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Thermodynamic Properties of Key Organic Oxygen Compounds in the Carbon Range C_1 to C_4. Part 2. Ideal Gas Properties

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The ideal gas thermodynamic properties of forty-four key organic oxygen compounds in the carbon range C_1 to C_4 have been calculated by a statistical mechanical technique. The properties determined are the heat capacity (C_p°), entropy $\{S^\circ(T) - S^\circ(0)\}$, enthalpy $\{H^\circ(T) - H^\circ(0)\}$, and Gibbs energy function $\{G^\circ(T) - H^\circ(0)\}/T$. The calculations have been performed, in most cases, over the temperature range 0 to 1500 K and at 1 bar. The contributions to the thermodynamic properties of compounds having internal- or pseudo-rotations have been computed by employing a partition function formed by the summation of the internal rotational or pseudorotational energy level for each rotor in the given molecule. These energy levels have been calculated by solving the wave equation using appropriate barrier heights, rotational constants, and potential functions for the given rotations. The thermodynamic properties have been calculated using a rigid-rotor and harmonic-oscillator molecular model for each species. The sources of molecular data and the selection of the values used in the calculation are described. The calculated C_p° and $\{S^\circ(T) - S^\circ(0)\}$ values are compared with experimental results where appropriate.

Key words: critically evaluated data; enthalpy; entropy; gaseous organic oxygen compounds; Gibbs energy function; heat capacity; ideal gas thermodynamic properties.

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1. Introduction

1.1. Scope and Objectives

The critical evaluation of the thermodynamic properties of simple chemical substances in the crystal, liquid, and ideal gas states has been a principal research project at the Thermodynamic Research Center (TRC) for many years. The results reported here constitute part of a research contract entitled "Thermodynamic Properties of Key Organic Oxygen Compounds in the Carbon Range C_1 to C_4," between TRC and the Office of Standard Reference Data of the National Bureau of Standards during the period 1970–1984. In Part 1 of this series, the thermodynamic properties of organic oxygen compounds (C_1–C_4) in the condensed phases (including the glass phase where possible) were critically evaluated and recommended values were tabulated.

Part II (this report) contains the thermodynamic properties of a number of organic oxygen compounds (C_1 to C_4) in the ideal gas phase. The values were calculated using a standard statistical mechanical method in which a rigid-rotor and harmonic-oscillator molecular model modified where appropriate for internal rotations, was assumed for each compound. The molecular, spectroscopic, and thermal constants needed for the statistical mechanical calculations were selected from the literature. In a few cases missing data were estimated by analogy to related compounds.

The ideal gas thermal functions calculated include the heat capacity (C_p°), entropy $\{S^\circ(T)\text{-}S^\circ(0)\}$, Gibbs energy function $\{G^\circ(T)\text{-}H^\circ(0)\}/T$, and enthalpy $\{H^\circ(T)\text{-}H^\circ(0)\}$. The standard state is the ideal gas at a pressure of 1 bar. Thermochemical properties are being reviewed in the next part of the series.

Calculations were made from 0 up to 1500 K at 1 bar. All calculations were based on the 1973 Fundamental Physical Constants recommended by the CODATA Task Group[1] and on the 1975 Atomic Weights: C=12.011, H=1.0079, and O=15.9994.[2] Where necessary, previous results were converted to SI units using the conversion factors: 1 cal=4.184 joules and 1 atm=1.01325 bar.

Whenever possible the calculated entropies and heat capacities were compared to those derived from calorimetric measurements. It is intended that these values will serve as a basis for extrapolation to higher members of the various homologous series.

1.2. Statistical Mechanical Method

The thermodynamic properties for the ideal gaseous state were calculated from molecular partition functions,

$$Q=\Sigma g_i e^{-\epsilon_i/kT} \qquad (1)$$

where ϵ_i is the energy of a molecule in the i-th quantum state (relative to the energy in the ground state) and g_i

the corresponding degeneracy. The relationship between the partition function and the thermodynamic properties is discussed in several standard textbooks on statistical mechanics [4-9,21] and various review articles.[10,11]

The energies of molecular quantum states were based primarily on observed molecular spectra. For molecules without an internal rotation the rigid-rotor harmonic-oscillator (RRHO) model was used. For this model the energy of each state was the sum of energies for translational, rotational, vibrational, and electronic states.

$$\epsilon_i = \epsilon_j(trans) + \epsilon_k(rot) + \epsilon_l(vib) + \epsilon_m(elec) \tag{2}$$

Excited electronic states were not significant for the molecules surveyed in this report. Thus the total partition function was the product of independent partition functions the three types of energy.

$$Q = Q_{trans}Q_{rot}Q_{vib} \tag{3}$$

Equations (2) and (3) are suitable for the low energy states, but not for the higher energy states where corrections are required for anharmonic intramolecular potentials, centrifugal stretching of chemical bonds, and vibration–rotation interactions. Available information is insufficient to permit such corrections for any of the molecules considered here. At a fixed temperature the contribution to Q decreases as the quantum state increases. However the higher energy terms become relatively more important as the temperature increases. Thus the RRHO model has limited accuracy at higher temperatures.

A molecule has $3N$ degrees of freedom, where N is the number of atoms in the molecule. These include 3 for translation and 3 for molecular rotation of a non-linear molecule. The remaining $3N-6$ can be assigned to the normal modes of vibration. A linear molecule has 2 degrees of rotational freedom and $3N-5$ normal vibrations.

The relations between thermodynamic properties and the partition function are:

$$\{G^\circ(T) - H^\circ(0)\}/T = -R\ln\frac{Q}{N_A} \tag{4}$$

$$\{H^\circ(T) - H^\circ(0)\} = RT^2\frac{\mathrm{d}\ln Q}{\mathrm{d}T} \tag{5}$$

$$\{S^\circ(T) - S^\circ(0)\} = R\ln\frac{Q}{N_A} - RT\frac{\mathrm{d}\ln Q}{\mathrm{d}T} \tag{6}$$

$$C_p^\circ = RT^2\frac{\mathrm{d}^2\ln Q}{\mathrm{d}T^2} + 2RT\frac{\mathrm{d}\ln Q}{\mathrm{d}T}. \tag{7}$$

N_A is Avogadro's number. The functions for translation, vibration, and rotation for the RRHO model expressed in closed algebraic forms are listed in Table A-1. The values of the fundamental frequences selected for the molecules and species are listed in Table A-2.

1.3. Internal Rotation

If a molecule contains two non-linear groups of atoms connected by a single chemical bond and if both groups contain atoms which do not lie on the bond axis, then the molecule has a mode of internal rotation or torsional oscillation. The groups of concern here are methyl, hydroxyl, carbonyl, carboxyl, and alkoxy and require some special approximations to evaluate the partition function.[9,12,13,18,20,21,26,27]

The approximations depend on the magnitude of the potential energy associated with the relative rotational motion. Where the potential was so high that all the corresponding terms, ϵ/kT, are large, the mode was treated as harmonic torsional oscillation. Where the barriers in the rotational potential are small the internal rotation can be approximated as free rotation with the partition function given by equation (13). However this was not assumed for any molecules discussed here.

For intermediate cases the internal rotation energy levels were obtained by a solution of the Schröedinger equation with the appropriate Hamiltonian. For a single symmetric rotor this was

$$H = p^2/2I_r + V(\theta), \tag{8}$$

where p is the angular momentum operator for internal rotation, I_r is the reduced moment of inertia, and $V(\theta)$ the potential energy as a function of rotational angle, θ. The Schröedinger equation was

$$\frac{h^2}{8\pi^2 I_r}\frac{\mathrm{d}^2\psi}{\mathrm{d}\theta^2} + [\epsilon - V(\theta)]\psi = 0, \tag{9}$$

or, with the energy in units of cm^{-1},

$$F\frac{\mathrm{d}^2\psi}{\mathrm{d}\theta^2} + [\epsilon' - V(\theta)']\psi = 0. \tag{10}$$

The rotational constant, F, is defined by

$$F = \frac{h}{8\pi^2 cI_r}. \tag{11}$$

The potential energy function is usually expressed by the series

$$V(\theta) = \frac{1}{2}\Sigma\, V_n(1 - \cos n\theta). \tag{12}$$

Equation (12) reflects the symmetry in the rotor. For example, a methyl group is a symmetric top with a 3-fold symmetry. The potential energy function contains terms in which n is a multiple of 3. Usually one term with V_3 is used for a methyl group. The function should contain only terms which are multiples of three. The three equivalent minima in V correspond to positions in which the C–H bonds in the methyl group are intermediate between two of the bonds on the frame to which it is attached.

The substitution of one term from equation (12) into equation (10) gives rise to the Mathieu differential equation. Tables of solutions for this equation have been published.[29–31]

Pitzer and co-workers[15,18,21] published tables for the contributions of an internal rotation mode to several thermodynamic properties. The values are functions of the partition function for a free rotor,

$$Q_f = (8\pi^2 I_r kT)^{1/2}/nh \qquad (13)$$

and V_n/RT. They are applicable only to a single symmetric top rotor and have been extensively used since their publication.

The contributions to internal rotations used here were obtained with the direct sum indicated in equation (1). The energy levels were obtained from an approximate solution to equation (10) with the appropriate potential energy function.[19,28,33] This method is valid for both symmetric and asymmetric rotors. In most cases the parameters, V_n, in equation (12) were taken from the published literature and were based on spectroscopic observations. In some cases these values were modified slightly to obtain a better fit to measured thermodynamic properties. In some cases only the $0 \rightarrow 1$ torsional transition for a methyl group was reported. The value of the parameter V_3 was calculated from the reported torsional frequency, the rotational constant, F, and a table of Mathieu functions by a procedure given by Fately and Miller.[32]

Pitzer and co-workers published methods of calculating the reduced moments of inertia.[14–17] In some cases we used values of the reduced moments reported in the literature, but usually we calculated them using reported molecular geometry with a computer program based on reference (17).

Because complete sets of energy levels were not available for molecules which exhibit internal rotation, approximations were employed to calculate the internal rotational contribution. Two methods were used. The first was to assume that the internal rotational partition function could be factored out. Thus,

$$Q = Q_{trans}Q_{rot}Q_{vib}Q_{ir} \qquad (14)$$

where Q_{ir} is the partition function for internal rotation, or the product of such partition functions if there is more than one mode of internal rotation. The number of vibrational modes in Q_{vib} was reduced by one for each mode of internal rotation.

The second method of approximation was to consider that the system of molecules consisted of an equilibrium mixture of conformers.[9] Each conformer corresponded to one of the minima of the potential energy function for an internal rotation. The different conformers had different ground state energies, as well as different fundamental vibrational frequencies. When the rotating groups were asymmetric the conformers also had different molecular moments of inertia and different reduced moments of inertia.

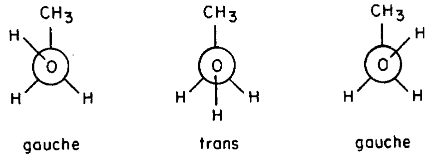


Fig. 1. The three stable rotational isomers of ethanol.

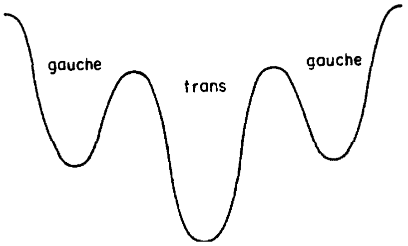


Fig 2. The potential curve of an asymmetric rotor.

Figure 1 shows the three conformers for the rotation of the -OH group in ethanol. They correspond to local minima in the potential energy function curve. The two *gauche* forms differ only in their optical activity. Their thermodynamic properties are identical but they were considered as two distinct species. Figure 2 is a schematic plot of the potential energy function for this rotation. The *gauche* forms have a higher energy than the *trans*.

The thermodynamic properties of such a mixture were calculated by the following steps.

1) Calculate the properties of each conformer separately with equation (14) where all energies are referred to the same ground state.
2) Calculate the equilibrium constants for isomerization from the differences in Gibbs energies.
3) Calculate the equilibrium mole fraction of each species.
4) Calculate the enthalpy, entropy and Gibbs energy function of the equilibrium mixture, including the entropy of mixing.
5) Calculate the heat capacity of the mixture from the temperature derivative of enthalpy.

This procedure is mathematically equivalent to calculating the thermodynamic properties from the following partition function,

$$Q = \sum_{q=1}^{s} Q_q \qquad (15)$$

where the Q_q are the partition functions of the individual species in the mixture. As in equation (14), the Q_q are products of factors which correspond to separable energy terms. Some of these, such as the translational function, may be the same for all species. Let Q_c be the product of all the common factors. Then the partition function for the mixture can be written as,

$$Q = Q_c \sum_{q=1}^{s} Q'_q \qquad (16)$$

where Q'_q are the product of partition functions that remain for each species after Q_c is factored out. Each Q'_q contains at least one factor for internal rotation. Thus

$$Q'_q = Q'_{q,c}\, Q'_{q,ir}. \qquad (17)$$

For equation (16) to be a valid approximation to the partition function of the real molecule, its terms should correspond approximately to the terms in equation (1) for the real molecular quantum states. Thus, the terms for the quantum states of an internal rotational mode should be partitioned among the $Q'_{q,ir}$ for the several conformers.

The wave function for each internal rotational state is a function of the rotational angle, θ. The probability function derived from the wave function has a maxima at angles corresponding to minima in the potential energy. It is reasonable to assign a particular state to that conformer which corresponds to the angle which has the maximum in the probability function. This assignment is unequivocal for the lower energy states but becomes increasingly less obvious as the energy increases.

This procedure requires reliable and detailed information about the structure and potential energies of the various conformers. Unfortunately in this work this kind of information was not available for molecules which exhibit relative rotation of unsymmetric tops. In such cases a complete set of internal rotational levels was used for each term, $Q'_{q,ir}$, in equations (16) and (17). A constant, ϵ_o, was added to the levels for the higher energy species to reflect the difference in energy between the ground states of the two species. This gave an overabundance of terms in the total partition function. To correct for this, the partition function is divided by s, the number of species assumed for the model. In effect, this procedure assigned an average of terms for the various conformers to each conformer in equation (16). Mathematically the factor, s, has the same effect as a symmetry number. However s is not a measure of molecular symmetry.

In some cases we approximated the energy levels for an asymmetric top rotor with two symmetric potentials, one for a *gauche*- and one for a *trans*- species.

In molecules that contain more than one rotor, the potential energy of internal rotation is a function of all the angular coordinates which describe the rotational motions.[38-40,46] However, we assumed that this function was separable and that the total internal rotational contribution was a sum of the contributions for independent rotors. The interaction of internal rotation with overall rotation was considered by Herschbach,[36] however we neglected such effects.

Molecules which have two rotors with C_{2v} symmetry exhibit two torsional modes for each kind of rotating top. Examples are dimethyl and diethyl ether and propanone. See Fately and Miller[170] and Myers and Wilson.[37] Although the potential energy function was the same for any two equivalent tops, the two modes gave rise to different reduced moments and consequently, different rotational constants. These corresponded to the a_2 and b_1 symmetry species in the spectra. Each pair of equivalent rotors yields two different contributions to the partition function. However, since the effect is nearly the same as two identical contributions based on the geometric mean of the reduced moments for the two modes and average values for the energy levels for the two species, we have used this approximation as well.

The various parameters associated with internal rotations in the molecules considered here are collected in Table A-3.

1.4. Hydrogen Bonding

Hydrogen bonding is an interaction between a covalently bound H atom and a region of high electron density on an electronegative atom or group of atoms. A typical example is the acetic acid dimer. The hydrogen atom of the O–H group of one CH_3COOH molecule forms a strong hydrogen bond with the oxygen atom of a carbonyl group in another CH_3COOH molecule, *i.e.* –O···H–O– where the dotted line is the hydrogen bond. The acetic acid dimer has two hydrogen bonds so the species is very stable. Fig. 3 illustrates the molecular structure of the CH_3COOH and $(CH_3COOH)_2$ molecules. Formation of a dimeric species results in the loss of two internal rotational degrees of freedom from the presence of two linear hydrogen bonds in the dimer instead of two free OH tops in the two monomers.

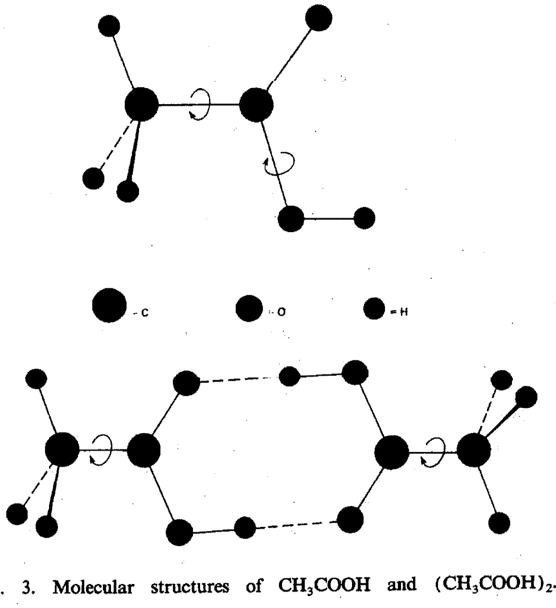


Fig. 3. Molecular structures of CH_3COOH and $(CH_3COOH)_2$.

At room temperature and atmospheric pressure, acetic acid vapor contains more dimers than monomers. As the temperature increases, the concentration of dimers decreases until at 500 K the vapor is composed predominantly of monomers. To provide a complete analysis, the thermodynamic properties for the monomers, dimers, and the equilibrium mixture of monomers and dimers have been calculated for both acetic and formic acids.

1.5. Deuterated Analogs

When pertinent molecular and spectroscopic constants were available, the thermodynamic properties of the deuterated analogs of the selected compounds were calculated. For the deuterated species, the bond distances and bond angles which were used in computing the moments of inertia were assumed to be the same as those of the undeuterated compounds when no experimental values were available.

The potential barrier height of a deuterated rotor was taken to be the same as that for the undeuterated one for generating the internal rotational energy levels. The data usually missing were the complete sets of the fundamental vibrational assignments for such deuterated species. Therefore, only a limited number of deuterated substances are included in this report.

1.6. Methylene Increment Method

The methylene (CH_2) increment method has been used extensively for estimating the ideal gas thermodynamic properties of higher members of a homologous series of paraffinic hydrocarbons from those for the lower members of the series.[48,49] A refined method of increments has been employed by Scott[50] for calculating the thermodynamic properties of organic sulfur compounds. The methylene increment method was adopted for calculating the ideal gas thermodynamic properties for some higher members of a few homologous series of organic oxygen compounds in the present work. Values of the increments to the properties were taken from reference 49.

1.7. Presentation of Results

The values for the ideal gas thermodynamic properties calculated by the statistical mechanical method are given as numerical tables. These tables are arranged in the order of increasing carbon numbers in the molecular formulas in each homologous series of compounds. The order of the homologous series follows that of Part I.

The property tables of deuterated species are always listed after those of the undeuterated species of the same compound in increasing order of the degree of deuterium substitution. A few of the tables have been reproduced directly from the open literature, with a suitable change of units, because no new molecular data were available for these compounds. For these cases, the source of data and method of calculation were still given.

A comparison of the calculated C_p° and/or $\{S^\circ(T)-S^\circ(0)\}$ values with experimental values was given for some selected compounds. Before a comparison was made, the ideal gas values were calculated from the experimental vapor heat capacity and third law entropy values. In particular, a detailed comparison has been made with the experimental values calculated using the critically selected properties given in Part I and in Part III (to be published) of this report. The best available physical constants and equations of state have been used for these conversions and the results calculated in this report were obtained using the most recent molecular and spectroscopic constants. Hence the values should be more reliable than those based on earlier spectroscopic and thermodynamic data

1.8. Uncertainty Assignment

The sources of errors in the calculated thermodynamic properties of ideal gases are considered in two groups. One is the errors in calculating the RRHO contributions to thermodynamic properites. The other is errors related to the deviations of real molecules from the RRHO model.

1.8.a. Errors in RRHO Contributions

Errors of this type reflect the errors in the molecular parameters used for the calculation. Specifically, they are the moments of inertia of the molecules and the values of the vibrational frequencies. As an approximation we assumed them to be independent and applied the usual statistical formula for calculating the standard deviations of a function from those of its arguments. Errors in vibrational frequencies affect all of the calculated thermodynamic properties.

The total uncertainty in the vibrational contribution (U) to each thermodynamic property (X) at a given temperature (T) was calculated as the sum of the separate uncertainties in the vibrational contributions (U_i) caused by the error ($\Delta\tilde{\nu}$) in assignment for each wavenumber ($\tilde{\nu}$), which is represented by the following (for a nonlinear molecule):

$$U(X)=\left[\sum_{1}^{3N-6}U_i^2\right]^{\frac{1}{2}}=\left[\sum_{1}^{3N-6}\left(\frac{\partial X}{\partial x_i}\right)^2(\Delta x_i)^2\right]^{\frac{1}{2}} \qquad (18)$$

where x is $hc\tilde{\nu}/kT$ and h is the Planck constant, c is the speed of light, and k is the Boltzmann constant. Based upon the standard statistical formulas for calculating the vibrational contributions to C_p°, $\{S^\circ(T)-S^\circ(0)\}$, $\{H^\circ(T)-H^\circ(0)\}$, and $\{G^\circ(T)-H^\circ(0)\}/T$, the following equations were derived:

$$\frac{\partial C_p^\circ}{\partial x}=\frac{Rx^2e^{-x}}{(1-e^{-x})^2}\left[\frac{2}{x}-1-\frac{2e^{-x}}{(1-e^{-x})}\right] \qquad (19)$$

$$\frac{\partial\{H^\circ(T)-H^\circ(0)\}}{\partial x}=RT\left[\frac{e^{-x}(1-x)}{1-e^{-x}}-\frac{xe^{-2x}}{(1-e^{-x})^2}\right] \quad (20)$$

$$\frac{\partial\left(\frac{\{G^\circ(T)-H^\circ(0)\}}{T}\right)}{\partial x}=\frac{Re^{-x}}{1-e^{-x}} \quad (21)$$

$$\frac{\partial\{S^\circ(T)-S^\circ(0)\}}{\partial x}=\frac{1}{T}\left[\frac{\partial\{H^\circ(T)-H^\circ(0)\}}{\partial x}\right]-\frac{\partial\left(\frac{\{G^\circ(T)-H^\circ(0)\}}{T}\right)}{\partial x}. \quad (22)$$

The above quantities were substituted into Eq. (18) to give the uncertainties in the respective thermodynamic properties caused by uncertainties in the vibrational assignments for the given compound. There is no general rule for estimating the uncertainties, Δx_i, in the vibrational assignments as they are unique for each individual substance.

The rotational contributions to the Gibbs energy function, $\{G^\circ(T)-H^\circ(0)\}/T$, and entropy, $\{S^\circ(T)-S^\circ(0)\}$, for a nonlinear polyatomic molecule require the value of $I_aI_bI_c$. The uncertainties in the $\{G^\circ(T)-H^\circ(0)\}/T$ value caused by the uncertainties in the principal moments of inertia were estimated by the following relations:

$$\Delta\left(\frac{\{G^\circ(T)-H^\circ(0)\}}{T}\right)_{\text{ROT}}=-\frac{R}{2}\frac{\Delta(I_aI_bI_c)}{I_aI_bI_c} \quad (23)$$

or

$$\Delta\left(\frac{\{G^\circ(T)-H^\circ(0)\}}{T}\right)_{\text{ROT}}=-\frac{R}{2}\left[\left(\frac{\Delta I_a}{I_a}\right)^2+\left(\frac{\Delta I_b}{I_b}\right)^2+\left(\frac{\Delta I_c}{I_c}\right)^2\right]^{\frac{1}{2}}=-\frac{R}{2}\left[\sum_1^3\left(\frac{\Delta I_i}{I_i}\right)^2\right]^{\frac{1}{2}} \quad (24)$$

where the values of ΔI_a, ΔI_b, and ΔI_c were estimated.

The total uncertainties in the calculated $\{G^\circ(T)-H^\circ(0)\}/T$, caused by uncertainties in both the vibrational and rotational contributions, were calculated as follows:

$$\Delta\left(\frac{\{G^\circ(T)-H^\circ(0)\}}{T}\right)=\left[\sum_1^{3n-6}\left(\frac{\partial\left(\frac{\{G^\circ(T)-H^\circ(0)\}}{T}\right)}{\partial x_i}\right)^2\times(\Delta x_i)^2+\frac{R^2}{4}\sum_1^3\left(\frac{\Delta I_i}{I_i}\right)^2\right]^{\frac{1}{2}}. \quad (25)$$

Equation (26) was used to calculate the total uncertainties in the calculated $\{S^\circ(T)-S^\circ(0)\}$, which includes the uncertainties in both the vibrational and rotational contributions, *i.e.*

$$\Delta\{S^\circ(T)-S^\circ(0)\}=\left[\sum_1^{3n-6}\left(\frac{\partial S^\circ}{\partial x_i}\right)^2(\Delta x_i)^2+\frac{R^2}{4}\sum_1^3\left(\frac{\Delta I_i}{I_i}\right)^2\right]^{1/2}. \quad (26)$$

Based upon the estimated Δx_i, ΔI_a, ΔI_b, ΔI_c, and the above equations, the uncertainties in the calculated C_p°, $\{S^\circ(T)-S^\circ(0)\}$, $\{G^\circ(T)-H^\circ(0)\}/T$, and $\{H^\circ(T)-H^\circ(0)\}$ were determined at the selected temperatures. These values are given in parentheses after the calculated value in each table.

1.8.b. Errors in Molecular Models

One source of deviation from the RRHO model is non-linear dependence of intramolecular force constants on atomic displacements, and on phenomena such as centrifugal stretching of bonds and rotation-vibration interaction. Although there is little direct evidence on the magnitude of these effects, it is likely that they do not affect the calculated heat capacity by more than 1% at temperature below 1000 K.

The other source of error arises from the approximation made to model internal rotation as described in section 1.3. In fact this is the principal source of error for those molecules which have internal rotations. In molecules which contains only symmetric top rotors, such as the methyl group where potential energy functions are based on reliable spectroscopic evidence, the errors in calculated heat capacity are expected to be within 1%. For more complex cases the errors are probably larger, and depend on temperature. Errors from deviations from the RRHO model were not included in the estimated errors given in the tables of thermodynamic functions.

2. Evaluation of Thermodynamic Properties

2.1. Alkanols

The calculated ideal gas properties such as C_p° and $\{S^\circ(T)-S^\circ(0)\}$ were compared, where possible, with experimental values to check the reliability of the input data and the computational method employed. The experimental heat capacities were corrected to their zero pressure value, C_p°, by correction for gas imperfections. When P-V-T data for the given compound was available, this correction was done using well-known thermodynamic relationships. However, alkanol vapors contain polymeric species in addition to the monomeric molecules, thus a special treatment, described below, was used to account for the effects of gas imperfection.

