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by

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ABSTRACT

Measurements of the thermal conductivities of methanol [1], trifluoroethanol, ethanol, and water vapors have been made as a function of pressure and temperature with a thick hot wire cell using a relative method in which the cell was calibrated with N_2, Ar, and Kr. Comparisons of the results for the different vapors can readily be made since all the measurements were performed with the same apparatus. At any given temperature (330-400 K), the thermal conductivities increased with pressure (7-160 kPa) indicating the presence of associated species in all the vapors. From the data, we deduced association constants as well as standard enthalpies and standard entropies for the formation of the associated vapor species. Dimeric molecules were detected in trifluoroethanol, ethanol, and water vapor; and a tetramer species was detected in methanol and ethanol. In quantum mechanical calculations, we find a special stability for the cyclic hydrogen bonded tetrameric species, supporting our conclusions that most of the effect we see on the pressure dependence of the thermal conductivities of methanol and ethanol is related to the presence of tetramer. Consistent with the quantum mechanical calculations, the measurements indicate that the trifluoroethanol dimer bond is strongest. We also report on transport parameters deduced from the data.

I. Introduction

We report measurements of the pressure dependence of the thermal conductivity for vapors of ethanol, 2,2,2-trifluoroethanol, and water. Analyses of the thermal conductivities of methanol [1] and the other substances indicate the presence of dimers in ethanol, TFE, and water and the presence of tetramers in methanol and ethanol. These results are consistent with ab initio quantum mechanical calculations that we have carried out on a number of polymers.

The importance of developing an understanding of hydrogen bonding between molecules has long been recognized as a prerequisite for attacking many fundamental questions on the structure of liquids (such as water) and on nucleation and condensation. There have been a large number of experimental studies of alcohols and water which indicate that associated hydrogen bonded species exist in the vapor [4-14]. Much of the data has been reviewed by Zwolinski and Wilhoit [12]. However, the information obtainable from these studies is limited by ambiguous interpretations of the data in calculating the thermodynamic quantities for the dimer and by the insensitivity of the measuring techniques to the presence of higher associated species. In contrast, thermal conductivities are especially sensitive to the presence of large aggregates, and even a small fraction of large polymeric species can be detected [1-3]. Consequently, measurements of the thermal conductivities of molecules which tend to form hydrogen bonds can provide information on large associated species which cannot be readily obtained by other types of measurements and, perhaps, help resolve some of the differences between investigators concerning the dimeric species.

In this paper, we present enthalpies and entropies of association, as well as equilibrium constants for associated species of ethanol, TFE,

and water. These results are compared to previous thermal conductivity measurements on methanol which detected tetramers [1]. Our results are compared to the results of other measurements. Finally, the results of *ab initio* molecular orbital calculations on TFE dimers and methanol polymers are discussed and compared to the experimental results.

II. The Thermal Conductivity of an Associating Gas

If a pure non-reacting gas is placed between a hot and a cold plate, heat is conducted principally by molecular collisions. In an associating gas having sufficiently fast rates of association, a steady-state chemical composition gradient will exist between the plates due to the temperature dependence of the association equilibrium. This leads to the diffusion of larger associated species to higher temperatures and the smaller species (monomers) to lower temperatures. The smaller species associate at the lower temperature releasing the enthalpy of association which becomes part of the total heat flux. The effective thermal conductivity is thus enhanced due to the heat transported as the chemical enthalpy of association.

An expression for the enhancement of the thermal conductivity of a gas due to chemical reactions, λ_R, over that of a "frozen" (i.e., non-reacting) gas was developed by Butler and Brokaw [3], based on the work of Hirschfelder [2]. This result, applicable to the steady-state conditions described above, may be written as:

$$\lambda_R = -\frac{1}{RT^2} \begin{vmatrix} 0 & \Delta H_1 \cdots \Delta H_\nu \\ \Delta H_1 & A_{11} \cdots A_{1\nu} \\ \vdots & \vdots \\ \Delta H_\nu & A_{\nu} \quad A_{\nu\nu} \end{vmatrix} \div \begin{vmatrix} A_{11} \cdots A_{1\nu} \\ \vdots \quad \vdots \\ A_{\nu 1} \cdots A_{\nu\nu} \end{vmatrix}, \qquad (1)$$

where ν is the number of independent chemical reactions; R is the gas constant; T is the absolute temperature; and ΔH_1, ΔH_2, ..., ΔH_ν are the standard enthalpies of each of the ν unique reactions (standard state = 1 atm). The numerical coefficients, A_{ij}, are evaluated from the general form given by Brokaw [15]:

$$A_{ij} = A_{ji} = \sum_{k=1}^{u-1} \sum_{\ell=k+1}^{u} \left(\frac{RT}{pD_{k\ell}}\right) x_k x_\ell \left[\frac{n_{ik}}{x_k} - \frac{n_{i\ell}}{x_\ell}\right] \cdot \left[\frac{n_{jk}}{x_k} - \frac{n_{j\ell}}{x_\ell}\right], \qquad (2)$$

where i,j = 1,2, ..., ν; P is the total gas pressure; u is the number of distinct chemical species; and $D_{k\ell}$ is the binary diffusion coefficient for species k and ℓ. The subscripted stoichiometric coefficients, n, refer to the kth or ℓth chemical species in the ith or jth chemical reaction. All reactions must be written in the form:

$$\sum_{k=1}^{u} n_{ik} X^k = 0 \qquad i = 1,2,\ldots,j,\ldots,\nu, \tag{3}$$

where X^k represents the kth chemical species. Note that any substance that does not participate in reaction i or j must be included in the general expression, Eq. (3), but has a zero valued stoichiometric coefficient.

The measured thermal conductivity of the reacting gas may now be expressed as a function of the temperature and pressure by the sum of the frozen thermal conductivity, λ_f, and the reaction contribution, λ_R:

$$\lambda(p,T) = \lambda_f + \lambda_R \tag{4}$$

The non-reacting contribution, λ_f, is essentially the thermal conductivity of a compositionally frozen mixture of all the species in the vapor. The pressure dependence of λ_f is generally very small; therefore, the major pressure dependence of $\lambda(p,T)$ in Eq. (4) lies in the λ_R term. An insight into the usefulness of Eqs. (1) and (4) for the analysis of experimental thermal conductivities of associating gases can be gained by expansion of Eq. (1) for some specific association reactions.

