of data points minus the number of fitting parameters).

Examination of the results in Table II-1 shows that only one of the χ^2 values for the one-parameter (two-wavelength) fits, the 3-4 combination, is near the expectation value. This indicates that, while only one species may absorb at wavelengths 3 and 4, one species is not sufficient to explain all of the data. The group of two-parameter (three-wavelength) fits is satisfactory, as is the 1-2-3-4 fit; thus, two chemical species are sufficient to explain the entire collection of spectral data. (A group of fits is judged to be "acceptable" if the distribution of χ^2 values about the expectation value is not badly skewed toward the high χ^2, low probability side

TABLE II-1

Results of Linear Dependence Tests on Hypothetical Absorbance Data

Combination of Wavelengths[a]	χ^2 Observed	χ^2 Probability[b]	Degrees of Freedom[c]	Mean χ^2
1-2	451.5	<0.001	14	3547.0
1-3	4078.9	<0.001		
1-4	9308.6	<0.001		
2-3	2475.0	<0.001		
2-4	4353.9	<0.001		
3-4	14.3	0.43		
1-2-3	11.6	0.56	13	11.5
1-2-4	9.8	0.71		
1-3-4	12.3	0.50		
2-3-4	12.4	0.49		
1-2-3-4	8.7	0.73	12	8.7

[a] Integers designate selected wavelengths; e.g., 3-4 indicates that absorbance data at wavelengths 3 and 4 are fitted in the form $A_3=rA_4$.

[b] The probability that a random variable, distributed according to the χ^2 distribution, would be greater than the observed χ^2 value.

[c] χ^2 has an expectation value (0.5 probability level) slightly lower than the number of degrees of freedom (the number of concentration sets less the number of fitting parameters).

and if the mean χ^2 value is not significantly greater than the number of degrees of freedom.)

CHAPTER III

EXAMPLES

Literature data for several systems were fitted according to the scheme explained in the preceding chapter. The first three examples are presented here because the interpretation of the results is reasonably straightforward and leads to plausible conclusions concerning the number of species. Unfortunately, no method for determining the number of species is able to yield clear results in all instances. The remaining examples (alcohol systems) are discussed here to illustrate that point; the results are not clear-cut but they prove to be of value anyway. In each case, the results are presented in a table in which the distribution of χ^2 values among the probability levels is shown for each group of fits. The data from which the least squares fits were produced are given in Appendix B.

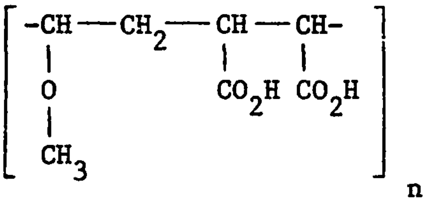
I_2-Br_2 in CCl_4

The absorbances of fifteen solutions of iodine and bromine in CCl_4 were measured at five wavelengths in a region in which I_2, Br_2, and IBr absorb (580, 550, 518, 460, and 430 nm).[41] The data were taken on a Beckman DU-2 spectrophotometer. Errors of 0.3 percent transmittance were assumed in both the 100% setting and in the actual transmittance reading; absorbance errors were calculated using propagation of error formulas. Uncertainties of 1% were assumed in all of the concentrations. I_2 and Br_2 concentrations were combined with the absorbances to give seven "wavelengths" for use in the least squares analyses. The results of these analyses are given in Table II-2.

Clearly, all three-parameter (four-wavelength) fits and higher fits are acceptable. Thus, three species are necessary and sufficient to explain the entire collection of data. It is also evident that there may be spectral regions in which only two species absorb, since a few of the two-parameter (three-wavelength) fits are quite good. These results are consistent with our knowledge of the association of I_2 and Br_2 to produce IBr. The absorbance errors have evidently been slightly overestimated, since one would not expect the acceptable groups of fits to be skewed so much toward the low χ^2, high probability values.

Fe^{+++} - Gantrez in H_2O

Fifteen aqueous solutions of Fe^{+++} and Gantrez were prepared with a pH of about 1.5.[42] Gantrez is a copolymer of maleic anhydride and methyl vinyl ether,



$$\left[\begin{array}{llll} -\mathrm{CH}- & \mathrm{CH_2}- & \mathrm{CH}- & \mathrm{CH}- \\ | & & | & | \\ \mathrm{O} & & \mathrm{CO_2H} & \mathrm{CO_2H} \\ | & & & \\ \mathrm{CH_3} & & & \end{array}\right]_n$$

Absorbances were measured at 325, 337.5, 350, 362.5, and 372.5 nm (a region in which Gantrez does not absorb significantly) using a

TABLE II-2

Results of Linear Dependence Tests on I_2-Br_2 Data

χ^2 Probability level	Number of fits using 1 Parameter	2 Parameters	3 Parameters	4 Parameters	5 Parameters	6 Parameters
0.0-0.1	20	25	--	--	--	--
0.1-0.2	--	1	--	--	--	--
0.2-0.3	--	--	--	--	--	--
0.3-0.4	--	--	--	--	--	--
0.4-0.5	--	--	--	--	--	--
0.5-0.6	--	--	--	--	--	--
0.6-0.7	--	1	--	--	--	--
0.7-0.8	--	--	--	--	--	--
0.8-0.9	--	2	--	--	--	--
0.9-1.0	1	6	35	21	7	1
Mean χ^2	8335.3	140.2	2.3	1.2	0.8	0.4
(Degrees of Freedom)	(14)	(13)	(12)	(11)	(10)	(9)

Hitachi Perkin-Elmer Model 124 (double beam) spectrophotometer. Absorbance errors were calculated by assuming an error of 0.3 percent transmittance both in the baseline reading and in the reading on the spectral curve of interest. The results of the least squares analyses are given in Table II-3.

The group of fits using two parameters (three wavelengths) seems to give a reasonable distribution about the expectation value of χ^2 and has a mean χ^2 value lower than the number of degrees of freedom. Thus, the results are indicative of two spectrally unique species, Fe^{+++} and a Fe^{+++}- Gantrez complex. Chemically, one would expect many types of complexes, since many ferric ions can complex with one Gantrez polymer. Evidently, the absorbances of the higher complexes are related linearly to the absorbance of the 1:1 complex, a fact which would preclude their appearance as spectrally unique species in this analysis.