DeVries and Collins[52] determined the heat capacity of methanol vapor and found that the C_p° values increased with decreasing temperature near the saturation curve. Sinke and DeVries[53] and Stromsoe *et al.*[54] reached a similar conclusion from C_p° measurements on the aliphatic alcohols CH_3OH to $C_5H_{11}OH$. Weltner and Pitzer[55] measured the heat capacity of gaseous methanol at a series of pressures and temperatures. From an analysis of the pressure dependence of C_p near the saturation curve, they proposed the existence of a polymerization phenomenon somewhat similar to that proposed for hydrogen fluoride. Based upon an assumption that the enthalpy of polymerization was constant and ΔC_p° of polymerization was zero, they developed an equation of state for methanol vapor:

$$PV = RT + BP + DP^{n-1} \tag{27}$$

where

$$B = b - \frac{RT}{K_2} = b - RT(\mathrm{e}^{-\Delta S_2/R})(\mathrm{e}^{\Delta H_2/RT}) \tag{28}$$

and

$$D = -(n-1)\, RT\, (\mathrm{e}^{-\Delta S_n/R})(\mathrm{e}^{\Delta H_n/RT}). \tag{29}$$

In the above equations, b is the covolume, n is the number of monomer units in the higher polymer, and K_2 and K_n are the pressure based equilibrium constants for the dissociation of the dimer and higher polymers, respectively. The resulting expression for the heat capacity, as proposed by Weltner and Pitzer[55] is

$$C_p = C_p^\circ + aP + cP^{n-1} \tag{30}$$

where

$$a = \frac{\Delta H_2^2}{RT^2}(\mathrm{e}^{-\Delta S_2/R})(\mathrm{e}^{\Delta H_2/RT}) \tag{31}$$

$$c = \frac{\Delta H_n^2}{RT^2}(\mathrm{e}^{-\Delta S_n/R})(\mathrm{e}^{\Delta H_n/RT}). \tag{32}$$

They found that the heat capacity data at 345.6 K were fitted best by $n = 4$. The following equation was used[55] to calculate the ideal gas entropy:

$$\{S^\circ(T)-S^\circ(0)\} - S_p(T) = R \ln P + \frac{\mathrm{d}B}{\mathrm{d}T}\cdot\frac{P^3}{3} \tag{33}$$

where $\{S^\circ(T)-S^\circ(0)\}$ is the standard entropy of the ideal gas monomer at 1 bar and S_p is the entropy of the real gas at pressure P.

Kretschmer and Wiebe[56] measured P-V-T data for methanol, ethanol, and 2-propanol and found that Eq. (26) fitted their results. They concluded that the above equations gave satisfactory agreement with vapor heat capacity measurements[52,53,55,57] and also gave satisfactory agreement with the saturated vapor densities calculated from the heats of vaporization measured by Fiock *et al.*[58]

Using the above model which assumes alkanol vapor to contain monomeric, dimeric, and tetrameric species, Barrow[57] and Green[59] made the gas imperfection corrections to the C_p and S values for ethanol and compared the resulting C_p° and $\{S^\circ(T)-S^\circ(0)\}$ values with those calculated by the statistical mechanical method. McKetta and co-workers have made a similar comparison of the ideal gas thermodynamic properties of 1-propanol,[60] 2-butanol,[61] and 2-methyl-2-propanol.[62] The ideal gas thermodynamic properties of n-alkanols (C_1 to C_4) were reported by Chermin[63] and Green[64] and others,[510] using the molecular, spectroscopic, and thermal constants available at that time. The sources of input data and the method of evaluation used for each alkanol are described below. The calculated C_p° and $\{S^\circ(T)-S^\circ(0)\}$ are compared with experimental results where available.

2.1.a. Methanol

The ideal gas thermodynamic properties of methanol (methyl alcohol, CH_3OH) were reevaluated recently by Chen *et al.*[65] They employed the molecular structural parameters and rotational constants determined from microwave spectroscopy by Lees and coworkers[66-69] for computing the values of $I_aI_bI_c$ and F.

The fundamental vibrational assignment of Shimanouchi[80] was adopted for evaluating the vibrational contributions. Although the vibrational frequencies of CH_3OH vapor have been determined by numerous investigators from infrared and Raman spectra,[70-79] some of the reported assignments[70,71,75,76] are in conflict. Shimanouchi critically reviewed the reported spectral data on methanol and its deuterated analogs, in both the gas and liquid phases, and made a complete set of fundamental frequency assignments for these species which is internally consistent. His results were adopted in this work. For generating internal rotational energy levels for CH_3OH, the potential function $V = 1/2[V_3(1 - \cos 3\theta) + V_6(1 - \cos 6\theta)]$ was used. The values of V_3 and V_6 were obtained from Kwan and Dennison.[81]

Using the molecular constants given in Tables A-2 and A-3, we recalculated the thermodynamic properties by the standard method of statistical mechanics. The results are presented in Table 1.

Ivash *et al.*[465] calculated the ideal gas thermodynamic properties of methanol (g) over the temperature range from 100 to 1000 K, and these were adopted by Stull *et al.* in their book on "The Chemical Thermodynamics of Organic Compound".[466] Their results are in excellent agreement with our new values.

Kaushik *et al.*[467] observed the microwave spectrum of CH_3OD (g) and determined the rotational and internal rotational constants, *i.e.*, A, B, C, F, and V_3 for this species. Based upon these data, we obtained the $I_aI_bI_c$ and 108 internal rotational energy levels for calculating the rotational and internal rotational contributions to the thermodynamic properties of CH_3OD (g). The vibrational wavenumbers for this compound, taken from Shimanouchi,[80] are given in Table A-2. The calculated results are listed in Table 2.

The thermodynamic properties for CD_3OH and CD_3OD, given in Tables 3 and 4, were calculated using the methods described. In these calculations, the molecular structure of each deuterated species was assumed to be the same as that of the CH_3OH molecule. The vibrational wavenumbers for these species were taken from Shimanouchi[80] and are listed in Table A-2. The potential function employed for generating the internal rotational energy levels for each deuterated species was assumed to be the same as that for CH_3OH.

TABLE 1. Ideal gas thermodynamic properties of methanol (CH_3OH) at 1 bar[a]
$M = 32.0420$

T / K	C_p° / J K^{-1} mol^{-1}	$\{S^\circ(T)-S^\circ(0)\}$ / J K^{-1} mol^{-1}	$-\{G^\circ(T)-H^\circ(0)\}/T$ / J K^{-1} mol^{-1}	$\{H^\circ(T)-H^\circ(0)\}$ / J mol^{-1}
0	0	0	0	0
100	36.90(0.07)	196.71(0.03)	161.62(0.01)	3509(2)
150	38.59(0.07)	212.04(0.06)	176.02(0.02)	5402(6)
200	39.68(0.06)	223.28(0.08)	186.49(0.03)	7358(9)
273.15	42.57(0.04)	236.12(0.09)	198.12(0.05)	10353(12)
298.15	44.04(0.03)	239.81(0.09)	201.46(0.05)	11435(13)
300	44.16(0.03)	240.08(0.09)	201.69(0.05)	11517(13)
400	51.62(0.03)	253.77(0.10)	213.04(0.06)	16291(16)
500	59.69(0.03)	266.16(0.11)	222.44(0.07)	21859(18)
600	67.19(0.03)	277.71(0.11)	230.70(0.08)	28209(20)
700	73.86(0.02)	288.58(0.11)	238.20(0.08)	35268(22)
800	79.75(0.02)	298.84(0.11)	245.15(0.09)	42955(23)
900	84.95(0.02)	308.54(0.11)	251.66(0.09)	51196(25)
1000	89.54(0.02)	317.73(0.11)	257.81(0.09)	59925(26)
1100	93.57(0.02)	326.46(0.11)	263.65(0.09)	69085(28)
1200	97.12(0.02)	334.76(0.12)	269.24(0.09)	78624(29)
1300	100.24(0.02)	342.06(0.12)	274.58(0.10)	88496(30)
1400	102.98(0.02)	350.19(0.12)	279.72(0.10)	98660(32)
1500	105.40(0.02)	357.38(0.12)	284.66(0.10)	109081(33)

[a]Values in parenthesis are estimated uncertainties.

TABLE 2. Ideal gas thermodynamic properties of methanol-d_1 (CH_3OD) at 1 bar[a]
$M = 33.0482$

T / K	C_p° / J K^{-1} mol^{-1}	$\{S^\circ(T)-S^\circ(0)\}$ / J K^{-1} mol^{-1}	$-\{G^\circ(T)-H^\circ(0)\}/T$ / J K^{-1} mol^{-1}	$\{H^\circ(T)-H^\circ(0)\}$ / J mol^{-1}
0	0	0	0	0
100	38.24(0.10)	199.11(0.07)	163.94(0.03)	3517(5)
150	39.82(0.07)	214.97(0.11)	178.47(0.05)	5475(9)
200	40.88(0.05)	226.56(0.13)	189.11(0.07)	7491(12)
273.15	44.04(0.03)	239.71(0.14)	200.97(0.08)	10583(15)
298.15	45.61(0.03)	243.63(0.14)	204.38(0.09)	11703(16)
300	45.73(0.03)	243.92(0.14)	204.63(0.09)	11788(16)
400	53.40(0.03)	258.09(0.15)	216.26(0.10)	16732(18)
500	61.52(0.03)	270.88(0.15)	225.92(0.11)	22481(20)
600	69.07(0.03)	282.78(0.15)	234.42(0.12)	29017(22)
700	75.85(0.03)	293.95(0.15)	242.13(0.12)	36270(23)
800	81.85(0.02)	304.47(0.16)	249.27(0.13)	44161(25)
900	87.15(0.02)	314.43(0.16)	255.96(0.13)	52617(26)
1000	91.79(0.02)	323.85(0.16)	262.29(0.13)	61568(27)
1100	95.84(0.02)	332.80(0.16)	268.29(0.13)	70954(29)
1200	99.36(0.02)	341.29(0.16)	274.03(0.14)	80718(30)
1300	102.43(0.02)	349.37(0.16)	279.51(0.14)	90812(31)
1400	105.10(0.02)	357.06(0.16)	284.78(0.14)	101191(33)
1500	107.43(0.02)	364.39(0.16)	289.84(0.14)	111820(34)

[a]Values in parenthesis are estimated uncertainties.

Vapor heat capacities of methanol from 341 to 585.35 K have been measured by DeVries and coworkers,[52,53] Stromsoe *et al.*,[54] and Weltner and Pitzer.[55] The reported C_p were converted to the ideal gas heat capacities, C_p°, by corrections for the gas imperfection effects.[55,56] These experimental C_p° values are compared with our calculated values in Table A-4. The differences are within the experimental uncertainties of ± 1.3 J K^{-1} mol^{-1}.

Table A-5 gives a comparison of the third-law entropies with our calculated $\{S^\circ(T)-S^\circ(0)\}$ for methanol vapor in the temperature range from 313.1 to 383.15 K. The third-law entropies were calculated based upon the value S(liq, 298.15 K) = (127.24 ± 0.21) J K^{-1} mol^{-1},[82] the liquid heat capacities[83] and the enthalpies of vaporization.[55,58] The entropy of liquid methanol at 298.15 K was reported as (134.9 ± 8) J K^{-1} mol^{-1} [84] and (127.19 ± 0.12) J K^{-1} mol^{-1}.[83] Carlson and Westrum[83] reported $\{S^\circ(298.15\ \mathrm{K})-S^\circ(0)\} = 239.60$ J K^{-1} mol^{-1} for methanol compared with our statistical thermodynamic value of 239.81 J K^{-1} mol^{-1} at 1 bar. This value is in agreement with our selected experimental value given in Table A-26 of 241.78 J K^{-1} mol^{-1} based on the evaluations in Part I and III of this report.

TABLE 3. Ideal gas thermodynamic properties of methanol-d_3 (CD_3OH) at 1 bar[a]
$M = 35.0606$

T/K	C_p°/J K^{-1} mol^{-1}	$\{S^\circ(T)-S^\circ(0)\}$/J K^{-1} mol^{-1}	$-\{G^\circ(T)-H^\circ(0)\}/T$/J K^{-1} mol^{-1}	$\{H^\circ(T)-H^\circ(0)\}$/J mol^{-1}
0	0	0	0	0
100	37.20(0.08)	202.24(0.04)	167.18(0.02)	3506(3)
150	39.16(0.07)	217.72(0.07)	181.57(0.03)	5418(7)
200	41.38(0.06)	229.27(0.09)	192.11(0.04)	7427(10)
273.15	47.03(0.04)	242.91(0.10)	203.95(0.06)	10644(13)
298.15	49.41(0.04)	247.13(0.11)	207.39(0.06)	11849(14)
300	49.58(0.04)	247.43(0.11)	207.64(0.06)	11941(14)
400	59.79(0.03)	263.12(0.11)	219.56(0.07)	17410(17)
500	69.25(0.03)	277.47(0.12)	229.73(0.08)	23870(19)
600	77.32(0.03)	290.86(0.12)	238.81(0.09)	31208(21)
700	84.14(0.03)	303.28(0.12)	247.13(0.09)	39292(23)
800	89.87(0.03)	314.91(0.12)	254.92(0.10)	48003(25)
900	94.73(0.02)	325.79(0.13)	262.20(0.10)	57237(27)
1000	98.78(0.02)	335.96(0.13)	269.06(0.10)	66919(28)
1100	102.26(0.02)	345.54(0.13)	275.58(0.10)	76973(30)
1200	105.19(0.02)	354.58(0.13)	281.78(0.11)	87349(31)
1300	107.74(0.02)	363.11(0.13)	287.72(0.11)	97998(33)
1400	109.87(0.02)	371.15(0.13)	293.41(0.11)	108880(34)
1500	111.75(0.02)	378.80(0.13)	298.85(0.11)	119964(35)

[a] Values in parenthesis are estimated uncertainties.

TABLE 4. Ideal gas thermodynamic properties of methanol-d_4 (CD_3OD) at 1 bar[a]
$M = 36.0688$

T/K	C_p°/J K^{-1} mol^{-1}	$\{S^\circ(T)-S^\circ(0)\}$/J K^{-1} mol^{-1}	$-\{G^\circ(T)-H^\circ(0)\}/T$/J K^{-1} mol^{-1}	$\{H^\circ(T)-H^\circ(0)\}$/J mol^{-1}
0	0	0	0	0
100	38.66(0.13)	204.40(0.12)	169.14(0.04)	3531(8)
150	40.46(0.09)	220.52(0.16)	183.79(0.08)	5515(13)
200	42.63(0.06)	232.45(0.18)	194.50(0.10)	7586(17)
273.15	48.49(0.04)	246.51(0.20)	206.63(0.12)	10904(20)
298.15	51.00(0.04)	250.90(0.20)	210.15(0.13)	12146(21)
300	51.63(0.04)	251.19(0.20)	210.40(0.13)	12242(21)
400	61.59(0.03)	267.34(0.21)	222.66(0.15)	17882(24)
500	71.09(0.03)	282.15(0.21)	233.08(0.16)	24527(26)
600	79.24(0.03)	295.84(0.21)	242.41(0.17)	32058(28)
700	86.19(0.03)	308.60(0.21)	250.98(0.18)	40338(29)
800	92.01(0.03)	320.48(0.22)	258.93(0.18)	49254(31)
900	96.94(0.02)	331.61(0.22)	266.38(0.18)	58710(32)
1000	101.04(0.02)	342.09(0.22)	273.45(0.19)	68613(34)
1100	104.52(0.02)	351.86(0.22)	280.15(0.19)	78898(35)
1200	107.45(0.02)	361.06(0.22)	286.50(0.19)	89500(36)
1300	109.91(0.02)	369.77(0.22)	292.57(0.19)	100374(37)
1400	112.05(0.02)	378.01(0.22)	298.39(0.20)	111474(39)
1500	113.80(0.02)	385.79(0.22)	303.95(0.20)	122767(40)

[a] Values in parenthesis are estimated uncertainties.

Previous workers, using heat capacity,[55] *PVT*,[56] and spectroscopic methods,[468,469] concluded that the most probable major self-association species of methanol vapor were the dimer and the tetramer. However, Tucker *et al.*[470] and Cheam *et al.*[471] measured the association of methanol in *n*-hexadecane and of methanol vapor by *PVT* and vapor density methods and suggested that the predominant associated species are trimers and octamers.

Counsell and Lee[472] measured the vapor heat capacity of methanol in the temperature range 330 to 450 K and at pressures up to 1 bar. They interpreted the heat capacities on the assumption that dimers, tetramers, and one larger associated species (pentamer or hexamer) are present in the vapor. The results of this treatment have been combined with the enthalpies of vaporization and vapor pressure data to give further information on the deviation of the vapor from ideal-gas behavior.

2.1.b. Ethanol

The ethanol (ethyl alcohol, CH_3CH_2OH) molecule has two rotating tops: the methyl group ($-CH_3$) and the hydroxyl group ($-OH$). Modern spectroscopic studies have identified two conformers corresponding to the *trans* and *gauche* positions of the – OH rotor with respect to the C–C bond. Thermodynamic properties have been calculated for an equilibrium mixture of these two forms.

Lovas[473] obtained values for the moments of inertia, and the rotational constant and barrier for the rotation of the methyl group from microwave spectra of the *trans* conformer. These were adopted for the statistical calculation and are listed in Tables A-2 and A-3. Takano *et al.*[85] obtained similar values for the moments of inertia of this form. The first transition for the calculated energy states is 244 cm^{-1} which is close to the observed value of 253 cm^{-1} for the methyl torsion. Wavenumbers for the other vibrational modes were taken from Durig *et al.*,[86] Barnes and Hallam[47] and Green.[59]

The microwave spectra of the *gauche* conformer was investigated by Kakar and Seibt[90] and Kakar and Quade.[474] The overall moments of inertia and the barrier to rotation of the methyl group in the *gauche* form reported by Kakar and Quade were adopted for our calculation. The reduced moments for internal rotation of the methyl and hydroxyl groups were calculated from the molecular geometry. The bond lengths and angles were taken as the same as those of the *trans* form.[88] A dihedral angle of 70° for the hydroxyl rotation was assumed.

Kakar and Quade[474] also reported a three term potential energy function for the hydroxyl group rotation.The constants are listed in Table A-3. Energy levels for the hydroxyl rotation were calculated from this function and the rotational constants in the *trans* and *gauche* forms. The calculated torsional wavenumber ($0 \rightarrow 1$) for OH top in the *trans* isomer, 205.2 cm^{-1}, agrees with the observed values of 199 cm^{-1} [89] and 201 cm^{-1},[47] respectively. Durig *et al.*[86] gave the barrier height for the hydroxyl rotation in the *trans* conformer as 2.12 kJ mol^{-1}. The potential function of Kakar and Quade indicates it to be 4.97 kJ mol^{-1}. The ϵ_0 estimated by Kakar and Quade was included for the *gauche* energy levels.

Comparisons of the calculated C_p° and $\{S^\circ(T)-S^\circ(0)\}$ with the experimental values are presented in Tables A-6 and A-7, respectively. The differences are within the uncertainties of the experimental measurements.

Green[59] evaluated the thermodynamic properties of ethanol (g) in the temperature range from 273.16 to 1000 K; this evaluation was adopted by Stull *et al.*[466] His calculated results are slightly different from ours, because we employed a molecular model that assumed the ethanol vapor to be an equilibrium mixture of *trans* and *gauche* isomers while his calculations were based upon a molecular model which contains only one isomer. The calculated value for the entropy at 298.15 K, 280.64 J K^{-1} mol^{-1}, is in reasonable agreement with our selected third law value of 282.5 J K^{-1} mol^{-1}, given in table A-26.

2.1.c. 1-Propanol

The propanol (*n*-propyl alcohol) molecule contains three internal rotors. The CH_3–CH_2 rotation is symmetric. The CH_3CH_2–CH_2 and CH_2–OH rotations are asymmetric. Conformations about the latter two bonds may be designated by T, G, and G' for the *trans* and two *gauche* positions. These give rise to nine conformers. They may be designated by a pair of symbols, the first for the C–C conformation and the second for the C–O conformation. These include four pairs of mirror images, so that only five conformations are energetically distinct. They are TT, (TG,TG'), $(GT,G'T)$, $(GG,G'G')$ and $(GG',G'G)$. The mirror image pairs are enclosed in parentheses. Fukushima and Zwolinski[476] carried out a normal coordinate analysis on the five distinct forms and reported the bond force constants and fundamental frequencies.

TABLE 5. Ideal gas thermodynamic properties of ethanol (C_2H_5OH) at 1 bar[a]
$M = 46.0688$

$\frac{T}{K}$	$\frac{C_p^\circ}{J\,K^{-1}\,mol^{-1}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{J\,K^{-1}\,mol^{-1}}$	$\frac{-\{G^\circ(T)-H^\circ(0)\}/T}{J\,K^{-1}\,mol^{-1}}$	$\frac{\{H^\circ(T)-H^\circ(0)\}}{J\,mol^{-1}}$
0	0	0	0	0
100	41.70(0.31)	225.44(0.17)	187.03(0.05)	3841(12)
150	46.94(0.26)	243.37(0.29)	202.96(0.11)	6061(27)
200	52.02(0.20)	257.56(0.36)	214.89(0.16)	8533(38)
273.15	61.46(0.15)	275.10(0.40)	228.73(0.22)	12668(50)
298.15	65.20(0.14)	280.64(0.41)	232.85(0.24)	14250(53)
300	65.49(0.14)	281.04(0.41)	233.14(0.24)	14371(53)
400	81.22(0.14)	302.04(0.44)	247.77(0.29)	21706(64)
500	95.78(0.13)	321.76(0.46)	260.62(0.33)	30573(73)
600	108.24(0.12)	340.36(0.47)	272.37(0.34)	40792(81)
700	118.83(0.11)	357.86(0.48)	283.35(0.36)	52159(89)
800	127.92(0.10)	374.34(0.48)	293.70(0.37)	64508(97)
900	135.81(0.09)	389.87(0.49)	303.53(0.39)	77704(104)
1000	142.68(0.08)	404.54(0.49)	312.91(0.40)	91636(110)
1100	148.68(0.08)	418.43(0.49)	321.88(0.40)	106210(116)
1200	153.92(0.07)	431.60(0.50)	330.47(0.41)	121350(121)
1300	158.49(0.07)	444.10(0.50)	338.74(0.42)	136970(126)
1400	162.50(0.06)	456.00(0.50)	346.69(0.42)	153030(131)
1500	166.01(0.06)	467.33(0.50)	354.36(0.43)	169450(135)

[a] Values in parenthesis are estimated uncertainties.

Berthelot[103] and Golik *et al.*[104] reported that the form in which the central C–C bond was in the *trans* position was the one with lowest energy. Mathews and McKetta[60] calculated the ideal gas thermodynamic properties of this *trans* conformer, including restricted internal rotational contributions for the methyl and hydroxyl rotors. Based upon the infrared and Raman spectral data,[96–100] they assigned the fundamental vibrational wavenumbers. The barriers to rotation were estimated by analogies with related compounds.[101,102] The potential function for the central C–C rotation was assumed to be similar to that of propanethiol. The two parameters, V°, the height of the *trans–gauche* barrier, and ϵ_o, the energy of the *gauche* conformer relative to the *trans* were adjusted to fit experimental heat capacity data. This gave $V^\circ = 9.66$ kJ mol^{-1} and $\epsilon_o = 3.56$ kJ mol^{-1}. Berthelot had previously obtained $\epsilon_o = 3.43$ kJ mol^{-1}, from a study of the temperature dependence of the Raman spectra of the liquid.

The calculations presented here represent an equilibrium mixture of the *trans* and *gauche* conformations about the central C–C bond. The vibrational wavenumbers of the normal modes were those reported for forms I and II by Fukushima and Zwolinski. Abdurakhmanov *et al.*[480] calculated the relative energies of several conformers from the microwave spectra. They found that the energy differences were small but that the *GG* form was the lowest. The structure of this form was established by an energy minimization computation. It corresponds to the II′ form of Fukushima and Zwolinski. The relative energies of three other forms were given as 0.25 (*TG*), 0.31 (*GT*) and 1.46 (*TT*) kJ mol^{-1}.

In our calculations the energy states of the three rotors were based on three-fold symmetric potential functions. The V_3 for the methyl rotation was taken from Dreizler and Scappini[475] for the *trans* conformer and from Abdurakhamov *et al.*[480] for the *gauche*. The V_3 value used by Mathews and McKetta[60] for the hydroxyl rotation was used for both forms here. The V_3 for the central C–C bond was taken from Mathews and McKetta for the *trans* conformer. For the *gauche* conformer it was calculated to match the corresponding torsional frequency given by Fukushima and Zwolinski.

The moments of inertia of the two conformers were based on the spectroscopic observations of Abdurakhmanov *et al.*[479] The values for the *trans*-isomer are consistent with those of Abdurahmanov *et al.*[95] determined by microwave spectroscopy. The reduced moments for internal rotation and the corresponding rotational constants for the three internal rotors were calculated from structural parameters obtained by Aziz and Rogowski[94] by electron diffraction.

The energy of the *trans* conformer relative to the *gauche* was taken to be 0.837 kJ mol^{-1}. This was obtained by adjustment to give a good agreement between calculated and observed gas phase heat capacities and entropies. It is the same order of magnitude as values obtained by Abdurakhmanov *et al.* All these parameters are collected in Tables A-2 and A-3.

The internal rotational energy levels for the *trans* and *gauche* isomers were calculated using the V_3 values for the OH and C_2H_5 rotors in the *trans* isomer and the OH rotor in the *gauche* isomer reported by Mathews and McKetta.[60] The V_3 values for the CH_3 group in the *trans* and *gauche* isomers have been reported by Dreizler and Scappini[475] and Abdurakhmanov *et al.*,[480] respectively. We selected the value of $V_3(C_2H_5)$ for the *gauche* isomer so that the calculated torsional frequency ($0 \rightarrow 1$) was consistent with the reported value [476]

Stull *et al.*[466] adopted the thermodynamic properties of Mathews and McKetta.[60] These values are slightly different from ours, as their calculations were based upon a molecular model which assumes that the 1-propanol molecules contain only *trans* isomers which were assumed to be more stable than the *gauche*.

A comparison between the calculated and experimental C_p° and $\{S^\circ(T) - S^\circ(0)\}$ values is presented in Table A-8. The average deviations are 0.09% and 0.96%, respectively, which are within the estimated experimental uncertainties.

Vapor heat capacities of 1-propanol have been measured by Sinke and DeVries,[53] and Bennewitz and Rossner.[106] Jatkar and Lakshimarayan[107] derived C_p° from velocity of sound measurements. Their results agree with those adopted here. The calculated value for the entropy at 298.15 k, 322.58 J K^{-1} mol^{-1}, is in good agreement with our selected third law entopy value of 322.62 J K^{-1} mol^{-1} given in Table A-26.

2.1.d. 2-Propanol

The existence of *trans* and *gauche* for the -OH rotation isomers on the 2-propanol (isopropyl alcohol, $(CH_3)_2CHOH$) vapor was reported by Tanaka[112] from infrared study and by Kondo and Hirota[113] from an anaylsis of the rotational spectrum, respectively. Hirota[477] investigated the internal rotation by microwave spectroscopy and found that the energy difference between *trans* and the more stable *gauche* isomers to be (1.88 ± 0.88) kJ mol^{-1}. Hirota[477] and Konda and Hirota[113] have also determined the rotational constants for these two isomers.

Imanov *et al.*[478] recorded about 1000 lines on a gas radiospectrometer with electrical molecular modulation and a number of molecular parameters were determined. Comparison of calculated results for the three possible isomeric forms of the molecule with the experimental results indicates that the molecule exists in the *trans* form. Abdurakhmanov *et al.*[479] calculated the coordinates of the atoms from the experimental structural parameters of the *trans* and *gauche* isomers. The structure obtained was compared with the parameters of other related molecules.

The ideal gas thermodynamic properties of 2-propanol were calculated using the statistical mechanical method by Schmann and Aston,[108] Kobe *et al.*,[109] and Zhuravlev and Rabinovich.[110] Green[111] assigned the fundamental frequencies and used the molecular structure data to calculate the thermodynamic functions of the compound.

