Thermodynamic Properties of Gas-Phase Hydrogen-Bonded Complexes

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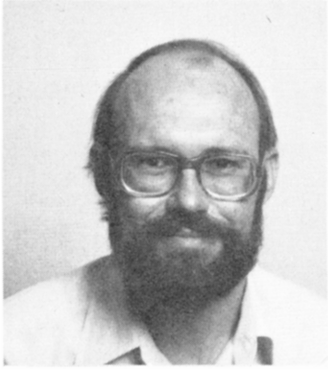
Contents

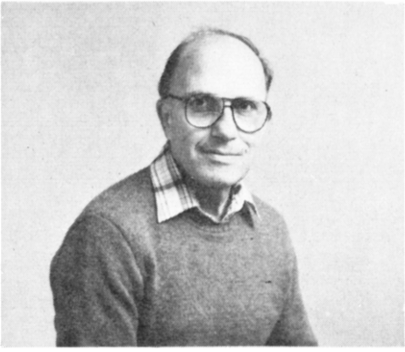
I. Introduction

Since the concept of hydrogen bonding was first proposed,[1] it has been the subject of much research in both chemistry and biology. One focus of research has been the energetics of hydrogen bond formation.[2,3] Methods based on spectroscopy, calorimetry, nonideal gas behavior, and transport properties have been used to obtain thermodynamic properties of hydrogen-bonded complexes. The majority of these studies have been done in "inert" solvents, while relatively few have been done in the gas phase. Gas-phase thermodynamic data on hydrogen-bonded species, the subject of this review, are fundamentally simpler than data from solvents since only energetic effects related to hydrogen bonding are included. In addition, the molecules involved are generally small enough to perform reliable quantum mechanical calculations of potential energy surfaces so that gas phase data can provide good tests of calculational methods. There have been numerous reviews[4] of applications of molecular orbital methods to the study of hydrogen bonding. In general, coupling analyses of experimental measurements with theoretical calculations enhances the reliability of both. Gas-phase measurements of association also provide a means of obtaining the energetics of the formation of polymers larger than the dimer, which is often indeterminate in solution. This can give insight into cooperative effects in hydrogen bonding[5,6] and is important in the derivation of equations of state for gases, such as steam, where higher polymers may be important. Finally, the gas-phase data provide a base line for determining solvent effects on hydrogen bonding in solution.

The purpose of this paper is to review the thermodynamic properties of gas-phase hydrogen-bonded complexes derived from nonideal gas measurements,



Larry A. Curtiss was born in Madison, WI, in 1947 and received his B.S. degree in chemistry from the University of Wisconsin in 1969. He received his Ph.D. degree in physical chemistry in 1973 working with Professor John A. Pople. He then spent about 2 years as a Battelle Institute Fellow at Battelle Memorial Institute (working with Professor C. W. Kern) in Columbus, OH. In 1976 he joined the Chemical Technology Division at Argonne National Laboratory. His research interests include experimental studies of gas-phase association reactions and theoretical studies of van der Waals complexes, molten salts, zeolites, heterogeneous charge-transfer reactions, and small molecules and their cations.



Milton Blander was born in Brooklyn, NY, in 1927. He received his B.S. degree in chemistry from Brooklyn College in 1950 and his Ph.D. at Yale in 1953. After 2 years of postdoctoral work at Cornell University, he joined the Oak Ridge National Laboratory in 1955 to initiate his work on molten salts and their vapors. In 1962 he joined the Rockwell International Science Center in Thousand Oaks, CA, where he worked on ionic materials, lunar samples, the origin of meteorites, and nucleation. He joined the Chemical Technology Division at Argonne National Laboratory in 1971 where his work has included studies on high-temperature solutions and their vapors, nucleation phenomena, alloys, vapor association, meteorites, and pyrometallurgy.

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spectroscopy, and transport properties. Emphasis is placed on the enthalpy of association, ΔH, which is directly related to the stabilization energy of the complex, and on the entropy of association ΔS, which makes a significant contribution[7] to the standard free energy of formation of the complex and, hence, the amount present in the gas. Included in this review are dimers between molecules of the same type and of different types. The majority of these dimers are present in only small amounts in the vapor (water vapor contains about 1% dimer at 373 K and 1 atm), although some gases, such as carboxylic acids, contain a large fraction of associated species (saturated acetic acid vapor contains about 56% dimer at 386 K). Also covered in this review will be polymers larger than dimer, which are present in some vapors in large enough quantities to be detected. This review does not cover hydrogen-bonded complexes involving charged species (anions or cations) which have been reviewed elsewhere.[8] In addition, a great deal of interesting structural and dynamical information on hydrogen bonded complexes has been obtained in recent years from molecular beam experiments. This also has been reviewed elsewhere.[9]

Some of the earliest work on thermodynamic properties of gas-phase hydrogen-bonded complexes took place in the 1940s and was based on the fact that gases with associated species show much greater deviations from the perfect gas laws than gases with no association.[10–15] The virial coefficients in the equation of state are one of the ways to express nonideal gas behavior and can be obtained by different techniques, such as vapor density, compressibilities, PVT, heat capacities, etc. The second virial coefficient, B, is the largest and most often studied virial coefficient and is usually related to dimer formation. The use of transport properties, such as thermal conductivities, to study association in gases also began about the same time as the use of virial coefficients.[16–18] The subsequent development of theories of transport properties of associating gases[19–22] provided a method for analyzing data from thermal conductivity measurements in terms of the thermodynamic properties of gas-phase complexes. Spectroscopic methods provide the most direct method of measuring thermodynamic properties of hydrogen-bonded complexes. However, the small amounts of complexes usually present in most gases often make accurate analyses difficult. Recent developments in high-resolution spectroscopy[9a] provide the promise of more accurate hydrogen bond energies in the future. Finally, in recent years, computational quantum chemistry has advanced to the point where it plays an important role in supplementing experimental measurements of thermodynamic properties.

In section II, the experimental techniques used in the analysis of the thermodynamic properties of gas-phase hydrogen-bonded complexes are reviewed, with emphasis on the method of analysis. The three general areas mentioned above (nonideal gas behavior, thermal conductivity, and spectroscopy) are covered. In section III, specific studies will be reviewed. The tables include a compilation of association enthalpies and entropies of many gas-phase hydrogen-bonded complexes. Critical evaluation, where appropriate, is done in the text. Since ab initio molecular orbital theory plays an important role in supplementing experimental results, we will note such results when it provides insight into the energetics of the hydrogen bonding. Trends in the enthalpies and entropies of associated species will also be noted. Finally, general conclusions are presented in section IV.

II. Experimental Methods

A. Deviations from Ideal Gas Behavior

A widely used technique for studying molecular association in the gas phase is the analysis of gas imperfections as determined by PVT, vapor density, heat capacity, ultrasound velocity, etc. techniques.[23–55] The data may be treated in several ways. In one treatment (virial coefficient), the data are used to define a virial equation of state[56] of the type

$$p\bar{V}/RT = 1 + B(T)/\bar{V} + C(T)/\bar{V}^2 + D(T)/\bar{V}^3 + \ldots \quad (1)$$

where $B(T)$, $C(T)$, and $D(T)$ are referred to as the second, third, and fourth virial coefficients, respectively. Analysis of one or more of the virial coefficients gives information on the thermodynamic properties of dimers and higher polymers.

Several different methods have been used to relate the second virial coefficient $B(T)$ to an equilibrium constant for dimerization. In one commonly used method, the dimerization constant K_2 is related to $B(T)$ by[15a,57]

$$-K_2RT = B(T) - B_{\text{nonpolar}} \quad (2)$$

where B_{nonpolar} is the nonpolar part of the second virial coefficient. This latter quantity, also referred to as the "excluded" volume (b_0), contains contributions to nonideality from effects other than association. It is commonly obtained from the physical properties of a nonpolar homomorph of the polar species being considered. For example, the nonpolar homomorph of acetonitrile would be propane. An alternative definition for B_{nonpolar} was suggested by Lambert et al.[11] They assume the nonpolar part of $B(T)$ to be given by the Berthelot equation of the form $a - bT^{-2}$. The use of the Berthelot equation introduces a temperature dependence into B_{nonpolar} and also gives values for B_{nonpolar} that are generally much larger and of the opposite sign than those obtained from the nonpolar homomorph definition. Finally, it has also been suggested[58–60] that the second virial coefficient should be related exactly to an association constant, $-K_2RT = B(T)$. This approach avoids the artificial division of the second virial coefficient into contributions from polar and nonpolar interactions.

The slope of a plot of log K_2 versus $1/T$ gives values for ΔH_2. The entropy ΔS_2 is related to ΔH_2 and K_2 by

$$K_2(T) = \exp(\Delta S_2/R - \Delta H_2/RT) \quad (3)$$

where R is the gas constant. Analysis of the third and higher virial coefficients is done in terms of the thermodynamic properties of polymers larger than dimer in ways analogous to that of the second virial coefficient for the dimer.

To illustrate the dependence of the analysis of second virial coefficient data on how $B(T)$ is related to the equilibrium constant K_2, we have calculated thermodynamic properties of the acetone dimer from the

TABLE I. Dependence of ΔH_2, ΔS_2, and K_2 on the Value of B_{nonpolar} (See Eq 2) Used in Analysis of Second Virial Coefficient Data[a] for Acetone

B_{nonpolar}, cm^3 mol^{-1}	ΔH_2, kcal mol^{-1}	ΔS_2, cal mol^{-1} K^{-1}	K_2, atm^{-1} (at T = 360 K)
-200	-3.84	-17.94	0.0258
-100	-3.55	-16.89	0.0291
0	-3.28	-15.92	0.0325
100	-3.09	-15.18	0.0359
200	-2.92	-14.39	0.0393
300	-2.78	-13.99	0.0427

[a] Recommended virial coefficients (for $T \geq 330$ K) from ref 61.

recommended second virial coefficient values of Dymond and Smith[61] using various values for B_{nonpolar} in eq 2. The ΔH_2, ΔS_2, and K_2 resulting from B_{nonpolar} values ranging from −200 to 300 cm^3 mol^{-1} are listed in Table I. The enthalpy of association ranges from −3.84 to −2.78 kcal mol^{-1}, while the entropy of association ranges from −17.94 to −13.99 cal mol^{-1} K^{-1}.