$(CH_3)_3N$-C_2H_2 in the Gas Phase

Nine mixtures of trimethylamine and acetylene were prepared in which the ratio of total acetylene to total trimethylamine remained constant.[43] Absorbances were measured with a Beckman IR-18A spectrophotometer at 2312, 2016, 1967.5, 1963, and 1954 cm^{-1}. The last three wavenumbers are in the region of the C≡C stretching mode in acetylene, which becomes IR-active upon complexation with $(CH_3)_3N$. Absorbance errors were calculated as in the last example, by assuming an error of 0.5 in percent transmittance. The results of the least squares fits are given in Table II-4.

TABLE II-3

Results of Linear Dependence Tests on Fe^{+++} - Gantrez Data

χ^2 Probability level	Number of fits using 1 Parameter	2 Parameters	3 Parameters	4 Parameters
0.0-0.1	8	--	--	--
0.1-0.2	--	2	--	--
0.2-0.3	1	2	--	--
0.3-0.4	--	--	--	--
0.4-0.5	--	--	--	--
0.5-0.6	--	--	--	--
0.6-0.7	--	1	--	--
0.7-0.8	--	--	--	--
0.8-0.9	--	1	--	--
0.9-1.0	1	4	5	1
Mean χ^2	157.4	10.2	2.2	0.8
(Degrees of Freedom)	(14)	(13)	(12)	(11)

TABLE II-4

Results of Linear Dependence Tests on $(CH_3)_3N\text{-}C_2H_2$ Data

χ^2 Probability level	Number of fits using 1 Parameter	2 Parameters	3 Parameters	4 Parameters
0.0-0.1	7	--	--	--
0.1-0.2	1	--	--	--
0.2-0.3	--	--	--	--
0.3-0.4	--	--	--	--
0.4-0.5	--	--	--	--
0.5-0.6	--	--	--	--
0.6-0.7	1	2	--	--
0.7-0.8	--	1	--	--
0.8-0.9	--	1	1	--
0.9-1.0	1	6	4	1
Mean χ^2	32.4	3.2	1.9	1.3
(Degrees of Freedom)	(8)	(7)	(6)	(5)

All of the two-parameter (three-wavelength) fits are acceptable; therefore, only two species are indicated. At first glance this result seems unreasonable, since the two original compounds both absorb in this region and there is evidence for a third species, a complex whose presence is indicated by a peak at 1963 cm^{-1}. The dilemma is resolved if one realizes that the ratio of total pressures of amine and acetylene is the same in all of the experiments. Complexation occurs to a small enough extent that this proportionality is not significantly disturbed.[43] Thus, the absorbances of $(CH_3)_3N$ and C_2H_2 will be linearly related, and they will count as only one spectrally unique species.

$(CH_3)_3C\text{-}OH$ in $C_{16}D_{34}$ at 25°

IR spectra of ten solutions of tert-butyl alcohol in deuterated hexadecane were run at 25°C.[30] The infrared spectra were produced with a Perkin-Elmer 521 Spectrometer through the hydroxyl-stretching region (3800-3200 cm^{-1}); in particular, absorbances were calculated at 3625, 3510, 3470, 3400, and 3350 cm^{-1}. Figure II-1 shows some of the measured spectra. Concentrations employed were in the range from 0.0304 M to 0.4661 M. Absorbance errors were calculated by assuming an error of 0.5 percent transmittance both in the baseline reading and in the readings from the spectral curves. A variable pathlength cell was used for the samples, and absorbances were normalized to a 1 cm pathlength. Formal (total) alcohol concentration was employed in the fitting procedure so that a total of six "wavelengths" were used. Errors of 0.0003 moles/ℓ were assumed in the concentrations. The results of the least squares analyses are given in Table II-5.