If a gas consists of a mixture of monomers and one polymer species, the chemical reaction occurring in the mixture may then be represented as:

$$nX \rightleftarrows X_n \tag{5}$$

The corresponding equilibrium constant is given by:

$$K_n = p_n/p_1^n, \tag{6}$$

where p_n and p_1 are the equilibrium partial pressures of the n-mer and the monomer, respectively. Recognizing that the required mole fractions in Eq. (2) are given by $x_n = K_n p_1^n/p$, then Eq. (1) can be easily shown to reduce to the very simple form:

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

If the extent of polymerization in the vapor is small, then at moderate pressures $nK_n p_1^{n-1} << 1$, and Eq. (7) reduces to:

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

The product of the pressure, p, and the diffusion coefficient, $D_{k\ell}$, is dependent only on the temperature (see Section IV). Thus, for the case of a monomer-dimer reaction, Eq. (8) predicts that, for a small fraction of the associated n-mer, the measured thermal conductivity will depend on p^{n-1}. Thus, when only monomers and a small fraction of dimer are present, a plot of λ_R versus p will be linear. For trimer, the plot will be quadratic, and for tetramer it will be cubic. Furthermore, it can be shown that, if we allow for the existence of more than one polymeric species, then at pressures where there is only a very small amount of polymerization, Eq. (1) can easily be shown to reduce to a sum of terms of exactly the same form as Eq. (8):

$$\lambda_R = \sum_n \left(\frac{pD_{1n}}{RT}\right)\left(\frac{\Delta H_n^2}{RT^2}\right)K_n p_1^{n-1} \tag{9}$$

Thus, for a gas which consists of dimers plus some higher polymers, we then would expect the thermal conductivity to increase linearly at low pressures and to a higher power of p at higher pressures. Thus, an analysis of the pressure dependence of thermal conductivities can provide direct information about the associated species which are present.

It should be noted that, if the pressure is sufficiently high or the equilibrium constant large enough so that $nK_n p_1^{n-1}$ is not small relative to unity, then λ_R will not depend exactly on p^{n-1}. For the case of a monomer-dimer equilibrium, the thermal conductivity may bend over with increasing pressure.

These qualitative features of the theory prove to be valuable in the interpretation of experimental thermal conductivity measurements, and even a visual examination of the data is quite revealing. For quantitative analyses, the data is fitted to Eq. (1) and Eq. (4) to determine the amounts of the various species present and their enthalpies of association.

III. Experimental Method

Thermal conductivities of ethanol, 2,2,2-trifluoroethanol (TFE), and water were measured at various temperatures between 307 and 385 K and pressures ranging from 50-1200 torr (6.7-160 kPa) in a thick hot-wire cell using an apparatus and a procedure which has been previously used for measurements on methanol [1]. The cell was calibrated with nitrogen, argon, and krypton at each temperature. The voltage drop across the cell wire, V, was found to vary linearly with the reciprocal of the thermal conductivity as

$$V = A + B/\lambda \tag{10}$$

where A and B are constants determined by the calibration procedure. The purity of the three alcohols (obtained from J. T. Baker Co.) was checked by gas chromatographic analyis. The resulting mole percents of of methanol, ethanol, and TFE were 99.6, 99.5, and 99.9, respectively. In all three alcohols, trace amounts of water were found to be the only impurity. Each substance was contained in a glass bulb connected to the cell and repeatedly frozen and outgassed to remove dissolved gases. The sample was transferred to the cell by vaporizing the liquid through evacuated heated metal connecting tubes until the vapor pressure of the liquid at the cell temperature was approached or the limiting cell pressure, ca. 1200 torr (160 kPa), was reached. The voltage drop across the cell was then measured as a function of a stepwise reduction of pressure and the thermal conductivity was calculated using Eq. (10). At the end of each run, the reference gas calibration was double checked. Two separate runs at each temperature were performed. The uncertainty in the measured pressure was less than 2 torr (.27 kPa) over the whole range. The uncertainty in the absolute values of the thermal conductivity is ca. 1% of the measured

value while the relative uncertainty is less than .5%. Figure 1 shows typical experimental thermal conductivity-pressure isotherms for each of the four substances studied.

IV. Data Reduction

We have shown earlier [Eq. (9)] that it is simple to qualitatively deduce the character of the polymeric species present in each vapor solely from inspection of the typical experimental λ-p isotherms such as in Fig. 1! In the case of TFE, the thermal conductivity increases with pressure almost linearly with bending down from a straight line at higher pressures. The isotherm for water vapor is more linear. In both cases, this behavior is indicative of a predominant dimeric species in the vapor. In order to interpret the bending over of the TFE isotherm, the dimerization-equilibrium constant must be sufficiently large so that the denominator in Eq. (7) is significant. The slight upward bend in the TFE data at the highest pressures may be due to higher polymers, but is not enough to be analyzed in terms of higher polymers. Although not evident from the single water isotherm plotted in Fig. 1, a definite upward curvature due to higher polymers is present on an expanded scale. This is discussed further below.

By contrast, the isotherms for methanol and ethanol show much larger upward curvatures with pressure, indicative of the presence of associated species larger than dimer. A close comparison indicates that the two curves have slightly different shapes. At low pressures ($p \lesssim 300$ torr), the ethanol curve increases linearly with pressure while in the same range the methanol plot is more horizontal. This behavior probably indicates a significant contribution to λ_R from dimeric species in ethanol. It has been shown that the contribution to λ_R from dimeric species in methanol is too small to determine [1]. Thus, it seems likely that ethanol vapors contain more dimers than methanol.

A more analytical data reduction was performed in order to obtain quantitative information about the vapor species. To accomplish this, Eq. (4) [with an appropriate form of Eq. (1) containing the probable species present commensurate with the above discussion] was fitted to the experimental data using the SIMPLEX version of the minimization subroutine STEPIT [16]. The function, Δ, that was minimized with respect to the unknown parameters, ΔH_n and K_n, may be written as:

$$\Delta = \sum_{i=1}^{N} [\lambda_i(\text{obs}) - \lambda_i(p,T)]^2, \tag{11}$$

where N is the number of data points, $\lambda_i(\text{obs})$ is the measured thermal conductivity, and $\lambda_i(p,T)$ is given by Eq. (4) with the appropriate form of λ_R [Eq. (4)]. The pressure-diffusion coefficient product, $pD_{k\ell}$ [Eq. (2)], can be expressed in terms of the monomer-monomer diffusion coefficient by the semi-empirical relation [1]:

$$pD_{k\ell} \cong pD_{11} \cdot \left(\frac{k+\ell}{2k\ell}\right)^{1/2} \left(\frac{2}{k^{1/3}+\ell^{1/3}}\right)^2 \tag{12}$$