A related method, based on heat capacities, was developed by Pitzer and Weltner[30] for methanol. They used heat capacity expressions corresponding to the virial equation to calculate virial coefficients. This type of method has been used to analyze data for a large number of alcohols[32,33,47,48,51,52] as well as other systems.[26,40] Heat capacities are particularly sensitive to association enthalpies. *PVT* data are often combined with heat capacity data in the analysis.

Other treatments of *PVT* and vapor density data are based on the assumption that all deviations are due to specific complex formation, but do not express these deviations in terms of the virial equation explicitly. Equilibrium constants are derived from fitting of pressure–volume relationships. Enthalpies of association are obtained from the temperature dependence of the equilibrium constants. Most of the data for mixed dimers from nonideal gas measurements have been obtained using this method.[37,45,46,49]

In summary, analysis of nonideal gas behavior is subject to problems due to the arbitrariness of the division of contributions to gas nonideality. However, as will be discussed in section III, these methods have contributed useful information on the thermodynamic properties of gas-phase hydrogen-bonded complexes.

B. Thermal Conductivity

The dependence of the thermal conductivity of a gas on temperature and pressure can be used to determine thermodynamic data for associated species in the gases. This technique eliminates some of the ambiguities of the nonideal gas methods and is also quite sensitive to the presence of higher polymers. One of the first studies to recognize the potential for thermal conductivity measurements in studying association in gases was that by Schäfer and Foz Gazulla[16] in 1942. In the early fifties, Lambert et al.[17] and Vines[18] also used thermal conductivity measurements to study association in a series of gases. In 1957, Hirschfelder[19] presented a theoretical treatment for the thermal conductivity of a reacting gas mixture when local chemical equilibrium is assumed. Butler and Brokaw[21,22] subsequently generalized the theory for thermal conductivity of chemically reacting gas mixtures; this work has been the basis for numerous analyses of the thermal conductivity of associating gases.[62–75]

The thermal conductivity of vapors of associating molecules can be expressed by[20]

$$\lambda = \lambda_f + \lambda_c + \lambda_R \tag{4}$$

where λ_f is the thermal conductivity of a frozen (nonreacting) composition of all the vapor species, λ_c is the contribution due to an effect referred to as "collisional transfer", and λ_R is the contribution to thermal conductivity arising from transport of association enthalpy in a thermal gradient. Generally, for an associating gas, the λ_R term makes the major contribution to the increase in thermal conductivity with pressure, and the other two terms, λ_f and λ_c, are not very pressure dependent.

The expression for λ_R is given by

$$\lambda_R = -\frac{1}{RT^2}\begin{vmatrix} 0 & \Delta H_1 & \cdots & \Delta H_\nu \\ \Delta H_1 & A_{11} & \cdots & A_{1\nu} \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \Delta H_\nu & A_{\nu 1} & \cdots & A_{\nu\nu} \end{vmatrix} \div \begin{vmatrix} A_{11} & \cdots & A_{\nu\nu} \\ \cdot & & \\ \cdot & & \\ \cdot & & \\ \cdot & & \\ A_{\nu 1} & \cdots & A_{\nu\nu} \end{vmatrix} \tag{5}$$

where ν is the number of independent chemical reactions (associations to form polymers in this case) occurring in the mixture, ΔH_n is the enthalpy change for the ith or jth reaction, and the A_{ij} are numerical factors that depend on m, the stoichiometric coefficients; x, the mole fractions of the species in the gas; p, the total pressure; and D_{kl}, the binary interdiffusion coefficient for species k and l. The A_{ij}'s are defined by

$$A_{ij} = A_{ji} = \sum_{k=1}^{\mu-1} \sum_{l=k+1}^{\mu} \left(\frac{RT}{pD_{kl}}\right) x_k x_l \left[\frac{m_{ik}}{x_k} - \frac{m_{il}}{x_l}\right]\left[\frac{m_{jk}}{x_k} - \frac{m_{jl}}{x_l}\right] \tag{6}$$

The subscripts on the coefficients, m, and mole fractions, x, refer to the kth or lth chemical species in the ith or jth reaction. The subscripts i and j can have values between 1 and ν. The parameter μ is the number of distinct chemical species.

If there is only one association reaction $n\mathrm{A(g)} \rightleftharpoons \mathrm{A}_n\mathrm{(g)}$ occurring in the vapor, then eq 5 and 6 simplify to

$$\lambda_R = \left(\frac{pD_{1n}}{RT}\right)\left(\frac{\Delta H_n^2}{RT^2}\right)\frac{K_n p_1^{n-1}}{(1 + nK_n p_1^{n-1})^2} \tag{7}$$

where p_1 is the partial pressure of the monomer, R is the gas constant, and K_n is the equilibrium constant for the association reaction. The pressure–binary diffusion coefficient, pD_{1n}, is dependent on temperature, but not on pressure. If there is more than one association reaction and there are relatively low concentrations of associated species, eq 5 and 6 reduce approximately to

$$\lambda_R = \sum_n (pD_{1n}/RT)(\Delta H_n^2/RT^2)K_n p_1^{n-1} \tag{8}$$

From eq 7 and 8, the dependence of thermal conductivity on pressure can be understood. Four types of thermal conductivity pressure dependence are illustrated in Figure 1. If dimers are the only associated species present and the extent of dimerization is small (i.e., $2K_2p_1 \ll 1$), then λ_R will increase linearly with pressure as in plot C (Figure 1) for water vapor.[62] If the association equilibrium constant is large enough such that $2K_2p_1$ is not small relative to unity, the λ versus p plot will bend over with increasing pressure

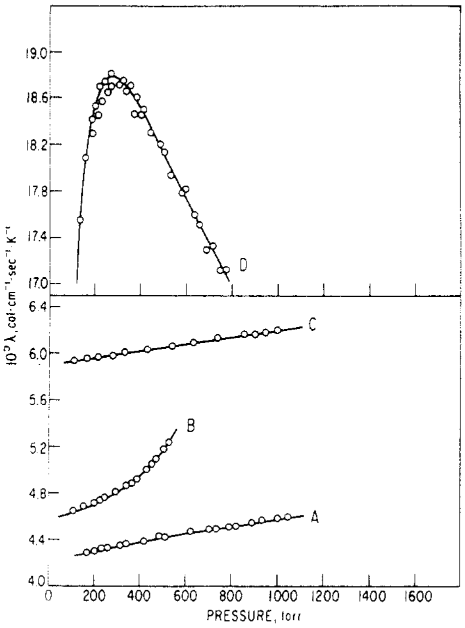


Figure 1. Thermal conductivity pressure dependence of some representative vapors: (A) 2,2,2-trifluoroethanol at 371 K; (b) ethanol at 347 K; (C) water at 386 K; (D) acetic acid at 398 K. Circles represent observed values; solid lines are from fits to data.

because of the denominator in eq 7. This is illustrated by the thermal conductivity of trifluoroethanol vapor[64] (plot A, Figure 1). From eq 7 it can be shown that when there is a large degree of association, the thermal conductivity will reach a maximum and then fall off. This is illustrated by the λ versus p plot for acetic acid vapor[71] (plot D, Figure 1). Finally, the sensitivity of the thermal conductivity to higher polymers is illustrated by the λ versus p plot (plot B, Figure 1) for ethanol vapor,[63,65] which, because of 0.2% tetramer, rises sharply to a value 14% higher than the thermal conductivity at low pressure. This is because of the p^{n-1} (and $\Delta H_n{}^2$) dependence of λ_R in eq 8. A similar relation holds for heat capacity,[21,22] which is also a sensitive technique for studying higher polymers.

From thermal conductivity data collected at different pressures over a range of temperatures, the thermodynamics of gas-phase association reactions can be determined from fitting the data to eq 4 with λ_R given by eq 5. In the fitting procedure, the enthalpies of association, ΔH_n, and equilibrium constants, K_n, are taken as fitting parameters, while the diffusion coefficients, pD_{kl} (eq 6), and λ_f and λ_c (eq 4) are estimated.[62-66,68,69,71,72] In most cases, the increase in thermal conductivity with pressure is due primarily to one associated species so that the λ versus p data can be fit by considering only one association reaction. In some cases, such as alcohol vapors, more than one association reaction needs to be included.

As with all the methods that have been used for studying the thermodynamics of gas-phase association complexes, the thermal conductivity technique has its weaknesses. First, because it is based on transport properties, it is an indirect method of studying microscopic properties of hydrogen-bonded complexes. Second, the fitting procedure depends on an estimation of the diffusion coefficients, although generally the results are not very sensitive to this quantity. Finally, when more than one association reaction contributes significantly to the enhancement in thermal conductivity, it is often not possible to unambiguously separate the contributions of the different species (see section III.B.1). This also applies to the other methods. Overall, the analysis of thermal conductivity data has proved to be effective because it avoids the ambiguities of the virial coefficient analyses in dividing up the gas nonideality and is very sensitive to the presence of higher polymers. It has also been systematically applied to a large number of gas-phase hydrogen-bonded complexes, which is important when trying to make comparisons between different systems.[67]

C. Spectroscopy

Spectroscopy is potentially the most accurate way to determine the thermodynamic properties of gas-phase hydrogen-bonded complexes. It is a direct method as opposed to the thermal conductivity and nonideal gas methods, which are indirect methods. Spectroscopic techniques have been used[76-99] to obtain data on the thermodynamics of hydrogen-bonded complexes, with most of the work being done on mixed dimers.