TABLE 6. Ideal gas thermodynamic properties of 1-propanol (C_3H_7OH) at 1 bar[a]
$M = 60.0956$

T/K	C_p°/J K^{-1} mol^{-1}	$\{S^\circ(T)-S^\circ(0)\}$/J K^{-1} mol^{-1}	$-\{G^\circ(T)-H^\circ(0)\}/T$/J K^{-1} mol^{-1}	$\{H^\circ(T)-H^\circ(0)\}$/J mol^{-1}
0	0	0	0	0
100	51.53(0.33)	252.41(0.35)	210.84(0.14)	4156(22)
150	58.92(0.23)	274.75(0.46)	228.59(0.23)	6924(35)
200	66.37(0.17)	292.69(0.51)	242.43(0.29)	10051(44)
273.15	80.19(0.14)	315.33(0.54)	258.99(0.36)	15391(53)
298.15	85.56(0.14)	322.58(0.55)	264.02(0.37)	17462(55)
300	85.96(0.14)	323.11(0.55)	264.38(0.37)	17621(56)
400	108.03(0.15)	350.88(0.57)	282.57(0.42)	27324(65)
500	128.19(0.15)	377.20(0.58)	298.88(0.45)	39158(75)
600	145.41(0.15)	402.14(0.59)	314.03(0.47)	52862(85)
700	160.05(0.15)	425.68(0.60)	328.32(0.49)	68154(95)
800	172.62(0.15)	447.89(0.61)	341.89(0.50)	84802(106)
900	183.51(0.15)	468.87(0.61)	354.84(0.51)	102620(116)
1000	192.97(0.15)	488.70(0.62)	367.25(0.52)	121460(127)
1100	201.22(0.15)	507.49(0.62)	379.15(0.53)	141180(138)
1200	208.40(0.15)	525.32(0.62)	390.59(0.54)	161670(149)
1300	214.67(0.15)	542.25(0.63)	401.61(0.54)	182830(160)
1400	220.14(0.14)	558.36(0.63)	412.24(0.55)	204570(171)
1500	224.93(0.13)	573.72(0.63)	422.50(0.56)	226830(182)

[a] Values in parenthesis are estimated uncertainties.

TABLE 7. Ideal gas thermodynamic properties of 2-propanol $\{(CH_3)_2CHOH\}$ at 1 bar[a]
$M = 60.0956$

T/K	C_p°/J K^{-1} mol^{-1}	$\{S^\circ(T)-S^\circ(0)\}$/J K^{-1} mol^{-1}	$-\{G^\circ(T)-H^\circ(0)\}/T$/J K^{-1} mol^{-1}	$\{H^\circ(T)-H^\circ(0)\}$/J mol^{-1}
0	0	0	0	0
100	46.04(0.24)	238.99(0.14)	201.15(0.06)	3784(9)
150	57.98(0.23)	259.49(0.23)	217.37(0.10)	6394(21)
200	68.28(0.18)	278.10(0.28)	230.33(0.13)	9553(31)
273.15	83.72(0.15)	301.62(0.33)	246.33(0.18)	15104(42)
298.15	89.32(0.15)	309.20(0.34)	251.29(0.19)	17266(45)
300	89.74(0.15)	309.75(0.34)	251.64(0.19)	17432(45)
400	112.15(0.16)	338.66(0.37)	269.82(0.23)	27536(57)
500	131.96(0.17)	365.88(0.39)	286.34(0.26)	39771(69)
600	148.30(0.16)	391.44(0.40)	301.75(0.28)	53811(81)
700	161.75(0.16)	415.34(0.41)	316.29(0.30)	69334(93)
800	173.04(0.15)	437.70(0.42)	330.08(0.31)	86090(105)
900	182.67(0.15)	458.65(0.43)	343.22(0.32)	103887(117)
1000	190.97(0.15)	478.33(0.44)	355.75(0.33)	122580(128)
1100	198.16(0.14)	496.88(0.44)	367.75(0.34)	142045(139)
1200	204.41(0.14)	514.40(0.45)	379.25(0.35)	162181(150)
1300	209.85(0.13)	530.98(0.45)	390.29(0.36)	182900(160)
1400	214.60(0.13)	546.71(0.46)	400.90(0.36)	204130(171)
1500	218.75(0.12)	561.66(0.46)	411.13(0.37)	225800(180)

[a] Values in parenthesis are estimated uncertainties.

The best overall agreement with the experimental values of entopy and heat capacity was obtained with the selected barrier heights, V_3, of 16.7 kJ mol^{-1} and 3.3 kJ mol^{-1} for the CH_3 and OH groups, respectively.

Green[111] employed estimated molecular parameters for computing the values of $I_aI_bI_c$ and F for the methyl and hydroxyl groups. Their estimated values are consistent with those determined by electron diffraction by Aziz and Rogowski[94]

Inagaki *et al.*[114] examined the far-infrared spectra of 2-propanol and its deuterated species. From the observed torsional transitions they obtained the potential function for the OH rotor as $V = 1/2\Sigma\ V_n(1 - \cos n\theta)$, where $V_1 = 30.4$ cm^{-1}, $V_2 = -86.2$ cm^{-1}, and $V_3 = 401.3$ cm^{-1}. The derived torsional wavenumbers of 210 and 234 cm^{-1} for *trans* ($0 \rightarrow 1$) and *gauche* ($0 \rightarrow 1$), respectively, are in good agreement with the observed values of 209 and 234 cm^{-1}.

For calculating the thermodynamic properties, we adopted the I_a, I_b and I_c values determined by Kondo and Hirota[113] to obtain $I_aI_bI_c$. The vibrational frequencies and V_3 and F for the CH_3 rotor were those assigned by

Green.[111] The F value and potential function for the OH rotor were taken from Inagaki *et al.*[114] The molecular constants used are listed in Tables A-2 and A-3, and the results are presented in Table 7. The calculated C_p° and $\{S^\circ(T)-S^\circ(0)\}$ of 2-propanol (g) are compared with the experimental values in Table A-9. The agreement between the calculated values for the third law entropy, 309.20 J K^{-1} mol^{-1} and the selected experimental value of 310.86 J K^{-1} mol^{-1} at 298.15 K given in Table A-26 is excellent.

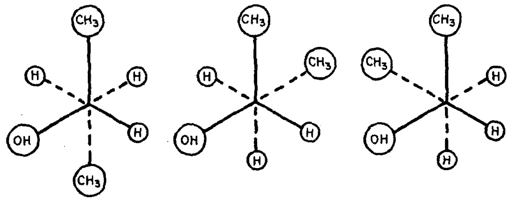
2.1.e. 1-Butanol

Dyatkina,[118] using statistical mechanics, calculated the thermodynamic properties of 1-butanol. Chermin,[63] adopting the same molecular constants as Dyatkina, but using estimated values for the potential barriers for CH_3, C_2H_5, C_3H_7, and OH rotors, calculated C_p°, $\{H^\circ(T)-H^\circ(0)\}/T$, $\{G^\circ(T)-H^\circ(0)\}/T$, $\{S^\circ(T)-S^\circ(0)\}$, $\Delta_f H^\circ$ and $\Delta_f G^\circ$ in the temperature range from 298.15 to 1000 K and at 1 atm for 1-butanol (g). Green[64] obtained values for the above properties by adding the methylene increment contributions[48] to the values for 1-propanol. These latter values were adopted by Stull *et al.*[466] As no new experimental molecular data on this compound were available, we adopted the molecular constants reported by Chermin[63] to recalculate the thermodynamic properties. The results are presented in Table 8. The calculated C_p° at temperatures from 398.15 to 453.15 K and $\{S^\circ(298.15\ K)-S^\circ(0)\}$ are in agreement with the experimental vapor heat capacities measured by Counsell *et al.*[120] and the reported third-law value $\{S^\circ(298.15\ K)-S^\circ(0)\}$, respectively, as shown in Table A-10. Our recalculated value at 298.15 K, 361.59 J K^{-1} mol^{-1}, agrees well with the selected experimental third law entropy value of 361.98 J K^{-1} mol^{-1} given in Table A-26. The molecular constants used in the calculations are given in Tables A-2 and A-3.

2.1.f DL-2-Butanol

The 2-butanol (*sec*-butyl alcohol, $CH_3CH_2C^*HOHCH_3$) molecule has an asymmetric carbon atom (marked with the asterisk). It exists in both the D- and L- form. Hindered internal rotation about the central C–C* bond produces three isomers, shown below, which are more stable than the "eclipsed" forms. These stable configurations correspond to the three minima of the potential energy curve as a function of the angle of internal rotation.

Bernstein and Pedersen[121] measured the specific optical rotation of 2-butanol in dilute solutions of cyclohexane at temperatures from 20 to 70 °C and found the concentrations of rotational isomers I, II, and III to be 42.35%, 42.35%, and 15.3%, respectively, at 20 °C and 43.0%, 43.0% and 14.0% at 70 °C, respectively. Assuming the configurations I and II have about the same energy, they derived the enthalpy of isomerization $\Delta H = (3.36 \pm 0.25)$ kJ mol^{-1} for the reactions: 2-butanol (I) = 2-butanol (III) and 2-butanol (II) = 2-butanol (III).



I II III

Fig. 4. The rotational conformations of 2-butanol.

Berman and McKetta[61] measured the vapor heat capacity, enthalpy of vaporization, and vapor pressure of 2-butanol. A model of an equilibrium mixture containing monomers, dimers, and tetramers was used to obtain constants for an equation of state which fitted the C_p data and the gas imperfections calculated from the Clapeyron equation.

Based upon the assumed molecular parameters, the fundamental vibrational frequencies assigned from infrared[96,100] and Raman[97,98] data, and the derived C_p°, Berman and McKetta[61] selected the internal rotational barrier heights for the CH_3, OH, and C_2H_5 rotors in the D-2-butanol molecule. Using these results, they evaluated the ideal gas thermodynamic properties for D-2-butanol by standard statistical mechanical methods. Their results were adopted by Stull *et al.*[466]

We recalculated the ideal gas properties of 2-butanol using the molecular parameters of Berman and McKetta[61] and a similar procedure. We used the model of two *gauche* conformers in equilibrium with one *trans* conformer, with the energy difference given by Bernstein and Pedersen. The other parameters were taken to be the same for both species. This calculation applies to a single enantiomer. The properties of the DL mixture were obtained by adding Rln 2 to the entropy and subtracting it from the Gibbs energy function. The results are given in Table 9. Table A-26 shows that the calculated entropy at 298.15 K is 4.1 J K^{-1} mol^{-1} higher than the third-law value. This is greater than the expected experimental uncertainty and undoubtedly reflects the approximations made in the calculated value.

2.1.g. 2-methyl-2-propanol

Beynon and McKetta[62] measured the vapor heat capacity of 2-methyl-2-propanol (*tert*-butyl alcohol, $(CH_3)_3OH$), over the temperature range 363.15 to 437.15 K and a pressure range from 0.3 to 1.3 bar. The enthalpy of vaporization from 330.15 to 355.65 K and the vapor pressure from 330.55 to 363.15 K were also determined. Using a molecular model of an equilibrium mixture of monomers, dimers, and tetramers, they correlated the vapor heat capacity data, and this correlation was used to extrapolate the C_p data to zero pressure. These

TABLE 8. Ideal gas thermodynamic properties of 1-butanol (C_4H_9OH) at 1 bar[a]
$M = 74.1224$

$\frac{T}{\text{K}}$	$\frac{C_p^\circ}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{-\{G^\circ(T)-H^\circ(0)\}/T}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{\{H^\circ(T)-H^\circ(0)\}}{\text{J mol}^{-1}}$
0	0	0	0	0
100	58.33(0.47)	276.82(0.46)	232.81(0.20)	4392(28)
150	70.10(0.35)	302.68(0.61)	251.93(0.31)	7613(47)
200	81.28(0.26)	324.36(0.69)	267.39(0.39)	11393(61)
273.15	100.68(0.24)	352.46(0.74)	286.47(0.48)	18025(76)
298.15	108.03(0.25)	361.59(0.75)	292.39(0.50)	20633(80)
300	108.58(0.25)	362.26(0.75)	292.82(0.50)	20834(80)
400	138.16(0.31)	397.59(0.79)	314.63(0.57)	33184(98)
500	164.42(0.33)	431.32(0.82)	334.62(0.61)	48350(120)
600	186.38(0.31)	463.30(0.84)	353.43(0.65)	65923(144)
700	204.83(0.29)	493.25(0.86)	371.30(0.67)	85509(168)
800	220.56(0.28)	521.86(0.87)	388.36(0.69)	106800(191)
900	234.15(0.26)	548.64(0.89)	404.70(0.71)	129550(213)
1000	245.93(0.25)	573.94(0.90)	420.37(0.73)	153570(234)
1100	256.18(0.24)	597.87(0.91)	435.43(0.74)	178690(253)
1200	265.10(0.22)	620.55(0.92)	449.92(0.76)	204760(272)
1300	272.86(0.21)	642.08(0.92)	463.88(0.77)	231670(289)
1400	279.63(0.20)	662.56(0.93)	477.34(0.78)	259300(306)
1500	285.54(0.19)	682.06(0.93)	490.35(0.79)	287560(321)

[a] Values in parenthesis are estimated uncertainties.

TABLE 9. Ideal gas thermodynamic properties of DL-2-butanol (C_4H_9OH) at 1 bar[a]
$M = 74.1224$

$\frac{T}{\text{K}}$	$\frac{C_p^\circ}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{-\{G^\circ(T)-H^\circ(0)\}/T}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{\{H^\circ(T)-H^\circ(0)\}}{\text{J mol}^{-1}}$
0	0	5.76	5.76	0
100	59.06(0.28)	270.07(0.39)	226.35(0.19)	4372(21)
150	74.17(0.23)	296.99(0.47)	245.54(0.27)	7718(32)
200	86.94(0.19)	320.10(0.51)	261.35(0.32)	11750(40)
273.15	105.90(0.17)	349.97(0.54)	281.16(0.37)	18795(51)
298.15	112.74(0.17)	359.53(0.55)	287.33(0.39)	21526(54)
300	113.25(0.17)	360.23(0.55)	287.78(0.39)	21735(54)
400	140.74(0.20)	396.60(0.57)	310.49(0.43)	34443(66)
500	165.63(0.22)	430.75(0.59)	331.16(0.46)	49792(81)
600	186.83(0.22)	462.87(0.60)	350.47(0.48)	67445(97)
700	204.82(0.21)	493.06(0.62)	368.70(0.50)	87052(113)
800	220.27(0.20)	521.45(0.63)	386.04(0.51)	108330(130)
900	233.65(0.19)	548.18(0.63)	402.58(0.52)	131040(145)
1000	245.30(0.18)	573.42(0.64)	418.42(0.53)	155000(160)
1100	255.45(0.17)	597.28(0.65)	433.60(0.54)	180050(174)
1200	264.30(0.16)	619.90(0.65)	448.19(0.55)	206040(188)
1300	272.03(0.15)	641.37(0.66)	462.23(0.56)	232870(201)
1400	278.77(0.15)	661.78(0.66)	475.76(0.56)	260420(213)
1500	284.66(0.14)	681.22(0.67)	488.82(0.57)	288600(224)

[a] Values in parenthesis are estimated uncertainties.

derived ideal gas heat capacities, C_p°, were used, in conjunction with molecular structure and spectroscopic information from the literature, to calculate the barriers to internal rotation.

The vibrational frequencies of this compound have been assigned by Pritchard and Nelson[122] and Tanaka.[123] Tanaka's assignment was chosen by Beynon and McKetta[62] for the thermodynamic calculations because it was based upon a normal coordinate analysis which yielded better agreement with the frequencies for which assignments are well established. The numerical values are given in Table A-2.

Beynon and McKetta[62] calculated the values of $I_aI_bI_c$ and I_r for the CH_3 and OH tops using an assumed molecular structure. Simple cosine potential barriers of the type $V = 1/2\ V_3(1 - \cos 3\theta)$ were employed for the methyl and hydroxyl internal rotations, with the three methyl tops being considered as equivalent and independent. The barrier heights were selected so that the calculated C_p° and $\{S^\circ(T)-S^\circ(0)\}$ were consistent with the experimental data. These internal rotational constants are presented in Table A-3.

From the above data, Beynon and McKetta computed the ideal gas thermodynamic properties in the temperature range from 0 to 1000 K and at 1 atm. Their results were adopted by Stull *et al.*[466] Because of the lack of new values for the molecular constants, we employed the vibrational assignments, reduced moments for the CH_3 and OH rotors and the individual internal rotation barrier heights reported by Beynon and McKetta[62] for recalculating the ideal gas thermodynamic properties. The value of $I_aI_bI_c$ was determined by Valenzuela[481] from microwave spectroscopy. The results are listed in Table 10. The calculated C_p° and $\{S^\circ(T)-S^\circ(0)\}$ values agree with the experimental values as shown in Table A-12. The calculated ideal gas entropy value at 298.15K, 326.70 J K^{-1} mol^{-1}, agrees well with our selected third law entropy value of 327.00 J K^{-1} mol^{-1} given in Table A-26.

2.2. Alkandiols

Data sufficient for the calculation of ideal gas thermodynamic properties were found only for 1,2-ethanediol (ethylene glycol). They are summarized below.

Numerous studies of spectra and molecular stucture of 1,2-ethanediol have been published over the past fifty years. It is highly associated in condensed phases. It has long been recognized that an intramolecular hydrogen bond between the two hydroxyl groups is present in isolated molecules. The interpretation of molecular spectra of this compound has been a challenge during this period.

Internal rotation takes place about the two C–O bonds and the C–C bond. Although the intramolecular hydrogen bond is comparatively weak, it does exert a strong influence on the potential energy governing internal rotation. In fact the three modes are strongly interacting. The molecular spectra of solid and liquid phases are dominated by associated species. The spectra of the gas phase at room temperature and above is complicated by rotational-vibrational interactions and by the numerous energy states associated with internal rotations. In recent years the availability of spectra of isolated molecules trapped in inert gas matrices have made possible improved assignments of the fundamental modes.

As a reasonable approximation, 1,2-ethanediol may be treated as mixture of conformers. Consider labelling the three staggered rotational conformations corresponding to potential energy minima about a bond by T (*trans*, $\theta=180°$), G (*gauche*, $\theta=60°$), and G' (*gauche*, $\theta=300°$). Any conformation of 1,2-ethanediol may be identified by a combination of three symbols, such as TGG'. The first symbol applies to one hydroxyl group, the second to the C–C rotation, and the third to the other hydroxyl group. There are 27 combinations, but only 12 are energetically different. An intramolecular hydrogen bond can exist only when the C–C rotation is in a *gauche* position.

From his electron diffraction study Bastiansen[414] concluded that the configuration about the C–C bond was entirely *gauche*. He could not determine the positions of the hydrogen atoms in the hydroxyl groups. In 1950 Allen and Sutton[324] published a compilation of molecular structure of 1,2-ethanediol based on electron diffraction studies, including some unpublished work of Bastiansen and Donahue.

Several partial assignments of vibrational modes, such as those by Kuroda and Kugo[415] and White and Lovell,[416] were made before 1960. They were largely based on spectra of condensed phases. They also assumed that both the *trans* and *gauche* configurations of

TABLE 10. Ideal gas thermodynamic properties of 2–methyl–2-propanol (C_4H_9OH) at 1 bar[a]
M = 74.1224

T/K	C_p°/J K^{-1} mol^{-1}	$\{S^\circ(T)-S^\circ(0)\}$/J K^{-1} mol^{-1}	$-\{G^\circ(T)-H^\circ(0)\}/T$/J K^{-1} mol^{-1}	$\{H^\circ(T)-H^\circ(0)\}$/J mol^{-1}
0	0	0	0	0
100	52.73(0.35)	240.24(0.21)	201.11(0.11)	3912(14)
150	70.40(0.31)	265.07(0.33)	218.37(0.15)	7004(30)
200	85.29(0.25)	287.40(0.41)	232.88(0.20)	10904(44)
273.15	106.29(0.21)	317.07(0.47)	251.52(0.26)	17907(58)
298.15	113.63(0.21)	326.70(0.48)	257.42(0.28)	20656(62)
300	114.18(0.21)	327.40(0.48)	257.85(0.28)	20867(63)
400	142.99(0.23)	364.24(0.52)	279.89(0.34)	33742(79)
500	168.39(0.25)	398.96(0.54)	300.27(0.37)	49346(96)
600	189.64(0.24)	431.60(0.57)	319.46(0.40)	67280(114)
700	207.48(0.22)	462.21(0.58)	337.69(0.42)	87162(132)
800	222.71(0.21)	490.93(0.60)	355.07(0.44)	108690(149)
900	235.85(0.20)	517.94(0.61)	371.68(0.46)	131630(165)
1000	247.26(0.19)	543.40(0.62)	387.59(0.47)	155800(181)
1100	257.10(0.18)	567.44(0.62)	402.86(0.49)	181040(195)
1200	265.84(0.17)	590.20(0.63)	417.53(0.50)	207200(209)
1300	273.37(0.16)	611.78(0.64)	431.65(0.51)	234170(222)
1400	279.92(0.15)	632.29(0.64)	445.26(0.52)	261840(234)
1500	285.62(0.14)	651.80(0.65)	458.38(0.52)	290120(246)

[a] Values in parenthesis are estimated uncertainties.

the C–C rotation were present. Raman spectra were reported by several investigators during this period.[417–419]

In 1967 Buckley and Giguere[420] published a detailed IR study of 1,2-ethanediol and several deuterated derivatives in the solid, liquid, and gas phases. They concluded that the configuration of the C–C rotation is entirely *gauche*. They also gave a nearly complete assignment, including the torsional modes. They made a rough estimate of the barriers to internal rotation but recognized the strong interactions among these modes. They compared the statistical entropy of the RRHO model with the third-law value. The calculated value was about 10 J K^{-1} mol^{-1} lower than the experimental one. A value calculated by assuming free rotation was high by about 44.8 J K^{-1} mol^{-1}. They concluded that the internal rotations were governed by a complicated three dimensional function.

Newer IR studies of 1,2-ethanediol in inert gas matrices have been published.[421–423] Gunthard and co-workers[421,422] also concluded that the C–C rotation was in the *gauche* position and assigned the fundamental vibrations accordingly. They calculated an entropy of 293.76 J K^{-1} mol^{-1} at 298.15 K for the RRHO model. This is 18.1 J K^{-1} mol^{-1} below the third law value.

Takeuchi and Tasumi[423] identified the *TGG'* and *GGG'* forms of 1,2-ethanediol when freshly deposited in an Ar matrix. After suitable infrared irradiation they found evidence for other forms. They carried out normal coordinate analysis for the *TGG'*, *GGG'*, *TTT* and *TTG* forms of $HOCH_2CH_2OH$, $DOCH_2CH_2OD$ and $DOCD_2CD_2OD$. They gave partial assignments of frequencies and listed the bond force constants.

Several microwave studies have been published. Marstokk and Mollendal[424] could not account for their observations by assuming a rigid rotor model. They concluded that the two mirror image forms, *TGG* and *GGT*, were present and that tunneling occurred between them. They also concluded that extensive coupling between vibration and rotation was present. Walder, Bauder and Gunthard[508] interpreted the microwave spectra of $DOCH_2CH_2OD$ in terms of a semi-rigid model. The large amplitudes of motion caused a splitting of all rotational transitions. These would be even greater for $HOCH_2CH_2OH$. They could not identify particular conformers and did not assume tunneling between forms. They found that the two hydroxyl groups rotate in a concerted manner which could be approximated by a one dimensional potential function.

Caminati and Corbelli[509] identified only the *TGG* species from microwave spectra of 1,2-ethanediol and several of its derivatives with deteurium in the hydroxyl groups. They did assume an intramolecular hydrogen bond. They did not find evidence of tunneling but could not rule it out for the mono-deuterated species.

The relative energies of various conformers have been calculated by *ab initio* SCF methods.[421,422,425,426] The most complete and probably most accurate are those of Van Alsenoy and Van Den Enden.[426] They optimized the geometries of ten conformers without constraints.

At present it appears impractical to calculate directly the energy states for the internal rotation modes. We therefore assume a RRHO model for an equilibrium mixture of the first four low energy conformers, *TGG'*, *GGG'*, *TTT*, and *TTG'*. The energies and geometries calculated by Van Alsenoy and Van Den Enden were adopted. The frequencies for the skeletal vibrations assigned by Takeuchi and Tasumi[423] and for the O–H and C–H stretching modes by Buckley and Giguere[420] were used. The symmetrical C–H stretch was taken to be the same as the asymmetric C–H stretch. The parameters used in this calculation are included in Tables A-2 and A-3.

We expect that the harmonic oscillator energy levels are separated more than those for the real internal rotation modes. The incorporation of the four conformers roughly approximates the interactions among these modes. At 298.15 K only the *TGG'* form makes an appreciable contribution to the thermodynamic functions.

The contribution of the three internal rotors was also approximated by two free rotors, one for a hydroxyl group and one for the C–C bond, and one restricted hydroxyl rotor. The restricted rotor was assumed to have a three-fold symmetrical barrier of 8.12 kJ mol^{-1} and a rotational constant of 22.39 cm^{-1}. The frequencies of the other vibrational modes were taken for a *TGG* conformer, and the overall symmetry number was 2. This gives the heat capacity and entropy of 71.7 and 314.5 J K^{-1} mol^{-1} respectively at 298.15 K and 142.2 and 418.4 J K^{-1} mol^{-1} at 800 K. The free rotor functions give a constant contribution to the heat capacity which is too large at low temperatures and too small at higher temperatures. The entropies for the two calculations cross at 700 K.

Table A-26 shows that the calculated entropy at 298.15 K is 8.04 J K^{-1} mol^{-1} below the accepted third law value. However, since the third law value is based on heat capacity data only down to 90 K, and the vaporization data involve an appreciable uncertainty, the overall uncertainty is around 4 J K^{-1} mol^{-1}. For a single species it would probably be even larger at higher temperatures. This is compensated to some extent by the contributions of the other three species assumed for this model. Because of the various uncertainties we terminated the table of thermodynamic values at 1000 K.

2.3. Ethers

The ideal gas thermodynamic properties of dimethyl (CH_3OCH_3), ethyl methyl ($C_2H_5OCH_3$), and diethyl ($C_2H_5OC_2H_5$) ethers have been evaluated by Chao and Hall[157] using statistical mechanical methods. For calculating the internal rotational contributions, each CH_3 rotor was treated as an independent rotor. In other words, no allowance was made for interactions between the two CH_3 rotors in each of these molecules.

2.3.a. Dimethyl Ether

Numerous researchers have investigated the molecular structure and the torsional frequencies of dimethyl

TABLE 11. Ideal gas thermodynamic properties of 1,2-ethanediol (CH_2OHCH_2OH) at 1 bar[a]
$M = 68.0682$

T K	C_p° J K^{-1} mol^{-1}	$\{S^\circ(T)-S^\circ(0)\}$ J K^{-1} mol^{-1}	$-\{G^\circ(T)-H^\circ(0)\}/T$ J K^{-1} mol^{-1}	$\{H^\circ(T)-H^\circ(0)\}$ J mol^{-1}
0	0	0	0	0
100	46.1(0.18)	236.5(0.18)	199.2(0.10)	3729(15)
150	56.3(0.16)	257.2(0.22)	215.2(0.12)	6300(23)
200	65.0(0.14)	274.6(0.25)	227.9(0.15)	9335(32)
273.15	77.9(0.13)	296.7(0.26)	243.5(0.16)	14554(35)
298.15	82.7(0.13)	303.8(0.26)	248.2(0.16)	16560(35)
300	83.0(0.14)	304.3(0.29)	248.6(0.18)	16713(46)
400	102.2(0.15)	330.8(0.30)	265.9(0.20)	25978(57)
500	119.4(0.15)	355.5(0.32)	281.3(0.22)	37081(68)
600	133.9(0.14)	378.6(0.33)	295.6(0.23)	49768(79)
700	145.8(0.13)	400.2(0.34)	309.1(0.25)	63770(90)
800	155.9(0.12)	420.3(0.34)	321.7(0.26)	78870(100)
900	164.5(0.11)	439.2(0.35)	333.7(0.26)	94900(110)
1000	171.9(0.10)	456.9(0.36)	345.2(0.27)	111730(118)

[a] Values in parenthesis are estimated uncertainties.

ether. It has two equivalent rotors of three-fold symmetry attached to a central atom. Pauling and Brockway[163] and Kimura and Kubo[164] determined the molecular structure of this compound by electron diffraction. From the microwave spectra, Kasai and Myers,[165] Blukis *et al.*,[166] Durig *et al.*,[45] and Lovas *et al.*[485] determined the rotational constants and molecular structure of CH_3OCH_3 (g). The rotational constants of Lovas *et al.*[485] were selected for the calculation of $I_aI_bI_c$ and F.