The term pD_{11} is evaluated from [1,17]:

$$pD_{11} = \frac{6}{5} \frac{R}{M_1} A_{11}^* \, T \, \eta, \tag{13}$$

where M_1 is the monomer molecular weight; A_{11}^* is the ratio of two reduced collision integrals determined from the Leonard-Jones potential parameters [18]; and η is the gas viscosity [19] at the temperature, T. For all gases investigated, A_{11}^* is constant within the experimental temperature range and very close to unity. Since the viscosity of TFE vapor has not been measured, we used an equivalent formulation of pD_{11} which may be written as [20]:

$$pD_{11} = \frac{8}{25} A^*_{11} T \frac{\lambda_1}{E} \tag{14}$$

where λ_1 is the value of the frozen thermal conductivity, λ_f, at zero pressure (obtained by extrapolating the experimental thermal conductivity, λ, to zero pressure) and E is the Eucken factor given in terms of the experimentally measured [21] constant pressure heat capacity, C_p, as:

$$E = \frac{4(C_p - R)}{15R} + \frac{3}{5} \tag{15}$$

The temperature and pressure dependence of the frozen thermal conductivity, although slight, was included in the fitting procedure as in a previous study of acetonitrile vapor done in this laboratory [22]. For each substance, all isotherms were fitted simultaneously (at least four separate temperature runs were performed for each substance).

Both water and TFE were reduced using the monomer-dimer form of Eq. (4) [i.e., λ_R from Eq. (7) with n = 2]. It was decided that any higher polymers in water make, at most, a tiny contribution to the measured thermal conductivity. The simultaneous fits of all the data at different temperatures and pressures were in good agreement with the experimental data and are shown as the solid lines in Fig. 1. Note that with the theory of Butler and Brokaw we were able to reproduce, within the experimental scatter, the slight downward bending of the TFE isotherm. The standard enthalpy and entropy of association of the dimers are listed in Table I. We also calculated the corresponding equilibrium constants for each experimental temperature, which are given in Table I.

Reduction of the methanol data was fully discussed in Ref. 1. Briefly, the best fits to the data were obtained

with a monomer-tetramer equilibrium [i.e., Eq. (7) was used with n = 4]. They were not able to extract reliable thermodynamic data for the dimer due to the dominating effect of the tetramer. However, the same results for the tetramer were obtained if they forced the dimer values to be those of a previous PVT study of Weltner and Pitzer [4] (ΔH_2 = -3.22 kcal mole^{-1}, ΔS_2° = -16.5 cal mole^{-1} K^{-1}, where ΔS_n° represents the standard entropy change in the association reaction at a standard state of one atmosphere pressure). The tetramer results are listed in Table I.

The ethanol data presented a more difficult problem. It was fairly obvious from the shapes of the ethanol isotherms that there was more than one type of associated species affecting the thermal conductivity. This fact was confirmed when a fit to the data assuming a monomer-tetramer (1,4) model, as for methanol, was performed. The 1,4 fits, shown for a typical isotherm as the dashed line in Fig. 1, were always too low in the middle pressure range and did not reproduce the initial and final slopes. A simultaneous fit of the data to a 1,2,3,4 model gave a better fit and is shown as the solid line in Fig. 1. Thermodynamic data from the 1,2,3,4 fits to ethanol are given in Table I. As in methanol, no trimer was detected (i.e., the final values of K_3 and ΔH_3 obtained from the least squares analyses were so small that only a negligible contribution to λ_R was made by the trimer terms). The thermodynamic properties of the ethanol dimer deduced from the data had large uncertainties. The uncertainties in ΔH_2 and ΔS_2° are coupled and the uncertainty in -RT ln K_2 is smaller than the uncertainty in ΔH_2.

In addition to the thermodynamic parameters, we have also calculated values of the frozen thermal conductivities of the monomer, λ_1. These are listed in Table I. This quantity is used in the fitting procedure

to calculate λ_f, the frozen thermal conductivities of the mixture of different species [22]. The quantity, pD_{11}, also listed in Table I, is used to calculate the various pD_{1n} of Eq. (2) in the manner previously discussed.

V. Quantum Mechanical Calculations

In order to gain more insight into the phenomenon of gas phase hydrogen bonding and to provide a basic underpinning for the analyses of experimental measurements, we undertook a program of quantum mechanical calculations to determine binding energies and structures of some of the alcohol polymers. Specifically, we sought a theoretical explanation of two questions: (1) why were higher polymers experimentally found in methanol and ethanol vapors while only dimers were found in TFE vapor, and (2) is there some special stability for the methanol tetramer over, say, trimer or pentamer? To accomplish this, we carried out ab initio molecular orbital calculations on various associated species of methanol $[(CH_3OH)_n$ n = 3,4,5,6] and the ethanol and TFE dimers using a minimal basis set. Standard LCAO-SCF methods were employed using the STO-3G [23] basis set. This small basis has been found to give reasonable structures and binding energies for hydrogen bonded complexes [24,25,26] and has the advantage that relatively large clusters of molecules can be handled. The intermolecular binding energy is obtained by subtracting the sum of monomer energies from the total energy computed for the polymer. The theoretical binding energies do not include differences in vibrational, rotational, and translational energies between the monomers and dimers which is included in the experimental enthalpies. In the TFE calculations, a standard experimental model [28] was used for all bond distances and angles.

We shall present here only the major results and conclusions of these calculations without any of the details on the computations or on the structures obtained. More complete discussions on some of these calculations have been or will be published elsewhere [27,28].

A. Methanol Polymers

Two structural types of methanol polymers were investigated — chain and cyclic. In both cases, the STO-3G geometry of the methanol monomer previously optimized by Lathan et al. [26] was used. Del Bene [25] has found a nearly linear hydrogen bond and a binding energy of -5.57 kcal mole^{-1} for the methanol dimer (Fig. 2a). The open structure chain polymers (Fig. 2b) were always found to be significantly less stable than the corresponding cyclic structures (except for the dimer) and will not be discussed further.