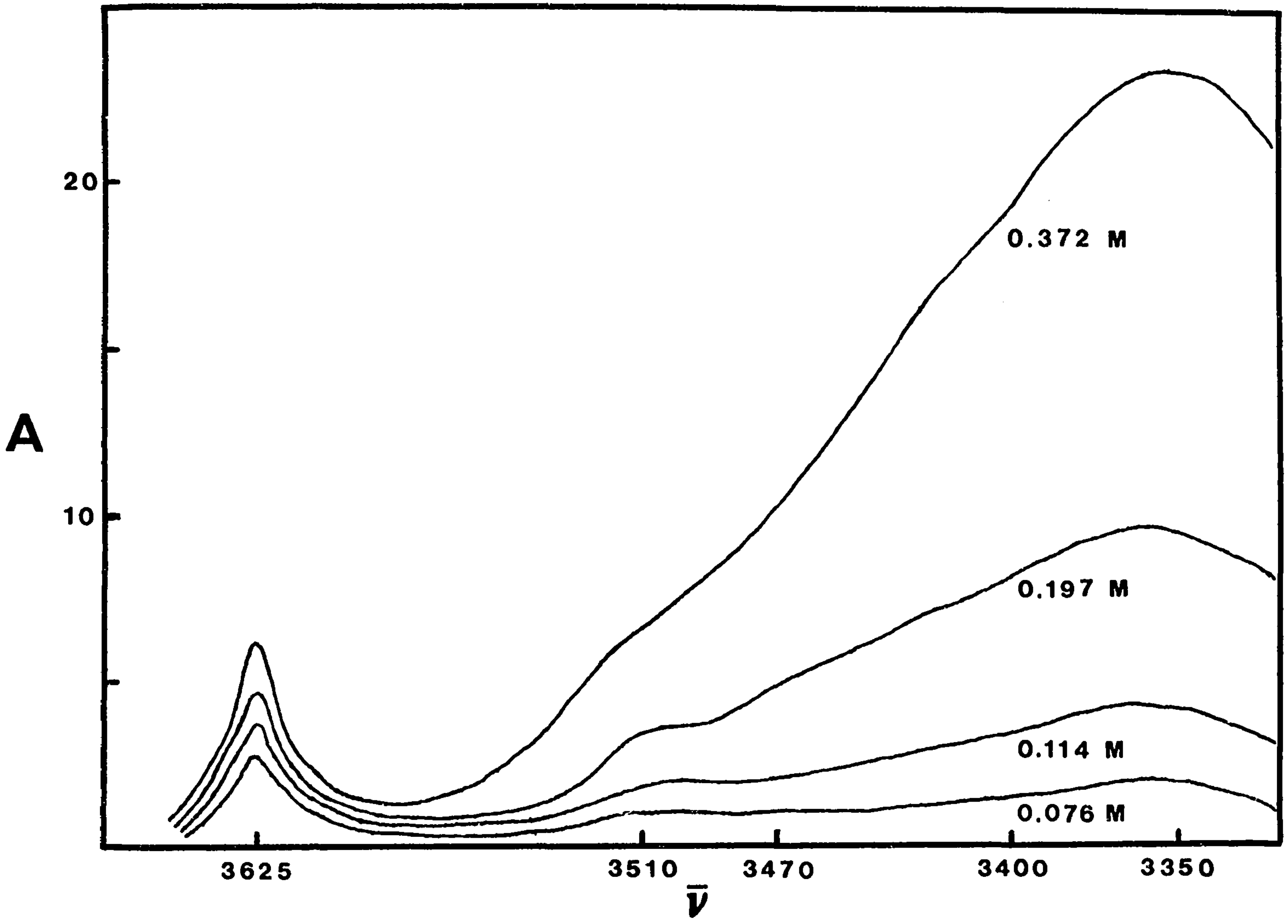


Figure II-1. Spectra of $(CH_3)_3COH$ in $C_{16}D_{34}$ at 25°C.[44]

TABLE II-5

Results of Linear Dependence Tests on t-BuOH Data at 25°

χ^2 Probability level	Number of fits using 1 Parameter	2 Parameters	3 Parameters	4 Parameters	5 Parameters
0.0-0.1	14	7	--	--	--
0.1-0.2	--	1	1	--	--
0.2-0.3	--	--	--	--	--
0.3-0.4	--	--	--	--	--
0.4-0.5	--	--	1	--	--
0.5-0.6	--	3	--	--	--
0.6-0.7	--	2	3	--	--
0.7-0.8	1	2	--	--	--
0.8-0.9	--	4	3	1	--
0.9-1.0	--	1	7	5	1
Mean χ^2	3155.2	12.5	4.0	1.6	0.9
(Degrees of Freedom)	(9)	(8)	(7)	(6)	(5)

The interpretation of the results is not so clear-cut as for the previous examples. There seem to be quite a few of the two-parameter (three-wavelength) fits which are acceptable. However, the distribution is skewed toward the high χ^2 end, and the mean χ^2 value for this group of fits ($\overline{\chi^2}$ = 12.5, 8 degrees of freedom) would have only a 13% chance of occurring if all of these fits were truly "good" and the residuals were random and normally distributed. Thus, it seems that two species may explain part of the data but that three species are probably necessary to account for the complete set of spectral and concentration data. It should be noted that the complete set of three-parameter (four-wavelength) fits is acceptable.

$(CH_3)_3C\text{-}OH$ in $C_{16}D_{34}$ at 35°

Ten solutions of tert-butyl alcohol in deuterated hexadecane were also examined at 35°C.[30] Infrared spectra were taken in the same manner as at 25°. Absorbances were calculated for the same wavelengths, and errors were estimated in an identical fashion. Figure II-2 shows a portion of the IR spectra. The concentrations employed ranged from 0.0301 M to 0.4616 M; errors in concentration were estimated as 0.0003 M. In addition to using the total concentration in the least squares fits, vapor pressures of the ten solutions were also utilized; errors in pressure were taken as 0.02-0.03 torr. Thus, seven "wavelengths" were employed in the analyses. The results are given in Table II-6.

The linear dependence tests on the same alcohol system at a lower temperature indicated three species. There is no reason to