The infrared and Raman spectra of dimethyl ether have been reported by many researchers.[167-173] Fundamental vibrational wavenumbers were assigned for this compound by Snyder and Zerbi,[172] Shimanouchi,[80] Blom *et al.*,[173] and Herzberg.[174] Blom and coworkers[173] recently re-examined the infrared and Raman spectra of CH_3OCH_3 (g). A complete, general valence force field calculation on this compound has been made from *ab initio* (4–31 G) energies. The observed and calculated wavenumbers for dimethyl ether and six deuterated analogs were compared. Their assignments of the fundamental vibrational wavenumbers for CH_3OCH_3 (g), given in Table A-2, were employed for evaluating the vibrational contributions.

The CH_3OCH_3 molecule has C_{2v} symmetry with two torsional modes, namely the b_2 and a_2 species. The wavenumber values of b_2 were reported to be from 239.1 to 270 cm^{-1}.[175] Based upon $b_2 = 241$ cm^{-1},[41,43,170] normal coordinate calculations[176,177] predicted $a_2 = 199$ to 202 cm^{-1}.[43,173] Using a two-dimensional Fourier series in torsional angles, Lutz and Dreizler[486] determined the coefficients V_3 and V'_{12} of the internal rotational potential function for CH_3OCH_3 molecule in excited torsional states.

For generating the internal rotational energy levels for the statistical calculations, we used the average of the two torsional wavenumbers, $\tilde{\nu}_{\text{tor}} = 214.5$ cm^{-1}, as the torsional frequency of each of the two independent CH_3 rotors. This torsional frequency was derived from a potential barrier height V_3 of 10.807 kJ mol^{-1} and $F =$ 6.524 cm^{-1} as reported by Lovas *et al.*[485] The V_3 of the CH_3 top in the CH_3OCH_3 molecule has been previously reported as (11.38 ± 0.58) kJ mol^{-1},[165] (11.32 ± 0.18) kJ mol^{-1},[43] and (11.81 ± 0.50) kJ mol^{-1}.[178]

Based upon the molecular and spectroscopic constants shown in Tables A-2 and A-3, the thermodynamic properties of CH_3OCH_3 (g) were evaluated. The results are presented in Table 12. A comparison of the observed and calculated C_p° and $\{S^\circ(T)-S^\circ(0)\}$ for this compound is given in Table A-13.

Stull *et al.*[466] calculated the thermodynamic properties of this compound in the temperature range 298.15 to 1000 K, employing the vibrational assignments of Kanazawa and Nukada,[487] the moments of inertia of Kasai and Myers,[165] and a barrier to internal rotation of 11.38 kJ mol^{-1}. Their C_p° values are 0.4% and 3.4% higher than ours at 298.15 K and 1000 K, respectively. Their entropy at 298.5 K, 267.06 J K^{-1} mol^{-1}, compares well with our value of 267.34 J K^{-1} mol^{-1}. The thermodynamic properties of dimethyl ether have been reported by many other researchers.[488-492]

2.3.b. Dimethyl Ether-d_3

The rotational constants for dimethyl ether-d_3 (CH_3OCD_3) have been reported by Blukis *et al.*[16] and Durig *et al.*[45] from an analysis of the microwave spectra. The rotational constants determined by Blukis *et al.*[166] were selected for the calculation of the three principal moments of inertia: $I_a = 2.71477 \times 10^{-39}$ g cm^2, $I_b = 9.71814 \times 10^{-39}$ g cm^2, and $I_c = 1.08317 \times 10^{-38}$ g cm^2.

Shimanouchi[80] assigned a complete set of fundamental vibrational frequencies for CH_3OCD_3 (g) where the torsional wavenumbers for CH_3 and CD_3 rotors were given as 227 and 164 cm^{-1}, respectively. Blom *et al.*[173] reported the vibrational assignments for this compound which were slightly different from the values of Shimanouchi. Their two torsional wavenumbers were calculated from the data of Labarbe *et al.*[176] and Labarbe and Forel[177] to be 224 and 163 cm^{-1}. These values were consistent with

TABLE 12. Ideal gas thermodynamic properties of dimethyl ether (CH_3OCH_3) at 1 bar[a]
$M = 46.0688$

T K	C_p° J K^{-1} mol^{-1}	$\{S^\circ(T)-S^\circ(0)\}$ J K^{-1} mol^{-1}	$-\{G^\circ(T)-H^\circ(0)\}/T$ J K^{-1} mol^{-1}	$\{H^\circ(T)-H^\circ(0)\}$ J mol^{-1}
0	0	0	0	0
100	42.27(0.20)	210.25(0.14)	174.36(0.04)	3589(10)
150	48.99(0.16)	228.72(0.21)	189.53(0.09)	5879(19)
200	54.47(0.11)	243.58(0.25)	201.24(0.12)	8467(25)
273.15	62.56(0.09)	261.73(0.27)	215.08(0.16)	12742(31)
298.15	65.57(0.08)	267.34(0.28)	219.23(0.17)	14344(33)
300	65.80(0.08)	267.74(0.28)	219.53(0.17)	14465(33)
400	78.68(0.10)	288.42(0.29)	234.21(0.20)	21683(39)
500	91.36(0.10)	307.36(0.30)	246.97(0.22)	30193(46)
600	102.86(0.10)	325.05(0.31)	258.52(0.23)	39915(53)
700	113.03(0.10)	341.68(0.32)	269.23(0.24)	50720(60)
800	121.99(0.09)	357.38(0.32)	279.27(0.25)	62480(67)
900	129.84(0.09)	372.21(0.33)	288.78(0.26)	75080(74)
1000	136.70(0.09)	386.25(0.33)	297.84(0.27)	88415(81)
1100	142.69(0.08)	399.57(0.33)	306.48(0.27)	102390(88)
1200	147.89(0.08)	412.21(0.34)	314.77(0.28)	116930(94)
1300	152.41(0.08)	424.23(0.34)	322.73(0.28)	131950(100)
1400	156.35(0.07)	435.67(0.34)	330.39(0.29)	147390(106)
1500	159.77(0.07)	446.58(0.34)	337.78(0.29)	163200(111)
1750	166.57(0.06)	471.75(0.35)	355.15(0.30)	204040(124)
2000	171.50(0.05)	494.33(0.35)	371.16(0.30)	246330(135)
2250	175.15(0.04)	514.75(0.35)	386.00(0.31)	289680(144)
2500	177.91(0.04)	533.35(0.35)	399.82(0.31)	333830(152)
2750	180.03(0.03)	550.41(0.35)	412.75(0.31)	378590(159)
3000	181.70(0.03)	566.15(0.35)	424.88(0.32)	423810(165)

[a] Values in parenthesis are estimated uncertainties.

those observed by Groner and Durig[44] from infrared spectra. Therefore, their vibrational assignments were adopted in this work.

Based upon the molecular constants listed for CH_3OCD_3 (g) in Tables A-2 and A-3, the thermodynamic properties of this compound were evaluated. Table 13 contains the calculated results.

2.3.c. Dimethyl Ether-d_6

The three principal moments of inertia: $I_a = 3.26586 \times 10^{-39}$ g cm^2, $I_b = 1.12135 \times 10^{-38}$ g cm^2, and $I_c = 1.23448 \times 10^{-38}$ g cm^2 were derived from the rotational constants determined by Kasai and Myers[165] from the microwave spectrum of the CD_3OCD_3 molecule. Snyder and Zerbi[172] and Blom *et al.*[173] reported the fundamental vibrational assignments for this compound. Those given by Blom *et al.* were adopted.

Dimethyl ether-d_6 has two torsional frequencies, *i.e.* ν_{b_1} and ν_{a_2}. Möller *et al.*[41] observed the far-infrared torsional vibrational spectra of one–, two–, and three–(CX_3) top molecules. They assigned the b_1 torsional band at 195.5 cm^{-1} as an upper limit and obtained $V_3 = 1217.2$ cm^{-1} for CD_3OCD_3 (g). Based upon $b_1 = 192.0$ cm^{-1}, Tuazon and Fateley[43] calculated the a_2 torsional wavenumbers as 152.8 cm^{-1}.

Blom *et al.*[173] investigated the infrared spectrum of this compound and observed the torsional wavenumber of b_1 as 187 cm^{-1}. From their theoretical calculation, they estimated the a_2 torsional wavenumbers to be 145 cm^{-1}. Their assignments were adopted in this work.

The microwave data[45] predicted the two torsional fundamental wavenumbers at 190.2 and 141.5 cm^{-1}. From normal coordinate analysis,[176,177] these two wavenumbers were calculated to be 186 and 142–144 cm^{-1}. In view of the above predictions, Groner and Durig[44] assigned the b_1 torsional wavenumber observed in the infrared spectrum at 188.6 cm^{-1} for the CD_3OCD_3 (g) molecule. Durig *et al.*[42] studied the far infrared spectrum of solid CD_3OCD_3, and assigned the b_2 and a_2 torsional wavenumbers at 207 and 182 cm^{-1}, respectively.

Lutz and Dreizler[486] have determined the coefficients V_3 and V'_{12} of the internal rotation potential function for this compound in excited torsional states, using a two-dimensional Fourier series in torsional angles. For evaluation of the internal rotational energy levels, an average torsional wavenumber of $1/2(187.0 + 145.0) = 166.0$ cm^{-1} and a calculated internal rotation constant $F = 3.637$ cm^{-1} were employed for each CD_3 rotor. In the calculation, each rotor was treated independently, as in the case of treating the CH_3 rotors in the CH_3OCH_3 molecule. From these molecular constants, the internal rotation barrier height (V_3) of each CD_3 rotor was evaluated to be 931.0 cm^{-1} or 11.138 kJ mol^{-1}. Based upon a semirigid rotor model, Durig *et al.*[45] obtained $V_{30} = V_{03} = 897.0$ cm^{-1}.

Groner and Durig[44] analyzed the torsional far infrared and Raman spectra of the CD_3OCD_3 (g) molecule, employing a semirigid two-top model. The analysis allowed

TABLE 13. Ideal gas thermodynamic properties of dimethyl ether-d_3 (CH_3OCD_3) at 1 bar[a]
M = 49.0874

$\frac{T}{K}$	$\frac{C_p^\circ}{J\ K^{-1}\ mol^{-1}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{J\ K^{-1}\ mol^{-1}}$	$\frac{-\{G^\circ(T)-H^\circ(0)\}/T}{J\ K^{-1}\ mol^{-1}}$	$\frac{\{H^\circ(T)-H^\circ(0)\}}{J\ mol^{-1}}$
0	0	0	0	0
100	43.81(0.15)	220.21(0.15)	183.49(0.06)	3673(9)
150	50.53(0.11)	239.30(0.20)	199.05(0.10)	6037(16)
200	56.84(0.09)	254.69(0.23)	211.09(0.13)	8719(20)
273.15	67.50(0.09)	273.93(0.24)	225.40(0.16)	13256(25)
298.15	71.49(0.10)	280.01(0.25)	229.73(0.16)	14993(27)
300	71.79(0.10)	280.46(0.25)	230.04(0.16)	15125(27)
400	87.93(0.12)	303.33(0.26)	245.54(0.19)	23115(34)
500	102.74(0.12)	324.58(0.27)	259.25(0.20)	32664(43)
600	115.61(0.11)	344.47(0.28)	271.81(0.21)	43597(52)
700	126.62(0.11)	363.14(0.29)	283.54(0.22)	55723(61)
800	136.00(0.10)	380.68(0.30)	294.60(0.23)	68867(70)
900	143.99(0.09)	397.17(0.30)	305.09(0.24)	82877(78)
1000	150.78(0.08)	412.71(0.31)	315.08(0.24)	97625(85)
1100	156.56(0.08)	427.36(0.31)	324.63(0.25)	113000(92)
1200	161.49(0.07)	441.20(0.31)	333.77(0.25)	128910(98)
1300	165.69(0.07)	454.29(0.31)	342.54(0.26)	145270(104)
1400	169.30(0.06)	466.71(0.32)	350.97(0.26)	162030(109)
1500	172.40(0.06)	478.49(0.32)	359.08(0.26)	179120(114)
1750	178.50(0.05)	505.51(0.32)	378.11(0.27)	223000(124)
2000	182.80(0.04)	529.61(0.32)	395.61(0.28)	268200(133)
2250	185.90(0.03)	551.41(0.33)	411.71(0.28)	314300(141)
2500	188.30(0.03)	571.11(0.33)	426.71(0.29)	361100(147)
2750	190.00(0.02)	589.11(0.33)	440.61(0.29)	408400(152)
3000	191.40(0.02)	605.71(0.33)	453.71(0.29)	456100(157)

[a] Values in parenthesis are estimated uncertainties.

the calculation of the torsional wavenumber of the infrared forbidden transition for this compound to be 141.7 cm^{-1}, as compared with 141.5 cm^{-1} from the microwave data.[45]

Using the selected molecular constants given in Tables A-2 and A-3, we calculated the thermodynamic properties of CD_3OCD_3 (g) given in Table 14.

2.3.d. Ethyl Methyl Ether

Ethyl methyl ether ($C_2H_5OCH_3$) has two rotational isomers, *trans* and *gauche*, in the vapor phase.[179-183] The infrared spectra observed by Kitagawa and Miyazawa,[180] and infrared and Raman spectra obtained by Perchard[181] indicate that the more stable isomer is the *trans* form. They reported the energy difference, ϵ_0, as 5.65 kJ mol^{-1}.

Hayashi and Kuwada[184] measured the microwave spectra of *trans*-ethyl methyl ether and its eleven isotopically substituted species. From the derived moments of inertia they reported: $I_a = 2.99803 \times 10^{-39}$ g cm^2, $I_b = 2.01758 \times 10^{-38}$ g cm^2, and $I_c = 2.15669 \times 10^{-38}$ g cm^2. They obtained $\epsilon_0 = 6.28$ kJ mol^{-1} for the difference between *gauche* and *trans* conformers. These were adopted.

The fundamental vibrational frequencies assigned by Shimanouchi *et al.*[185] were employed for computing the vibrational contributions to the thermodynamic properties of *trans*-$C_2H_5OCH_3$ (g). The two torsional wavenumbers, $\tilde{\nu}_{tor}(CH_3\text{–}O) = 202$ cm^{-1} and $\tilde{\nu}_{tor}(CH_3\text{–}CH_2) = 248$ cm^{-1} observed by Kitagawa *et al.*[182] and Hayashi and Kwada,[184] and the two rotational constants $F = 7.867$ cm^{-1} and 5.306 cm^{-1} were employed for the evaluation of the internal rotational barrier heights (V_3) of the two methyl rotors in the *trans* isomer molecule. From $\tilde{\nu}_{tor}$ and F for the methyl rotors in the $C_2H_5OCH_3$ molecule, we obtained the values, $V_3 = 8.31$ kJ mol^{-1} and $V_3 = 17.01$ kJ mol^{-1} which compare with the reported values of (10.46 ± 0.42) kJ mol^{-1} and (13.81 ± 0.42) kJ mol^{-1};[182] and (10.67 ± 0.42) kJ mol^{-1} and 13.77 kJ mol^{-1},[184] respectively. The V_3 for the $CH_2\text{–}CH_2$ rotation was calculated from the torsional wavenumber of 115 cm^{-1} reported by Hayashi and Kuwada.[184]

Vibrational assignments for the *trans*-$C_2H_5OCH_3$ molecule were also reported by Snyder and Zerbi,[172] where the two torsional wavenumbers were given as $\tilde{\nu}_{tor}(CH_3\text{–}O) = 199$ cm^{-1} and $\tilde{\nu}_{tor}(CH_3\text{–}CH_2) = 238$ cm^{-1}. Shimanouchi *et al.*[185] assigned these two wavenumbers as 200 cm^{-1} and 252 cm^{-1}. They are consistent with our adopted values. Shiki and Hayashi[493] measured the microwave spectra of *trans*-ethyl methyl ether and its four deuterated species in the ground and the four lowest torsionally excited states. The coupling amongst the two methyl and the skeletal torsions were analyzed. Ninety-six internal rotational energy levels were generated, using the selected $\tilde{\nu}_{tor}$ and F for each rotor.

The molecular structure of *gauche*-$C_2H_5OCH_3$(g) was not available. The molecular parameters of the *trans* isomer[184] were employed for calculating $I_aI_bI_c$ and F values

TABLE 14. Ideal gas thermodynamic properties of dimethyl ether-d_6 (CD_3OCD_3) at 1 bar[a]
$M = 52.1060$

$\frac{T}{\text{K}}$	$\frac{C_p^\circ}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{-\{G^\circ(T)-H^\circ(0)\}/T}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{\{H^\circ(T)-H^\circ(0)\}}{\text{J mol}^{-1}}$
0	0	0	0	0
100	45.67(0.23)	216.55(0.26)	178.91(0.11)	3764(16)
150	52.37(0.15)	236.37(0.33)	194.91(0.17)	6220(25)
200	59.50(0.11)	252.38(0.37)	207.33(0.22)	9010(31)
273.15	72.61(0.12)	272.80(0.39)	222.18(0.26)	13827(37)
298.15	77.45(0.13)	279.37(0.39)	226.70(0.27)	15703(39)
300	77.81(0.13)	279.85(0.39)	227.93(0.27)	15846(39)
400	96.48(0.15)	304.84(0.41)	243.39(0.30)	24578(48)
500	112.56(0.15)	328.14(0.42)	258.04(0.32)	35053(58)
600	125.98(0.14)	349.89(0.43)	271.56(0.34)	47001(70)
700	137.11(0.13)	370.17(0.44)	284.21(0.35)	60173(81)
800	146.31(0.12)	389.10(0.45)	296.15(0.36)	74359(91)
900	153.90(0.11)	406.79(0.45)	307.47(0.37)	89381(101)
1000	160.16(0.10)	423.34(0.46)	318.24(0.38)	105094(110)
1100	165.35(0.10)	438.85(0.46)	328.51(0.39)	121377(118)
1200	169.65(0.09)	453.43(0.47)	338.32(0.39)	138134(126)
1300	173.25(0.08)	467.16(0.47)	347.71(0.40)	155285(133)
1400	176.28(0.07)	480.11(0.47)	356.71(0.40)	172766(139)
1500	178.84(0.07)	492.36(0.47)	365.34(0.41)	190526(145)
1750	183.70(0.06)	520.31(0.48)	385.51(0.42)	235900(158)
2000	187.10(0.04)	545.11(0.48)	403.91(0.42)	282300(168)
2250	189.50(0.04)	567.31(0.48)	420.91(0.43)	329400(177)
2500	191.30(0.03)	587.31(0.48)	436.51(0.43)	377000(184)
2750	192.60(0.03)	605.61(0.48)	451.11(0.44)	424900(190)
3000	193.50(0.02)	622.41(0.48)	464.71(0.44)	473200(195)

[a]Values in parenthesis are estimated uncertainties.

for the three rotors in the *gauche* isomer molecule. The dihedral angle of this molecule was estimated to be the same as that in paraffinic hydrocarbons.

The vibrational wavenumbers for the *gauche* isomer were taken from Shimanouchi *et al.*[185] Based upon the reported torsional wavenumbers and the calculated F values, we calculated the barrier heights to be $V_3(CH_3\text{–}O) = 9.57$ kJ mol^{-1}, $V_3(CH_3\text{–}C) = 15.04$ kJ mol^{-1} and $V_3(CH_3CH_2\text{–}) = 14.76$ kJ mol^{-1}. From these molecular constants, 108 internal rotational energy levels were generated for each CH_3 rotor.

Kitagawa *et al.*[182] measured the far-infrared spectra of ethyl methyl ether and its deuterated species in the crystalline, liquid, and gaseous states. From an analysis of the isotope effects on the infrared frequencies, the torsional wavenumbers of the two CH_3 rotors in the *gauche* isomer were assigned at 192 cm^{-1} and 239 cm^{-1}. Normal vibrations treated with a local-symmetry force field and force constants, adjusted by the method of least squares, gave $\tilde{\nu}_{\text{tor}}(CH_3\text{–}O) = 197$ cm^{-1} and $\tilde{\nu}_{\text{tor}}(CH_3\text{–}C) = 224$ cm^{-1}.

Using the molecular constants for the *trans* and *gauche* isomers given in Tables A-2 and A-3, their thermodynamic properties were calculated separately. These values, along with the known equilibrium compositions of the *trans–gauche* mixture, were used to calculate the thermodynamic properties of ethyl methyl ether (g) in the temperature range from 0 to 1500 K and at 1 bar. They are presented in Table 15.

Neither vapor heat capacity nor third law entropy measurements of ethyl methyl ether were available for comparison with our calculated values.

Oyanagi and Kuchitsu[156] investigated the molecular structure and conformation of this compound by gas electron diffraction and determined the molar composition of the *trans–gauche* isomeric equilibrium mixture at 20 °C. The composition of *trans* (80 ± 8)% in the equilibrium mixture is in agreement with our calculated molar composition of ethyl methyl ether at 20 °C which was 84% of *trans* isomer.

The thermodynamic properties reported by Stull *et al.*[466] were estimated by comparison with those of the related hydrocarbons.

2.3.e. Diethyl Ether

The infrared and Raman spectra of this compound have been studied by many researchers.[155,172,186,187] At least two rotational isomers, namely the *trans–trans* (*TT*) and the *trans–gauche* (*TG*), exist in the gas and liquid states. Hayashi and Kuwada[188] determined the molecular structural parameters of the *TT* isomer from the microwave spectra of six isotopic species of diethyl ether. They reported that the *TT* isomer was more stable than the *TG* isomer by from 4.6 to 5.7 kJ mol^{-1}.[186,187] Based upon their rotational constants and molecular structural parameters, we obtained the following constants: $I_a = 4.67366 \times 10^{-39}$ g cm^2, $I_b = 3.73948 \times 10^{-38}$ g cm^2, $I_c = 3.99288 \times 10^{-38}$ g cm^2, and $F = 6.715$ cm^{-1}.

TABLE 15. Ideal gas thermodynamic properties of *ethyl methyl ether* ($C_2H_5OCH_3$) at *1 bar*[a]
$M = 60.0956$

$\frac{T}{\text{K}}$	$\frac{C_p^\circ}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{\{G^\circ(T)-H^\circ(0)\}/T}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{\{H^\circ(T)-H^\circ(0)\}}{\text{J mol}^{-1}}$
0	0	0	0	0
100	51.19(0.19)	233.28(0.25)	193.73(0.12)	3955.8(14)
150	63.43(0.14)	256.42(0.31)	210.89(0.17)	6829.0(21)
200	73.95(0.11)	276.14(0.33)	224.79(0.21)	10269(26)
273.15	88.30(0.10)	301.31(0.36)	241.99(0.25)	16204(32)
298.15	93.30(0.11)	309.25(0.36)	247.30(0.25)	18473(34)
300	93.67(0.11)	309.83(0.36)	247.68(0.25)	18646(34)
400	113.88(0.13)	339.55(0.37)	266.99(0.28)	29026(42)
500	132.66(0.14)	367.03(0.38)	284.28(0.30)	41372(51)
600	149.06(0.14)	392.70(0.39)	300.24(0.31)	55478(61)
700	163.24(0.13)	416.77(0.40)	315.18(0.32)	71110(72)
800	175.54(0.12)	439.39(0.41)	329.31(0.33)	88063(82)
900	186.25(0.11)	460.70(0.41)	342.73(0.34)	106170(92)
1000	195.58(0.10)	480.81(0.42)	355.55(0.35)	125270(100)
1100	203.71(0.09)	499.84(0.42)	367.81(0.35)	145240(109)
1200	210.77(0.09)	517.88(0.42)	379.57(0.36)	165970(116)
1300	216.92(0.08)	535.00(0.43)	390.87(0.36)	187370(123)
1400	222.27(0.07)	551.27(0.43)	401.75(0.37)	209330(130)
1500	226.94(0.07)	566.77(0.43)	412.24(0.37)	231800(136)

[a] Values in parenthesis are estimated uncertainties.

Vibrational frequencies of the *TT*-isomer have been reported by Snyder and Zerbi,[172] Wieser *et al.*,[186] Perchard,[181] and Perchard *et al.*[187] Recently, Shimanouchi and coworkers[185] critically reviewed the infrared and Raman spectra of the isomeric diethyl ethers. Their assigments for the fundamental vibrations of the *TT*-isomer were adopted here. See Table A-2 for numerical values.

We treated the two CH_3 rotors in the *TT*-$CH_3CH_2OCH_2CH_3$ molecule as two identical independent rotors, as before. From $\tilde{\nu}_{\text{tor}} = 238$ cm^{-1} and $F = 6.715$ cm^{-1}, the potential barrier height (V_3) was calculated to be 12.79 kJ mol^{-1} for each rotor. The torsional wavenumber 238 cm^{-1} is the average of two reported torsional wavenumbers, 231 and 245 cm^{-1}.[185] One hundred and eight (108) internal rotational energy levels were generated for each rotor for computing the internal rotational contributions to the thermodynamic properties of *TT*-$C_2H_5OC_2H_5$ (g). The value of V_3 for the potential function of the ethyl rotor was calculated from the corresponding torsional wavenumber of Shimanouchi *et al.*[185]

The molecular structure of *TG*-diethyl ether was not available. Thus the molecular parameters for the *TT*-isomer[188] and an estimated dihedral angle of 59.2° from the *trans* position were employed for calculating $I_aI_bI_c$ and F for this isomer.

The vibrational wavenumbers for the *TG*-isomer were taken from Shimanouchi *et al.*[185] From $\tilde{\nu}_{\text{tor}} = 227$ cm^{-1} and $F = 5.933$ cm^{-1} for the *trans*-CH_3 rotor; a potential barrier height of $V_3 = 13.01$ kJ mol^{-1} was obtained. With the above molecular constants, two sets of internal rotational energy levels, with 108 levels (up to 16000 cm^{-1}) for each species, were generated. The V_3 for the ethyl rotor was calculated from the mean value of the two torsional wavenumbers assigned by Shimanouchi *et al.*.

The thermodynamic properties of diethyl ether were evaluated based upon a molecular model which contained an equilibrium mixture of *TT*- and *TG*-isomeric species. The energy $\epsilon_0 = 5.73$ kJ mol^{-1} was used for the *TG* conformer. All the molecular parameters are listed in Table A-2 and Table A-3. The calculated results appear in Table 16.

Using flow calorimetry, Counsell *et al.*[160] and Jennings and Bixler[178] measured the vapor heat capacities of diethyl ether. Jatkar[161] determined C_p° for this compound in the temperature range from 310 to 620 K by measuring the speed of sound in the vapor. From equilibrium studies on the gas-phase dehydration of ethyl alcohol to ethyl ether, Valentin[162] derived the heat capacities for diethyl ether from 400 to 500 K. These reported C_p° values are compared with our calculated values in Table A-14.

Counsell *et al.*[160] evaluated the third law entropy of diethyl ether (g) at 298.15 K to be 342.2 J K^{-1} mol^{-1}, based upon their low temperature thermal measurements. Using the same low temperature thermal data, we calculated the entropy as 342.55 J K^{-1} mol^{-1} while our selected value in Table A-26 is 342.71 J K^{-1} mol^{-1}.

Stull *et al.*[466] calculated the thermodynamic properties of this compound in the temperature range 298.15 to 1000 K, using a selected value of the ideal gas entropy at 298.15 K of 342.67 J K^{-1} mol^{-1} and the vapor heat capacities estimated by an empirical structural correlation method.