One method of determining the thermodynamic properties of a gas-phase association reaction

$$\mathrm{M} + \mathrm{M} \rightleftharpoons \mathrm{D} \tag{9}$$

is from the temperature dependence of the relative infrared (Raman) intensities of the free components and the complex. In practice, it is often hard to separate the bands, due to the complex, from those of the monomeric bands. As a result, the method is usually simplified to use only one band, either that of the monomer[93] or that of the dimer.[84,92] Alternatively, Thomas[85] has treated an infrared absorption band of the complex like a charge-transfer band and determined the equilibrium constant from its intensity using the Benesi–Hildebrand approximation[100] to separate the equilibrium constant from the extinction coefficient. This can be used if an infrared band of the complex is very intense and in a region where there is little overlap.

Pine and Howard[91] have recently obtained dissociation energies, including zero-point energies, D_0, of HCl and HF dimers from absolute infrared intensities. They used the relationship

$$K_2 = [\mathrm{D}]/[\mathrm{M}]^2 = (Q_\mathrm{D}/Q_\mathrm{M}{}^2)\exp(D_0/RT) \tag{10}$$

where Q_D and Q_M are the total partition functions for the dimer and monomers, respectively. The partition functions are determined from statistical mechanics and require information on the rotational and vibrational properties of the dimer. Correction to the electronic dissociation energy D_e was done by estimated zero-point energies. A similar method has recently been used by Legon et al.[89,90] to derive D_0 values for a series of dimers involving hydrogen fluoride from absolute rotational intensity measurements. From measured intermolecular vibrational frequencies they were also able to obtain values for D_e. The methods based on absolute intensity measurements have the advantage that the intensity needs to be measured at only one temperature.

Finally, nuclear magnetic resonance (NMR) has been used to study the energetics of hydrogen bonding in the gas phase. Govil, Clague, and Bernstein[80] showed that analysis of the temperature and pressure dependence of the proton signal from the hydrogen directly involved in hydrogen bond formation could be used to obtain

TABLE II. Enthalpies and Entropies of Association for the Water Dimer

ΔH_2, kcal mol^{-1}	ΔS_2, cal mol^{-1} K^{-1}	K_2 at 373 K, atm^{-1}	temp range, K	method[a]	ref
-5.7[b,c]	-25.8	0.0050	313-673	AN[d]	10
-4.6			361-487	HC	26
-3.75	-17.9	0.0193	423-723	*PVT*	27, 29
-5.2 ± 1.5			294-323	IR	76
-4.6[b]			289-353	SS	50
-3.59 ± 0.5	-18.59 ± 1.3	0.0111	358-386	TC	62

[a] *PVT* = pressure-volume-temperature, VD = vapor density, HC = heat capacity (*PVT* data are often used in the analysis of heat capacity data; see, for example, ref 30), SS = speed of sound measurements analyzed in terms of virial coefficients, TC = thermal conductivity, IR = infrared intensities, RAM = Raman intensities, ROT = rotational intensities, NMR = nuclear magnetic resonance, AN = analysis of prior data. [b] ΔU value given in reference; correction to ΔH given in this table ($\Delta H = \Delta U - RT$) at 373 K. [c] $\Delta H_2 = -5.2$ kcal mol^{-1} is obtained by using an alternate method (Stockmayer's formulation of second virial coefficients). [d] Analysis of second virial coefficient data from Keyes, F. G. *J. Chem. Phys.* **1947**, *15*, 602.

values of ΔH_2 and ΔS_2. The results were in agreement with other measurements for the dimethyl ether-HCl complex. However, later work[88] on the trimethylamine-methanol complex gave data that was in disagreement with other methods (see section III.F.1). The NMR method has been used to obtain the thermodynamics of only a limited number of gas-phase hydrogen-bonded complexes.[3c,80,88,95,101]

III. Specific Studies of Gas-Phase Hydrogen-Bonded Complexes

A. Water

1. Dimer

Very few experimental studies have been carried out to determine the thermodynamic properties of the water dimer. This is probably due to the low concentration of dimers present in water vapor (around 1% at 1 atm and 373 K), which makes accurate thermodynamic measurements difficult. All three of the major methods discussed in section II have been used. The reported values for ΔH_2 and ΔS_2 are listed in Table II, along with values of K_2 at 373 K.

Analyses of second virial coefficient data have given association enthalpies that range from -3.75 to -5.7 kcal mol^{-1}. The more negative values of Rowlinson[10] (-5.7 kcal mol^{-1}), McCullough, Pennington, and Waddington[26] (-4.6 kcal mol^{-1}), and Bohlander and Gebbie[50] (-4.6 kcal mol^{-1}) are due to their use of large negative values for B_{nonpolar} in eq 2 based on the Berthelot equation (for example, -292 cm^3 mol^{-1} at 373 K in ref 10). Rowlinson[10] also used Stockmayer's statistical mechanical formulation of B, which he said was more reasonable than use of the Berthelot equation, and obtained a ΔH_2 of -5.2 kcal mol^{-1}. Kell, McLaurin, and Whalley[29] used the "excluded" volume concept for B_{nonpolar} (40 cm^3 mol^{-1}) and obtained -3.75 kcal mol^{-1} from their *PVT* data. Finally, an analysis[62] of three sets of second virial coefficient data considered to be most reliable (including the data analyzed by Rowlinson[10]) using B_{nonpolar} values of 0 and 38.5 cm^3 mol^{-1} gave ΔH_2 values ranging from -3.29 to -4.53 kcal mol^{-1}, ΔS_2 values ranging from -17.07 to -19.91 cal mol^{-1} K^{-1}, and K_2 values ranging from 0.0200 to 0.0144 atm^{-1} at 373 K. Hence, there is considerable uncertainty in thermodynamic properties for the water dimer derived from virial coefficient data. This is due not only to differences in the measured B values but also to the different choices of B_{nonpolar}. The ambiguities in the analysis of virial coefficient data were discussed in more detail in section II.A.

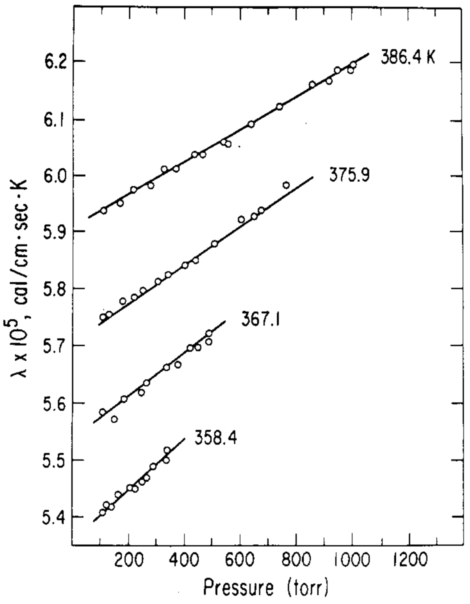


Figure 2. Thermal conductivity of H_2O vapor versus pressure at four temperatures. The circles represent the observed values and the solid lines were calculated from a monomer-dimer fit. (Reproduced from ref 62; copyright 1979 American Institute of Physics.)

In the only spectroscopic study of the association energy of the water dimer, Gebbie et al.[76] derived a value for ΔH_2 of -5.2 kcal mol^{-1} from the temperature variation of submillimeter wave absorption (rotational transitions in the region 5-30 cm^{-1}) of water vapor. However, this value has large uncertainty limits of ±1.5 kcal mol^{-1}.

From analyses of thermal conductivity data, Curtiss, Frurip, and Blander[62] derived a value for ΔH_2 of -3.59 ± 0.5 kcal mol^{-1} and a value for ΔS_2 of -18.59 ± 1.3 cal mol^{-1} K^{-1}.[102] The fit of the data is shown in Figure 2. Most of the increase in thermal conductivity with increase in pressure is due to the dimer. The ΔH_2 and ΔS_2 for water dimer formation from thermal conductivity fall within the range of the values determined from virial coefficient analyses[29,62] in which B_{nonpolar} values from 0 to 40 cm^3 mol^{-1} were used. The value of K_2 from thermal conductivity (0.0111 atm^{-1} at 373 K) is somewhat smaller than the K_2 values from virial coefficient data (0.0144-0.0200 atm^{-1} at 373 K). Factor of 2 differences in K_2 from the thermal conductivity and virial coefficient methods are common for dimer formation in other vapors containing small amounts (<5%) of dimer (see, for example, the results for alcohol, acetonitrile, and acetone). The reasons for the differences have been explored and are not at all obvious.[68]

In making comparisons between ΔH_2 values for the water dimer as well as other associated species, one must consider the temperature range in which they were determined. Theoretical ΔH_2 values as a function of temperature are given in Table III. They indicate that, for example, between 298 and 373 K, the approximate

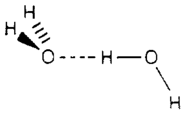
TABLE III. Theoretical Results for Dimerization Entropies and Enthalpies for HF, H_2O, and NH_3

dimer	T, K	ΔE, kcal mol^{-1}	$\Delta H_2(T)$, kcal mol^{-1}	$\Delta S_2(T)$, cal mol^{-1} K^{-1}	method
HF	200	−5.03	−3.89	−20.35	*a*
	298	−5.03	−3.94	−20.60	*a*
	373	−5.03	−3.93 (−3.89)	−20.54 (−19.6)	*a*
	500	−5.03	−3.81	−20.28	*a*
		−4.56			*b*
H_2O	200	−5.34	−3.76	−21.50	*a*
	298	−5.34	−3.61	−20.86	*a*
	373	−5.34	−3.46 (−3.41)	−20.34 (−19.04)	*a*
	500	−5.34	−3.08	−19.50	*a*
	373	−5.63	−3.64	−17.97	*c*
	373	−5.0 ± 0.45	−3.15 ± 0.65	−18.92	*d*
NH_3	298	−3.8	−2.25	−15.94	*e*
	373	−3.8	−2.01	−15.23	*e*

[a] $\Delta H_2(T)$ and $\Delta S_2(T)$ calculated from MP2/6-311++G** (2d,2p) vibrational frequencies and structures in ref 103a. ΔE is from ref 103a. (Values in parentheses are from HF/6-31G* frequencies.) [b] Reference 111. [c] Reference 104 (based on CI calculations of ref 103b). [d] Reference 62 (ΔE is from the Hartree–Fock value in ref 103e and correlation correction from ref 103b and 103c; 4-31G vibrational frequencies from ref 103e used to calculate ΔH_2 and ΔS_2). [e] $\Delta H_2(T)$ and $\Delta S_2(T)$ calculated from MP2/6-31+G* vibrational frequencies and structures in ref 103a. ΔE is from ref 103a.

range of many of the measurements quoted in this review, the value of ΔH_2 for water dimer changes by 0.15 kcal mol^{-1}.