Since water and methanol dimers have nearly the same intermolecular geometries [24,25], the configurations of the cyclic methanol polymers were chosen to be the same as the cyclic water polymers which were optimized by Del Bene and Pople [24]. The cyclic structures can be illustrated schematically as, for example, the methanol tetramer shown in Fig. 2c. To test the validity of using the water polymer geometries, the methanol tetramer geometry was optimized and found to have a binding energy within 0.3 kcal mole^{-1} of the result using the water tetramer geometry. The calculated binding energies for the most stable structures are given in Table II. By performing similar molecular orbital calculations on pairs of closest neighbor molecules which have the same relative positions as in the cyclic structures, it was found that their hydrogen bond energies are at least 2.5 kcal mole^{-1} less stable than in the optimized open dimer. Hence, a cooperative effect must be occurring in the cyclic structures and, as a result, the hydrogen bond energies are far from additive. By analyzing the gross atomic populations [27], this enhanced stability was shown to be due to a mutual polarization of the O-H···O bonds.

It is interesting to construct a plot of the incremental gain in binding energy of the methanol polymers, i.e., $|E_n - E_{n-1}|$, versus the number of monomers comprising the cluster, n, for the most stable geometry. This is shown in Fig. 3 and the peak at n = 4 indicates that the tetramer does indeed possess a special stability over the other clusters. Our experimental results for methanol are consistent with the theoretical calculations; both indicate that the tetramer has a special stability.

We have also plotted the incremental gain in binding energy of the cyclic water polymers of Del Bene and Pople [24] in Fig. 3. The similarity of the two plots for water and methanol strongly suggests that tetramers may be significant in water vapor and may be as stable, relatively, as methanol tetramers. Their presence is not as obvious as in methanol because the saturation vapor pressure of water is much lower than that of methanol. For example, at the boiling point of methanol, the vapor pressure is about four times as large as that of water. Saturated methanol vapor will then have about 250 times more tetramer than saturated water vapor if the two tetramers have the same association constants. Consequantly, tetramers should be harder to detect in water. Despite this, a careful examination of our data reveals an apparent slight upward curvature in our λ-p water plots. If significant, this would indicate the presence of a species larger than dimers, probably the tetramer. This point will be examined further in the discussion section.

Our quantum mechanical calculations performed on the ethanol [28] dimer indicate that its stability is similar to that reported for methanol.

B. 2,2,2-Trifluoroethanol

The TFE monomer has various possible rotational isomers. The STO-3G basis set predicts that the two lowest energy configurations are the gauche-staggered and the trans-staggered isomers. These are illustrated schematically in Fig. 4a. The g-staggered form is 0.7 kcal $mole^{-1}$ more stable than the t-staggered form, apparently due to the formation of an intramolecular F···H hydrogen bond. This is in consonance with an infrared study [29] in which it was found that g-staggered form is predominant. Various dimeric structures using each isomer were considered and contained both O-H···F and O-H···O bonds. The lowest energy structure found (ΔE = -6.46 kcal $mole^{-1}$) was the dimer constructed of g-staggered monomers and is shown in Fig. 4b. Note that this structure contains two F···H internal hydrogen bonds, an O-H···O bond, and an external F···H bond involving the same fluorine that is taking part in the intramolecular bond.

The cyclic structure determined for the TFE dimer and the presence of an intramolecular hydrogen bond in the monomer provides a possible explanation for the fact that only dimers are detected in TFE vapor as opposed to methanol and ethanol vapors where higher polymers (tetramers) are found. The formation of cyclic tetramers (as other cyclic polymers) is apparently facilitated by the formation of linear hydrogen bonds similar to those for methanol in Fig. 2. In the case of TFE tetramer, linear hydrogen bonds would be hindered by F···H internal hydrogen bonds. Consequently, such F···H bonds probably are not present in the tetramer. TFE tetramers are relatively less stable than tetramers of water and methanol because the internal F···H bond in the TFE monomers are broken in forming the

tetramer, thus reducing the magnitude of the energy change. These calculations, although not complete, provide a basis for understanding and interpreting the experimental results.

VI. Discussion

The analyses of thermal conductivity measurements appear to provide reliable quantitative information on the nature of hydrogen bonded gas phase polymers. The experimental data have shown that higher polymers exist in methanol and ethanol vapors while in TFE and water vapors, only dimers are clearly evident.

A comparison of the enthalpies of association derived from the thermal conductivity data indicates that the TFE dimer (ΔH_2 = -4.59 kcal mole^{-1}) is energetically more stable than both the water dimer (ΔH_2 = -3.62 kcal mole^{-1}) and the methanol dimer ($|\Delta H_2| < 4$ kcal/mole [1]). The difficulty in separating the contribution to λ_R of the dimers from that of the tetramers leads to large uncertainties in the ΔH_2 of ethanol (-3.0 to -5.0 kcal mole^{-1}). Thus, we cannot compare the ethanol dimer enthalpy of association with the other substances. These results are consistent with quantum mechanical calculations [28] which indicate that the TFE dimer is energetically more stable than the methanol or ethanol dimers. These calculations also indicate that the energetics of formation of the methanol and ethanol dimers are very similar, a point we could not completely confirm experimentally.

Most other studies of association in vapors involve the determination of the second virial coefficient, B [12]. However, there is a diversity of data reduction techniques used to extract thermodynamic information about the polymeric species from the experimental values of B. The discrepancies in the results obtained from the different analyses on the same experimental data can be substantial. Probably, the most unambiguous approach is to describe a non-ideal gas as an ideal mixture of monomers and associated species. The second virial coefficient is then directly related to the association constant for the formation of dimers [30] as

$B = -RT\ K_2$. Using this type of analysis on second virial coefficient data obtained from other studies, we obtained enthalpies of association [from the van't Hoff equation, $d \ln K_2/d(1/T) = -\Delta H_2/R$] that are in general agreement with the thermal conductivity results. A value of ΔH_2 of -3.56 kcal $mole^{-1}$ for water dimer from the PVT data of Keyes [13] is in good agreement with the value $\Delta H_2 = -3.62$ kcal $mole^{-1}$ determined from the thermal conductivity data. For the ethanol dimer, Barrow [7] finds a value of -3.4 kcal $mole^{-1}$ from heat capacity data and Kretschmer and Wiebe [8] derive a value of -4.0 kcal mole[1] from their PVT data. These values fall in the range of uncertainty of our values of ΔH_2 for the ethanol dimer derived from the thermal conductivity data. No value of ΔH_2 for the TFE dimer in the vapor has been reported. A vapor density study [13] has led to the conclusion that trimers and octamers are the major species in TFE vapor. The thermal conductivity data indicates that dimers are the major associated species present in the vapor and, therefore, do not lend support to this conclusion.

A comparison of the dimerization constants determined from this study indicates that, in the range of temperatures considered, the dimerization constants are in the order K_2(TFE) > K_2(ethanol) > K_2(water). Thermal conductivity data on methanol gave no indication of the presence of dimers [1]. which implies that K_2(methanol) must be smaller than K_2(ethanol).