TABLE 16. Ideal gas thermodynamic properties of diethyl ether ($C_2H_5OC_2H_5$) at 1 bar[a]
$M = 74.1224$

$\frac{T}{\mathrm{K}}$	$\frac{C_p^\circ}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{-\{G^\circ(T)-H^\circ(0)\}/T}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{\{H^\circ(T)-H^\circ(0)\}}{\mathrm{J\,mol^{-1}}}$
0	0	0	0	0
100	62.50(0.25)	242.85(0.62)	199.29(0.41)	4355.5(23)
150	84.80(0.20)	272.54(0.67)	218.84(0.48)	8054.8(32)
200	99.70(0.16)	299.17(0.69)	235.66(0.53)	12701(39)
273.15	114.30(0.15)	332.45(0.71)	257.26(0.57)	20539(47)
298.15	119.46(0.15)	342.67(0.72)	263.99(0.59)	23459(49)
300	119.86(0.15)	343.42(0.72)	264.48(0.59)	23680(50)
400	142.81(0.16)	380.98(0.73)	289.00(0.62)	36795(60)
500	165.77(0.17)	415.35(0.74)	310.87(0.64)	52239(71)
600	186.35(0.16)	447.43(0.75)	330.99(0.66)	69867(83)
700	204.35(0.15)	477.54(0.76)	349.80(0.67)	89422(95)
800	220.04(0.14)	505.88(0.76)	367.55(0.68)	110660(106)
900	233.74(0.13)	532.61(0.77)	384.42(0.69)	133360(117)
1000	245.68(0.13)	557.86(0.77)	400.52(0.70)	157350(128)
1100	256.08(0.12)	581.78(0.77)	415.92(0.70)	182450(137)
1200	265.12(0.11)	604.46(0.78)	430.69(0.71)	208520(146)
1300	272.97(0.11)	626.00(0.78)	444.89(0.71)	235430(155)
1400	279.81(0.10)	646.48(0.78)	458.57(0.72)	263080(163)
1500	285.76(0.09)	665.99(0.78)	471.75(0.72)	291370(171)

[a] Values in parenthesis are estimated uncertainties.

2.4. Alkanones

Propanone (acetone, CH_3COCH_3) and 2-butanone (ethyl methyl ketone, $CH_3CH_2COCH_3$) are the two simplest aliphatic alkanones. Their thermodynamic properties in the ideal gaseous state have been reported,[189-193] but the calculations used incomplete and inaccurate input data for the molecular and spectroscopic parameters. Due to the availability of a more complete and reliable set of data on the molecular structure, vibrational assignments, and torsional frequencies for these two compounds, Chao and Zwolinski[194] reevaluated their thermodynamic properties. The selection of the input data and method for calculating the thermodynamic properties of these compounds are briefly described.

2.4.a. Propanone

The molecular structure, rotational constants, and potential barrier to internal rotation of propanone has been investigated by electron diffraction[195-199] and microwave spectroscopy.[35,494-496] For computing $I_aI_bI_c$, the values of I_a, I_b, and I_c determined by Nelson and Pierce[495] were used.

Many researchers have observed the infrared[170,200-209] and Raman[210-218] spectra of propanone (g). The fundamental vibrational wavenumbers of this compound have been reported.[219-221] Recently Shimanouchi[80] critically reviewed the spectral data in the literature and assigned a complete set of fundamental vibrational wavenumbers for the CH_3COCH_3 molecule. These values were employed for calculating the vibrational contributions.

In the calculation of the internal rotational contributions we treated the two CH_3 groups in the molecule as two independent identical symmetrical rotors. We adopted $V_3 = (3.255 \pm 0.084)$ kJ mol^{-1} and $F = 5.727$ cm^{-1} [495] for calculating the internal rotational energy levels (0–16780 cm^{-1}). The torsional wavenumber ($0 \rightarrow 1$) was 104.8 cm^{-1}.

Based upon the two torsional wavenumbers, $\tilde{\nu}_{12} = 105$ cm^{-1} and $\tilde{\nu}_{24} = 109$ cm.$^{-1}$ and the internal rotational constants reported by Fateley and Miller,[170] the barrier height was evaluated to be 3.473 kJ mol^{-1} for each CH_3 rotor. The value of V_3 was reported to be (3.28 ± 0.17) kJ mol^{-1} by Swalen and Costain.[35]

The ideal gas thermodynamic properties were calculated using the selected molecular and spectroscopic constants listed in Tables A-2 and A-3. The results appear in Table 17.

Pennington and Kobe[189] measured the vapor heat capacities of this compound as a function of pressure, from 1/3 to 5/3 atm, and at four temperatures, 338.2, 371.2, 405.2 and 439.2 K. From the C_p values measured at 1/3 atm and the second virial coefficients given in the literature,[135] the heat capacities of propanone vapor in the ideal gaseous state, C_p°, were calculated at these four temperatures and presented in Table A-17. The agreement between our calculated C_p° and the experimental values is excellent.

Based upon low temperature thermal measurements, an experimental third-law entropy of (294.6 ± 1.0) J K^{-1} mol^{-1} at 298.15 K is given in Table A-26. Our statistical entropy value is 297.62 J K^{-1} mol^{-1}. The entropies of propanone (g) calculated by Pennington and Kobe[189] and Schumann and Aston[108] are given in Table A-18.

Ideal gas thermodynamic properties of propanone were calculated by Pennington and Kobe[189] in the temperature range from 0 to 1500 K. These results were adopted by Stull *et al.*[466]

TABLE 17. Ideal gas thermodynamic properties of propanone (CH_3COCH_3) at 1 bar[a]
$M = 58.0798$

$\frac{T}{K}$	$\frac{C_p^\circ}{J\,K^{-1}\,mol^{-1}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{J\,K^{-1}\,mol^{-1}}$	$\frac{-\{G^\circ(T)-H^\circ(0)\}/T}{J\,K^{-1}\,mol^{-1}}$	$\frac{\{H^\circ(T)-H^\circ(0)\}}{J\,mol^{-1}}$
0	0	0	0	0
100	51.73(0.14)	232.11(0.37)	190.00(0.20)	4210(18)
150	56.18(0.10)	253.95(0.41)	207.87(0.26)	6911(23)
200	61.20(0.10)	270.76(0.43)	221.56(0.30)	9840(27)
273.15	71.09(0.10)	291.22(0.44)	237.55(0.34)	14660(31)
298.15	75.02(0.11)	297.62(0.45)	242.32(0.35)	16486(33)
300	75.32(0.11)	298.08(0.45)	242.67(0.35)	16625(33)
400	92.06(0.12)	322.03(0.46)	259.56(0.37)	24990(40)
500	108.08(0.13)	344.33(0.46)	274.30(0.39)	35011(48)
600	122.20(0.12)	365.31(0.47)	287.74(0.40)	46542(57)
700	134.43(0.11)	385.09(0.48)	300.25(0.41)	59388(66)
800	145.00(0.11)	403.75(0.48)	312.03(0.42)	73372(75)
900	154.15(0.10)	421.37(0.48)	323.21(0.43)	88340(83)
1000	162.09(0.09)	438.03(0.49)	333.87(0.43)	104162(91)
1100	168.96(0.09)	453.81(0.49)	344.06(0.44)	120723(99)
1200	174.92(0.08)	468.77(0.49)	353.83(0.44)	137924(105)
1300	180.09(0.08)	482.98(0.49)	363.23(0.44)	155681(112)
1400	184.58(0.07)	496.49(0.50)	372.27(0.45)	173920(118)
1500	188.49(0.07)	509.37(0.50)	380.98(0.45)	192578(124)

[a] Values in parenthesis are estimated uncertainties.

2.4.b. 2-Butanone

Infrared spectroscopy,[223] electron diffraction,[224] and microwave spectroscopy,[497] indicate that the *trans* rotational isomer of 2-butanone is far more stable than the *gauche* isomer. Therefore, for evaluation of the thermodynamic properties of this compound, the *trans* isomer was selected.

Romers and Creutzberg[195] and Abe, *et al.*[224] have elucidated the molecular structure of *trans*-2-butanone byelectron diffraction. From microwave spectroscopy, Pierce *et al.*[497] determined the ground-state rotational constants for *trans*-2-butanone and V_3 and F for the CH_3 rotor. These molecular constants were adopted to obtain $I_aI_bI_c$ and the internal rotational energy levels for the CH_3 rotor.

The molecular structural parameters of Romers and Creutzberg[195] were employed for calculating the internal rotational constants for the two rotors, *i.e.* CH_3 in C_2H_5, and CH_2H_5. They are listed in Table A-3.

The infrared[200, 214, 223, 225-227, 230, 231] and Raman[200, 214, 228, 229, 232-234] spectra have been observed by many investigators. Shimanouchi[80] critically reviewed the reported infrared and Raman spectra and the related theoretical calculations for 2-butanone (g) and assigned a complete set of fundamental vibrational frequencies for *trans*-$CH_3CH_2COCH_3$ (g). The assignments were employed in this work.

The torsional frequencies and potentional barriers to internal rotation in 2-butanone were reported by Shimanouchi,[80] Nickerson *et al.*,[193] and Sinke and Oetting.[192] Based upon the three torsional wavenumbers, ν_{31} = 199.6 cm^{-1}, $\tilde{\nu}_{32}$ = 83.27 cm^{-1}, and $\tilde{\nu}_{33}$ = 60.6 cm^{-1} and the three internal rotation constants (see Table A-3), we evaluated the potential barrier heights as: V_3 (CH_3) = 2.17 kJ mol^{-1}, V_3 (CH_3 in C_2H_5) = 11.0 kJ mol^{-1}, and $V(C_2H_5) = 1/2[V_1(1 - \cos 30)]$ where V_1 = 7.99 kJ mol^{-1} and V_3 = 4.00 kJ mol^{-1}.

Sinke and Oetting[193] selected two methyl barriers in the propanone molecule as 5.02 and 12.34 kJ mol^{-1} and adopted the skeletal rotational potential function for the ethyl rotor similar to that used by Nickerson *et al.*,[193] *i.e.* the potential function shows three minima per cycle of internal rotation with two equal minima higher than the third.

To calculate the contribution to the thermodynamic properties of this compound from the internal rotation of the three rotors in the molecule, Nickerson *et al.*[193] used $V_3(CH_3)$ = 4.18 kJ mol^{-1} and $V_3(CH_3$ in $C_2H_5)$ = 10.04 kJ mol^{-1}. They employed an equilibrium model between rotational isomers to compute the contribution for the internal rotation of the ethyl group. The barrier for rotation of the *trans* form was 4.18 kJ mol^{-1}. The energy difference between *trans* and *gauche* isomers was taken as 2.93 kJ mol^{-1} (the value found in butane[235]) plus a quantity which represented the energy due to the attractive force between oxygen and the extended methyl group. They adopted a value of 2.51 kJ mol^{-1} for this interaction term to obtain the best fit between the calculated and experimental heat capacities.

Using the molecular constnats given in Tables A-2 and A-3, we calculated the thermodynamic properties for 2-butanone (g) which are presented in Table 18. A comparison of observed and calculated C_p° and $(S^\circ(T)\text{–}S^\circ(0))$ values appears in Table A-19.

TABLE 18. Ideal gas thermodynamic properties of 2-butanone ($C_2H_5COCH_3$) at 1 bar[a]
$M = 72.1066$

T K	C_p° J K^{-1} mol^{-1}	$\{S^\circ(T)-S^\circ(0)\}$ J K^{-1} mol^{-1}	$-\{G^\circ(T)-H^\circ(0)\}/T$ J K^{-1} mol^{-1}	$\{H^\circ(T)-H^\circ(0)\}$ J mol^{-1}
0	0	0	0	0
100	57.03(0.18)	257.11(0.58)	212.04(0.37)	4507(22)
150	68.98(0.14)	282.50(0.62)	231.44(0.45)	7659(28)
200	80.20(0.13)	303.90(0.64)	246.94(0.49)	11392(33)
273.15	96.12(0.13)	331.25(0.66)	265.94(0.53)	17839(39)
298.15	101.68(0.14)	339.90(0.66)	271.78(0.54)	20312(41)
300	102.09(0.14)	340.54(0.66)	272.20(0.54)	20500(41)
400	124.37(0.16)	372.97(0.67)	293.40(0.57)	31828(50)
500	145.05(0.17)	402.99(0.68)	312.35(0.59)	45319(61)
600	163.15(0.16)	431.07(0.69)	329.82(0.61)	60751(74)
700	178.77(0.15)	457.43(0.69)	346.19(0.62)	77866(86)
800	192.25(0.14)	482.20(0.70)	361.66(0.63)	96433(98)
900	203.91(0.13)	505.53(0.70)	376.36(0.63)	116260(109)
1000	213.99(0.13)	527.55(0.71)	390.39(0.64)	137160(120)
1100	222.69(0.12)	548.37(0.71)	403.81(0.64)	159010(130)
1200	230.21(0.12)	568.07(0.71)	416.69(0.65)	181660(139)
1300	236.70(0.11)	586.76(0.71)	429.06(0.65)	205020(148)
1400	242.31(0.10)	604.51(0.72)	440.96(0.66)	228970(157)
1500	247.17(0.10)	621.40(0.72)	452.43(0.66)	253450(165)

[a]Values in parenthesis are estimated uncertainties.

The thermodynamic properties of 2-butanone in the ideal gas state were calculated by Nickerson *et al.*[193] and Sinke and Oetting.[192] The results of Sinke and Oetting[192] were adopted by Stull *et al.*[466] For the evaluation of the internal rotational contributions, Nickerson *et al.* used the tables of Pitzer and Gwinn,[15] whereas Sinke and Oetting employed the tables published by Scott and McCullough.[237] Their calculated entropies at 298.15 K corrected to 1 bar are compared with our calculated value in Table A-17. The calculated ideal entropy at 298.15 K, 339.90 J K^{-1} mol^{-1}, agrees well with the selected value of 338.91 J K^{-1} mol^{-1} given in Table A-26.

2.5. Alkanals

Recently Chao *et al.*[87] evaluated the ideal gas thermodynamic properties of methanal, ethanal, and their deuterated species. The selection of the molecular constants used in the calculations were discussed in detail. Their calculated results were adopted in this work. The numerical values of the input data used appear in Tables A-2 and A-3.

2.5.a. Methanal

The molecular structure of methanal (formaldehyde, HCHO) is planar with C_{2v} symmetry. Reported bond distances and angles determined do not agree.

Chu *et al.*[93] observed weak transitions of the type $\Delta J = \pm 1$, $\Delta K_a = \pm 2$, $\Delta K_c = \pm 3$ in HCHO and DCDO using double resonance method and by direct absorption using a Stark modulated spectrometer. Adding these new transitions into the previously known microwave and millimeterwave data, and employing a least-squares analysis, they obtained an improved set of rotational constants. Based upon their reported rotational constants, we derived the three principal moments of inertia as: $I_a = 2.97626 \times 10^{-40}$ g cm^2, $I_b = 2.16096 \times 10^{-39}$ g cm^2, and $I_c = 2.46807 \times 10^{-39}$ g cm^2, respectively. Dangoisse *et al.*[482] investigated the microwave spectra of methanal and its isotopic species and obtained the rotational constants of H_2CO, HDCO, and D_2CO in the ground state. Their results are in excellent agreement with those reported by Chu *et al.*[93] The values of $I_aI_bI_c$ used are given in Table A-2.

The vibrational assignments recommended by Shimanouchi[80] were employed for evaluating the vibrational contributions. The calculated thermodynamic functions appear in Table 19. Stull *et al.*[466] adopted the thermal functions calculated by Pillai and Cleveland.[483]

2.5.b. Methanal-d_1

Oka[124] determined the rotational constants for the isotopic methanals from the parameters used in the analysis of the K-type doubling spectra and the frequencies of $1_{01} \leftarrow 0_{00}$ transitions. Dangoisse *et al.*,[482] used microwave spectroscopy to determine the rotational constants of this compound in the ground state. From the reported rotational constants for HCDO(g), $A = 198112 \pm 25$ MHz, $B = 34910.84 \pm 1$ MHz, and $C = 29561.07 \pm 1$ MHz, we calculated $I_a = 4.23606 \times 10^{-40}$ g cm^2, $I_b = 2.40388 \times 10^{-39}$ g cm^2, $I_c = 2.83892 \times 10^{-39}$ g cm^2, and $I_aI_bI_c = 2.89087 \times 10^{-117}$ g^3 cm^6. The rotational constants, B and C, were later confirmed by analysis of the millimeterwave spectrum of HCDO (g) by Takagi and Oka.[125] The fundamental vibrational wavenumbers used, see Table A-2, were assigned by Shimanouchi.[80] The calculated results are given in Table 20.

TABLE 19. Ideal gas thermodynamic properties of methanal (HCHO) at 1 bar[a]
$M = 30.0262$

$\frac{T}{\text{K}}$	$\frac{C_p^\circ}{\text{J K}^{-1}\,\text{mol}^{-1}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\text{J K}^{-1}\,\text{mol}^{-1}}$	$\frac{-\{G^\circ(T)-H^\circ(0)\}/T}{\text{J K}^{-1}\,\text{mol}^{-1}}$	$\frac{\{H^\circ(T)-H^\circ(0)\}}{\text{J mol}^{-1}}$
0	0	0	0	0
100	33.26(0.00)	182.02(0.04)	148.77(0.04)	3326(0)
150	33.28(0.00)	195.51(0.04)	162.25(0.04)	4989(0)
200	33.50(0.01)	205.11(0.04)	171.83(0.04)	6657(0)
273.15	34.70(0.02)	215.69(0.04)	182.22(0.04)	9144(1)
298.15	35.39(0.02)	218.76(0.04)	185.16(0.04)	10020(2)
300	35.44(0.03)	218.98(0.04)	185.36(0.04)	10085(2)
400	39.24(0.04)	229.67(0.04)	195.15(0.04)	13809(5)
500	43.74(0.05)	238.90(0.04)	202.99(0.04)	17956(10)
600	48.18(0.05)	247.27(0.05)	209.68(0.04)	22554(15)
700	52.28(0.05)	255.01(0.06)	215.61(0.04)	27581(20)
800	55.94(0.05)	262.24(0.06)	220.99(0.04)	32996(25)
900	59.16(0.05)	269.02(0.07)	225.96(0.04)	38754(30)
1000	61.95(0.05)	275.40(0.07)	230.59(0.04)	44813(35)
1100	64.37(0.04)	281.42(0.07)	234.94(0.05)	51132(39)
1200	66.45(0.04)	287.11(0.08)	239.05(0.05)	57676(43)
1300	68.25(0.04)	292.50(0.08)	242.96(0.05)	64413(46)
1400	69.80(0.04)	297.62(0.08)	246.68(0.05)	71318(50)
1500	71.15(0.03)	302.48(0.08)	250.24(0.05)	78367(53)

[a] Values in parenthesis are estimated uncertainties.

TABLE 20. Ideal gas thermodynamic properties of methanal-d_1 (DCHO) at 1 bar[a]
$M = 31.0324$

$\frac{T}{\text{K}}$	$\frac{C_p^\circ}{\text{J K}^{-1}\,\text{mol}^{-1}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\text{J K}^{-1}\,\text{mol}^{-1}}$	$\frac{-\{G^\circ(T)-H^\circ(0)\}/T}{\text{J K}^{-1}\,\text{mol}^{-1}}$	$\frac{\{H^\circ(T)-H^\circ(0)\}}{\text{J mol}^{-1}}$
0	0	0	0	0
100	33.26(0.00)	190.69(0.07)	157.43(0.07)	3326(0)
150	33.33(0.00)	204.18(0.07)	170.92(0.07)	4990(0)
200	33.78(0.01)	213.82(0.07)	180.49(0.07)	6665(0)
273.15	35.62(0.03)	224.58(0.07)	190.92(0.07)	9194(2)
298.15	36.54(0.04)	227.74(0.07)	193.88(0.07)	10096(3)
300	36.61(0.04)	227.97(0.07)	194.09(0.07)	10164(3)
400	41.18(0.05)	239.10(0.07)	203.99(0.07)	14046(7)
500	46.15(0.06)	248.83(0.08)	212.00(0.07)	18412(13)
600	50.87(0.06)	257.66(0.08)	218.89(0.07)	23267(19)
700	55.09(0.06)	265.83(0.09)	225.02(0.07)	28570(24)
800	58.75(0.06)	273.43(0.09)	230.60(0.07)	34267(30)
900	61.89(0.05)	280.54(0.10)	235.76(0.07)	40303(35)
1000	64.55(0.05)	287.20(0.10)	240.57(0.08)	46629(39)
1100	66.81(0.05)	293.46(0.10)	245.10(0.08)	53200(44)
1200	68.73(0.04)	299.36(0.10)	249.38(0.08)	59980(48)
1300	70.36(0.04)	304.93(0.11)	253.44(0.08)	66936(51)
1400	71.75(0.04)	310.19(0.11)	257.30(0.08)	74043(55)
1500	72.94(0.03)	315.18(0.11)	261.00(0.08)	81279(58)

[a] Values in parenthesis are estimated uncertainties.

2.5.c. Methanal-d_2

The ground state rotational constants, $A = 141653.3$ MHz, $B = 32283.57$ MHz, and $C = 26185.34$ MHz, were reported by Dangoisse *et al.*[482] These constants agreed with those obtained by Tatematsu *et al.*[132] and Chu *et al.*[93] The corresponding moments of inertia were $I_a = 5.9244 \times 10^{-40}$ g cm^2, $I_b = 2.5995 \times 10^{-39}$ g cm^2, and $I_c = 3.2049 \times 10^{-39}$ g cm^2, which were adopted for computing the value of $I_aI_bI_c$.

Shimanouchi[80] recommended the six vibrational wavenumbers observed by Cossee and Schachtschneider[133] as the best values for DCDO (g). The thermodynamic properties of this compound given in Table 21 were calculated with the above data.

2.5.d. Ethanal

The molecular structure of ethanal (acetaldehyde, CH_3CHO) has been investigated by electron diffraction[126-128] and microwave spectroscopy.[129-131] The two

TABLE 21. Ideal gas thermodynamic properties of methanal-d_2 (DCDO) at 1 bar[a]
M = 32.0386

$\frac{T}{\text{K}}$	$\frac{C_p^\circ}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{-\{G^\circ(T)-H^\circ(0)\}/T}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{\{H^\circ(T)-H^\circ(0)\}}{\text{J mol}^{-1}}$
0	0	0	0	0
100	33.26(0.00)	187.55(0.10)	154.29(0.10)	3326(0)
150	33.42(0.00)	201.06(0.10)	167.78(0.10)	4991(0)
200	34.24(0.02)	210.76(0.10)	177.36(0.10)	6679(1)
273.15	36.93(0.04)	221.89(0.10)	187.84(0.10)	9272(3)
298.15	38.14(0.05)	225.07(0.10)	190.83(0.10)	10210(4)
300	38.23(0.05)	225.31(0.10)	191.04(0.10)	10281(4)
400	43.65(0.06)	237.04(0.10)	201.11(0.10)	14371(9)
500	49.10(0.06)	247.37(0.11)	209.35(0.10)	19011(15)
600	54.06(0.06)	256.77(0.11)	216.48(0.10)	24173(21)
700	58.36(0.06)	265.43(0.12)	222.86(0.10)	29800(27)
800	61.99(0.06)	273.47(0.12)	228.69(0.10)	35823(31)
900	65.02(0.05)	280.95(0.12)	234.09(0.10)	42178(37)
1000	67.52(0.05)	287.93(0.13)	239.13(0.10)	48809(42)
1100	69.59(0.05)	294.47(0.13)	243.86(0.11)	55668(46)
1200	71.32(0.04)	300.60(0.13)	248.34(0.11)	62716(50)
1300	72.75(0.04)	306.37(0.13)	252.58(0.11)	69922(54)
1400	73.96(0.03)	311.81(0.13)	256.62(0.11)	77259(57)
1500	74.98(0.03)	316.94(0.14)	260.47(0.11)	84707(60)

[a] Values in parenthesis are estimated uncertainties.

carbon atoms and the hydrogen and oxygen of the carbonyl group are in a single plane. In this work, the structural parameters determined by Nösberger *et al.*[131] from the moments of inertia of isotopically substituted species were used to calculated the three principal moments of inertia as $I_a = 1.4752 \times 10^{-39}$ g cm^2, $I_b = 8.2479 \times 10^{-39}$ g cm^2, and $I_c = 9.1889 \times 10^{-39}$ g cm^2. The reduced moment and the internal rotational constant of the CH_3 top were calculated as 3.648×10^{-40} g cm^2 and 7.673 cm^{-1}, respectively.

The reported torsional frequency and internal rotational barrier height of the methyl rotor in CH_3CHO were reviewed by Chao *et al.*[87] The torsional wavenumber of 150 cm^{-1} observed by Fateley and Miller[32] and the derived internal rotational constant, 7.673 cm^{-1}, were employed for evaluating the barrier height as $V_3 = 4.929$ kJ mol^{-1}. Based upon a potential function $V = 1/2\ V_3\ (1 - \cos 3\theta)$, 96 energy levels (up to 17000 cm^{-1}) were generated.[28] These energy levels were used for computing the internal rotational contribution. The agreement between our calculated energy levels and those reported by Fateley and Miller[32] is excellent.[87]

Using the selected molecular constants listed in Tables A-2 and A-3, the thermodynamic properties of ethanal were calculated and are presented in Table 22. Stull *et al.*[466] adopted the evaluations of Pitzer and Weltner.[136]

A comparison of heat capacities calculated in this work with some experimental data is given in Table A-13. The C_p values listed in column 2 of Table A-13 were determined by Coleman and DeVries[134] and are the only experimental measurements available. Two sets of second virial coefficients for this compound were reported[135,136] for converting the measured real gas heat capacities to ideal gas heat capacities. In general, the agreement between C_p° (exptl.) and C_p° (calc.) is good. The average deviations are 0.2 and 0.59 J K^{-1} mol^{-1} or 0.2% and 0.9%, respectively. Our calculated C_p°, $\{H^\circ(T)-H^\circ(0)\}$, and $\{S^\circ(T)-S^\circ(0)\}$ values are consistent with those calculated previously.[136,137,138]

2.5.e. Ethanal-d_1

The molecular structural parameters of CH_3CDO by Nösberger *et al.*[131] were employed for calculating the three principal moments of inertia: $I_a = 1.8621 \times 10^{-39}$ g cm^2, $I_b = 8.2517 \times 10^{-39}$ g cm^2, and $I_c = 9.5797 \times 10^{-39}$ g cm^2. The reduced moment and rotational constant for the CH_3 rotor in CH_3CDO were computed to be 3.982×10^{-40} g cm^2 and 7.030 cm^{-1}, respectively.

The vibrational assignments were those given by Shimanouchi.[80] These are consistent with the assignments reported by Cossee and Schachtschneider[133] with the exception of two wavenumbers, *i.e.* 3014(2) cm^{-1} which were reassigned as 3028 and 2917 cm^{-1} by Shimanouchi.

Using the torsional wavenumber $\tilde{\nu}^{15} = 145$ cm^{-1} and the calculated rotational constant, the internal rotation barrier height (V_3) was derived to be 5.067 kJ mol^{-1}. Following the procedure mentioned previously, 96 internal rotation energy levels (0 – 16000 cm^{-1}) were generated for computing the internal rotational contributions. The calculated results are presented in Table 23.