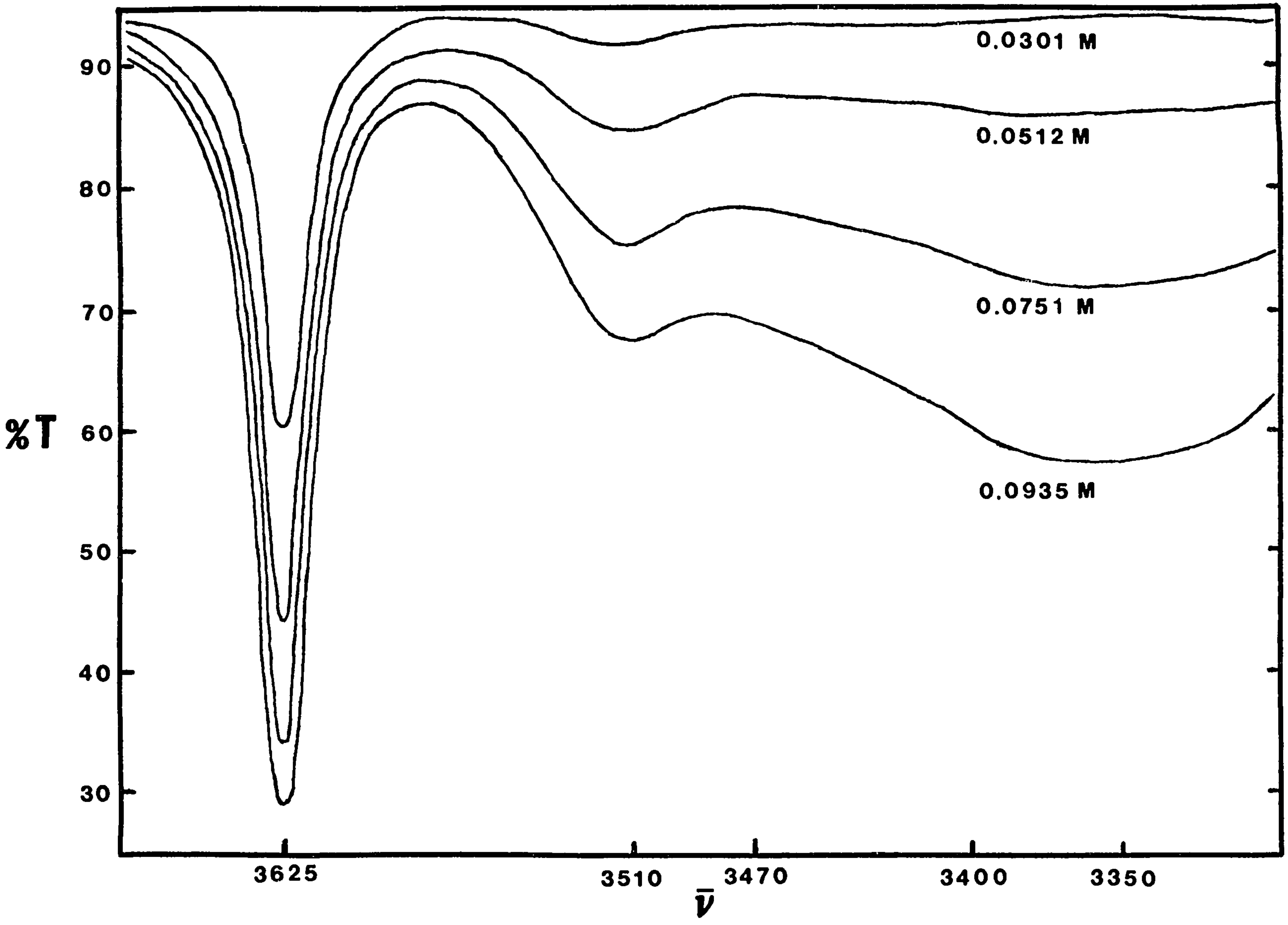


Figure II-2. Spectra of t-BuOH in $C_{16}D_{34}$ at 35°C.[44]

TABLE II-6

Results of Linear Dependence Tests on t-BuOH Data at 35°

χ^2 Probability level	Number of fits using 1 Parameter	2 Parameters	3 Parameters	4 Parameters	5 Parameters	6 Parameters
0.0-0.1	21	27	14	2	--	--
0.1-0.2	--	--	1	--	--	--
0.2-0.3	--	--	4	3	--	--
0.3-0.4	--	1	--	--	--	--
0.4-0.5	--	--	--	--	--	--
0.5-0.6	--	--	--	--	--	--
0.6-0.7	--	--	--	--	--	--
0.7-0.8	--	--	2	2	1	--
0.8-0.9	--	2	2	2	--	--
0.9-1.0	--	5	12	12	6	1
Mean χ^2	11820.9	77.5	12.7	4.3	1.2	0.5
(Degrees of Freedom)	(9)	(8)	(7)	(6)	(5)	(4)

expect a different conclusion in the present case. However, an examination of the least squares results shows that the group of fits using three parameters (four wavelengths) is not acceptable. More than half of the fits have χ^2 values below the 0.3 probability level, and the mean χ^2 value for the group ($\overline{\chi^2}$ = 12.7, 7 degrees of freedom) is at the 8% probability level. Thus, it is rather unlikely that three species could give rise to the measured spectra and vapor pressures; four species are necessary to explain the data.

Since experimental conditions other than temperature were the same for the two sets of alcohol data, it is difficult to understand why different numbers of species are indicated. Because vapor pressures were added to the second set of data, it might be surmised that this type of data does not "mix" well with the absorbances and concentrations and causes worse least squares fits with the higher temperature data. However, a close examination of the linear dependence tests shows that, among the group of three-parameter fits, two-thirds of the fits which included vapor pressure data had χ^2 at a probability level of 0.7 or higher (they were good fits). Thus, the inclusion of vapor pressures does not appear to be the reason for the increased number of species.

C_2H_5OD in n-$C_{10}H_{22}$

The near-infrared spectra of ten solutions of ethanol-d_1 in n-decane were studied at 25°C.[45] Specifically, absorbances were measured at 1.86 μm, 1.89 μm, 1.92 μm, 2.03 μm, and 2.18 μm, all of which are in the hydroxyl overtone region. In this study, Fletcher used concentrations of up to 17 M (neat ethanol), but only the data from those solutions with concentrations in the 0.017-1.392 M range are included here. Formal concentration was employed as a sixth "wavelength"; errors of 0.0005 M were assumed in the concentrations.

The spectra were recorded on a Cary Model 14RI spectrophotometer with the full scale of the chart paper set to equal 20% transmittance; thus, transmittance values should be recorded with excellent precision. %T values were calculated from the absorbances reported in the literature (T_o assumed to be 100%), and then 0.1 %T errors were assumed in both T and T_o. Absorbance errors were calculated from a propagation-of-errors formula. The results of the least squares fits are presented in Table II-7.

Although some of the data can apparently be explained with only two species (note the number of good fits using two parameters), the entire group of three-wavelength fits is not acceptable. There is a large number of poor fits which cause the mean χ^2 value to be quite high ($\overline{\chi^2}$ = 16.1, 8 degrees of freedom). In contrast, the group of fits using three parameters (four wavelengths) yields χ^2 values much lower than would be expected from an acceptable group of fits ($\overline{\chi^2}$ = 2.0 for 7 degrees of freedom). Perhaps the absorbance errors have been overestimated. Nevertheless, it would appear that three species are necessary and sufficient to explain the concentration and spectral data.

TABLE II-7

Results of Linear Dependence Tests on C_2H_5OD Data

χ^2 Probability level	Number of fits using 1 Parameter	2 Parameters	3 Parameters	4 Parameters	5 Parameters
0.0-0.1	13	8	1	--	--
0.1-0.2	--	1	--	--	--
0.2-0.3	--	--	--	--	--
0.3-0.4	--	1	--	--	--
0.4-0.5	--	--	--	--	--
0.5-0.6	--	1	--	--	--
0.6-0.7	1	--	1	--	--
0.7-0.8	--	1	--	--	--
0.8-0.9	--	--	1	--	--
0.9-1.0	1	8	12	6	1
Mean χ^2	2812.8	16.1	2.0	0.5	0.2
(Degrees of Freedom)	(9)	(8)	(7)	(6)	(5)

CHAPTER IV

DISCUSSION

Since it has been claimed that the least squares method presented here for determining the number of chemical species has advantages over other methods, it should be worthwhile to consider the results obtained from one of the matrix rank-eigenvalue methods and to compare the two techniques. Data presented in Appendix B and utilized in the linear least squares demonstration in the preceding chapter were also processed with a program provided by Hugus.[15]

Before results from the Hugus method can be discussed, two statistical tests used by Hugus for determining the number of species must be explained. In the first test, the eigenvalues determined from the absorbance matrix are listed in order of decreasing magnitude. For each eigenvalue, a propagation-of-errors calculation is used to estimate the variance in the eigenvalue. Any eigenvalues which are significantly greater than the square roots of their variances are considered non-zero and count as unique species.