The water dimer (1) has been one of the hydrogen-bonded complexes that has been most extensively studied theoretically.[103] In order to compare the enthalpy of association of a dimer with the binding energy, ΔE, calculated from molecular orbital theory, the ΔE must be corrected for differences in vibrational energy (ΔE_{vib}), rotational energy (ΔE_{rot}), and translational energy (ΔE_{trans}):


1

$$\Delta H_2(T) = \Delta E + \Delta E_{vib}(T) + \Delta E_{trans}(T) + \Delta E_{rot}(T) + \Delta(PV) \quad (11)$$

Usually $RT/2$ is assigned to each degree of translational and rotational freedom so that eq 11 becomes

$$\Delta H_2(T) = \Delta E + \Delta E_{vib}(T) - 4RT \quad (12)$$

The $\Delta E_{vib}(T)$ is generally calculated from theoretically determined harmonic vibrational frequencies of the dimer and monomers. However, large anharmonicities in the low-frequency modes are possible, and this could introduce errors into the calculation of $\Delta E_{vib}(T)$, which is very dependent on the low-frequency modes.

Thermodynamic properties (ΔE, ΔH_2, ΔS_2) of the water dimer from recent ab initio molecular orbital calculations are listed in Table III. Included in this table are the results of Slanina,[104] based on the configuration interaction (CI) study of Matsuoka, Clementi, and Yoshimine[103b] (MCY). Slanina obtains a value for ΔH_2 at 373 K of −3.64 kcal mol^{-1}, in good agreement with the value of −3.59 kcal mol^{-1} from the thermal conductivity measurements[62] and −3.75 kcal mol^{-1} from the virial coefficient analysis of Kell et al.[29] Slanina[104] calculated association entropies for the water dimer from harmonic vibrational frequencies obtained from the MCY potential energy surface. At 373 K, they report a theoretical value of −17.97 cal mol^{-1} K^{-1}, in good agreement with the experimental value from the measurements of thermal conductivity[62] (−18.59 cal mol^{-1} K^{-1}) and virial coefficients[29] (−17.9 cal mol^{-1} K^{-1}). Recently, Frisch et al.[103a] reported high level calculations on the water dimer using fourth-order Møller–Plesset (MP4) perturbation theory. These results are also included in Table III. Their best basis set gave a value of −5.34 kcal mol^{-1} for ΔE. Using MP2 vibrational frequencies they obtained a value for ΔH_2 at 298 K of −3.6 kcal mol^{-1} (−3.45 kcal mol^{-1} at 373 K), also in good agreement with experiment. Frisch et al.[103a] indicate that due to basis set superposition error (BSSE), the theoretical value may be too negative by about 0.7 kcal mol^{-1} (i.e., ΔH^{373} = −2.7 kcal mol^{-1}). The experimental values support the uncorrected theoretical result, i.e., without correction for BSSE. We have calculated association entropies for the water dimer from the MP2 structure and vibrational frequencies of Frisch et al.[103a] and have listed them in Table III. The ΔS_2 value of −20.34 cal mol^{-1} K^{-1} is about 2.3 cal mol^{-1} K^{-1} more negative than that of Slanina,[104] apparently due to differences in vibrational frequencies. Further theoretical and experimental studies are needed on the thermodynamics of the water dimer.

TABLE IV. Effect of Isotopic Substitution on Thermodynamic Parameters of Water Dimer[a]

$\Delta(\Delta H_2)$, kcal mol^{-1}	$\Delta(\Delta S_2)$, cal mol^{-1} K^{-1}	% change in K_2 at 373 K, atm^{-1}	temp, K	method[b]	ref
−0.02	+0.03	+4.6	423–723	*PVT*	28
−0.07	−0.08	+4.5	358–386	TC	62
−0.17			40	IR	77
−0.47	−0.20	+13.6	298	*c*	*d*
−0.33	−0.27	+11.0	373	*c*	*d*
−0.20	−0.16	+12.3	500	*c*	*d*
−0.24	−0.26	+18.0	373	*c*	104
−0.19	−0.19	+18.1	373	*c*	62

[a] Change in ΔH_2, ΔS_2, and K_2 upon deuteriation. [b] See Table II, footnote *a*, for abbreviations. [c] Theory. [d] Calculated from MP2-FU/6-311++G**(2d,2p) frequencies in ref 103a. (HF/6-31G* frequencies give similar results.)

Finally, we note that several studies have been done on deuteriated water vapor to determine the effects of isotopic substitution on the thermodynamic properties of the water dimer. The results are summarized in Table IV, along with several theoretical calculations of this effect. The changes are primarily a measure of the effect of changes of the vibrational frequencies on the thermodynamics. While there is general agreement that both ΔH_2 and ΔS_2 become more negative because of lower intermolecular vibrational frequencies, there is quite a spread of values. From 4 to 20% more dimer is indicated to be present in D_2O vapor than in H_2O vapor, with the larger change in K_2 occurring at the theoretical level. There is much uncertainty in the experimental values because the differences in thermodynamic quantities are much smaller than the experimental uncertainties. The theoretical values are calculated from harmonic frequencies; anharmonic effects could also be significant.

2. Evidence for Higher Polymers

No measurements of the thermodynamics of n-mers larger than dimer have been reported for water.[105]

TABLE V. Enthalpies and Entropies of Association for Alcohol Dimers

	ΔH_2, kcal mol^{-1}	ΔS_2, cal mol^{-1} K^{-1}	K_2 at 373 K, atm^{-1}	type of fit	temp range, K	method[a]	ref
methanol	−3.22	−16.5	0.0191	1–2–4	340–390	HC	30
	−3.3	−16.7	0.0192	1–2–3	423–573	*PVT*	29
	−3.5 ± 0.2[b]			1–2–4	305–335	IR	78b
	−4		0.0177[c]	1–2–4	313–393	VD	31
	−4.1 ± 0.5	−17.5 ± 3	0.0378	1–2	333–468	NMR	88
	−3.51 ± 0.9	−17.42 ± 0.7	0.0177	1–2–4	338–420	TC	63
	−4.3[d]	−24.9[d]	0.0012[d]	1–2	298–473	*PVT*	55
ethanol	−3.4	−16.6	0.0231	1–2–4	368–476	HC	32
	−5.0 ± 1.2			1–2	290–330	IR	81
	−4		0.0236[c]	1–2–4	313–393	VD	31
	−3.70 ± 0.9	−16.36 ± 0.7	0.0391	1–2–4	329–419	TC	63
1-propanol	−3.4	−15.4	0.0423	1–2–4	371–451	HC	33
2-propanol	−4.09 ± 0.9	−16.15 ± 0.7	0.0736	1–2–4	340–420	TC	63
	−4		0.0290[c]	1–2–4	313–393	VD	31
	−5.3	−22.4	0.0162	1–2–4	371–451	HC	47
	−4.5	−19.5	0.0237	1–2–4	359–473	HC	48
tert-butyl alcohol	−4.26 ± 0.9	−16.67 ± 0.7	0.0712	1–2–4	348–420	TC	63
	−4.6	−19.0	0.0349	1–2–4	363–437	HC	52
2-butanol	−5.25	−21.4	0.0268	1–2–4	365–455	HC	51
2,2,2-trifluoroethanol	−5.7 ± 1.2				290–330	IR	81
	−4.75	−18.73	0.0489	1–2	338–385	TC	64

[a] See Table II, footnote *a*, for abbreviation. [b] For CH_3OD dimer, ref 78b reports $\Delta H_2 = -4.9 \pm 0.2$ kcal mol^{-1}, a much larger shift than found for H_2O dimer (see Table III). [c] Calculated from their virial coefficients with $K = -B/RT$ (at 373 K). [d] The values given in this reference are inconsistent with their reported B values. Reanalysis in the region 348–448 K (where $1/T$ vs log K is a straight line) gives $\Delta H_2 = -4.0$ kcal mol^{-1}, $\Delta S_2 = -18.8$ cal mol^{-1} K^{-1}, and $K_2 = 0.0170$ atm^{-1}. Reanalysis with $b_0 = 80$ cm^3 mol^{-1} gives $\Delta H_2 = -3.5$ kcal mol^{-1}, $\Delta S_2 = -17.1$ cal mol^{-1} K^{-1}, and $K_2 = 0.021$ atm^{-1}.

However, the thermal conductivity method, which is sensitive to the presence of larger clusters, has been used to provide upper limits to the amounts of water clusters (n = 3–6) present in water vapor at 373 K.[70] The equilibrium constant for the formation of methanol tetramer ($\sim 2 \times 10^{-4}$ atm^{-3} at 373 K, Table VI) is significantly larger than the upper limit equilibrium constant for water tetramer formation (6.0×10^{-5} atm^{-3} at 373 K from ref 70). The upper limits are consistent with equilibrium constants calculated[70] from the thermodynamic functions for water clusters derived by Owicki et al.[106] from an empirical pair potential (EPEN). Ab initio molecular orbital calculations could provide useful information on the thermodynamics of water clusters and the reason for the difference in stabilities between the water n-mers and methanol n-mers.