2.5.f. Ethanal-d_4

Based upon an approximation that the molecular structural parameters of CD_3CDO (g) are the same as those of CH_3CHO (g),[131] the three principal moments of inertia and the reduced moment of the CD_3 top were calculated to be $I_a = 2.4015 \times 10^{-39}$ g cm^2, $I_b = 9.7752$

TABLE 22. Ideal gas thermodynamic properties of ethanal (CH_3CHO) at 1 bar[a]
$M = 44.0530$

$\frac{T}{\mathrm{K}}$	$\frac{C_p^\circ}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{-\{G^\circ(T)-H^\circ(0)\}/T}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{\{H^\circ(T)-H^\circ(0)\}}{\mathrm{J\,mol^{-1}}}$
0	0	0	0	0
100	40.27(0.11)	214.07(0.15)	178.12(0.07)	3595(9)
150	43.26(0.08)	230.98(0.19)	193.07(0.10)	5686(13)
200	46.47(0.07)	243.85(0.20)	204.22(0.12)	7926(16)
273.15	52.80(0.08)	259.22(0.22)	216.95(0.15)	11545(20)
298.15	55.32(0.08)	263.95(0.22)	220.69(0.15)	12896(21)
300	55.51(0.08)	264.29(0.22)	220.96(0.15)	12999(22)
400	66.28(0.08)	281.73(0.23)	234.01(0.17)	19085(27)
500	76.68(0.08)	297.65(0.24)	245.17(0.18)	26241(33)
600	85.94(0.07)	312.47(0.24)	255.17(0.19)	34382(38)
700	94.04(0.07)	326.34(0.25)	264.35(0.20)	43390(44)
800	101.07(0.06)	339.37(0.25)	272.92(0.20)	53154(49)
900	107.19(0.06)	351.63(0.25)	280.99(0.21)	63574(54)
1000	112.49(0.06)	363.21(0.26)	288.64(0.21)	74565(58)
1100	117.08(0.05)	374.15(0.26)	295.92(0.22)	86049(63)
1200	121.06(0.05)	384.51(0.26)	302.82(0.22)	97961(67)
1300	124.50(0.05)	394.34(0.26)	309.54(0.22)	110240(71)
1400	127.49(0.05)	403.68(0.26)	315.93(0.23)	122850(74)
1500	130.09(0.04)	412.57(0.26)	322.08(0.23)	135730(78)

[a] Values in parenthesis are estimated uncertainties.

TABLE 23. Ideal gas thermodynamic properties of ethanal-d_1 (CH_3CDO) at 1 bar[a]
$M = 45.0592$

$\frac{T}{\mathrm{K}}$	$\frac{C_p^\circ}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{-\{G^\circ(T)-H^\circ(0)\}/T}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{\{H^\circ(T)-H^\circ(0)\}}{\mathrm{J\,mol^{-1}}}$
0	0	0	0	0
100	40.45(0.11)	215.62(0.16)	179.59(0.07)	3603(9)
150	43.94(0.08)	232.69(0.20)	194.60(0.11)	5713(14)
200	47.95(0.08)	245.86(0.21)	205.82(0.13)	8006(17)
273.15	55.32(0.09)	261.85(0.23)	218.75(0.15)	11775(21)
298.15	58.11(0.09)	266.82(0.23)	222.57(0.16)	13192(22)
300	58.32(0.09)	267.18(0.23)	222.84(0.16)	13300(22)
400	69.69(0.08)	285.52(0.24)	236.26(0.18)	19702(28)
500	80.29(0.08)	302.23(0.25)	247.81(0.19)	27211(35)
600	89.61(0.07)	317.71(0.25)	258.18(0.20)	35717(40)
700	97.65(0.07)	332.14(0.26)	267.73(0.21)	45090(46)
800	104.56(0.07)	345.64(0.26)	276.63(0.21)	55208(51)
900	110.49(0.06)	358.31(0.26)	285.01(0.22)	65968(56)
1000	115.58(0.06)	370.22(0.27)	292.94(0.22)	77279(61)
1100	119.95(0.06)	381.45(0.27)	300.48(0.23)	89061(65)
1200	123.71(0.05)	392.06(0.27)	307.68(0.23)	101250(69)
1300	126.94(0.05)	402.08(0.27)	314.56(0.23)	113780(73)
1400	129.73(0.05)	411.60(0.27)	321.15(0.23)	126620(77)
1500	132.14(0.04)	420.63(0.27)	327.48(0.24)	139720(80)

[a] Values in parenthesis are estimated uncertainties.

$\times 10^{-39}$ g cm^2, $I_c = 1.1109 \times 10^{-38}$ g cm^2, and $I_r = 6.407 \times 10^{-40}$ g cm^2, respectively.

Cossee and Schachtschneider[133] measured the infrared and Raman spectra of this compound and performed the normal-coordinate calculations for many of the isotopic species of acetone, acetaldehyde, and formaldehyde. Their complete set of 14 fundamental vibrational assignments were adopted in this work. The missing wavenumber, $\tilde{\nu}_{14}$, was assigned to be 670 cm^{-1} by Shimanouchi.[80]

The torsional wavenumber ($\tilde{\nu}_{15}$) has been reported to be 116 cm^{-1}.[80,133,139] The barrier height for internal rotation of CD_3 top was determined as: $V_3 = (4.60 \pm 0.29)$ and $V_6 = 0.372$ kJ mol^{-1} by Lin and Kilb;[140] $V_3 = (4.82 \pm 0.13)$ kJ mol^{-1} and $V_6 = 0.243$ kJ mol^{-1} by Kilb *et al.*;[129] $V_3 = (4.87 \pm 0.03)$ kJ mol^{-1} by Herschbach;[36] and $V_3 = (5.06 \pm 0.42)$ kJ mol^{-1} by Iijima and Tsuchiya.[141]

Based upon the selected $\tilde{\nu}_{\mathrm{tor}}$ of 116 cm^{-1} and our calculated F of 4.370 cm^{-1}, a value of $V_3 = 4.858$ kJ mol^{-1} was obtained for the CD_3 top internal rotation barrier height in the CD_3CDO molecule. To calculate the internal rotational contributions to the thermodynamic properties, 120 internal rotational energy levels (0 - 16000 cm^{-1}) were employed. Table 24 gives the calculated thermodynamic properties.

2.5.g. 1-Propanal

Butcher and Wilson[144] studied the microwave spectrum of 1-propanal (propionaldehyde, CH_3CH_2CHO) vapor in the frequency region 8–38 GHz and confirmed the existence of two stable rotational isomers, *cis* and *skew*. The *cis* isomer which has a planar CCCO skeleton is more stable by (3.77 ± 0.42) kJ mol^{-1}. The *skew* isomer is similar but has a dihedral angle of about 131° relative to the *cis*. Abraham and Pople,[145] using nuclear magnetic resonance, determined the enthalpy difference between *cis* and *trans* rotamers in liquid 1-propanal to be 4.18 kJ mol^{-1}, while from the temperature dependence of infrared band intensities, Sbrana and Schettino[146] determined this value as (4.31 ± 0.54) kJ mol^{-1}. The value of ϵ_0 in the liquid state is higher than that in the vapor.

The vibrational frequencies of propanal (g) were reported by Chermin,[142] Vasilév and Vvedenskii,[143] Worden,[151] and many others (see reference[143] for details). The Raman and infrared spectra of this compound in the liquid (at room temperature) and crystalline state (at −190 °C) were measured between 4000 and 100 cm^{-1} by Sbrana and Schettino.[146]

Pickett and Scroggin[152] studied the gas-phase microwave spectrum of the *skew* isomer. They observed several predicted transitions and confirmed the theoretical treatment for determining the energy level splitting (471.80 ± 0.07 MHz) of the two lowest levels of the *skew* propanal. This information was used for elucidating the internal rotation potential. Their results were compared with the other recent theoretical calculations.[153,154]

From measuring the relative intensities of microwave spectra, Aleksandrov and Tysovskii[484] derived the potential barrier (V_3) for the CH_3 and CHO tops as (10.8 ± 0.8) kJ mol^{-1} and (5.23 ± 0.42) kJ mol^{-1}.

The ideal gas thermodynamic properties of this compound have been reported by Chermin[142] and Vasilév and Vvedenskii.[143] The values of Chermin were adopted by Stull *et al.*[466] In Chermin's calculation the existence of *cis* and *trans* rotamers in 1-propanal vapor was not mentioned, and Vasilév and Vvedenskii only calculated the thermodynamic properties of the *cis* isomer. Frankiss[147] has recalculated the ideal gas thermodynamic properties for 1-propanal using new molecular data. His calculated values of $\{S°(T)-S°(0)\}$ and C_p° agree with the experimental results within the experimental uncertainty, as shown in Table A-14. Therefore, his calculated values were adopted. Frankiss employed the molecular structural parameters determined by Butcher and Wilson[144] from microwave spectroscopy for calculating $I_aI_bI_c$, I_r(-CH_3) and I_r(-CHO) for both the *cis* and *skew* isomers. The fundamental vibrational wavenumbers were obtained from the infrared and Raman spectra of 1-propanal.[150] Frankiss used a partition function, equivalent in principle to equation (16), to calculate the internal rotation contribution. He used the classical equation corrected for quantum effects[51] to calculate the $Q'_{q,ir}$ terms. The parameters he adopted are listed in Tables A-2 and A-3. His calculated thermodynamic functions for CH_3CH_2CHO (g) are listed in Table 25.

TABLE 24. Ideal gas thermodynamic properties of ethanal-d_4 (CD_3CDO) at 1 bar[a]
$M = 48.0778$

T/K	C_p°/J K^{-1} mol^{-1}	$\{S°(T)-S°(0)\}$/J K^{-1} mol^{-1}	$-\{G°(T)-H°(0)\}/T$/J K^{-1} mol^{-1}	$\{H°(T)-H°(0)\}$/J mol^{-1}
0	0	0	0	0
100	41.90(0.10)	220.49(0.24)	183.50(0.13)	3699(12)
150	46.25(0.08)	239.27(0.27)	198.94(0.17)	5900(16)
200	51.70(0.09)	252.30(0.28)	210.58(0.19)	8343(19)
273.15	61.24(0.10)	269.79(0.29)	224.15(0.22)	12468(23)
298.15	64.64(0.10)	275.30(0.30)	228.21(0.22)	14041(25)
300	64.89(0.10)	275.70(0.30)	228.50(0.22)	14161(25)
400	77.86(0.10)	296.18(0.31)	242.91(0.24)	21310(32)
500	89.21(0.09)	314.81(0.31)	255.45(0.26)	29678(39)
600	98.91(0.08)	331.95(0.32)	266.79(0.26)	39097(46)
700	107.08(0.08)	347.83(0.32)	277.25(0.27)	49408(52)
800	113.90(0.08)	362.59(0.33)	287.00(0.28)	60467(58)
900	119.55(0.07)	376.34(0.33)	296.18(0.28)	72149(64)
1000	124.24(0.07)	389.19(0.33)	304.84(0.29)	84346(69)
1100	128.12(0.06)	401.22(0.34)	313.06(0.29)	96970(74)
1200	131.36(0.06)	412.51(0.34)	320.88(0.30)	109950(79)
1300	134.06(0.05)	423.13(0.34)	328.34(0.30)	123220(83)
1400	136.33(0.05)	433.15(0.34)	335.48(0.30)	136750(87)
1500	138.26(0.04)	442.62(0.34)	342.31(0.30)	150480(91)

[a] Values in parenthesis are estimated uncertainties.

TABLE 25. Ideal gas thermodynamic properties of 1-propanal (CH_3CH_2CHO) at 1 bar[a]
$M = 58.0798$

$\frac{T}{K}$	$\frac{C_p^\circ}{J\ K^{-1}\ mol^{-1}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{J\ K^{-1}\ mol^{-1}}$	$\frac{-\{G^\circ(T)-H^\circ(0)\}/T}{J\ K^{-1}\ mol^{-1}}$	$\frac{\{H^\circ(T)-H^\circ(0)\}}{J\ mol^{-1}}$
0	0	0	0	0
273.15	77.50(0.10)	297.61(0.32)	240.81(0.22)	15520(29)
298.15	80.73(0.10)	304.51(0.32)	245.81(0.23)	17490(31)
300	80.98(0.10)	305.01(0.32)	246.21(0.23)	17640(31)
400	96.39(0.12)	330.21(0.33)	264.01(0.25)	26470(38)
500	112.90(0.12)	353.51(0.34)	279.61(0.27)	36930(46)
600	128.50(0.11)	375.51(0.35)	293.81(0.28)	49020(54)
700	142.60(0.11)	396.51(0.36)	307.01(0.29)	62590(63)
800	155.20(0.10)	416.41(0.36)	319.51(0.30)	77510(71)
900	166.40(0.09)	435.41(0.37)	331.41(0.30)	93590(79)
1000	176.30(0.08)	453.51(0.37)	342.71(0.31)	110700(86)
1100	185.10(0.08)	470.81(0.37)	353.71(0.31)	128800(93)
1200	192.90(0.07)	487.31(0.37)	364.11(0.32)	147800(99)
1300	199.80(0.07)	503.01(0.38)	374.21(0.32)	167400(105)
1400	206.10(0.06)	518.11(0.38)	384.01(0.33)	187700(110)
1500	211.70(0.06)	532.51(0.38)	393.51(0.33)	208600(115)

[a] Values in parenthesis are estimated uncertainties.

2.5.h. 1-Butanal

The molecular and spectroscopic constants for this compound were not available so the values of the thermodynamic properties presented in Table 26 were estimated. The thermodynamic properties of 1-butanal were computed by addition of the contributions due to the presence of the CH_2 group (see section 1.6) in the molecule to the corresponding values for 1-propanal which are listed in Table 25. Stull *et al.*[466] obtained the thermodynamic properties for this compound from Chermin.[142]

2.6. Alkanoic Acids

As a result of hydrogen bonding alkanoic (carboxylic) acid vapor shows significant departure from ideal gas behavior at low temperatures and/or under high pressures. Vapor density[238-247] and heat capacity[248,249] measurements suggest the existence of polymeric species in the vapor, particularly dimers.

Many spectroscopic studies have been made in order to determine the nature of the hydrogen bonding in the dimeric molecules of methanoic and ethanoic acids. The enthalpy of dimerization of methanoic (formic) acid has been found to range from 46.0 to 61.9 kJ mol^{-1}.[265] The enthalpy of dimerization of methanoic acid has been determined from the infrared spectra of the dimers as a function of temperature.[250-258] Ramsperger and Porter[259] used the ultraviolet absorption spectra to determine the dissociation energy of dimers to monomers. Su[260] obtained the dissociation energy of the dimers from an electron diffraction study of the effect of temperature on the molecular structure.

The infrared spectra of ethanoic acid dimers has been investigated by Weltner,[248] Herman and Hofstadter,[261] and many others.[251-256,263] Cosaro and Atkinson[264] using the ultrasonic absorption in CH_3COOH-CH_3COCH_3 mixtures, studied the rapid ethanoic acid dimerization reaction.

In view of the above experimental evidence, a molecular model of an equilibrium mixture of monomers and dimers was employed for evaluation of the ideal gas thermodynamic properties of both methanoic and ethanoic acids.

Employing recent molecular and spectroscopic constants, Chao and Zwolinski[265] evaluated the ideal gas thermodynamic properties of methanoic and ethanoic monomers, dimers, and their monomer-dimer equilibrium mixtures. The sources of input data and methods of calculation are briefly described below.

2.6.a. Methanoic Acid Monomer

Methanoic acid (formic acid) monomer (HCOOH) has two rotational isomers, *i.e. cis* and *trans*. In the *cis* form the hydrogen on -OH eclipses the oxygen. The molecular structure of the *cis* isomer has been investigated extensively by many researchers using microwave,[266-275] electron diffraction,[276-280] and infrared[281-283] spectroscopy. The existence of *trans* isomer in the vapor was mentioned by Coop *et al.*,[284] Williams,[281] and Mariner and Bleakney.[285] Hocking[498] reviewed the studies on the rotational isomerism in methanoic acid.

From spectroscopic studies and additional theoretical calculations, the *cis* isomer was found to be more stable than the *trans* isomer by from 5.0 to 39.5 kJ mol^{-1}.[265] Using microwave relative intensity measurements, Hocking[498] determined the energy difference between the ground vibrational states of *cis* and *trans*-HCOOH and found the *cis* rotamers to lie at a higher energy than the *trans* rotamers by (1365 ± 30) cm^{-1} or (16.33 ± 0.36) kJ mol^{-1}.

Based upon $\epsilon_0 = 8.37$ kJ mol^{-1} for the reaction: *cis*-HCOOH (g) = *trans*-HCOOH (g), the concentration of *trans*-HCOOH in the equilibrium mixture was calcu-

TABLE 26. Ideal gas thermodynamic properties of 1-butanal $\{CH_3(CH_2)_2CHO\}$ at 1 bar[a]
$M = 72.1066$

T K	C_p° J K^{-1} mol^{-1}	$\{S^\circ(T)-S^\circ(0)\}$ J K^{-1} mol^{-1}	$-\{G^\circ(T)-H^\circ(0)\}/T$ J K^{-1} mol^{-1}	$\{H^\circ(T)-H^\circ(0)\}$ J mol^{-1}
0	0	0	0	0
273.15	98.63(0.10)	334.93(0.32)	263.45(0.22)	19528(29)
298.15	103.36(0.10)	343.67(0.32)	269.78(0.23)	22046(31)
300	103.74(0.10)	344.38(0.32)	270.27(0.23)	22238(31)
400	125.55(0.12)	377.03(0.33)	292.84(0.25)	33666(38)
500	147.80(0.12)	407.44(0.34)	312.75(0.27)	47348(46)
600	168.04(0.11)	436.22(0.35)	330.96(0.28)	63162(54)
700	185.78(0.11)	463.62(0.36)	348.01(0.29)	80874(63)
800	201.31(0.10)	489.50(0.36)	364.15(0.30)	100270(71)
900	214.81(0.09)	514.07(0.37)	379.53(0.30)	121080(79)
1000	226.51(0.08)	537.36(0.37)	394.13(0.31)	143130(86)
1100	236.98(0.08)	559.51(0.37)	408.10(0.31)	166460(93)
1200	246.04(0.07)	580.61(0.37)	421.85(0.32)	190480(99)
1300	254.19(0.07)	600.50(0.38)	434.88(0.32)	215520(105)
1400	261.33(0.06)	619.78(0.38)	447.19(0.33)	241260(110)
1500	268.18(0.06)	637.95(0.38)	459.62(0.33)	268010(115)

[a] Values in parenthesis are estimated uncertainties.

lated by Fukushima *et al.*[286] as 2.8% at 298.15 K and 23.7% at 1000 K, respectively. Assuming $\epsilon_0 = 16.74$ kJ mol^{-1} for that reaction, the *trans* isomer concentrations in the vapor mixture were evaluated as 0.1% at 298.15 K and 9.0% at 1000 K. From microwave spectroscopy, Lide[287] estimated the minimum possible value of ϵ_0 to be 16.74 kJ mol^{-1}. From the foregoing, the thermodynamic properties of the equilibrium *cis-trans* mixture are not significantly different from those of the pure *cis* form. Therefore, for the calculation of the ideal gas thermodynamic properties of HCOOH (g), the molecular structure of this compound was taken to be the *cis* form.

Many experimental determinations on the molecular structure of methanoic acid have been reported in the literature. However, only a few results agree. In this work, the rotational constants obtained from microwave spectroscopy by Willemot *et al.*[499] were selected to calculate the value of $I_aI_bI_c$, as shown in Table A-2.

Rotational spectra of the methanoic acid monomer have been studied by numerous investigators[281,288–292] and reviewed by Willemot *et al.*,[499] and the fundamental vibrational frequencies for this species have been assigned.[289–293] Several normal coordinate treatments[262,286,294–299] have been made. In this work, the vibrational assignments of Millikan and Pitzer[293] and Miyazawa and Pitzer[262] were used for evaluation of the vibrational contributions to the thermodynamic properties.

The internal rotational potential function, (V), for the OH rotor in the HCOOH (g) molecule has been suggested by Radom *et al.*[300] as $V = 1/2[V_1(1 - \cos\theta) + V_2(1 - \cos 2\theta) + V_3(1 - \cos 3\theta)]$ where θ = angle of internal rotation, $V_1 = 24.06$, $V_2 = 37.36$, and $V_3 = 2.301$ kJ mol^{-1}. Based upon this potential function and a calculated value of $F = 24.96$ cm^{-1}, derived from the molecular structural parameters of Bellet *et al.*,[266] we generated sixty internal rotational energy levels (0 to 24800 cm^{-1}) for evaluation of the internal rotational contributions to the thermodynamic properties of methanoic acid vapor. These represent both *cis* and *trans* forms.

The reported torsional wavenumber of the OH rotor in the HCOOH molecule varies from 452 to 695 cm^{-1} and the barrier height from 41.84 to 71.13 kJ mol^{-1}.[265] Our adopted potential curve indicated that the *cis* isomer was more stable than the *trans* isomer by 26.36 kJ mol^{-1} and the potential maximum was 51.04 kJ mol^{-1} at θ = 97° from the *cis* position. The barrier height of the OH rotor in HCOOH (g) was estimated to be 45.61 kJ mol^{-1} by Miyazawa and Pitzer[262] and was recalculated to be 55.23 kJ mol^{-1} by Bernitt *et al.*[301] using data of reference 262.

The thermodynamic properties given in Table 27 for methanoic acid monomer were calculated using the molecular constants listed in Tables A-2 and A-3. Our calculated C_p° values are higher than those reported by Green.[302] The C_p° and $\{S^\circ(T)-S^\circ(0)\}$ values of Green are smaller than ours by 1.0% and 0.06% at 298.15 K, and by 6.6% and 0.94% at 1000 K, respectively. Our C_p° values are lower than the values of Waring[303] below 550 K and are higher than his values at higher temperatures. The differences at 298.15 K and 1500 K are −6.6% and 4.8%, respectively. There are no experimental C_p° data available for direct comparison. Our calculated $\{S^\circ(298.15\text{ K})-S^\circ(0)\}$ agrees with the reported third-law values, (248.70 ± 0.42) J K^{-1} mol^{-1} [303] and (248.11 ± 1.26) J K^{-1} mol^{-},[323] respectively. Ideal gas thermodynamic properties of methanoic acid have been calculated by Green[302] using the available molecular constants. His results were adopted by Stull *et al.*[466]

2.6.b. Methanoic Acid Dimer

Pauling and Brockway,[304] using electron diffraction, suggested the molecular structure of this species, $(HCOOH)_2$, to be a planar ring with a D_{2h} symmetry.

TABLE 27. Ideal gas thermodynamic properties of methanoic acid monomer (HCOOH) at 1 bar[a]
$M = 46.0256$

T / K	C_p° / J K^{-1} mol^{-1}	$\{S^\circ(T)-S^\circ(0)\}$ / J K^{-1} mol^{-1}	$-\{G^\circ(T)-H^\circ(0)\}/T$ / J K^{-1} mol^{-1}	$\{H^\circ(T)-H^\circ(0)\}$ / J mol^{-1}
0	0	0	0	0
100	33.44(0.01)	208.29(0.01)	175.01(0.01)	3328(0)
150	34.91(0.04)	222.07(0.01)	188.54(0.01)	5030(1)
200	37.83(0.06)	232.48(0.03)	198.27(0.01)	6843(4)
273.15	43.54(0.07)	245.09(0.05)	209.17(0.02)	9812(9)
298.15	45.68(0.07)	248.99(0.05)	212.34(0.02)	10927(10)
300	45.84(0.07)	249.28(0.05)	212.57(0.02)	11012(10)
400	54.52(0.08)	263.66(0.07)	223.58(0.03)	16032(18)
500	62.63(0.07)	276.71(0.09)	232.92(0.04)	21897(24)
600	69.81(0.07)	288.78(0.10)	241.23(0.05)	28527(31)
700	76.04(0.06)	300.02(0.10)	248.84(0.05)	35827(36)
800	81.34(0.06)	310.53(0.11)	255.90(0.06)	43704(42)
900	85.77(0.05)	320.37(0.12)	262.52(0.07)	52066(46)
1000	89.40(0.05)	329.61(0.12)	268.77(0.07)	60831(51)
1100	92.33(0.04)	338.27(0.12)	274.70(0.08)	69923(55)
1200	94.65(0.04)	346.41(0.13)	280.34(0.08)	79276(58)
1300	96.48(0.04)	354.06(0.13)	285.72(0.08)	88837(61)
1400	97.91(0.04)	361.26(0.13)	290.86(0.09)	98559(64)
1500	99.02(0.03)	368.06(0.13)	295.78(0.09)	108410(67)

[a] Values in parenthesis are estimated uncertainties.

However, later studies using similar techniques[277,280,305] showed its molecular structure to be of C_{2h} symmetry.

We adopted the molecular parameters reported by Almenningen *et al.*[277] for calculating the three principal moments of inertia for methanoic acid dimer as: $I_a = 1.3615 \times 10^{-38}$ g cm^2, $I_b = 3.7724 \times 10^{-38}$ g cm^2, and $I_c = 5.1340 \times 10^{-38}$ g cm^2.

The fundamental vibrational assignments were determined by numerous researchers from a study of its infrared[250-252,292,306-317] and Raman[318,319] spectra. Using a rigid monomer model, Miyazawa and Pitzer[320] made a normal coordinate treatment of the low frequency vibrations of the dimer. A normal coordinate treatment of out-of-plane vibrations of this species was performed by them[262] using the results of the infrared spectra of four isotopic species of methanoic acid measured in the vapor phase as well as in the solid nitrogen matrix in the region 400–800 cm^{-1}. A normal coordinate analysis of the dimeric species has also been made by Kishida and Nakamoto,[321] using the spectral data of Millikan and Pitzer[250] and Bonner and Kirby-Smith.[319]

Alfheim *et al.*[322] employed the best available assignments of fundamental vibrational frequencies and performed a complete normal coordinate analysis of the $(HCOOH)_2$ (g) molecule. Their calculated values agreed well with the experimentally observed ones.[250,251,318-320] Therefore, the complete set of fundamental vibrational assignments reported by Alfeim *et al.* was adopted.

The thermodynamic properties of methanoic acid dimer (g) were calculated using the molecular constants as listed in Table A-2 and the results are presented in Table 28. The statistically calculated entropy at 298.15 K for methanoic acid dimer (g) was given as 348.74 J K^{-1} mol^{-1} by Waring[303] and 346.81 J K^{-1} mol^{-1} by Green,[302] while our recommended value is 332.67 J K^{-1} mol^{-1} at 1 atm.

2.6.c. Methanoic Acid Equilibrium Mixture

The thermodynamic properties of methanoic acid were calculated using a molecular model of an equilibrium mixture of monomers and dimers. Using a selected enthalpy of dimerization $\Delta_r H^\circ(0) = -61.59$ kJ mol^{-1} [265] and the calculated $\{H^\circ(T)-H^\circ(0)\}$, $\{S^\circ(T)-S^\circ(0)\}$ and C_p° for HCOOH (g) and $(HCOOH)_2$, (g), we calculated the ideal gas thermodynamic properties for the methanoic acid equilibrium mixture over the temperature from 50 to 1000 K and at 1 bar as shown in Table 29. Our calculations showed that at room temperature and atmospheric pressure the methanoic acid vapor contained 95% dimers. For evaluation of the thermodynamic properties of methanoic acid vapor, the presence of dimeric species in the vapor should not be ignored. The calculated equilibrium constants for dimerization are consistent with those reported by Coolidge[345] from vapor density measurements.

The values presented in Table 29 were evaluated based upon formation of the mixture from one mole of methanoic acid monomer. From our calculations,[265] the acid vapor contained pure dimers (0.5 mole) at temperatures below 200 K. As the temperature increases, some of the dimers decompose into monomers. This decomposition reaction approaches completion when the temperature reaches 700 K at 1 bar. If $P = 5$ bar, this decomposition temperature is 800 K and when $P = 0.1$ bar, all dimers decompose into monomers at $T = 600$ K.