In order to perform the second statistical test, approximations to the original absorbances are generated using as few of the eigenvectors as possible. Thus, if $B_{ij}^{(m)}$ is the approximation to the absorbance in the ith experiment at the jth wavelength (A_{ij}) which is calculated using m eigenvectors, one can obtain

$$\chi_m^2 = \sum_{i,j} \frac{(B_{ij}^{(m)} - A_{ij})^2}{\sigma_{A_{ij}}^2}$$

The number of degrees of freedom is (p-m)(n-m), where p is the number of wavelengths and n is the number of experiments. For each value of m, a comparison can be made between χ_m^2 and its expectation value. Table II-8 lists the results from Hugus' program for the six examples that were discussed in the preceding chapter.

In three cases the Hugus method produces similar results. The Fe^{+++}-Gantrez spectra reduce to a single non-zero eigenvalue; the $(CH_3)_3N$-C_2H_2 data also produce one eigenvalue which is significantly larger than zero; and the C_2H_5OD results give two eigenvalues which are non-zero (larger than their estimated standard deviations). Unfortunately, the interpretation of the results is not so straightforward, since in each case one additional eigenvector is required to reduce χ^2 to a reasonable level (i.e., approximately equal to or less than the expected value). Thus, the Hugus method indicates that either one or two species give rise to the Fe^{+++}-Gantrez spectra and to the $(CH_3)_3N$-C_2H_2 spectra. In both cases, it is obvious from the spectra that at least two species are present. Fe^{+++} absorbs in the region studied; addition of Gantrez alters that spectrum. Both $(CH_3)_3N$ and C_2H_2 absorb in the 1900-2300 cm^{-1} region; a new peak due to their complexation is also evident. (It was explained in the preceding chapter why only two spectrally unique species are likely to be found in these instances.) In addition, the eigenvalue method indicates that either two or three species are present inthe C_2H_5OD solutions.

TABLE II-8

Number of Species Results from the Hugus Method

Eigenvalue	Std. Dev. of Eigenvalue	χ^2_m	$\chi^2_{m, expected}$
A. I_2-Br_2 in CCl_4 (15 experiments; 5 wavelengths and 2 concentrations)			
15.06	0.04	260439.6	84
0.49	0.02	3674.1	65
0.003	0.011	37.9	48
0.0000	0.017	35.7	33
0.0000	0.007	35.0	20
0.00000	0.00005	0.9	9
0.00000	0.00002	0.0	0
B. Fe^{+++} - Gantrez in H_2O (15 experiments; 5 wavelengths)			
5.85	0.02	1008.4	56
0.006	0.010	27.0	39
0.0001	0.005	5.2	24
0.00003	0.00609	0.8	11
0.00001	0.00727	0.0	0
C. $(CH_3)_3N$-C_2H_2 (9 experiments; 5 wavelengths)			
5.65	0.05	204.3	32
0.003	0.018	10.5	21
0.0002	0.0264	4.4	12
0.00005	0.00493	1.4	5
0.00002	0.00850	0.0	0
D. t-BuOH in $C_{16}D_{34}$ at 25° (10 experiments; 5 wavelengths and concentration)			
3660.9	50.4	137076.1	45
32.4	10.3	1866.7	32
0.2	28.1	324.9	21
0.04	12.92	270.9	12
0.001	14.110	231.8	5
0.00002	1.22152	0.0	0

TABLE II-8 (continued)

Eigenvalue	Std. Dev. of Eigenvalue	χ_m^2	χ_m^2, expected
E. t-BuOH in $C_{16}D_{34}$ at 35° (10 experiments; 5 wavelengths, concentration, and vapor pressure)			
9458.6	29.6	519228.4	54
480.7	7.6	1224.9	40
1.4	15.1	453.3	28
0.09	13.48	153.6	18
0.03	4.44	102.5	10
0.003	3.779	35.5	4
0.00001	0.15977	0.0	0
F. C_2H_5OD in n-$C_{10}H_{22}$ (10 experiments; 5 wavelengths and concentration)			
3.620	0.002	25591.6	45
0.0115	0.0004	80.5	32
0.00002	0.00062	18.2	21
0.00001	0.00041	1.4	12
0.00000	0.00008	0.2	5
0.00000	0.00010	0.0	0

Unfortunately, the interpretation of the Hugus method's results grows more confusing with the remaining systems. Data from I_2-Br_2 and t-BuOH (at both 25° and 35°) produce, in each case, two non-zero eigenvalues. However, the X^2 test proves worthless in all these instances. With the I_2-Br_2 data, X^2 from three eigenvectors is satisfactorily small; however, X^2 calculated using five eigenvectors is improbably large. With both sets of t-BuOH data, <u>all</u> of the eigenvectors must be used to achieve a satisfactory fit of the data; therefore, no information about the number of species is gained from this statistical test.

It is likely that the failure of the Hugus method in these cases is due primarily to the inclusion of concentration data. A close examination of the results shows that it is the data points involving concentrations which are not fit well and thus produce the large X^2 values. Table II-9 illustrates the results from the Hugus routine when concentration data are omitted. It can be seen that removal of these data improves the results in all three cases. The X^2 test now indicates three species for I_2-Br_2, four species for t-BuOH at 25°, and five species for t-BuOH at 35°.