B. Alcohols

1. Methanol

Molecular association due to hydrogen bonding in alcohol vapors has been investigated by many researchers with varied results. The most studied alcohol system is methanol vapor. Weltner and Pitzer[30] suggested the presence of monomers, dimers, and tetramers, based upon available *PVT* data and a few measurements of the heat capacity of gaseous methanol. However, they were not absolutely able to distinguish between tetramer formation and the presence of a mixture of polymeric species larger than dimer. The vapor density measurements of Kretschmer and Wiebe[31] similarly seem to point to the existence of monomers, dimers, and tetramers. Inskeep, Kelliher, McMahon, and Somers[78] have interpreted the infrared absorption peaks of methanol vapor between 3200 and 3800 cm^{-1} as a function of pressure in terms of monomers, dimers, and tetramers. Kudchadker and Eubank[55] interpreted their compressibility data in terms of monomers, dimers, and tetramers. On the other hand, Kell and McLaurin[29] have interpreted their *PVT* data in terms of monomers, dimers, and trimers. Tucker, Farnham, and Christian[35] obtained best fits of *PVT* data in terms of a mixture of monomers, trimers, and octamers. Thermal conductivity measurements as a function of temperature and pressure were analyzed in terms of monomers and tetramers by Renner, Kucera, and Blander[65] and subsequently dimers were incuded in the fits by Frurip, Curtiss, and Blander.[63]

Thermodynamic parameters derived for the methanol dimer from the various studies are listed in Table V. The studies based on virial coefficient type analyses, with the exception of the compressibility study by Kudchadker and Eubank,[55] are in agreement on ΔH_2 (−3.2 to −4 kcal mol^{-1}) and ΔS_2 (−16.5 to −17.4 cal mol^{-1} K^{-1}). The more negative ΔH_2 found by Kudchadker and Eubank[55] is due to a problem with their analysis. Reanalysis (see Table V, footnote *d*) gives a value in line with the other results. The thermal conductivity values of ΔH_2 (−3.51 kcal mol^{-1}) and ΔS_2 (−17.42 cal mol^{-1} K^{-1}) are in agreement with the virial coefficient data. Likewise, the spectroscopic results for ΔH_2 and ΔS_2 are in agreement. The equilibrium constants for methanol dimer are in quite good agreement (0.018–0.019 atm^{-1} at 373), with the exception of the NMR study of Clague et al.,[88] which gave a value of K_2 nearly twice as large.

Thermodynamic parameters for the higher methanol polymers are given in Table VI. The choice of the higher polymer in a 1–2–n model to fit the data is somewhat arbitrary. On the basis of the heat capacity study of Weltner and Pitzer,[30] most workers used a 1–2–4 model for their virial coefficient data, i.e., monomers, dimers, and tetramers. Thermal conductivity, like heat capacity, is very sensitive to the presence of higher polymers. This has been demonstrated by Renner et al.[65] and is illustrated by the upward curvature in Figure 3. The presence of only dimers would result in a linear increase. Despite its sensitivity, the thermal conductivity analysis is also hampered by

TABLE VI. Enthalpies and Entropies of Association for Alcohol *n*-mers (Larger Than Dimer)

	n	ΔH_n, kcal mol^{-1}	ΔS_n, cal mol^{-1} K^{-1}	K_n at 373, atm$^{-(n-1)}$	type of fit	temp range, K	method[a]	ref
methanol	3	−12.53 ± 0.12	−44.2 ± 0.4	0.0048	1–3–8	288–308	*PVT*	35
		−4.59	−17.8	0.0629	1–2–3	423–573	*PVT*	29
	4	−24.2	−81.3	0.00026	1–2–4	340–390	HC	30
		−22.1			1–2–4	313–393	VD	31
		−18 ± 5[b]			1–2–4	305–335	IR	78b
		−23.01 ± 3	−78.22 ± 5	0.00024	1–2–4	338–420	TC	63
	8	−67.8 ± 0.28	−216.9 ± 0.9	2.1×10^{-8}	1–3–8	288–308	*PVT*	35
ethanol	4	−24.8	−81.4	0.00055	1–2–4	368–476	HC	32
		−20.1			1–2–4	313–393	VD	31
		−22.15 ± 3	−74.65 ± 5	0.00046	1–2–4	329–419	TC	63
1-propanol	4	−25.18	−75.4	0.01883	1–2–4	371–451	HC	33
2-propanol	4	−21.65 ± 3	−72.37 ± 5	0.00074	1–2–4	340–420	TC	63
		−22.6			1–2–4	313–393	VD	31
		−22.3	−74.2	0.00071	1–2–4	371–451	HC	47
		−22.9	−75.3	0.00091	1–2–4	359–473	HC	48
tert-butyl alcohol	4	−21.27	−71.23	0.00078	1–2–4	348–420	TC	63
	4	−25.1	−82.2	0.00055	1–2–4	363–437	HC	52
2-butanol	4	−23.1	−74.7	0.00162	1–2–4	365–455	HC	51
2,2,2-trifluoroethanol	3	−13.62 ± 0.15	−47.4 ± 0.5	0.00418	1–3–8	288–308	*PVT*	36, 37
1,1,1,3,3,3-hexafluoro-2-propanol	3	−13.97 ± 0.2	−50.5 ± 0.7	0.00141	1–3–8	288–308	*PVT*	37

[a] See Table II, footnote *a*, for abbreviations. [b] For CH_3OD tetramer, ref 78b reports ΔH_2 = −14 ± 4 kcal mol^{-1}.

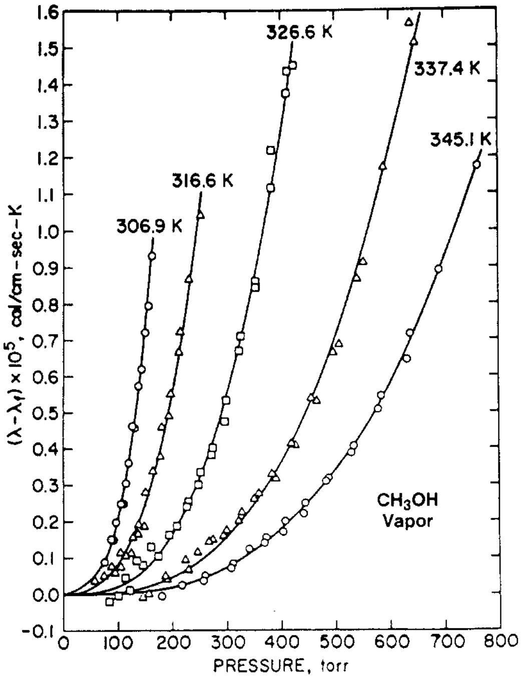


Figure 3. Difference between the observed thermal conductivity, λ, and frozen thermal conductivity, λ_f, of methanol vapor versus pressure at different temperatures. The symbols represent the observed values and the solid lines represent fits to data. (Reproduced from ref 65; copyright 1977 American Institute of Physics.)

choice of the n-mers in the fit. A monomer–dimer–tetramer mixture gave only a slightly better fit than most other 1–2–n mixtures,[63] with the exception of a 1–2–3 fit, which was significantly worse. Other combinations of n-mers also gave good fits to some data. For example, Tucker et al.[35] obtained the best fit to their *PVT* data using a 1–3–8 model.

Despite the arbitrariness of the choice of model, results in Table VI indicate that there is generally good agreement between the different studies on tetramerization enthalpy (−22 to −24 kcal mol^{-1}) and entropy (−78 to −81 cal mol^{-1} K^{-1}), as well as the equilibrium constant (ca. 2×10^{-4} atm^{-3}). The results of Tucker et al.[35] (ΔH_3 = −12.5 kcal mol^{-1}, ΔS_3 = −44.2 cal mol^{-1} K^{-1}) are also reasonable and in line with theoretical predictions (see section III.A.3) and the 1–2–3 fit of thermal conductivity data.[63] The *PVT* results of Kell and McLaurin[29] (ΔH_3 = −4.59 kcal mol^{-1}, ΔS_3 = −17.8 cal mol^{-1} K^{-1}) are out of line.

2. Other Alcohols

For ethanol dimer, the virial coefficient[32,33] and thermal conductivity analyses[63] are again in good agreement on ΔH_2 (−3.4 to −4 kcal mol^{-1}) and ΔS_2 (−16.4 to −16.6 cal mol^{-1} K^{-1}). The infrared result of Barnes, Hallam, and Jones[81] for ΔH_2 of −5.0 kcal mol^{-1} seems out of line and also significantly different from the infrared result[78b] for the methanol dimer (ΔH_2 = −3.5 kcal mol^{-1}).

For the 2-propanol and *tert*-butyl alcohol dimers, significant disagreement exists for the ΔH_2 and ΔS_2 values among the studies (see Table V). This difference is also reflected in the equilibrium constants. While the dimer equilibrium constants from virial coefficients (e.g., 0.019 atm^{-1} at 373 K) are in agreement with those deduced from thermal conductivity (e.g., 0.018 atm^{-1} at 373 K) for methanol, they differ by factors of 2.0–4.5 for the higher alcohols. Equation 2, relating K_2 to the second virial coefficient, indicates that B_{nonpolar} would have to be unreasonably large to obtain K_2 values approaching the thermal conductivity values. The differences in K_2 between the two methods are in the opposite direction to that found for the water dimer (see section III.B.1). There is no obvious reason for the discrepancy between the two methods.

In contrast to the dimerization results, the tetramerization enthalpies and entropies for these other larger alcohol systems are in quite good agreement. This is reflected by the general agreement of the K_4 values in Table VI. From the thermal conductivity analyses for the series of alcohols, it is noted that the tetramerization entropies tend to be less negative as the alcohol complexity increases (see Table VI). Frurip et al.[63] found that this is the result largely of the vibrational contribution to ΔS_4. The vibrational contribution ΔS_{vib} increases (more positive) as the alcohol size increases because of lower intermolecular vibrational frequencies.