TABLE 28. Ideal gas thermodynamic properties of methanoic acid dimer $\{(HCOOH)_2\}$ at 1 bar[a]
$M = 92.0512$

$\frac{T}{K}$	$\frac{C_p^\circ}{J\,K^{-1}\,mol^{-1}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{J\,K^{-1}\,mol^{-1}}$	$\frac{-\{G^\circ(T)-H^\circ(0)\}/T}{J\,K^{-1}\,mol^{-1}}$	$\frac{\{H^\circ(T)-H^\circ(0)\}}{J\,mol^{-1}}$
0	0	0	0	0
100	57.33(0.21)	252.17(0.48)	208.81(0.30)	4336(20)
150	68.03(0.15)	277.53(0.53)	227.66(0.37)	7481(27)
200	77.43(0.12)	298.40(0.55)	242.80(0.41)	11119(33)
273.15	91.32(0.10)	324.58(0.57)	261.28(0.45)	17288(38)
298.15	96.14(0.10)	332.78(0.57)	266.94(0.46)	19632(40)
300	96.50(0.10)	333.38(0.57)	267.34(0.46)	19810(40)
400	115.23(0.11)	363.74(0.58)	287.72(0.49)	30408(47)
500	131.80(0.11)	391.28(0.59)	305.72(0.51)	42781(54)
600	145.72(0.11)	416.58(0.59)	322.11(0.52)	56679(61)
700	157.28(0.10)	439.94(0.60)	337.30(0.53)	71846(69)
800	166.93(0.09)	461.59(0.60)	351.50(0.54)	88071(76)
900	175.04(0.08)	481.73(0.60)	364.86(0.55)	105180(82)
1000	181.91(0.08)	500.54(0.61)	377.50(0.55)	123040(88)
1100	187.76(0.07)	518.16(0.61)	389.49(0.56)	141530(94)
1200	192.76(0.06)	534.71(0.61)	400.91(0.56)	160560(99)
1300	197.05(0.06)	550.32(0.61)	411.81(0.56)	180060(104)
1400	200.74(0.05)	565.06(0.61)	422.24(0.57)	199950(108)
1500	203.94(0.05)	579.02(0.61)	432.23(0.57)	220190(112)

[a] Values in parenthesis are estimated uncertainties.

TABLE 29. Ideal gas thermodynamic properties of methanoic acid monomer–dimer equilibrium mixture $\{HCOOH–(HCOOH)_2\}$ at 1 bar[a]
$M = 46.0256$

$\frac{T}{K}$	$\frac{C_p^\circ}{J\,K^{-1}\,mol^{-1}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{J\,K^{-1}\,mol^{-1}}$	$\frac{-\{G^\circ(T)-H^\circ(0)\}/T}{J\,K^{-1}\,mol^{-1}}$	$\frac{\{H^\circ(T)-H^\circ(0)\}}{J\,mol^{-1}}$
0	0	0	0	0
100	28.66(0.21)	126.14(0.48)	104.47(0.30)	2167(20)
150	34.02(0.15)	138.82(0.53)	113.89(0.37)	3740(27)
200	38.86(0.12)	149.26(0.55)	121.45(0.41)	5562(33)
273.15	58.96(0.10)	163.36(0.57)	130.76(0.45)	8903(38)
298.15	84.15(0.10)	169.48(0.57)	133.74(0.46)	10655(40)
300	86.81(0.10)	170.01(0.57)	133.96(0.46)	10814(40)
400	343.17(0.11)	232.02(0.58)	149.27(0.49)	33099(47)
500	83.72(0.11)	275.02(0.59)	171.42(0.51)	51800(54)
600	71.47(0.11)	288.24(0.59)	189.91(0.52)	58997(61)
700	76.80(0.10)	299.47(0.60)	204.84(0.53)	66239(69)
800	82.19(0.09)	309.90(0.60)	217.40(0.54)	74000(76)
900	86.83(0.08)	319.67(0.60)	228.30(0.55)	82227(82)
1000	90.68(0.08)	328.83(0.61)	237.97(0.55)	90851(88)

[a] Values in parenthesis are estimated uncertainties.

2.6.d. Methanoic Acid-d_1

Willemot *et al.*[499] determined the rotational constants for this compound (*cis*-HCOOD) from microwave spectroscopy, and these values were adopted for computing $I_aI_bI_c$.

The infrared spectra of four isotopic species of methanoic acid, *i.e.* HCOOH, HCOOD, DCOOH, and DCOOD, were measured in the vapor phase by Millikan and Pitzer[293] and Miyazawa and Pitzer.[262] They assigned nine fundamental vibrational frequencies for the four *cis* isomers and two *trans* isomers. Incomplete frequency assignments were reported for the other two *trans* isomers (HCOOD and DCOOD).

Fukushima *et al.*[286] selected the fundamental frequencies of monomeric methanoic acid and its deutero-analogs by the product rule. On the basis of the selected frequencies and recent molecular structural parameters, they performed a normal coordinate treatment for in-plane and out-of-plane vibrations.

Because methanoic acid vapor contained predominantly *cis* isomers, we assumed that this was also true for its deutero-analogs. Therefore, we only considered the *cis* isomer for the evaluation of the thermodynamic properties of methanoic acid-d_1.

To calculate the vibrational contributions to the thermodynamic properties of this compound, the vibrational assignments, ν_1 to ν_8, reported by Fukushima *et al.*[286] were used.

The internal rotation potential function for the OD rotor in the *cis*-HCOOD molecule was adopted from that for the OH rotor in the HCOOH molecule. The value of I_r was calculated from the molecular structural parameters given by Bellet *et al.*[266] Sixty internal rotational energy levels were generated for calculating the internal rotational contributions. The calculated OD torsional wavenumber, 483 $\mathrm{cm^{-1}}$, was in fair agreement with that reported, 508 $\mathrm{cm^{-1}}$.[262] Using the selected molecular constants listed in Tables A-2 and A-3, the thermodynamic properties of methanoic acid-d_1 were calculated and are presented in Table 30.

2.6.e. Methanoic Acid-d_1

For computing the thermodynamic properties of (*cis*-DCOOH), the molecular and spectroscopic constants were obtained from the same sources as those for the *cis*-HCOOD molecule. Their numerical values are listed in Tables A-2 and A-3. Based upon the same potential function as that for OH rotor in HCOOH molecule and a calculated $F = 23.76\ \mathrm{cm^{-1}}$, we generated forty-eight internal rotational energy levels (0 to 16000 $\mathrm{cm^{-1}}$). The calculated OH torsional wavenumber of 595 $\mathrm{cm^{-1}}$ is in fair agreement with the value 629 $\mathrm{cm^{-1}}$ reported by Miyazawa and Pitzer.[262] The evaluated results are presented in Table 31.

2.6.f. Methanoic Acid-d_2

The $I_aI_bI_c$ for *cis*-DCOOD was calculated from the rotational constants determined from the rotational spectrum by Bellet *et al.*[266] The sources of additional molecular and spectroscopic data and the method of calculating the ideal gas thermodynamic properties of methanoic acid-d_2 were the same as those for the above deuterated methanoic acids. Based upon the selected potential function and a calculated F value, as listed in Table A-3, sixty internal rotational energy levels (0 to 15000 $\mathrm{cm^{-1}}$) were generated for computing the internal rotational contributions to the thermodynamic properties of DCOOD (g) caused by the presence of a OD rotor. The OD torsional wavenumber was calculated to be 464 $\mathrm{cm^{-1}}$, compared with the experimental value of 491 $\mathrm{cm^{-1}}$.[262] Using the selected molecular constants, the thermodynamic properties for methanoic acid-d_2 presented in Table 32 were calculated.

2.6.g. Ethanoic Acid Monomer

The molecular structure of ethanoic (acetic) acid monomer (CH_3COOH) has been studied by electron diffraction[280,324,325] and microwave spectroscopy.[326-328,500,501] The *cis*-ethanoic acid was reported to be more stable than the *trans*-ethanoic acid by from 34.7 to 45.6 kJ $\mathrm{mol^{-1}}$.[331]

Krisher and Saegebarth[328] have determined the rotational constants from microwave spectroscopy. Their results were confirmed by van Eijck *et al.*[501] and were adopted in this work for calculating $I_aI_bI_c$, as given in Table A-2. Using the principal axis method, extended to include terms through $n = 6$ in the perturbation series,[329] they identified 30 new E-type transitions.

The internal rotational barrier height V_3 of the CH_3 rotor was reported by numerous investigators to be from 1.67 to 3.68 kJ $\mathrm{mol^{-1}}$.[265] The values of $V_3 = (2.02 \pm 0.11)$ kJ $\mathrm{mol^{-1}}$ determined by Tabor[327] by microwave spectroscopy, (2.012 ± 0.004) kJ $\mathrm{mol^{-1}}$ by Krisher and Saegebarth,[328] and 2.008 kJ $\mathrm{mol^{-1}}$ by Chadwick and Katrib[330] are in good agreement and appeared to be more reliable than the others.

TABLE 30. Ideal gas thermodynamic properties of methanoic acid-d_1 (HCOOD) at 1 bar[a]
$M = 47.0318$

T/K	C_p°/J K^{-1} mol^{-1}	$\{S^\circ(T)-S^\circ(0)\}$/J K^{-1} mol^{-1}	$-\{G^\circ(T)-H^\circ(0)\}/T$/J K^{-1} mol^{-1}	$\{H^\circ(T)-H^\circ(0)\}$/J mol^{-1}
0	0	0	0	0
100	33.82(0.02)	209.57(0.02)	176.23(0.02)	3333(0)
150	36.28(0.06)	223.69(0.03)	189.83(0.02)	5078(2)
200	39.92(0.07)	234.60(0.04)	199.70(0.02)	6980(6)
273.15	46.07(0.07)	247.94(0.06)	210.88(0.03)	10122(11)
298.15	48.25(0.07)	252.07(0.07)	214.17(0.03)	11301(13)
300	48.41(0.07)	252.37(0.07)	214.40(0.03)	11390(13)
400	57.00(0.07)	267.48(0.09)	225.82(0.04)	16665(19)
500	64.94(0.07)	281.07(0.10)	235.53(0.05)	22769(26)
600	72.04(0.07)	293.55(0.11)	244.17(0.06)	29625(32)
700	78.29(0.06)	305.13(0.12)	252.07(0.07)	37148(37)
800	83.65(0.06)	315.95(0.12)	259.38(0.07)	45253(42)
900	88.13(0.05)	326.07(0.13)	266.24(0.08)	53849(47)
1000	91.78(0.05)	335.55(0.13)	272.70(0.08)	62851(51)
1100	94.70(0.05)	344.44(0.13)	278.82(0.09)	72181(55)
1200	96.97(0.04)	352.78(0.14)	284.64(0.09)	81770(59)
1300	98.73(0.04)	360.62(0.14)	290.19(0.10)	91559(62)
1400	100.07(0.04)	367.98(0.14)	295.48(0.10)	101500(65)
1500	101.08(0.03)	374.92(0.14)	300.55(0.10)	111560(68)

[a] Values in parenthesis are estimated uncertainties.

TABLE 31. Ideal gas thermodynamic properties of methanoic acid-d_1 (DCOOH) at 1 bar[a]
$M = 47.0318$

$\frac{T}{\text{K}}$	$\frac{C_p^\circ}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{-\{G^\circ(T)-H^\circ(0)\}/T}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{\{H^\circ(T)-H^\circ(0)\}}{\text{J mol}^{-1}}$
0	0	0	0	0
100	33.47(0.01)	209.97(0.01)	176.69(0.01)	3328(0)
150	35.17(0.04)	223.80(0.02)	190.23(0.01)	5036(1)
200	38.66(0.07)	234.36(0.03)	199.98(0.01)	6875(4)
273.15	45.42(0.08)	247.38(0.05)	210.97(0.02)	9944(9)
298.15	47.87(0.08)	251.46(0.06)	214.20(0.02)	11110(11)
300	48.05(0.08)	251.76(0.06)	214.43(0.02)	11199(12)
400	57.51(0.08)	266.90(0.08)	225.69(0.03)	16484(20)
500	65.92(0.08)	280.66(0.10)	235.33(0.04)	22665(27)
600	73.20(0.07)	293.33(0.11)	243.95(0.05)	29630(34)
700	79.41(0.07)	305.10(0.12)	251.86(0.06)	37268(40)
800	84.63(0.06)	316.05(0.12)	259.20(0.07)	45478(46)
900	88.93(0.05)	326.28(0.13)	266.09(0.07)	54164(51)
1000	92.39(0.05)	335.83(0.13)	272.60(0.08)	63236(55)
1100	95.13(0.04)	344.77(0.13)	278.76(0.08)	72617(59)
1200	97.26(0.04)	353.14(0.14)	284.61(0.09)	82241(63)
1300	98.90(0.04)	361.00(0.14)	290.19(0.09)	92053(66)
1400	100.14(0.04)	368.37(0.14)	295.51(0.09)	102010(69)
1500	101.09(0.03)	375.32(0.14)	300.60(0.10)	112070(72)

[a] Values in parenthesis are estimated uncertainties.

TABLE 32. Ideal gas thermodynamic properties of methanoic acid-d_2 (DCOOD) at 1 bar[a]
$M = 48.0380$

$\frac{T}{\text{K}}$	$\frac{C_p^\circ}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{-\{G^\circ(T)-H^\circ(0)\}/T}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{\{H^\circ(T)-H^\circ(0)\}}{\text{J mol}^{-1}}$
0	0	0	0	0
100	33.91(0.02)	211.13(0.03)	177.78(0.03)	3335(0)
150	36.66(0.06)	225.33(0.04)	191.39(0.03)	5091(3)
200	40.89(0.08)	236.43(0.05)	201.31(0.03)	7026(6)
273.15	48.09(0.08)	250.23(0.07)	212.61(0.04)	10277(12)
298.15	50.58(0.08)	254.55(0.08)	215.94(0.04)	11510(14)
300	50.76(0.08)	254.86(0.08)	216.18(0.04)	11604(14)
400	60.12(0.08)	270.77(0.10)	227.88(0.05)	17158(21)
500	68.33(0.08)	285.09(0.11)	237.91(0.06)	23589(29)
600	75.51(0.07)	298.20(0.12)	246.88(0.07)	30789(35)
700	81.72(0.06)	310.32(0.13)	255.09(0.08)	38658(41)
800	86.99(0.06)	321.58(0.14)	262.71(0.08)	47102(47)
900	91.33(0.06)	332.09(0.14)	269.84(0.09)	56025(51)
1000	94.81(0.05)	341.90(0.15)	276.56(0.10)	65339(56)
1100	97.52(0.05)	351.07(0.15)	282.92(0.10)	74962(60)
1200	99.60(0.04)	359.65(0.15)	288.96(0.10)	84823(64)
1300	101.17(0.04)	367.69(0.15)	294.71(0.11)	94865(67)
1400	102.32(0.04)	375.23(0.15)	300.20(0.11)	105040(70)
1500	103.16(0.03)	382.32(0.16)	305.44(0.11)	115320(73)

[a] Values in parenthesis are estimated uncertainties.

We selected the I_r and V_3 values determined by Krisher and Saegebarth[328] for calculating the internal rotational contributions of the CH_3 top in CH_3COOH (g). The torsional wavenumber (0 → 1) of the CH_3 top was calculated to be (75 ± 1) cm^{-1} (see Table A-3).

The potential function $V = 1/2[V_1(1 - \cos\theta) + V_2(1 - \cos 2\theta) + V_3(1 - \cos 3\theta)]$ with $V_1 = 24.06$, $V_2 = 37.36$, and $V_3 = 2.301$ kJ mol^{-1}, suggested for an OH rotor in HCOOH (g) by Radom *et al.*,[300] was used. The molecular structural parameters of Derissen[325] were employed to calculate the value $I_r = 1.317 \times 10^{-40}$ g cm^2. Based upon the selected V and calculated I_r, sixty internal rotational energy levels (0 to 21500 cm^{-1}) were generated. The OH torsional wavenumber (0 → 1) was 565 cm^{-1}.

The internal rotational contributions of the CH_3 and OH rotors were evaluated separately. The results of these two rotors were added to yield the total internal rotational contributions.

The infrared vibrational spectra of ethanoic acid vapor were reported by Sverdlov,[318] Weltner,[248] Wilmshurst,[332] and Haurie and Novak.[333] Recently, Shimanouchi[80] critically reviewed the vibrational spectra data and assigned a complete set of fundamental vibrational wavenumbers. His assignments were adopted for evaluating the vibrational contributions to the thermodynamic properties of CH_3COOH (g).

Using the molecular constants listed in Tables A-2 and A-3, we computed the ideal gas thermodynamic properties of ethanoic acid monomer, which are given in Table 33. The third law entropy (g, 298.15 K) was reported as 282.84 J K^{-1} mol^{-1} by Weltner.[248] The statistical value was calculated to be (296.2 ± 4.2) J K^{-1} mol^{-1} by Halford,[340] and 282.50 J K^{-1} mol^{-1} by Weltner,[248] respectively. Our value was 283.34 J K^{-1} mol^{-1} at 1 atm. The thermodynamic properties given in Stull *et al.*[466] were obtained from W. Weltner (private communication).

2.6.h. Ethanoic Acid Dimer

Ramsey and Young[242,339] measured the vapor pressures and vapor densities of ethanoic acid and showed that it was associated in the vapor state. The association of ethanoic acid vapor by hydrogen bonding was first suggested by Latimer and Rodebush[344] and was later verified by Pauling and Brockway[304] from electron diffraction measurements. Because of the importance of the dimer species in ethanoic acid vapor, its thermodynamic properties were evaluated.

The molecular structure of ethanoic acid dimer, $(CH_3COOH)_2$, has been elucidated by Derissen[325] and Karle and Brockway[280] by the electron diffraction method. This molecule, similar to the methanoic acid dimer, has two hydrogen bonds. It has, in addition, two methyl rotors.

From the molecular structural parameters determined by Derissen,[325] the three principal moments of inertia were calculated to be $I_a = 1.5049 \times 10^{-38}$ g cm^2, $I_b = 9.6817 \times 10^{-38}$ g cm^2, and $I_c = 1.1078 \times 10^{-37}$ g cm^2. The reduced moment of the CH_3 top was 5.221×10^{-40} g cm^2. The potential function was taken to be $V = \frac{1}{2}V_3(1 - \cos 3\theta)$, where $V_3 = 2.013$ kJ mol^{-1}, for each of the two identical CH_3 tops. Using the selected V_3 with a calculated F of 5.361 cm^{-1}, we generated 108 internal rotational energy levels (0 to 15000 cm^{-1}) for each CH_3 rotor.

The vibrational spectra of $(CH_3COOH)_2$ (g) have been analyzed from infrared,[248,250,311,315,332,334,335,342] far infrared,[251,252] near infrared,[256] and Raman[343] spectroscopy measurements. Incomplete vibrational assignments were reported. Normal coordinate treatment of this compound has been made by Fukushima and Zwolinski[336] and Kishida and Nakamoto.[321] The vibrational assignments of Haurie and Novak[333] and Weltner[248] were adopted in this work. Seven missing values were taken from reference 336. The numerical values of the selected 40 fundamental assignments are listed in Table A-2.

The torsional wavenumber (0 → 1) for each CH_3 top was obtained as 74 cm^{-1} from our internal rotation energy level calculation. Fukushima and Zwolinksi[336] reported the torsional wavenumber $\tilde{\nu}_{33} = \tilde{\nu}_{42} = 100$ cm^{-1}. Table 34 presents the calculated results for ethanoic acid dimer.

The third law entropy of ethanoic acid dimer at 298.15 K was determined as 410.87 J K^{-1} mol^{-1} by Weltner;[248] while the statistical entropy was calculated to be 416.73 J K^{-1} mol^{-1} by Halford[340] and 403.50 J K^{-1} mol^{-1} by Weltner,[248] respectively. We obtain 414.28 J K^{-1} mol^{-1} at 1 atm.

TABLE 33. Ideal gas thermodynamic properties of ethanoic acid monomer (CH_3COOH) at 1 bar[a]
$M = 60.0524$

T/K	C_p°/J K^{-1} mol^{-1}	$\{S^\circ(T)-S^\circ(0)\}$/J K^{-1} mol^{-1}	$-\{G^\circ(T)-H^\circ(0)\}/T$/J K^{-1} mol^{-1}	$\{H^\circ(T)-H^\circ(0)\}$/J mol^{-1}
0	0	0	0	0
100	40.42(0.08)	231.74(0.41)	193.70(0.25)	3804(16)
150	42.74(0.06)	248.44(0.43)	209.33(0.31)	5867(18)
200	48.34(0.09)	261.44(0.44)	220.78(0.34)	8133(20)
273.15	59.38(0.10)	278.09(0.45)	233.94(0.37)	12062(24)
298.15	63.44(0.11)	283.47(0.45)	237.86(0.37)	13597(26)
300	63.74(0.11)	283.86(0.45)	238.15(0.37)	13715(26)
400	79.66(0.11)	304.41(0.46)	252.17(0.39)	20894(33)
500	93.93(0.11)	323.75(0.46)	264.57(0.41)	29590(41)
600	106.18(0.10)	341.99(0.47)	275.97(0.41)	39612(50)
700	116.63(0.09)	359.16(0.47)	286.64(0.42)	50766(59)
800	125.50(0.08)	375.33(0.47)	296.73(0.43)	62885(67)
900	132.99(0.07)	390.56(0.48)	306.32(0.43)	75820(74)
1000	139.26(0.07)	404.91(0.48)	315.46(0.44)	89442(80)
1100	144.46(0.06)	418.43(0.48)	324.22(0.44)	103640(87)
1200	148.76(0.06)	431.19(0.48)	332.60(0.44)	118300(92)
1300	152.30(0.06)	443.24(0.48)	340.66(0.45)	133360(97)
1400	155.22(0.05)	454.64(0.49)	348.39(0.45)	148740(102)
1500	157.63(0.05)	465.43(0.49)	355.84(0.45)	164390(106)

[a] Values in parenthesis are estimated uncertainties.

2.6.i. Ethanoic Acid Equilibrium Mixture

The experimental vapor density of ethanoic acid suggests the presence of dimers,[240,241,243,248,253,254,337] trimers,[245] and tetramers.[244] In this work, we assumed the vapor contained monomers and dimers only. The ideal gas enthalpy, entropy, and heat capacity data for CH_3COOH (g) and $(CH_3COOH)_2$ (g) were obtained from Tables 25 and 26, respectively. The enthalpy of dimerization ($\Delta_r H$) was adjusted so that the calculated C_p° values for the monomer-dimer equilibrium mixture agreed with the experimental values at various temperatures.

The enthalpies of dimerization of ethanoic acid were determined as (57.7 ± 0.4) to (68.6 ± 3.4) kJ mol^{-1} (298–483 K; 0.667–153.32 kPa) from vapor density measurements, 47.7 to 71.1 kJ mol^{-1} by infrared spectroscopic method, and 63.0 ± 0.21 kJ mol^{-1} derived from calculation.[265] Using trial and error, we found that the value $\Delta_r H = -64.02$ kJ mol^{-1} at 0 K was optimal. Table A-20 compares the observed and calculated heat capacities of ethanoic acid (g). The evaluated thermodynamic properties of ethanoic acid are listed in Table 35.The average deviations are 1.0% at P/bar = 0.332, 1.5% at P/bar = 0.626, and 1.9% at 1 bar.

Based upon our calculated values of $\{S^\circ(400\ K) - S^\circ(0)\}$ for ethanoic acid monomers and dimers, the entropy of dimerization was derived as -149.54 J K^{-1} mol^{-1} which is consistent with the experimental value of (-153.9 ± 6.3) J K^{-1} mol^{-1} by Slutsky and Bauer[341] and Taylor.[246] This confirms that our molecular model used for calculating the ideal gas thermodynamic properties of ethanoic acid is adequate.

TABLE 34. Ideal gas thermodynamic properties of ethanoic acid dimer $\{(CH_3COOH)_2\}$ at 1 bar[a]
$M = 120.1048$

$\frac{T}{K}$	$\frac{C_p^\circ}{J\ K^{-1}\ mol^{-1}}$	$\frac{\{S^\circ(T)\ \ S^\circ(0)\}}{J\ K^{-1}\ mol^{-1}}$	$\frac{\{G^\circ(T)\ \ H^\circ(0)\}/T}{J\ K^{-1}\ mol^{-1}}$	$\frac{\{H^\circ(T)-H^\circ(0)\}}{J\ mol^{-1}}$
0	0	0	0	0
100	86.38(0.28)	299.65(1.22)	236.09(0.78)	6356(44)
150	96.44(0.18)	336.56(1.28)	263.73(0.94)	10923(53)
200	108.43(0.17)	365.89(1.31)	285.71(1.03)	16035(59)
273.15	129.50(0.17)	402.72(1.32)	312.22(1.10)	24718(66)
298.15	137.25(0.17)	414.39(1.33)	320.30(1.12)	28052(68)
300	137.83(0.17)	415.24(1.33)	320.88(1.12)	28307(69)
400	168.63(0.18)	459.16(1.34)	350.04(1.17)	43648(78)
500	196.49(0.17)	499.87(1.35)	375.98(1.21)	61944(88)
600	219.96(0.16)	537.83(1.35)	399.83(1.23)	82801(99)
700	239.62(0.15)	573.26(1.36)	422.11(1.25)	105810(110)
800	256.19(0.14)	606.37(1.36)	443.99(1.26)	130620(120)
900	270.27(0.12)	637.38(1.36)	462.98(1.27)	156960(130)
1000	282.29(0.11)	666.49(1.37)	481.89(1.28)	184610(139)
1100	292.61(0.10)	693.90(1.37)	499.93(1.29)	213370(147)
1200	301.48(0.09)	719.75(1.37)	517.18(1.29)	243080(155)
1300	309.14(0.09)	744.19(1.37)	533.71(1.30)	273620(162)
1400	315.77(0.08)	767.35(1.37)	549.58(1.30)	304880(168)
1500	321.52(0.07)	789.33(1.37)	564.83(1.31)	336750(174)

[a] Values in parenthesis are estimated uncertainties.

TABLE 35. Ideal gas thermodynamic properties of ethanoic acid monomer–dimer equilibrium mixture $\{CH_3COOH\text{–}(CH_3COOH)_2\}$ at 1 bar[a]
$M = 33.0482$

$\frac{T}{K}$	$\frac{C_p^\circ}{J\ K^{-1}\ mol^{-1}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{J\ K^{-1}\ mol^{-1}}$	$\frac{-\{G^\circ(T)-H^\circ(0)\}/T}{J\ K^{-1}\ mol^{-1}}$	$\frac{\{H^\circ(T)-H^\circ(0)\}}{J\ mol^{-1}}$
0	0	0	0	0
100	43.19(0.28)	149.88(1.22)	118.10(0.78)	3178(44)
150	48.22(0.18)	168.33(1.28)	131.92(0.94)	5462(53)
200	54.30(0.17)	183.00(1.31)	142.91(1.03)	8018(59)
273.15	71.81(0.17)	201.96(1.32)	156.20(1.10)	12498(66)
298.15	87.52(0.17)	208.85(1.33)	160.32(1.12)	14470(68)
300	89.09(0.17)	209.40(1.33)	160.62(1.12)	14634(69)
400	297.22(0.18)	258.29(1.34)	177.94(1.17)	32138(78)
500	162.30(0.17)	318.86(1.35)	200.94(1.21)	58959(88)
600	111.33(0.16)	341.60(1.35)	222.66(1.23)	71363(99)
700	117.30(0.15)	359.11(1.36)	240.92(1.25)	82728(110)
800	125.64(0.14)	375.32(1.36)	256.71(1.26)	94881(120)
900	133.03(0.12)	390.56(1.36)	270.75(1.27)	107820(130)
1000	139.27(0.11)	404.91(1.37)	283.46(1.28)	121450(139)

[a] Values in parenthesis are estimated uncertainties.

2.7. Alkyl Alkanoates

The ideal gas thermodynamic properties of the alkanoates (esters), methyl methanoate and methyl ethanoate, have been calculated from molecular and spectroscopic data. Based upon these results, the thermodynamic properties of the other members of this homologous series may be estimated by correlation methods.

2.7.a. Methyl Methanoate

The molecular structure of methyl methanoate (methyl formate, $HCOOCH_3$) has been studied by electron diffraction[346] and microwave spectroscopy.[347,348] O'Gorman *et al.*[346] reported that the molecular structure of methyl methanoate has a planar heavy-atom skeleton with the ester methyl group *cis* to the carbonyl oxygen atom. They also reported that the average dihedral angle of rotation was 25° from the planar configuration, *i.e.* a *gauche* conformation.

From microwave studies, Curl[347] and Bauder[348] confirmed that the stable species of $HCOOCH_3$ (g) was the *cis* isomer. They determined the rotational constants, molecular parameters, and the internal rotation barrier height for the CH_3 rotor.