The failure of the Hugus method to accommodate concentration data along with absorbance data is indicative of a major weakness in all factor analysis-matrix rank-eigenvalue-type techniques for determining number of species. The precision (weight) of individual data points has not been taken into account in determining rank or eigenvalues. When data of widely varying precision are employed, the technique fails. When data of closer precision are used, the

TABLE II-9

Number of Species Results from the Hugus Method

(Concentration Data Omitted)

Eigenvalue	Std. Dev. of Eigenvalue	χ_m^2	χ_m^2, expected
A. I_2-Br_2 in CCl_4 (15 experiments; 5 wavelengths)			
15.06	0.04	43590.8	56
0.49	0.02	286.6	39
0.003	0.011	4.7	24
0.00003	0.01715	2.1	11
0.00001	0.00743	0.0	0
B. t-BuOH in $C_{16}D_{34}$ at 25° (10 experiments; 5 wavelengths)			
3660.4	50.5	15062.0	36
32.4	10.3	76.2	24
0.2	28.1	49.9	14
0.04	12.92	1.0	6
0.001	14.155	0.0	0
C. t-BuOH in $C_{16}D_{34}$ at 35° (10 experiments; 5 wavelengths and vapor pressure)			
9458.1	29.6	455897.1	45
480.7	7.6	651.2	32
1.4	15.1	79.2	21
0.09	13.48	43.5	12
0.03	4.44	1.4	5
0.003	3.79	0.0	0

method appears to work, but it cannot truly succeed until individual weights are included.

One may notice that the Hugus method seems to succeed on data for C_2H_5OD, in which concentrations are included. In this one case, the absorbance errors are assumed to be quite low, and the absorbances have approximately the same size errors as the concentrations. Nevertheless, concentration data are always important, and number-of-species methods should be capable of using this information regardless of its precision.

Since these methods were introduced as likely to be particularly helpful in studies of alcohols, it should be worthwhile to consider these results in more detail. Table II-10 summarizes the results of the two methods described here. It would appear that the number of non-zero eigenvalues is not a useful statistic for these examples. In addition to indicating two species regardless of the fit of the data, the results of the eigenvalue test seem to disagree with spectral evidence for at least three unique species. For example, Fletcher[45] claims to have demonstrated the existence of three species in the spectrum of C_2H_5OD.

Tucker and Becker[30] discuss in detail the assignment of various bands in the t-BuOH spectrum to alcohol species (see figures II-1 and II-2). By comparison with vapor pressure and pmr data, they conclude that the peak at 3625 cm^{-1} is due to monomer and to the end -OH group of an acyclic trimer; the peak at 3510 cm^{-1} is attributed to the trimer. The broad absorption at lower frequencies is assigned to a higher (cyclic) polymer or polymers. Their vapor pressure and

TABLE II-10

Results of Number of Species Determinations on Alcohol Data

	Linear Least Squares Method	Hugus Method*	
		Non-zero Eigenvalues	χ^2 Test
A. t-BuOH in $C_{16}D_{34}$ at 25°	3	2	4
B. t-BuOH in $C_{16}D_{34}$ at 35°	4	2	5
C. C_2H_5OD in $C_{10}H_{22}$	3	2	3

---

*Concentrations were omitted from both sets of t-BuOH data.

pmr data seem to be fit best with a model that assumes stepwise polymer formation after the trimer (i.e.,

$$C_n = KC_1C_{n-1} \qquad\qquad n \geq 4$$

where C_n is the concentration of the cyclic polymer containing n monomeric alcohol units). Therefore, the linear least squares method for determining number of species gives an answer for t-BuOH which is no more definitive but basically in agreement with Tucker and Becker's conclusions. It indicates either three or four unique species, depending on the set of data employed. (One would expect that if polymers existed whose spectra were linear combinations of lower species' spectra, no number of species method would be able to detect them.)

Several advantages of the linear dependency method described above should be summarized here, along with warnings about use of the technique with various types of data. Two important features of the new fitting procedure are its conceptual simplicity and the generality of its application to different types of data and to results with widely varying uncertainties. Weighting factors, which take experimental errors into account, are employed at every step of the calculations. In current matrix-rank methods and other factor-analysis methods, matrices are manipulated or eigenvalues are calculated without regard for errors in the measured quantities. The errors are introduced at a later stage of the calculations where tests of significance are made.

Limitations of the linear-dependence technique are similar to those of the other methods. Obviously, chemical species which do not absorb at any of the chosen wavelengths (and which do not contribute to any of the other physical measurements incorporated in the analysis) are not included in the deduced number of species. Linear combination relations among the absorbances (or other properties being fitted) for the different species will similarly reduce the effective number of species. For example, different isomers of a solute species may have quite different spectral absorption bands; however, at least in the dilute solution region at a fixed temperature, the concentration of any one isomer will vary directly with that of each of the others. Thus, the isomers collectively will count as only one independent species. (In principle, one could fit data obtained at several temperatures together and thereby infer the presence of more than one isomer, provided the relative concentrations of the isomers depend significantly on temperature.)

Probably the most serious limitation on any of the various methods for determining number of species is the ambiguity arising from incorrect estimates of uncertainties in the data. For example, if it were determined that the uncertainties in individual absorbance values had been incorrectly estimated by a factor of two, the observed χ^2 values would all have to be changed by a factor of four. As a result it is quite likely that more or fewer species (depending on whether the errors had originally been overestimated or underestimated) would be required to explain the spectral data. There seems to be no way to remove this type of ambiguity in statistical analyses of limited numbers of data, but it is clear that careful attention to determination of probable errors in measured quantities is required in meaningful applications of all of the methods for inferring number of species. A corollary of this last statement is the observation that proper weighting of individual data points is extremely important in any number-of-species determination.

Finally, it should be noted that number-of-species determinations are a convenient starting point in numerical analyses for calculating equilibrium constants for formation of molecular complexes. Armed with the knowledge that a given number of species is probably present, one can propose reasonable stoichiometries for the various complexes and then apply conventional analytical methods to fit data to particular mass action models. The number of species techniques are by no means substitutes for this latter type of analysis, but they should prove particularly useful in the initial examination of spectral and other types of solution data.

APPENDIX A

LINEAR LEAST SQUARES ANALYSIS WITH ERRORS IN ALL OF THE VARIABLES

The linear least squares analysis involved in the method for determining number of species has one main difference from many linear least squares techniques. The method requires the fitting of experimental data in which <u>all</u> of the independent and dependent variables are subject to errors of measurement. In most examples of linear least squares curve-fitting, the independent variables are assumed to be free of error. Such an assumption cannot be made in the present situation.