TABLE VII. Comparison of Theoretical and Experimental Enthalpies of Association for $(CH_3OH)_n$ in kcal mol^{-1}

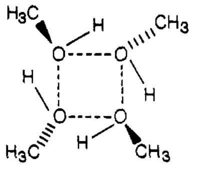
	theory (at 325 K)				
species	ΔE_{el}[a]	ΔE_{vib}[b]	$[\Delta E_{tr} + \Delta E_{rot} + \Delta(PV)]$[c]	ΔH_n[c]	exptl ΔH_n
$(CH_3OH)_2$	-5.6	4.5	-2.58	-3.7	-3.2,[d] -3.5[e]
$(CH_3OH)_3$	-15.3	9.0 (13.5)	-5.17	-11.5 (-7.0)	-12.5[f]
$(CH_3OH)_4$	-35.3	13.5 (18.0)	-7.75	-29.6 (-25.0)	-24.2,[d] -23.0[e]
$(CH_3OH)_5$	-48.3	18.0 (22.5)	-10.30	-40.6 (-36.1)	
$(CH_3OH)_6$	-59.5	22.5 (27.0)	-12.92	-49.9 (-45.4)	

[a] Binding energy for lowest energy structures determined in ref 107; STO-3G results. [b] Upper and lower estimates (in parentheses) from ref 107. [c] Calculated according to eq 11 and 12. [d] Reference 30. [e] Reference 63. [f] Reference 35.

Two fluorinated alcohols have been studied. These are trifluoroethanol and hexafluoro-2-propanol. Thermal conductivity results[64] indicate that dimers are the primary associated species in trifluoroethanol vapor with a ΔH_2 of -4.75 kcal mol^{-1}. There was no evidence for higher polymers. An infrared study by Barnes et al.[81] gave a ΔH_2 of -5.7 kcal mol^{-1}, but with a large uncertainty of ±1.2 kcal mol^{-1}. In disagreement with these studies, a vapor density study by Farnham et al.[36,37] finds trimers and octamers. Similar results are found for hexafluoro-2-propanol from vapor density studies.[36,37]

3. Theoretical Considerations

Hydrogen-bonded complexes of alcohols have been much less studied theoretically than the water dimers and at lower levels of theory. A theoretical study[107] of methanol polymers at the STO-3G level has led to the conclusion that for all polymers other than dimers, cyclic structures (**2**) are more stable than chain structures (**3**). Binding energies for the most stable methanol polymers from the theoretical study are listed in Table VII. The largest increment in binding energy occurs in going from the trimer to the tetramer, as shown in Figure 4. This is consistent with the detection of tetramer in most measurements. However, binding energy is only part of the story and entropy must also be considered in any justification of the detection of tetramer over other species. This is evidenced by the fact that higher water polymers are not detected in water vapor (section III.A.2) despite similarities in the binding energies of methanol and water polymers (see Figure 4).



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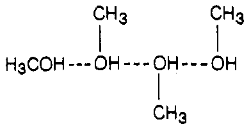


$H_3COH---\overset{CH_3}{OH}---\underset{CH_3}{OH}---\overset{CH_3}{OH}$

3

Estimated theoretical values from ref 107 for the enthalpies of association for $(CH_3OH)_n$ (n = 2–6) are given in Table VII and are compared to experiment. There is reasonable agreement with experiment. Higher level calculations would give more accurate enthalpies, as well as entropies, which could give insight into the amounts of the various polymers, expected to be present in the vapor. The existence of cooperativity in hydrogen bonding is evidenced by the nonadditive theoretical and experimental enthalpies of association in Table VII. The decreasing amounts of polymers with increasing cluster size (Table VI) are evidence for the opposing effect of entropy.

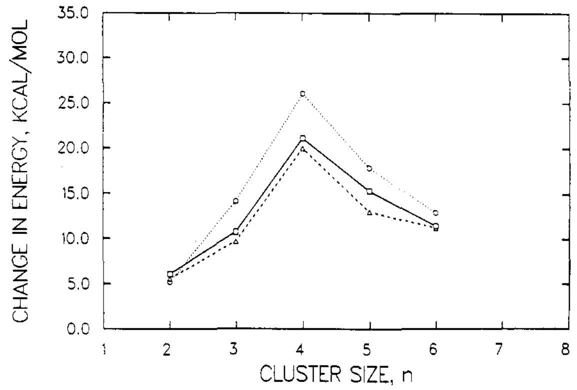
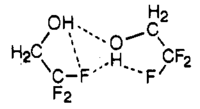


Figure 4. Calculated increments in binding energy $|\Delta E_n - \Delta E_{n-1}|$ versus the size, n, of the cluster. Results are shown for water (ref 103h, solid line), methanol (ref 107, dashed line), and hydrogen fluoride (ref 113a, dotted line) clusters. All results are from minimal basis set calculations, which may overestimate the increments (see, for example, ref 113b), but the trends should be reasonable.

Trifluoroethanol dimer is bound more strongly (-4.75 kcal mol^{-1}) than any of the nonfluorinated alcohol dimers according to the thermal conductivity measurements. Theoretical calculations[64,108] suggest that this may be due to a cyclic hydrogen-bonded structure (**4**) for trifluoroethanol dimer resulting from the intramolecular F···H bond in trifluoroethanol monomer.



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The cyclic structure and internal hydrogen bond may also explain why only dimers were detectable in thermal conductivity measurements as opposed to the other alcohols where higher polymers are evident.

C. Hydrogen Fluoride

The presence of polymers in hydrogen fluoride vapor has been deduced from a variety of *PVT*,[38,39] heat capacity,[40] and spectroscopic[81,82] data. In addition, there have been a number of studies that have analyzed and reviewed previous data.[41,53,109,110] The most broad-based of these is the JANAF tables,[109] which include enthalpies and entropies of all of the polymers (n = 2–7) derived from measured association properties as well as a statistical mechanical analysis. Vanderzee and Rodenburg[110] compiled thermodynamic properties of gaseous hydrogen fluoride from vapor densities, heat capacities, and enthalpies of vaporization. Maclean, Rossotti, and Rossotti[53] analyzed the *PVT* data of Briegleb and Strohmeier.[39] Finally, Redington[41] derived a nonideal associated vapor model for hydrogen fluoride

TABLE VIII. Enthalpies and Entropies of Association for Hydrogen Fluoride Polymers

n	ΔH_n	ΔS_n	K_n at 373, $\text{atm}^{-(n-1)}$	type of fit	temp range, K	method[a]	ref
2	−6.5	−26.0	0.012	1–2–6	299–329	*PVT*	53
	−5.0			1–2–4–6		IR	82
	−6.7	−25.8	0.019	1–2–4–6	253–373	HC	40
	−4.27	−22.6	0.0037		293–329	AN	41
	−6.6	−26.0	0.015			AN	109
	(−2.97)[b]					IR	91
3	−14.7	−55.6	2.9×10^{-4}			AN	109
4	−20.1	−77.5	6.8×10^{-6}	1–2–4–6	253–373	HC	40
	−18.9			1–2–4–6		IR	82
	−23.2[c]	−84.8[c]	1.1×10^{-5}		293–329	AN	41
	−22.4	−82.7	1.1×10^{-5}			AN	109
5	−30.4	−110.0	5.8×10^{-7}			AN	109
6	−40.8	−133.8	4.5×10^{-6}	1–6	273–311	*PVT*	38
	−40.4	−132.6	4.8×10^{-6}	1–2–6	299–329	*PVT*	53
	−40.2	−133.1	2.9×10^{-6}	1–2–4–6	253–373	HC	40
	−39.9			1–2–4–6		IR	82
	−39.4	−131.5	2.2×10^{-6}		293–329	AN	41
	−41.2	−137.6	1.1×10^{-6}			AN	109
7	−46.5	−165.5	1.2×10^{-9}			AN	109

[a] See Table II, footnote *a*, for abbreviations. [b] D_0 value. [c] Ring structure.

from fitting vapor density, heat capacity, excess enthalpy, excess entropy, and infrared data.

The thermodynamic properties of the hydrogen fluoride polymers derived from the various studies are listed in Table VIII. Evidence seems strongest for the presence of significant concentrations of dimers and hexamers and for lower concentrations of trimers, tetramers, and pentamers.[40,53,109] There is also evidence for at least one unidentifiable polymer larger than the hexamer at the higher pressures of some of the measurements in the lower range of temperatures.[53] Because of their low concentrations, the species other than dimers and hexamers could not be identified unambiguously and their thermodynamic parameters have large uncertainties. As a result, the following discussion is limited to the thermodynamic properties of the dimers and hexamers of hydrogen fluoride.

The data for the dimer are difficult to assess, with values of ΔH_2 ranging from −4.27 to −6.6 kcal mol^{-1} and with ΔS_2 values ranging from −22.6 to −26.0 cal mol^{-1} K^{-1}. In addition, the values of K_2 vary by about a factor of 5 at 373 K and by about 11 at 300 K. There are definable uncertainties in such data. First is the correction for nonideal gas behavior discussed earlier, which was specifically included in the analyses of Redington.[41] In addition, the presence of hexamers makes the extraction of data on dimer properties more difficult, especially at low temperatures. This is especially true for the heat capacity data of Franck and Meyer,[40] which are considerably more sensitive to the presence of hexamer than to the presence of dimer.