Dimerization constants derived from thermal conductivity measurements and those from other techniques are in general agreement. Values of K_2

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[1]In the review of Wilhoit and Zwolinski [12], a value of $\Delta H_2 = -5.2$ kcal $mole^{-1}$ for ethanol is reported from the data of Kretschmer and Wiebe [8]. This result appears to be determined from an equation representing the PVT data in Ref. 8 and is not the value reported by the authors.

for water [obtained from the PVT data of Keyes [13] using Eq. (16)] are about 30% larger than the thermal conductivity values given in Table I. If the so-called excluded volume, b_o, is taken into account ($B = b_o - RT K_2$), as discussed by Hirschfelder et al. [31], then the PVT data yields values for K_2 which are only 20% larger than the thermal conductivity result. In the case of ethanol, the values of K_2 from the thermal conductivity data are very close to the values of K_2 of Kretschmer and Wiebe [8] and of Barrow [7]. For example, at 60°C and 100°C, our values of K_2 in atm^{-1} are 0.044 and 0.021, respectively, as compared to 0.047 and 0.024 from the results of Kretschmer and Wiebe and 0.041 and 0.023 from the results of Barrow.

The small differences between our values of the equilibrium constants for dimers and those deduced from PVT measurements may be real and could be related to the different methods of measurement which "see" dimers differently. In our measurements, dimers constitute a "kinetic" unit which can interdiffuse with other species. The second virial coefficient, on the other hand, may include an additional contribution from short-lived species such as "collision pairs" which exist for a few molecular vibrations or rotations [32].

The thermal conductivity technique is generally much more sensitive than other methods to the presence of higher polymers. The thermal conductivity data reported here indicate the presence of tetramers in both methanol and ethanol with values of K_4 for ethanol being somewhat larger than those for methanol. This is due to the more negative standard entropy of association for methanol. Our values of K_4 for ethanol (K_4 at 100°C = 4.0×10^{-4} atm^{-1}) are in reasonable agreement with the values deduced from both the data of Barrow [7] (K_4 at 100°C = 5.3×10^{-4} atm^{-1}) and of Kretschmer and Wiebe (K_4 at 100°C = 5.0×10^{-4} atm^{-1}) [8]. Also,

our values of ΔH_4 (-22.26 kcal mole^{-1}) and ΔS_4° (-75.2 cal mole^{-1} K^{-1}) are consistent with those of the same two studies (ΔH_4 = -21.4, -24.8 kcal mole^{-1} and ΔS_4° = -72.21, -81.45 cal mole^{-1} K^{-1}, respectively).

The slight upward curvature in the thermal conductivity data for water is an indication that a species larger than dimer is present in the vapor. An analysis performed by fitting the data to a polynomial in the pressure [i.e., Eq. (9)] led to a value of ΔH_4 similar to those of methanol and ethanol but with large uncertainties. The corresponding values of K_4 we obtained for water were about five to ten times lower than those for ethanol. However, using this method of analysis, the derived values of the dimerization constants, K_2, also had very large uncertainties and no reliable values of ΔH_2 could be derived. A similar analysis of the data for TFE vapor did not give any indication that TFE tetramer is a significant species.

VII. Conclusions

Although our data analyses are not complete, the thermal conductivity measurements indicate that tetramers exist in methanol and ethanol and dimers exist in water, ethanol, and 2,2,2-trifluoroethanol. Although dimers undoubtedly exist in methanol, their presence is masked by tetramers in thermal conductivity measurements [1]. Quantum mechanical calculations are consistent with the presence of tetramers in methanol, ethanol, and water, and the internal F···H bond may be the reason why TFE vapor contains more dimer and less tetramer than in the two other alcohols. Although water tetramers may have energetic stabilities close to those of methanol or ethanol, the lower vapor pressure of water leads to a much smaller fraction of tetramers in saturated water vapor than in saturated methanol and ethanol vapors.

Further analyses of the data and measurements of higher molecular weight alcohols, substituted alcohols, and of their mixtures are under way to obtain a more complete picture of the factors which influence hydrogen bonding.

VIII. Acknowledgments

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Table I. Association Reaction Equilibrium Constants, K_n,[a] Saturation Vapor Pressures, p_{sat}, Polymer Mole Fractions at Saturation, x_n, Monomer Thermal Conductivities, λ_1,[b] Pressure-Binary Diffusion Coefficients, pD_{11}[c] and Cluster Thermodynamic Data

Methanol, CH_3OH [1]

$\Delta H_4 = -23.73$ kcal mole^{-1}, $\Delta S_4^\circ = -80.92$ cal mole^{-1} K^{-1}

T (K)	$10^3 K_4$ (atm^{-3})	p_{sat} (atm)	x_4 at Saturation	$10^5 \lambda_1$ (cal cm^{-1} sec^{-1} K^{-1})	$10^5 pD_{11}$ (cal cm^{-1} sec^{-1})
306.9	164	0.250	0.0025	4.025	253
316.6	49.9	0.397	0.0031	4.358	269
326.6	15.7	0.620	0.0036	4.645	286
337.4	4.87	0.971	0.0043	4.950	305
345.1	2.21	1.322	0.0050	5.164	319

Ethanol, CH_3CH_2OH, Preliminary Analysis

($\Delta H_2 = -4.5 \begin{smallmatrix} + 0.5 \\ - 1.5 \end{smallmatrix}$ kcal mole^{-1}, $\Delta S_2^\circ = -19.7 \begin{smallmatrix} + 1.0 \\ - 2.0 \end{smallmatrix}$ cal mole^{-1} K^{-1})

$\Delta H_4 = -22.26$ kcal mole^{-1}, $\Delta S_4^\circ = -75.2$ cal mole^{-1} K^{-1}

T (K)	$10^3 K_4$ (atm^{-3})	$10^2 K_2$ (atm^{-1})	p_{sat} (atm)	x_2 at Saturation	x_4 at Saturation	$10^5 \lambda_1$ (cal cm^{-1} sec^{-1} K^{-1})	$10^5 pD_{11}$ (cal cm^{-1} sec^{-1})
328.7	23.2	4.9	0.362	0.017	0.0010	4.098	184
337.4	9.64	4.1	0.536	0.021	0.0014	4.318	193
347.2	3.78	3.4	0.829	0.027	0.0019	4.562	204
357.1	1.54	2.8	1.257	0.033	0.0027	4.806	216
366.7	0.68	2.4	1.855	0.041	0.0036	5.039	227
377.4	0.29	2.0	2.684	0.048	0.0045	5.295	240

Table I (Cont'd.)