Functions of the form

$$A_m = rA_1 + sA_2 + \ldots + zA_n \qquad \text{(A-1)}$$

are fit with weighted linear least squares analysis. A_i values are experimentally measured absorbances, concentrations, vapor pressures, etc. and are all clearly subject to error. The least squares problem is to find values of r, s, ..., z which minimize the sum of weighted squared residuals,

$$S = \sum_{i=1}^{p} W_i (A_{m,i} - rA_{1,i} - sA_{2,i} - \ldots - zA_{n,i})^2$$

for p data points. The weight for each point is proportional to the reciprocal of the variance of the residual. This variance can be expressed in terms of the individual errors as[46]

$$\frac{1}{W_i} = \sigma^2_{A_{m,i}} + r^2\sigma^2_{A_{1,i}} + s^2\sigma^2_{A_{2,i}} + \ldots + z^2\sigma^2_{A_{n,i}}$$

and the expression for S is therefore written as

$$S = \sum_{i=1}^{p} \frac{(A_{m,i}-rA_{1,i}-sA_{2,i}-\ldots-zA_{n,i})^2}{\sigma^2_{A_{m,i}}+r^2\sigma^2_{A_{1,i}}+s^2\sigma^2_{A_{2,i}}+\ldots+z^2\sigma^2_{A_{n,i}}} \qquad \text{(A-2)}$$

Equation A-2 makes it clear that, in attempting to determine the values of r, s,...,z which minimize S, one cannot legitimately neglect the dependence of W_i on the parameters unless one of the terms in the denominator is much larger than the sum of the others for each value of i. If one of the terms is dominant, equation A-2 simply reduces to the well-known form of least squares which applies when only one of the observables is subject to error.

In the general case, such as that found in the number of species method, it is not justifiable to ignore the variation of W_i with r, s,...,z in differentiating S to obtain $\partial S/\partial r$, $\partial S/\partial s$, ..., $\partial S/\partial z$. Yet, this is equivalent to what is done in most standard treatments of the problem. The procedure commonly developed corresponds to seeking a minimum in equation A-2 by treating the parameters r, s,..., z as variables in the numerator while holding them constant in the denominator. The fact that iterative procedures are sometimes used, in which estimated values of the least squares parameters determined in one cycle are employed to derive weights for use in the next cycle, does not overcome the basic fallacy in this method.

Furthermore, it is often found that when the usual (improper) weighted least squares methods are applied to data in the form of equation A-1, the results vary with the choice of dependent variable.[46] When A_m is fitted as a linear function of A_1, A_2,..., A_n, the results are often different from results obtained when A_1 is fit as a linear function of A_m, A_2 ..., A_n or when A_2 is fit as a linear function of A_m, A_1, ..., A_n. Disparate values of S are obtained at the "minimum" and the least squares constants are not algebraically consistent from one choice of dependent variable to the next. Clearly, this is unacceptable. There can be no meaningful distinction between the terms dependent and independent as applied to this problem, and the final least squares fit cannot be influenced by the order in which the variables are arranged.

Proper differentiation of S with respect to the least squares constants avoids this problem. There is no dependence on the arrangement of variables, and the minimum value of S is lower than any of the "minima" found by the usual least squares treatments.[46]

Equation A-2 can be properly minimized by an iterative procedure in which values of the least squares constants found in one cycle are used to calculate weights for the next cycle. Differentiation with respect to the constants is done properly, and the usual normal equations must be modified somewhat. Since the linear problem has effectively become nonlinear, it may be that an efficient nonlinear optimization routine would provide the fastest and easiest solution to this optimization problem. Such an approach is suggested for future investigators in this field.

APPENDIX B

DATA EMPLOYED IN THE NUMBER OF SPECIES CALCULATIONS

The following data (Tables II-11 to II-16) are, for the most part, not readily available in the literature. Therefore, they are presented here for the benefit of anyone seeking to reproduce the preceding results or to study in detail the methods for the determination of number of species.

TABLE II-11

Spectral and Concentration Data for I_2-Br_2 in CCl_4[41]

Solution No.	Absorbance at 580 nm	550 nm	518 nm	460 nm	430 nm	Total I_2 concentration	Total Br_2 concentration
1	0.245	0.577	0.890	0.348	0.102	0.0005312	0.0000961
2	0.213	0.509	0.820	0.408	0.151	0.0005291	0.0001912
3	0.183	0.435	0.751	0.475	0.204	0.0005271	0.0002860
4	0.154	0.364	0.682	0.532	0.257	0.0005249	0.0003798
5	0.147	0.353	0.675	0.552	0.265	0.0005244	0.0004032
6	0.139	0.335	0.655	0.562	0.275	0.0005239	0.0004265
7	0.133	0.322	0.642	0.573	0.289	0.0005234	0.0004497
8	0.124	0.304	0.620	0.600	0.309	0.0005223	0.0004961
9	0.120	0.291	0.615	0.616	0.322	0.0005218	0.0005192
10	0.117	0.287	0.612	0.620	0.331	0.0005213	0.0005423
11	0.117	0.283	0.610	0.632	0.341	0.0005208	0.0005653
12	0.116	0.280	0.608	0.634	0.355	0.0005203	0.0005883
13	0.116	0.278	0.608	0.661	0.378	0.0005188	0.0006570
14	0.115	0.281	0.615	0.684	0.414	0.0005168	0.0007479
15	0.116	0.281	0.620	0.707	0.450	0.0005148	0.0008381

TABLE II-12

Spectral Data for Fe^{+++} - Gantrez in H_2O[42]

Solution No.	Absorbance at 372.5 nm	362.5 nm	350 nm	337.5 nm	325 nm
1	0.024	0.028	0.038	0.048	0.064
2	0.034	0.042	0.052	0.066	0.090
3	0.038	0.046	0.060	0.078	0.108
4	0.045	0.054	0.070	0.092	0.124
5	0.054	0.064	0.082	0.106	0.148
6	0.058	0.074	0.096	0.124	0.168
7	0.070	0.088	0.116	0.150	0.198
8	0.084	0.108	0.144	0.180	0.230
9	0.098	0.130	0.176	0.214	0.266
10	0.116	0.160	0.216	0.262	0.318
11	0.146	0.204	0.270	0.318	0.380
12	0.186	0.260	0.344	0.400	0.472
13	0.230	0.320	0.426	0.494	0.566
14	0.276	0.384	0.514	0.588	0.664
15	0.336	0.472	0.626	0.710	0.794

The baseline was at 100% transmittance at all five wavelengths

TABLE II-13

Spectral Data for $(CH_3)_3N-C_2H_2$ in the Gas Phase[43]