Theoretical predictions of the thermodynamic properties (ΔE, ΔH_2, ΔS_2) of the HF dimer, based on the high-level ab initio molecular orbital calculations of Frisch et al.,[103a] are listed in Table III. The calculated values of ΔH_2 and ΔS_2 are less negative than all of the values given in Table VIII. The calculational method used for the HF dimer has been shown in section III.A.1 to agree with measured values of ΔH_2 and ΔS_2 for water dimer. This supports the reliability of the theoretical calculations. Also, the binding energies from the high-level calculations by Frisch et al.[103a] (−5.03 kcal mol^{-1}) and Michael et al.[111] (−4.56 kcal mol^{-1}) for the HF dimer are in agreement with the value of −4.57 kcal mol^{-1} measured by Pine and Howard[91] from absolute infrared intensities. Hence, the theoretical calculations suggest that the analysis of Redington[41] is to be given the greatest weight since it led to values of ΔH_2 and ΔS_2, which are closest to the theoretical values in Table III. In addition, values of K_2 (in atm^{-1}) deduced from the results of Frisch et al.[103a] are 2.3×10^{-2} at 300 K and 6.5×10^{-3} at 373 K. These are consistent with the values of 1.5×10^{-2} and 3.7×10^{-3} at 300 and 373 K, respectively, from Redington's analysis. These values of K_2 are significantly smaller than all of the other values in Table VIII. Clearly, a coupled reassessment of all the measurements and calculations is called for. However, we provisionally recommend the values of $\Delta H_2 = -4.27$ kcal mol^{-1} and $\Delta S_2 = -22.6$ cal mol^{-1} K^{-1} deduced by Redington.

The data for the hexamer in Table VIII are relatively self-consistent. The values for the enthalpies of association of the hexamer range from −39.4 to −41.2 kcal mol^{-1}. The entropies range from −131.2 to −137.6 cal mol^{-1} K^{-1}. Since the differences in the entropies and enthalpies are coupled, the differences in K_6 are considerably smaller than is implied by the differences between individual values of ΔH_6 or ΔS_6. The biggest difference in values of K_6 in Table VIII represents a difference in the free energy of formation of hexamer from the monomers of about 1.1 kcal mol^{-1}. Since the temperature cited, 373 K, is just out of the range of the large majority of measurements and represents the presence of minute concentrations of hexamer, a fairer comparison is made at lower temperatures. For example, at 300 K, values of K_6 range from 0.9[41,109] to 3.0[38] atm^{-5}, with the range representing a free energy difference of 0.74 kcal mol^{-1}. We place the greatest reliance on the thermodynamic parameters deduced by Redington[41] ($\Delta H_6 = -39.4$ kcal mol^{-1}, $\Delta S_6 = -131.5$ cal mol^{-1} K^{-1}) because of the thoroughness of his analysis.

The stabilities of higher polymers of hydrogen fluoride have been studied theoretically.[113] Results for the energy change upon addition of the nth molecule to a cluster from low level (minimal basis set) calculations[113a] for $n = 2$–6 are shown in Figure 4. No large increase in the binding energy for addition of the sixth molecule is predicted for the hexamer. Hence, entropic

TABLE IX. Enthalpies and Entropies of Association for Carboxylic Acid Dimers in the Gas Phase

	ΔH_2, kcal mol^{-1}	ΔS_2, cal mol^{-1} K^{-1}	K_2 at 373 K, atm^{-1}	temp range, K	method[a]	ref
formic acid	-15.15[b]	-39.2[b]	2.04		AN	97
acetic acid	-14.92[b]	-35.9[b]	7.73		AN	97
trifluoroacetic acid	-14.00	-36.2	1.96	353–403	VD	43b
	-14.05	-36.5	1.79	303–423	VD	34
	-14.5 ± 0.6	-38.4 ± 1.4	1.26	318–468	NMR	95
	-13.66 ± 2.0	-36.15 ± 5.0	1.26	350–413	TC	71
	-12.0 ± 1.0			293–443	IR	87

[a] See Table II, footnote *a*, for abbreviations. [b] Values at 373 K extrapolated from thermodynamic tables in ref 97.

TABLE X. Enthalpies and Entropies of Association of Other Dimers between Like Molecules

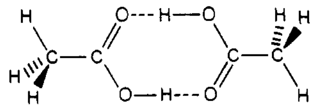
species	ΔH_2, kcal mol^{-1}	ΔS_2, cal mol^{-1} K^{-1}	K_2 at 373 K, atm^{-1}	temp range, K	method[a]	ref
acetone	-3.9	-17.7	0.0288	299–423	*PVT*	42
	-3.22 ± 0.35	-15.07 ± 0.40	0.0458	341–378	TC	72
acetaldehyde	-4.5	-22.3	0.00579	285–400	*PVT*	10, 11a
	-3.960[b]	-20.07[b]	0.00860	313–373	*PVT*	44
acetonitrile	-5.20	-20.6	0.0350	313–403	*PVT*	10, 11a
	-5.11[c]	-19.25[c]	0.0612	313–373	*PVT*	44
	5.00 ± 0.12	-21.15 ± 0.62	0.0206	338–387	TC	68
pyridine	-4.93	-22.2	0.0109	366–387	TC	69
hydrogen chloride	-2.44 ± 0.1			190–250	AN[d]	54
	-2.14 ± 0.2			195–300	IR	92
	[1.23 ± 0.06][e]				IR	91
ammonia	-4.4	-26.8	0.0005	263–413	*PVT*	10, 11c

[a] See Table II, footnote *a*, for abbreviations. [b] Recomputed with correct gas constant (see ref 68) to be $\Delta H_2 = -3.92$ kcal mol^{-1}, $\Delta S_2 = -20.5$ cal mol^{-1} K^{-1}, and $K_2 = 0.0066$ atm^{-1}. [c] Recomputed in ref 68 to be $\Delta H_2 = -5.09$ kcal mol^{-1}, $\Delta S_2 = -19.68$ cal mol^{-1} K^{-1}, and $K_2 = 0.048$ atm^{-1} at 373 K. [d] Analysis of virial coefficient data from: Schramm, W.; Leuchs, U. *Ber. Bunsenges. Phys. Chem.* **1979**, *83*, 847. [e] D_0 value.

factors as well as small differences in enthalpies may be important in determining the relative amounts of the various *n*-mers present in hydrogen fluoride vapor. Further theoretical calculations could shed light on the apparent special stability of the hexamer in hydrogen fluoride vapor.

D. Carboxylic Acids

Carboxylic acid vapors are characterized by the presence of large amounts of associated species. The extent of the dimerization is very large so that, for example, saturated acetic acid vapor is ca. 50% dimer at its normal boiling point (391 K). The thermodynamic properties of formic and acetic acid dimers have been the most studied of the carboxylic acids. In general, the second virial coefficient, thermal conductivity, and spectroscopic techniques are in good agreement on the thermodynamic properties of these dimers. A comprehensive review of the data has been done by Chao and Zwolinski.[97] In Table IX we include only the results of their review and not the individual studies. The large dimerization enthalpy (ca. −15 kcal mol^{-1}) of these dimers is due in large part to their cyclic structures (5), which contain two equivalent C═O···H—O hydrogen bonds.



5

The structures have been characterized both spectroscopically[98,99] and theoretically.[71,112] The possibility that higher polymers are present in acetic acid vapor has been considered in fits of thermal conductivity data,[71] but the results indicate that the amounts of trimer and tetramer present are extremely small (tetramer mole fraction at 1 atm is less than 8 × 10^{-4}) and that the dimer is by far the dominant associated species in the vapor.

Association in a number of other acid vapors has also been investigated.[114] Association enthalpies and entropies are similar to those of the formic and acetic acid dimers. Thermodynamic properties of trifluoroacetic acid dimer are included in Table IX. The different methods indicate that the hydrogen bond strength is very close to that of the acetic and formic acid dimers. Theoretical calculations[71] also yield similar binding energies.

E. Other Single-Component Systems

Associated species have been studied in a number of other single-component vapors not covered in sections III.A–D. Results for these other systems are summarized in Table X. In all cases, dimers were the only species reported.

Acetonitrile has been studied by both second virial coefficient[11a,44] and thermal conductivity measurements.[68] Agreement is quite good on ΔH_2, with ca. −5 kcal mol^{-1} reported in all three studies. Again, as in the case of the water dimer and some of the alcohol dimers, the various K_2 values (see Table X) are in disagreement due to differing values for ΔS_2. The pyridine dimer has a ΔH_2 value from thermal conductivity[69] close to that of acetonitrile dimer. This suggests a similarity of hydrogen bonding (C—N···H) in the two dimers. However, the acetonitrile dimer equilibrium constant is larger than that of the pyridine dimer because of an entropic effect.

Acetone and acetaldehyde vapors contain dimers with ΔH_2 values in the range of −3 to −4 kcal mol^{-1}.[10,11a,42,44,72] Entropic effects result in smaller amounts of acet-

TABLE XI. Enthalpies and Entropies of Association for Mixed Polymers (AB)

A	ΔH_2, kcal mol^{-1}	ΔS_2, cal mol^{-1} K^{-1}	K_2 at 373 K, atm^{-1}	temp range, K	method[a]	ref
		B = Methanol				
methylamine	-5.59 ± 0.2	-17.45 ± 1.0	0.2890	298-318	*PVT*	45
dimethylamine	-6.19 ± 0.2	-19.8 ± 0.7	0.1993	298-318	*PVT*	45
trimethylamine	-6.91 ± 0.2	-23.2 ± 0.7	0.0951	298-318	*PVT*	45
	-7.50 ± 0.3			283-321	VD	46
	-7.10 ± 0.2			283-313	IR	46
	-5.8 ± 0.7	-22.6 ± 0.3	0.0288	343-463	NMR	88
diethylamine	-7.3				VD	3c
triethylamine	-7.50 ± 0.5	-24.9 ± 1.9	0.0896	298-318	*PVT*	45
	-8.2[b]			292-308	IR	84
trifluoroethanol	-7.3 ± 0.2	-24.7 ± 0.7	0.0757	288-308	*PVT*	37
hexafluoropropanol	-10.4 ± 0.3	-32.7 ± 0.9	0.0885	288-308	*PVT*	37
		B = Hydrogen Fluoride				
dimethyl ether	-10.3	-28.7	0.5789	293-333	IR	85
methyl ethyl ether	-8.84	-23.9	1.249	293-333	IR	85
diethyl ether	-7.17	-19.1	1.063	293-333	IR	85
hydrogen cyanide	(4.52 ± 0.3)[c]			167-192	ROT	89
acetonitrile	(6.24 ± 0.14)[c]			223	ROT	90
HCCCN	(4.88 ± 0.17)[c]			195-205	ROT	90
water	-6.21	-22.7	0.24	315	IR	94
		B = Hydrogen Chloride				
dimethyl ether	-6.7 ± 0.4	-25.5 ± 1.3	0.0225	295-405	RAM	86
	-7.1 ± 0.8	-25.7 ± 1.3	0.0349	306-443	NMR	80
diethyl ether	-4.7 ± 0.7			300-330	IR	96
		B = Trifluoroacetic Acid				
acetone	-7 ± 1	-24.6	0.0536	293-443	IR	87
	-14.4 ± 1.0	-50.8 ± 3.3	0.00216	294-313	VD	49
cyclopentanone	-11.7 ± 1.0	-40.9 ± 3.2	0.00825	313-333	VD	49
dimethyl ether	-7.9 ± 0.2	-23.03	0.3932	293-443	IR	87
diethyl ether	-8.4 ± 0.2	-26.80	0.116	293-443	IR	87
acetic acid	-17			276-363	VD	24