H_2O, Preliminary Analysis[d]

$\Delta H_2 = -3.62$ kcal mole^{-1}, $\Delta S_2^\circ = -18.74$ cal mole^{-1} K^{-1}

T (K)	$10^2 K_2$ (atm^{-1})	p_{sat} (atm)	x_2 at Saturation	$10^5 \lambda_1$ (cal cm^{-1} sec^{-1} K^{-1})	10^5 pD_{11} (cal cm^{-1} sec^{-1})
358.4	1.298	0.578	0.007	5.355	592
367.1	1.151	0.804	0.009	5.530	626
375.9	1.025	1.112	0.011	5.705	660
386.4	0.898	1.562	0.014	5.911	703

2,2,2-Trifluoroethanol, CF_3CH_2OH[d]

$\Delta H_2 = -4.59$ kcal mole^{-1}, $\Delta S_2^\circ = -18.54$ cal mole^{-1} K^{-1}

T (K)	$10^2 K_2$ (atm^{-1})	p_{sat} (atm)	x_2 at Saturation	$10^5 \lambda_1$ (cal cm^{-1} sec^{-1} K^{-1})	10^5 pD_{11} (cal cm^{-1} sec^{-1})
338.0	8.24	0.685	0.051	3.566	115
347.4	6.19	1.03	0.057	3.752	123
359.8	5.45	1.72	0.079	3.993	132
370.8	4.07	2.63	0.089	4.203	141
385.1	3.57	4.40	0.121	4.471	154

---

[a] Equilibrium constants were calculated from simultaneous fits to all experimental isotherms.

[b] λ_1 values listed here were determined from the theoretical fits.

[c] All values of pD_{11} were calculated from Eq. (13) using the experimental viscosity [19] except TFE for which Eq. (15) was used. The values of A_{11}^* were calculated from the Leonard-Jones potential parameters [18] and are 1.104, 1.104, 1.095, and 1.089 for methanol, ethanol, TFE, and water, respectively.

[d] Results from monomer-dimer fits.

Table II. Binding Energies of Methanol Polymers

Species	Most Stable Structure	Binding Energy kcal/mole
$(CH_3OH)_2$[a]	linear	-5.57
$(CH_3OH)_3$	cyclic	-15.34
$(CH_3OH)_4$	cyclic	-35.34(-35.59)[b]
$(CH_3OH)_5$	cyclic	-48.28
$(CH_3OH)_6$	cyclic	-59.48

[a]The structure and binding energy of the methanol dimer was determined by Del Bene [25].

[b]Number in parenthesis is the value for the optimized geometry.

Figure Captions

Figure 1 Typical experimental thermal conductivity versus pressure isotherms for the three alcohols and water. The methanol data is taken from Ref. 1. The solid lines are the best fits obtained by the fitting procedure discussed in the text. In the ethanol isotherm, the dashed line is the best fit assuming a monomer-tetramer model.

Figure 2 Schematic structures of various methanol polymers.

Figure 3 The theoretically calculated gain in binding energy $|E_n - E_{n-1}|$ versus the number of molecules comprising the cluster, n, for methanol (solid line) and water [24] (dashed line).

Figure 4 (a) the most stable rotational isomers of the TFE monomer, and (b) the lowest energy TFE dimer.

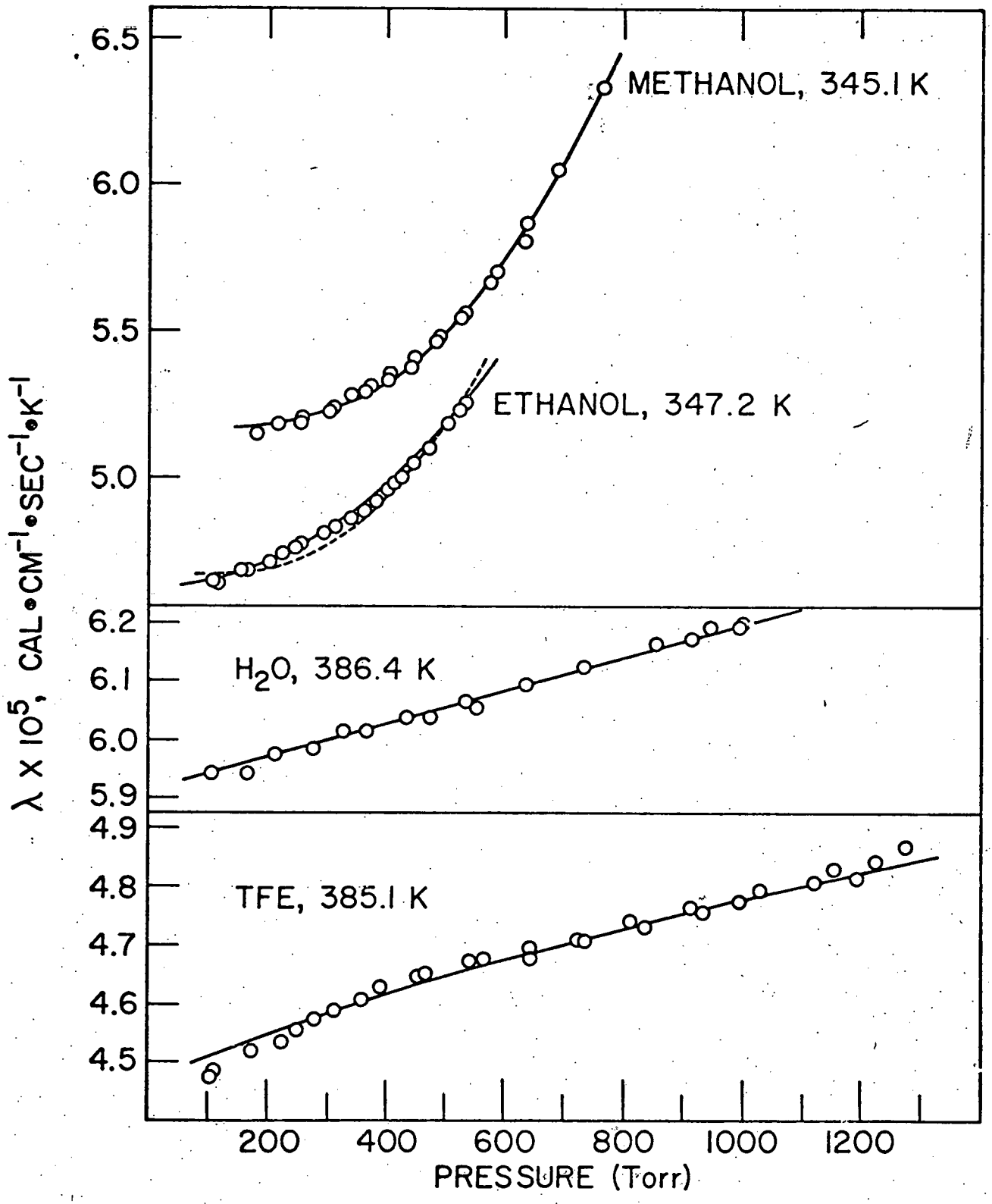
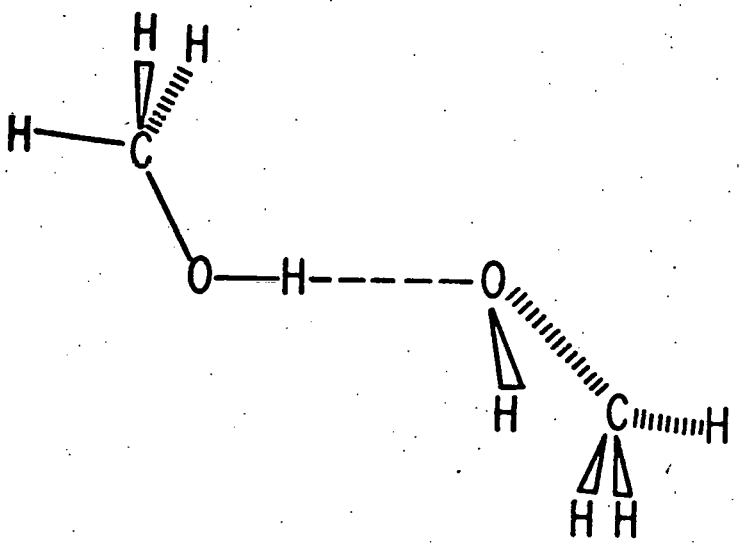
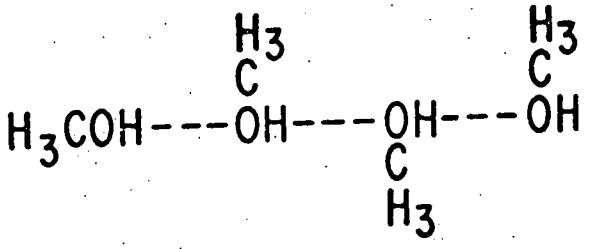