Mixture No.	Transmittance at 2312 cm^{-1}	2016 cm^{-1}	1967.5 cm^{-1}	1963 cm^{-1}	1954 cm^{-1}
1	78.5	84.1	95.7	95.7	95.9
2	66.5	73.1	92.9	91.0	92.3
3	50.0	60.7	86.9	84.1	85.5
4	38.3	50.0	80.5	77.3	80.0
5	28.0	39.0	73.6	69.5	72.4
6	21.5	31.7	68.1	63.1	67.5
7	16.7	25.5	61.5	56.5	62.5
8	13.2	21.7	56.9	50.0	58.1
9	10.6	18.7	51.0	44.6	53.3
Baseline Transmittance	92.7	94.7	100.0	100.0	100.0

TABLE II-14

Spectral and Concentration Data for t-BuOH in $C_{16}D_{34}$ at 25°C[44]

Solution No.*	Transmittance and (baseline transmittance) at 3625 cm^{-1}	3510 cm^{-1}	3470 cm^{-1}	3400 cm^{-1}	3350 cm^{-1}	Total t-BuOH Concentration
1	59.3 (95.4)	91.5 (96.1)	93.3 (96.2)	92.4 (96.3)	92.1 (95.7)	0.0304
2	44.9 (95.4)	82.7 (96.1)	84.7 (96.2)	79.5 (96.3)	77.2 (95.7)	0.0517
3	36.5 (95.4)	72.6 (96.1)	72.6 (96.2)	60.2 (96.3)	54.6 (95.7)	0.0759
4	31.5 (95.4)	64.3 (96.1)	61.5 (96.2)	45.8 (96.3)	38.1 (95.7)	0.0944
5	43.4 (95.0)	67.8 (95.3)	63.3 (95.5)	46.4 (95.5)	39.2 (95.3)	0.1138
6	37.9 (95.0)	56.4 (95.3)	47.5 (95.5)	26.6 (95.5)	20.0 (95.3)	0.1581
7	34.4 (95.0)	47.2 (95.3)	35.8 (95.5)	16.3 (95.5)	11.2 (95.3)	0.1968
8	59.2 (95.0)	63.2 (95.7)	51.5 (95.8)	29.2 (95.9)	22.0 (96.1)	0.2740
9	55.3 (95.0)	53.2 (95.7)	37.8 (95.8)	16.5 (95.9)	11.5 (96.1)	0.3716
10	52.7 (95.0)	45.3 (95.7)	28.8 (95.8)	10.1 (95.9)	6.6 (96.1)	0.4661

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*Solutions 1-4 were studied in a 1.55 mm cell, solutions 5-7 in a 1.00 mm cell, and solutions 8-10 in a 0.40 mm cell.

TABLE II-15

Spectral, Concentration, and Vapor Pressure Data for t-BuOH in $C_{16}D_{34}$ at 35°C[44]

Solution No.*	Transmittance and (baseline transmittance) at 3625 cm^{-1}	3510 cm^{-1}	3470 cm^{-1}	3400 cm^{-1}	3350 cm^{-1}	Total t-BuOH Concentration	Vapor Pressure
1	59.5 (95.6)	92.5 (96.2)	94.2 (96.3)	94.3 (96.3)	95.4 (96.5)	0.0301	8.15
2	44.3 (95.6)	85.4 (96.2)	88.5 (96.3)	87.1 (96.3)	87.4 (96.5)	0.0512	12.92
3	34.5 (95.6)	76.2 (96.2)	79.2 (96.3)	74.1 (96.3)	78.3 (96.5)	0.0751	17.19
4	29.5 (95.6)	67.8 (96.2)	69.7 (96.3)	61.4 (96.3)	58.3 (96.5)	0.0935	19.90
5	40.0 (95.1)	70.3 (95.5)	69.8 (95.5)	59.8 (95.7)	56.9 (96.0)	0.1127	22.29
6	33.3 (95.1)	57.6 (95.5)	53.4 (95.5)	37.7 (95.7)	33.6 (96.0)	0.1565	26.59
7	29.4 (95.1)	48.0 (95.5)	40.7 (95.5)	34.0 (95.7)	20.0 (96.0)	0.1949	29.38
8	54.9 (95.0)	62.8 (95.3)	54.5 (95.7)	36.0 (95.8)	31.1 (96.2)	0.2713	33.71

Table II-15 (continued)

Solution No.*	Transmittance and (baseline transmittance) at 3625 cm^{-1}	3510 cm^{-1}	3470 cm^{-1}	3400 cm^{-1}	3350 cm^{-1}	Total t-BuOH Concentration	Vapor Pressure
9	50.0 (95.0)	52.0 (95.3)	39.7 (95.7)	21.0 (95.8)	17.2 (96.2)	0.3681	37.62
10	46.9 (95.0)	43.8 (95.3)	30.0 (95.7)	13.1 (95.8)	10.1 (96.2)	0.4616	40.47

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[*] Solutions 1-4 were studied in a 1.55 mm cell, solutions 5-7 in a 1.00 mm cell, and solutions 8-10 in a 0.40 mm cell.

TABLE II-16

Spectral and Concentration Data for C_2H_5OD in n-$C_{10}H_{22}$ at 25°C[45]

Solution No.	Absorbance at 1.86 μm	1.89 μm	1.92 μm	2.03 μm	2.18 μm	Total C_2H_5OD Concentration
1	0.0004	0.0141	0.0004	0.0002	0.0000	0.01666
2	0.0005	0.0210	0.0008	0.0003	0.0002	0.02465
3	0.0013	0.0411	0.0017	0.0009	0.0007	0.05773
4	0.0040	0.0611	0.0043	0.0050	0.0035	0.12969
5	0.0067	0.0696	0.0052	0.0092	0.0057	0.19388
6	0.0089	0.0763	0.0059	0.0142	0.0084	0.27963
7	0.0153	0.0862	0.0056	0.0250	0.0144	0.41305
8	0.0249	0.0963	0.0140	0.0415	0.0238	0.63969
9	0.0390	0.1094	0.0222	0.0682	0.0390	0.94107
10	0.0587	0.1224	0.0329	0.1053	0.0600	1.3916

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