[a] See Table II, footnote *a*, for abbreviations. [b] ΔU value given in reference; correction for ΔH given in this table ($\Delta H = \Delta U - RT$) at 373 K. [c] D_0 value.

aldehyde being present in the vapor. Theoretical calculations[72] suggest that acetone dimer involves C=O···H—C hydrogen bonds with the possibility of a cyclic-type structure having two of these bonds. Acetaldehyde dimer also probably involves C=O···H—C hydrogen bonding. Theoretical calculations[72] at the STO-3G level give ΔE values of around -1 to -2 kcal mol^{-1} for acetone dimer, considerably underestimating the hydrogen bond strength. This also occurs for pyridine dimer.[68] This is in contrast to many other dimers, such as the water dimer, where this small basis set gives reasonable results.[103h] Inadequate treatment of the C=O double bond may be the cause. The 4-31G basis gives results for the binding energy of acetone dimer that is closer to values expected from experiment.[72]

The HCl dimer has been the subject of some recent studies. Second virial coefficients[54] and spectroscopic studies[92] are in agreement on the enthalpy of association (-2.15 to -2.44 kcal mol^{-1}). The virial coefficient data were analyzed[54] by using B_{nonpolar} from the Berthelot equation. A high-resolution measurement of absolute infrared line strengths by Pine and Howard[91] has given a zero-point dissociation energy, D_0, of 1.23 kcal mol^{-1} (D_e is estimated to be 2.28 kcal mol^{-1}).

Association in ammonia vapor has been studied by Rowlinson[10] and Lambert and Strong.[11c] They both obtain a ΔH_2 value of -4.4 kcal mol^{-1} using the Berthelot equation for B_{nonpolar} in eq 2. Theory (see Table III) gives a much less negative value for ΔH_2 (-2.25 kcal mol^{-1} at 298 K). An intermolecular potential derived by Duquette et al.,[115] based in part on virial coefficients and the lattice energy of the solid, also indicates that ΔH_2 should be much less negative than -4.4 kcal mol^{-1}. As in the case of water dimer, the use of the Berthelot type of analysis appears to give misleading thermodynamic results for association in gases. Lambert and Strong[11c] also give thermodynamic data for a series of amine complexes, but these results are not included in Table X because of the questionable nature of the analysis based on the Berthelot equation.

F. Mixtures

1. Dimers

The enthalpies and entropies of association of a series of gas-phase dimers between unlike molecules are listed in Table XI.

A number of amine complexes with methanol have been studied[45,46,84,88] using virial coefficient and spectroscopic techniques. The results in Table XI indicate a range of ΔH_2 values from -5.6 to -8.2 kcal mol^{-1}. In the most studied of these complexes, trimethylamine–methanol, the NMR results[88] seem out of line with the other studies based on virial coefficients. In the only systematic study of the amine complexes, that of Millen and Mines,[45] the results indicate that increasing the number of alkyl groups on the amine makes ΔH_2 more negative. If the hydrogen bond strength (N···H—O) in these complexes is measured by ΔH_2, then alkyl substitution increases the bond strength. Hence, increasing the number of alkyl groups makes the nitrogen lone pair a better hydrogen acceptor (i.e., electron donor). This is in line with charge-transfer concepts[5,116,117] of hydrogen bonding, i.e., that hydrogen bond strength increases with an increase in basicity of the hydrogen acceptor.

Thomas[85] has studied ether complexes with hydrogen fluoride using the temperature variation of the absorption band of the HF stretching vibration. The ΔH_2 values (−10.3 to −7.17 kcal mol^{-1}) become less negative with increasing alkyl size. Thomas interpreted this trend in terms of conformational rearrangements of the ethers when they form hydrogen bonds and suggests that the shifts in the HF stretching frequency upon hydrogen bonding and the increases in intensity are better measures of the hydrogen bond strengths than ΔH_2. The frequency and intensity shifts indicate that larger alkyl substituents increase the hydrogen bond strengths in contrast to the conclusion deduced from values of ΔH_2. Ether complexes with HCl studied by several workers[80,86,95] also exhibit the same trends as the HF complexes, i.e., diethyl ether has a smaller (less negative) value of ΔH_2 than dimethyl ether.

Legon et al.[89,94] have used measurements of absolute intensities of rotational transitions to determine zero-point and equilibrium dissociation energies, D_0 and D_e, of RCN···HF (R = H, CH_3, HCC) dimers. The D_0 values are listed in Table XI. High-level theoretical calculations by Benzel and Dykstra[118] on the HCN···HF complex give a D_e value of 6.9 kcal mol^{-1} compared with the experimental D_e value of 6.1 kcal mol^{-1}.

The thermodynamic data for binary complexes involving trifluoroacetic acid (TFAA) are consistent with the exception of the vapor density results of Lin et al.[49] Their ΔH_2 for the TFAA–acetone complex (−14.4 kcal mol^{-1}) is nearly twice as large as that obtained from an infrared study by Gerasimov and Tokhadze.[87] Since the TFAA–acetone complex is likely to have only one hydrogen bond compared to the TFAA or acetic acid dimers (see **5**), it is reasonable to expect that its hydrogen bond strength would be approximately half that of the TFAA dimer, i.e., ca. −7 kcal mol^{-1} as found in the infrared study. Theoretical calculations could help to resolve this question. The less negative value is also supported by a thermal conductivity study[73] of a binary acetic acid–water mixture which found the acetic acid–water complex to be much less stable than the acetic acid dimer.

2. Higher Polymers

Few measurements of mixed polymers larger than dimer have been reported. Thermal conductivity measurements[66] on methanol–water binary mixtures were analyzed and much of the increase in thermal conductivity with pressure could be accounted for by a 2:1 methanol:water trimer (as opposed to a 1:2 trimer) with a ΔH_3 of −10.5 kcal mol^{-1} and ΔS_3 of −38.2 cal mol^{-1} K^{-1}. This result was found to be consistent with theoretical calculations on methanol–water trimers.[66] Farnham[37] has determined thermodynamics for the 1:2 trimer in a methanol–hexafluoropropanol mixture from *PVT* measurements (ΔH_3 of −14.1 kcal mol^{-1}, ΔS_3 of −43 cal mol^{-1} K^{-1}).

IV. Conclusions

We have presented a review of the thermodynamic properties of gas-phase hydrogen-bonded complexes as obtained from nonideal gas, spectroscopic, and transport properties. Some general findings of this review include the following.

(a) Theory and experiment are in quite good agreement on the hydrogen bond strength in the water dimer, one of the most theoretically studied hydrogen-bonded systems, with a ΔH_2 value of −3.5 to −3.8 kcal mol^{-1} at 373 K (ΔE = −5.0 to −5.5 kcal mol^{-1}).

(b) The hydrogen bond strength in water and alcohol dimers is very similar, reflecting similar types of hydrogen bonding. The entropic factor (lower intermolecular frequencies for alcohols), in general, makes the association constants of the alcohol dimers larger than that of the water dimer. This also probably contributes to the larger concentration of higher polymers in alcohol vapors than in water vapor.

(c) The measured enthalpies of association of alcohol and hydrogen fluoride polymers (tetramers etc.) provide strong evidence for the importance of cooperativity in hydrogen bonding. The smaller amounts of higher polymers compared to the amounts of dimers are due to the opposing effect of entropy.

(d) The thermodynamic properties of these gas-phase hydrogen-bonded complexes are also useful in finding trends in hydrogen bonding, which can often be understood in terms of charge-transfer concepts.[5,116,117] Nitrogen, because it is a good electron donor, forms some of the strongest hydrogen bonds (N···H–X, where X $\neq$ N). For example, based on the series of hydrogen-bonded complexes between like molecules studied by the thermal conductivity technique, the nitriles (pyridine, acetonitrile) have the most negative ΔH_2 values, with the exception of doubly H-bonded complexes (carboxylic acids). Hydrogen fluoride, being a good electron acceptor, forms some of the strongest bonds among mixed dimers.

Spectroscopic techniques based on measurement of absolute intensities appear to be more accurate than those based on the temperature dependence of relative intensities for studying the energetics of hydrogen bonding. However, at the present time, the number of complexes to which they can be applied is limited. Of the indirect methods the thermal conductivity method avoids the ambiguities associated with virial coefficient analysis and has provided thermodynamic data on a series of hydrogen-bonded complexes, including the water dimer, using a single technique. There are unresolved differences in some of the measured values, primarily the dimerization constant for vapors (water, alcohols, acetonitrile, acetone) having small amounts of dimers. Theoretical calculations are of great value in interpreting experimental results as they can give information on structures and vibrational frequencies that are often difficult to obtain experimentally. This is evident from the results on the ammonia, water, and hydrogen fluoride dimers (see Table III), for which the highest level calculations have been reported. However, it is apparent that there are some significant differences between the theoretical calculations such as those on ΔS_2 for the water dimer. Larger basis sets, inclusion of more correlation energy, and anharmonic effects need to be included for more accuracy.

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