6.5
6.0
5.5
5.0
METHANOL, 345.1 K
ETHANOL, 347.2 K
6.2
6.1
6.0
5.9
H_2O, 386.4 K
4.9
4.8
4.7
4.6
4.5
TFE, 385.1 K
200
400
600
800
1000
1200
PRESSURE (Torr)
$\lambda \times 10^5$, CAL•CM^{-1}•SEC^{-1}•K^{-1}

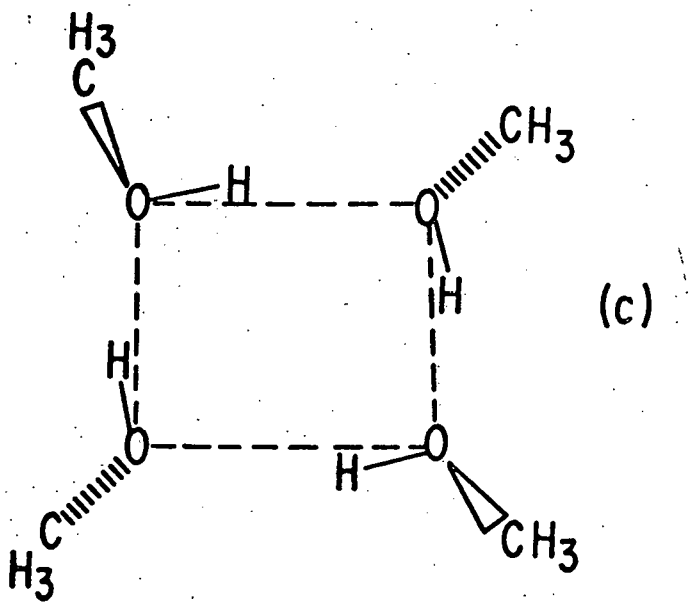
FIGURE 1



(a)

(b)





(c)

FIGURE 2

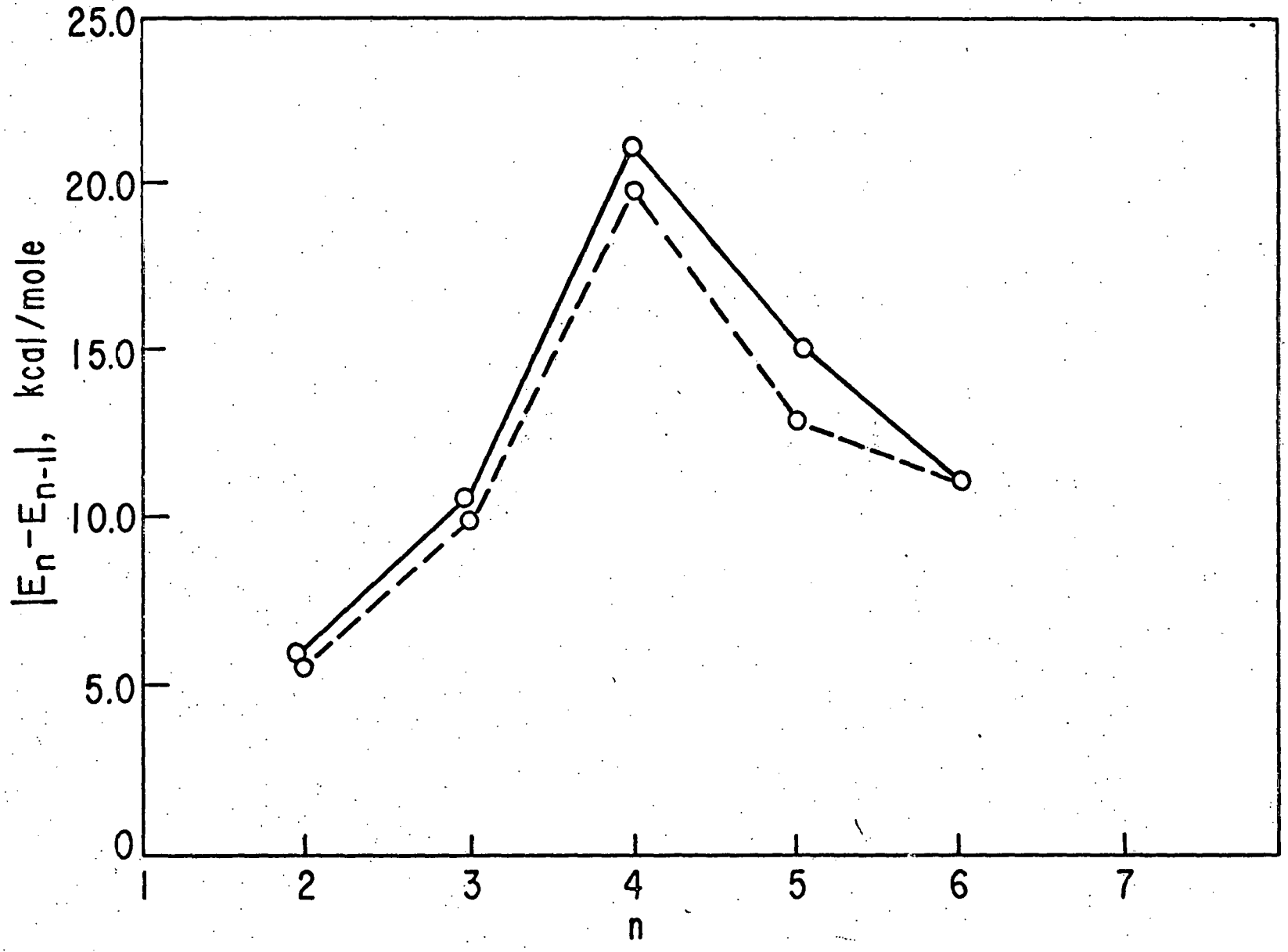
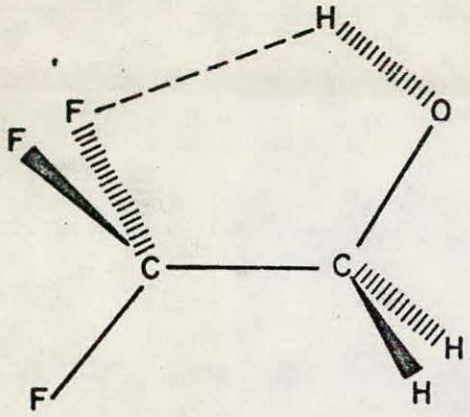
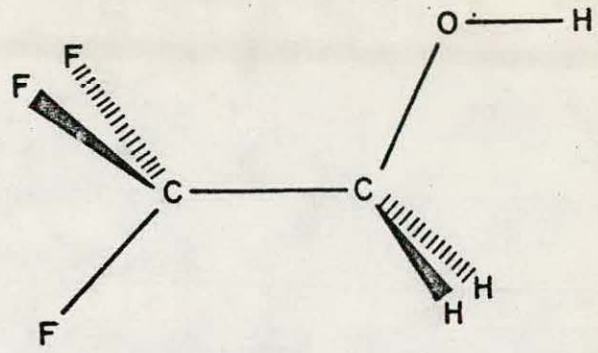


FIGURE 3

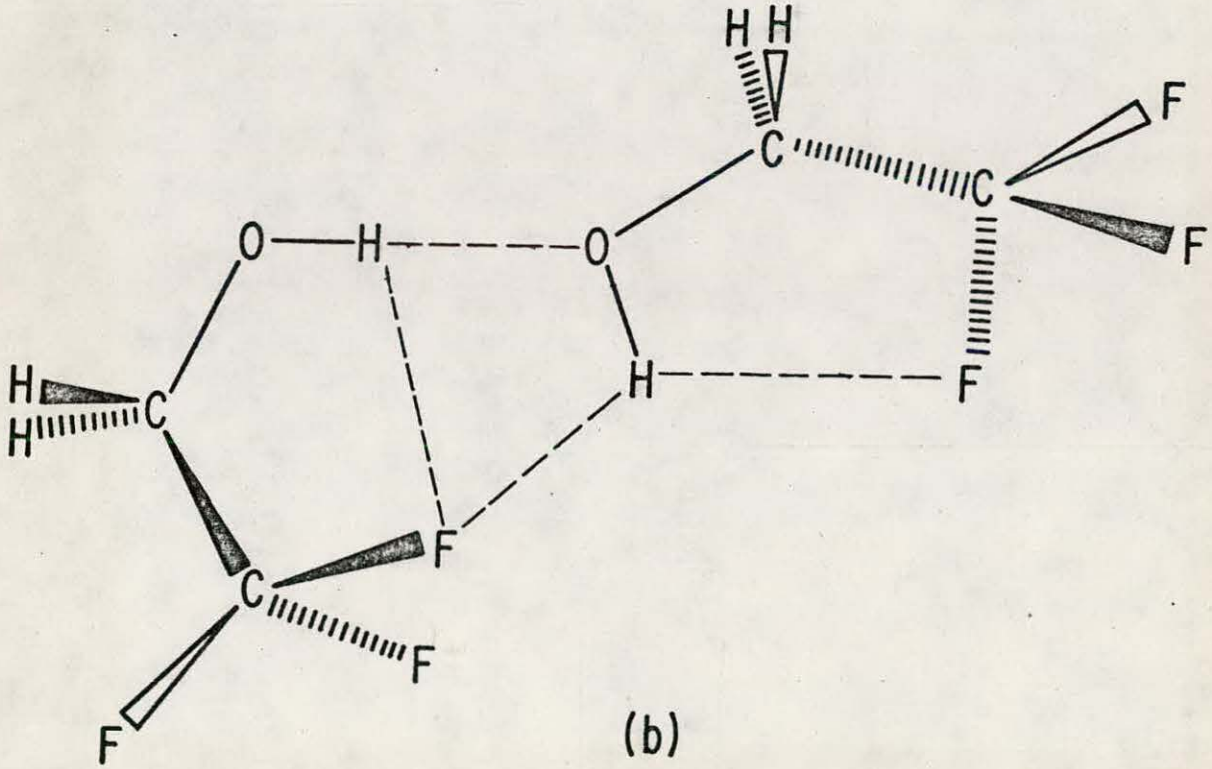


g- STAGGERED



t- STAGGERED
(III)

(a)



(b)

FIGURE 4