Harris *et al.*[349] analyzed the Raman spectra of $HCOOCH_3$, $DCOOCH_3$ and $HCOOCD_3$ in the gaseous, liquid, and crystalline states. They confirmed the skeletal planarity structure proposed from the microwave studies. However, they found no evidence for a second conformer like *trans* or *gauche* present in the methyl methanoate vapor. Consequently, we adopted a *cis* isomer molecular model for the evaluation of the ideal gas thermodynamic properties of this compound.

Karpovich[350] investigated the rotational isomers of methyl methanoate liquid using the ultrasound method and reported the existence of the *trans* isomer in the liquid phase. This proposal was rejected by the later study of the infrared spectrum of this compound by Wilmhurst.[351]

We adopted the three principal moments of inertia derived from the rotational constants determined by Bauder[348] from microwave spectroscopy. His results have been confirmed by the recent work of Demaison *et al.*[502]

The vibrational spectra of methyl methanoate[349,351-358] and the normal coordinate calculations[351-354,359] have been made by numerous researchers. Complete fundamental vibrational wavenumbers have been assigned by Harris *et al.*,[349] Wilmhurst[351] and Suzi and Scherer.[352] Shimanouchi[80] critically reviewed the spectral data and reported a complete set of vibrational assignments for this compound which we have used in this work.

Fateley and Miller[32] observed the CH_3 torsional wavenumber, $\tilde{\nu}_{tor}$ $(0 \rightarrow 1) = 130$ cm^{-1}, and determined the internal rotation potential barrier V_3 to be 4.87 kJ mol^{-1}. From microwave spectroscopy, Curl[347] and Bauder[348] determined V_3 as (4.98 ± 0.17) kJ mol^{-1} and 4.86 kJ mol^{-1} for the methyl rotor in the $HCOOCH_3$ molecule, respectively. We employed the values $V_3 =$ 4.86 kJ mol^{-1} and $F = 5.720$ cm^{-1} [348] for generating 108 internal rotational energy levels (0–16800 cm^{-1}) for calculating the internal rotational contributions.

Based upon the molecular and spectroscopic constants, as given in Tables A-2 and A-3, the ideal gas thermodynamic properties of methyl methanoate were evaluated. The results appear in Table 36. The thermodynamic properties of this compound reported by Stull *et al.*[466] were estimated based upon an assumption that the heat capacity of the gas was the same as that of ethanoic acid gas.

2.7.b. Methyl Ethanoate

The molecular structure of methyl ethanoate (methyl acetate, CH_3COOCH_3) was determined to be the *cis* form by spectroscopic methods.[351,360,361] This is consistent with findings for $HCOOCH_3$. Williams *et al.*[360] studied the microwave spectrum and found the complete absence of any strong non-*cis* isomer absorption lines. This placed a lower limit on the energy difference between the *cis* and *trans* conformations of about 8.4 kJ mol^{-1}. Therefore, the *cis* isomer molecular structure was used for evaluation of the thermodynamic properties of this substance.

Sheridan *et al.*[503] investigated the microwave spectrum of this compound and determined the three principal moments of inertia (I_a, I_b, and I_c) and V_3 and reduced barrier (S) for each of the two CH_3 rotors in the CH_3COOCH_3 molecule. Their results were selected for calculating the product of the three principal moments of inertia and for generating internal rotational energy levels for these two rotors.

The methyl ethanoate molecule has two methyl rotors, namely O–CH_3 and C–CH_3. The coupling between these two methyl torsional vibrations in the methyl ethanoate molecule was reported to be small.[360,503] Thus, we treated the two rotors independently for calculating the internal rotational contributions.

The fundamental vibrational wavenumbers assigned for this compound by Shimanouchi[80] were adopted, except for the two CH_3 rotor torsional wavenumbers, $\tilde{\nu}_{26}$ $= 136$ cm^{-1} for the C–C torsion and $\tilde{\nu}_{27} = 110$ cm^{-1} for the O–CH_3 torsion. We used 133.3 cm^{-1} and 65.0 cm^{-1} for $\tilde{\nu}_{26}$ $(0 \rightarrow 1)$ and $\tilde{\nu}_{27}$ $(0 \rightarrow 1)$ respectively, which were derived from our selected V_3 and F values for each rotor.[503] The vibrational wavenumber of 303 cm^{-1} was adjusted to 199 cm^{-1} in order to bring the calculated C_p° to agree with the experimental values.

Table 37 presents our calculated ideal gas thermodynamic properties for methyl ethanoate. The molecular data employed for evaluation are given in Tables A-2 and A-3.

Vapor heat capacities of methyl ethanoate for the temperature range from 335 to 450 K and at pressures from 25 kPa to 101.325 kPa were measured by vapor-flow calorimetry by Connett *et al.*[362] Extrapolation of the experimental heat capacities to zero pressure yielded the values of ideal gas heat capacities. A comparison of our

TABLE 36. Ideal gas thermodynamic properties of methyl methanoate ($HCOOCH_3$) at 1 bar[a]
$M = 60.0524$

$\frac{T}{\mathrm{K}}$	$\frac{C_p^\circ}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{-\{G^\circ(T)-H^\circ(0)\}/T}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{\{H^\circ(T)-H^\circ(0)\}}{\mathrm{J\,mol^{-1}}}$
0	0	0	0	0
100	44.06(0.13)	227.87(0.20)	190.72(0.09)	3715(11)
150	49.84(0.11)	246.92(0.24)	206.43(0.13)	6073(16)
200	54.18(0.09)	261.86(0.26)	218.48(0.16)	8675(20)
273.15	61.45(0.09)	279.77(0.27)	232.57(0.19)	12892(25)
298.15	64.38(0.09)	285.28(0.28)	236.76(0.20)	14465(27)
300	64.61(0.09)	285.67(0.28)	237.06(0.20)	14584(27)
400	77.56(0.11)	306.01(0.29)	251.80(0.22)	21684(34)
500	90.29(0.11)	324.71(0.30)	264.53(0.23)	30086(41)
600	101.57(0.11)	342.19(0.31)	276.03(0.24)	39693(50)
700	111.26(0.10)	358.59(0.31)	286.67(0.25)	50347(58)
800	119.53(0.09)	374.00(0.32)	296.63(0.26)	61897(66)
900	126.61(0.08)	388.50(0.32)	306.04(0.26)	74214(73)
1000	132.68(0.07)	402.16(0.33)	314.98(0.27)	87186(80)
1100	137.89(0.07)	415.06(0.33)	323.50(0.27)	100721(86)
1200	142.38(0.06)	427.26(0.33)	331.64(0.28)	114740(91)
1300	146.24(0.06)	438.81(0.33)	339.44(0.28)	129176(96)
1400	149.58(0.05)	449.77(0.33)	346.94(0.29)	143971(101)
1500	152.48(0.05)	460.19(0.34)	354.14(0.29)	159077(105)

[a] Values in parenthesis are estimated uncertainties.

TABLE 37. Ideal gas thermodynamic properties of methyl ethanoate (CH_3COOCH_3) at 1 bar[a]
$M = 74.0792$

$\frac{T}{\mathrm{K}}$	$\frac{C_p^\circ}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{-\{G^\circ(T)-H^\circ(0)\}/T}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{\{H^\circ(T)-H^\circ(0)\}}{\mathrm{J\,mol^{-1}}}$
0	0	0	0	0
100	55.78(0.18)	250.35(0.51)	206.13(0.31)	4422(21)
150	63.27(0.14)	274.46(0.55)	225.07(0.38)	7407(27)
200	70.02(0.12)	293.57(0.57)	239.89(0.43)	10738(31)
273.15	81.56(0.12)	317.04(0.58)	257.49(0.47)	16267(37)
298.15	86.03(0.12)	324.38(0.59)	262.79(0.48)	18362(39)
300	86.37(0.12)	324.91(0.59)	263.17(0.48)	18522(39)
400	105.31(0.14)	352.34(0.60)	282.09(0.50)	28101(47)
500	123.40(0.14)	377.82(0.61)	298.71(0.52)	39552(56)
600	139.25(0.14)	401.75(0.61)	313.91(0.54)	52704(66)
700	152.84(0.13)	424.26(0.62)	328.08(0.55)	67326(77)
800	164.47(0.12)	445.45(0.62)	341.44(0.56)	83207(86)
900	174.46(0.11)	465.42(0.63)	354.12(0.56)	100170(95)
1000	183.06(0.10)	484.25(0.63)	366.20(0.57)	118050(104)
1100	190.47(0.09)	502.06(0.63)	377.75(0.57)	136740(111)
1200	196.87(0.08)	518.91(0.63)	388.82(0.58)	156110(118)
1300	202.39(0.08)	534.89(0.63)	399.44(0.58)	176080(125)
1400	207.18(0.07)	550.07(0.64)	406.67(0.58)	196570(131)
1500	211.34(0.06)	564.51(0.64)	419.51(0.59)	217500(136)

[a] Values in parenthesis are estimated uncertainties.

calculated C_p° values with the reported experimental data appears in Table A-21. The average deviation is 0.3 percent.

Bennewitz and Rossner[106] determined the heat capacity of methyl ethanoate vapor at atmospheric pressure, using flow calorimetry with total condensation. Their results for C_p° (g) were 7 J K^{-1} mol^{-1} higher than those reported by Connett *et al.*.[362]

2.8. Epoxyalkanes

The thermodynamic properties of four epoxyalkanes (alkene oxides), *i.e.* C_2H_4O, C_2D_4O, C_3H_6O, and C_4H_8O, were evaluated. A large number of spectroscopic investigations have been made in order to determine the molecular structure and to assign the fundamental vibrational frequencies, but some fundamental frequency assignments of ethylene oxide are still subject to controversy. Because of the lack of molecular data, the thermodynamic properties of 1,2-epoxybutane were calculated from those for 1,2-epoxypropane using the CH_2 increment method.

2.8.a. Epoxyethane

The molecular structure of epoxyethane (ethylene oxide, C_2H_4O) has been elucidated by electron diffraction[128,363,364] and microwave spectroscopy.[365–374]

Cunningham *et al.*[368] observed the microwave spectra of $C_2^{12}H_4O$, $C^{12}C^{13}H_4O$ and $C_2^{12}D_4O$. For each isotopic species; three moments of inertia were derived. From the nine moments of inertia, they calculated a set of bond distances and angles. Their results have been reevaluated by Turner and Howe[370] who obtained the three principal moments of inertia as $I_a = 3.29413 \times 10^{-39}$ g cm^2, $I_b = 3.79489 \times 10^{-39}$ g cm^2, and $I_c = 5.95449 \times 10^{-39}$ g cm^2. These values were used for computing the value of $I_aI_bI_c$ given in Table A-2. The values of I_a, I_b, and I_c used have been confirmed by later measurements.[374,392]

The infrared and Raman spectra of epoxyethane have been extensively investigated. The infrared spectra was measured by Mecke and Vierling,[393] Bonner,[394] and Linnett.[375] Some overtone and combination bands in the near infrared were observed by Eyster.[395] The Raman spectra was measured by Lespiau and Gredy,[396] Timm and Mecke,[397] Bonner,[394] Ananthakrishnan,[398] and Kohlrausch and Reitz.[399]

Later spectroscopic investigations on epoxyethane include those by Thompson and Cave,[376] Lord and Nolin,[377] Potts,[378] and others.[379–386,402–404] A number of force field calculations[387–391] have been reported.

Complete fundamental vibrational assignments for this substance were reported by Shimanouchi,[80] Lord and Nolin,[377] Potts,[378] Freeman and Henshall,[389] Venkateswarlu and Joseph,[391] Cant and Armstead,[400] and Hirokawa *et al.*[401] Different authors have proposed considerably different frequencies for ν_7 (a_2, CH_2–twisting), ν_8 (a_2, CH_2–rocking), and ν_{12} (b_1, ring deformation), for which no direct spectral evidence has been obtained.[374]

For evaluation of the vibrational contributions to the thermodynamic properties of epoxyethane (g), the vibrational assignments $\nu_1 - \nu_5$ and $\nu_9 - \nu_{15}$ reported by Cant and Armstead,[400] and $\nu_6 - \nu_8$ reported by Shimanouchi[80] were selected. These values yielded calculated heat capacities and entropies consistent with those determined by Kistiakowski and Rice[158] and Giauque and Gordon.[405] Table A-22 presents a comparison of our calculated C_p° and $\{S^\circ(T)-S^\circ(0)\}$ with the experimental values corrected to 1 bar.

Based upon the adopted molecular constants, as given in Table A-2, the thermodynamic properties of epoxyethane in the temperature range from 0 to 3000 K and at 1 bar were evaluated. They appear in Table 38. Calculated values of the thermodynamic properties of epoxyethane have been reported by Zeise,[504] Gunthard and Hilbronner,[505] Kobe and Pennington,[506] and Stull *et al.*[466] The calculated statistical entropy at the boiling point of 283.71 K, 240.66 J K^{-1} mol^{-1}, agrees well with our selected third law entropy of 240.08 J K^{-1} mol^{-1}.

2.8.b. Epoxyethane-d_4

Cunningham *et al.*[368] studied the microwave spectrum of epoxyethane-d_4 (ethylene oxide-d_4,C_2D_4O) and obtained the three principal moments of inertia. From their microwave measurements, Turner and Howe[370] redetermined the structural parameters of C_2D_4O (g). The reported moments of inertia: $I_a = 4.11521 \times 10^{-39}$ g cm^2, $I_b = 5.43096 \times 10^{-39}$ g cm^2, and $I_c = 7.27186 \times 10^{-39}$ g cm^{2}[370] were employed for computing $I_aI_bI_c$, as listed in Table A-2.

The infrared and Raman spectra of this species have been investigated by many researchers[80,377,383,389,390,391,400] and complete sets of fundamental vibrational wavenumbers have been assigned.[80,377,391,400] In this work, we adopted the vibrational assignments $\nu_1 - \nu_5$ and $\nu_9 - \nu_{15}$ reported by Cant and Armstead[400] and $\nu_6 - \nu_8$ recommended by Shimanouchi[80] for evaluation of the vibrational contributions.

Using the data given in Table A-2, we calculated the thermodynamic properties of this species in the temperature range from 0 to 3000 K and at 1 bar. The results are presented in Table 39.

2.8.c. DL–1,2–Epoxypropane

To investigate the effects of hindered internal rotation of a methyl group for a high barrier, Swalen and Herschbach[408] observed the microwave spectrum of 1,2-epoxypropane (propylene oxide, C_3H_6O). Rotational transitions have been assigned up to J = 30 in the ground torsional state and to J = 10 in the first excited torsional state. The structure of the molecule was partially determined by combining the rotational constants derived from the spectrum with the known structure of epoxyethane. The reported three principal moments of inertia: $I_a = 4.65756 \times 10^{-39}$ g cm^2, $I_b = 1.25628 \times 10^{-38}$ g cm^2, and $I_c = 1.41055 \times 10^{-38}$ g cm^2 were used to compute the value of $I_aI_bI_c$ which is listed in Table A-2. These three principal moments of inertia[408] have been confirmed by Creswell and Schwendeman.[507]

The infrared spectra of DL–1,2–epoxypropane in the liquid and vapor phases have been investigated by Tobin.[413] Based upon the fundamental vibrational frequencies assigned by Lord and Nollin[377] for epoxyethane, he proposed a complete assignment of fundamental frequencies for DL–1,2–epoxypropane (g). These proposed assignments indicated that the substitution of a methyl group for a hydrogen atom had hardly perturbed the ethylene oxide spectrum. The major change in the spectrum, aside from the appearance of new bands ascribable to CH_3 motions, was the lowering of one wavenumber from about 810 cm^{-1} to 745 cm^{-1}.[413] The above set of vibrational assignments was the only set of data available, and it was adopted to compute the vibrational contributions.

The microwave spectra of the DL–1,2–epoxypropane molecule were studied by several investigators.[32,408–412]

TABLE 38. Ideal gas thermodynamic properties of epoxyethane (C_2H_4O) at 1 bar[a]
$M = 44.0530$

$\frac{T}{\mathrm{K}}$	$\frac{C_p^\circ}{\mathrm{J\ K^{-1}\ mol^{-1}}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\mathrm{J\ K^{-1}\ mol^{-1}}}$	$\frac{-\{G^\circ(T)-H^\circ(0)\}/T}{\mathrm{J\ K^{-1}\ mol^{-1}}}$	$\frac{\{H^\circ(T)-H^\circ(0)\}}{\mathrm{J\ mol^{-1}}}$
0	0	0	0	0
100	33.28(0.00)	202.80(0.04)	169.54(0.04)	13326(0)
150	33.97(0.01)	216.38(0.04)	183.04(0.04)	15001(0)
200	33.66(0.03)	226.46(0.04)	192.68(0.04)	16757(1)
273.15	44.50(0.06)	238.95(0.04)	203.43(0.04)	19702(4)
298.15	47.86(0.07)	242.99(0.05)	206.58(0.04)	10856(6)
300	48.11(0.07)	243.29(0.05)	206.80(0.04)	10945(6)
400	62.38(0.09)	259.08(0.06)	217.91(0.04)	16470(14)
500	75.42(0.09)	274.44(0.08)	227.69(0.04)	23377(22)
600	86.34(0.09)	289.19(0.09)	236.72(0.05)	31482(31)
700	95.40(0.08)	303.20(0.10)	245.22(0.05)	40582(39)
800	103.01(0.07)	316.45(0.11)	253.31(0.06)	50513(47)
900	109.47(0.07)	328.96(0.12)	261.02(0.06)	61146(53)
1000	115.01(0.06)	340.79(0.12)	268.42(0.07)	72377(59)
1100	119.77(0.06)	351.98(0.13)	275.51(0.07)	84120(65)
1200	123.87(0.06)	362.58(0.13)	282.33(0.08)	96310(70)
1300	127.43(0.05)	372.64(0.13)	288.89(0.08)	108880(74)
1400	130.51(0.05)	382.20(0.14)	295.22(0.09)	121780(78)
1500	133.19(0.05)	391.30(0.14)	301.32(0.09)	134970(82)
1750	138.50(0.04)	412.21(0.14)	315.71(0.10)	169000(91)
2000	142.40(0.03)	431.01(0.15)	328.91(0.10)	204100(99)
2250	145.20(0.03)	447.91(0.15)	341.31(0.11)	240100(105)
2500	147.30(0.02)	463.41(0.15)	352.71(0.11)	276700(110)
2750	149.00(0.02)	477.51(0.15)	363.51(0.12)	313700(115)
3000	150.40(0.02)	490.51(0.15)	373.51(0.12)	351200(119)

[a] Values in parenthesis are estimated uncertainties.

TABLE 39. Ideal gas thermodynamic properties of epoxyethane-d_4 (C_2D_4O) at 1 bar[a]
$M = 48.0778$

$\frac{T}{\mathrm{K}}$	$\frac{C_p^\circ}{\mathrm{J\ K^{-1}\ mol^{-1}}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\mathrm{J\ K^{-1}\ mol^{-1}}}$	$\frac{-\{G^\circ(T)-H^\circ(0)\}/T}{\mathrm{J\ K^{-1}\ mol^{-1}}}$	$\frac{\{H^\circ(T)-H^\circ(0)\}}{\mathrm{J\ mol^{-1}}}$
0	0	0	0	0
100	33.57(0.01)	207.18(0.04)	173.89(0.04)	3329(0)
150	36.19(0.04)	221.18(0.04)	187.44(0.04)	5060(1)
200	42.06(0.07)	232.32(0.05)	197.30(0.04)	7004(4)
273.15	54.17(0.11)	247.16(0.06)	208.69(0.04)	10509(10)
298.15	58.58(0.11)	252.09(0.07)	212.12(0.04)	11919(13)
300	58.91(0.11)	252.46(0.07)	212.37(0.04)	12028(13)
400	75.44(0.12)	271.73(0.10)	224.81(0.05)	18766(25)
500	89.12(0.11)	290.09(0.12)	236.05(0.06)	27019(36)
600	100.18(0.10)	307.35(0.14)	246.51(0.07)	36503(46)
700	109.14(0.09)	323.49(0.15)	256.37(0.08)	46985(55)
800	116.45(0.08)	338.56(0.16)	265.71(0.09)	58276(63)
900	122.42(0.08)	352.63(0.17)	274.60(0.10)	70230(70)
1000	127.33(0.07)	365.79(0.18)	283.06(0.11)	82726(77)
1100	131.38(0.06)	378.12(0.18)	291.15(0.11)	95667(83)
1200	134.73(0.06)	389.70(0.19)	298.89(0.12)	108980(88)
1300	137.54(0.05)	400.60(0.19)	306.30(0.12)	122600(93)
1400	139.89(0.05)	410.88(0.19)	313.40(0.13)	136470(97)
1500	141.88(0.04)	420.60(0.19)	320.23(0.13)	150560(101)
1750	145.70(0.04)	442.81(0.20)	336.21(0.14)	186500(110)
2000	148.30(0.03)	462.41(0.20)	350.71(0.15)	223300(116)
2250	150.20(0.02)	480.01(0.20)	364.11(0.15)	260600(122)
2500	151.60(0.02)	495.91(0.20)	376.51(0.16)	298400(127)
2750	152.60(0.02)	510.41(0.21)	388.11(0.16)	336400(131)
3000	153.40(0.01)	523.71(0.21)	398.81(0.17)	374600(134)

[a] Values in parenthesis are estimated uncertainties.

Swalen and Herschbach[408] determined the internal rotational barrier height for the CH_3 rotor as $V_3 = 11.34$ kJ mol^{-1} for the ground state and $V_3 = 10.71$ kJ mol^{-1} for the first excited state.

Herschbach and Swalen[409] measured several long progressions of perpendicular transitions in the microwave spectrum. Rotational transitions have also been assigned for the first and second excited torsional states. The barrier height V_3 for these two excited states was found to be identical with the ground state result.

Fateley and Miller[32] measured the transitions between excited torsional levels ($0 \rightarrow 1$, $1 \rightarrow 2$, $2 \rightarrow 3$) in the far infrared spectrum. They proposed the potential function: $V(\theta) = \frac{1}{2}[V_3(1 - \cos 3\theta) + V_6(1 - \cos 6\theta)]$ for the hindered internal rotation of the CH_3 rotor in the molecule, where θ was the angle of internal rotation. Based upon the observed torsional wavenumbers: 200 cm^{-1} ($0 \rightarrow 1$), 185.8 cm^{-1} ($1 \rightarrow 2$), 168.8 cm^{-1} ($2 \rightarrow 3A$), and 167.5 cm^{-1} ($2 \rightarrow 3E$), they found $V_3 = (10.77 \pm 0.10)$ kJ mol^{-1} and $V_6 = (0.108 \pm 0.01)$ kJ mol^{-1}.

From Raman spectra, Villarreal and Laane[34] confirmed the torsional transitions reported by Fateley and Miller.[32] They determined the potential function coefficients as $V_3 = 10.68$ kJ mol^{-1} and $V_6 = -0.084$ kJ mol^{-1}. The internal rotational barrier height of the methyl rotor was evaluated to be 10.68 kJ mol^{-1}, and the torsional wavenumber ($0 \rightarrow 1$) was calculated as 200 cm^{-1} which was consistent with the observed value. Employing $F = 5.841$ cm^{-1} and the above potential function, we generated 108 internal rotational energy levels for evaluating the internal rotational contributions.

Using the selected molecular constants listed in Tables A-2 and A-3, we calculated the ideal gas thermodynamic properties for DL–1,2–epoxypropane as shown in Table 40. Our calculated value, $\{S^\circ(298.15\ K) - S^\circ(0)\}$, was 286.91 J K^{-1} mol^{-1}. The value derived from the low temperature measurements of Oetting[407] was (288.4 ± 0.8) J K^{-1} mol^{-1}.

Thermodynamic functions reported by Green,[406] Oetting,[407] and Stull *et al.*,[466] were calculated using statistical mechanical methods and employing slightly different molecular constants. No vapor heat capacity data were available for comparison with our calculated C_p° values.

2.8.d. DL–1,2–Epoxybutane

The thermodynamic properties of DL–1,2–epoxybutane (butylene oxide, C_4H_8O) were estimated because of the lack of pertinent molecular and spectroscopic constants required for the statistical mechanical calculation. We evaluated the ideal gas thermodynamic properties of DL–1,2–epoxybutane (g) by addition of the thermodynamic properties of a methylene group to the corresponding properties of DL–1,2–epoxypropane (g) (see section 1.6).

The results are listed in Table 41. The selected third-law value given in Table A-26 is in reasonable agreement with the calculated value at 298.15 K.

TABLE 40. Ideal gas thermodynamic properties of DL–1,2–epoxypropane (C_3H_6O) at 1 bar[a]
$M = 58.0798$

$\frac{T}{K}$	$\frac{C_p^\circ}{J\ K^{-1}\ mol^{-1}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{J\ K^{-1}\ mol^{-1}}$	$\frac{-\{G^\circ(T)-H^\circ(0)\}/T}{J\ K^{-1}\ mol^{-1}}$	$\frac{\{H^\circ(T)-H^\circ(0)\}}{J\ mol^{-1}}$
0	0	5.76	5.76	0
100	39.74(0.05)	230.12(0.04)	195.06(0.03)	3506(1)
150	46.65(0.08)	247.53(0.05)	209.77(0.04)	5664(5)
200	54.27(0.09)	261.96(0.07)	221.05(0.04)	8182(9)
273.15	67.57(0.11)	280.78(0.10)	234.57(0.05)	12624(15)
298.15	72.55(0.12)	286.91(0.10)	238.70(0.05)	14375(17)
300	72.92(0.12)	287.36(0.11)	239.00(0.05)	14510(18)
400	92.99(0.14)	311.11(0.13)	254.08(0.07)	22813(29)
500	110.99(0.14)	333.85(0.15)	267.78(0.08)	33035(41)
600	126.16(0.13)	355.46(0.17)	280.61(0.09)	44915(53)
700	138.89(0.12)	375.89(0.19)	292.77(0.10)	58185(65)
800	149.68(0.11)	395.16(0.20)	304.38(0.12)	72628(76)
900	158.91(0.10)	413.34(0.21)	315.49(0.12)	88069(85)
1000	166.85(0.09)	340.51(0.22)	326.14(0.13)	104370(94)
1100	173.70(0.09)	446.74(0.22)	336.37(0.14)	121400(102)
1200	179.62(0.08)	462.11(0.23)	346.21(0.15)	139080(109)
1300	184.74(0.08)	476.70(0.23)	355.70(0.15)	157300(116)
1400	189.19(0.07)	490.55(0.24)	364.84(0.16)	176000(122)
1500	193.06(0.07)	503.74(0.24)	373.66(0.16)	195120(128)
1750	200.70(0.06)	534.11(0.25)	394.46(0.18)	244400(141)
2000	206.30(0.05)	561.29(0.25)	413.64(0.18)	295300(151)
2250	210.40(0.04)	585.84(0.25)	431.43(0.19)	347400(160)
2500	213.50(0.03)	608.17(0.26)	448.01(0.20)	400400(168)
2750	215.90(0.03)	628.64(0.26)	463.51(0.20)	454100(174)
3000	217.80(0.03)	647.50(0.26)	478.07(0.21)	508300(180)

[a] Values in parenthesis are estimated uncertainties.

TABLE 41. Ideal gas thermodynamic properties of DL–1,2–epoxybutane (C_4H_8O) at 1 bar[a]
$M = 72.1066$

T / K	C_p° / J K^{-1} mol^{-1}	$\{S^\circ(T)-S^\circ(0)\}$ / J K^{-1} mol^{-1}	$-\{G^\circ(T)-H^\circ(0)\}/T$ / J K^{-1} mol^{-1}	$\{H^\circ(T)-H^\circ(0)\}$ / J mol^{-1}
0	0	5.76	5.76	0
200	71.42(0.09)	292.9(0.07)	238.9(0.04)	10800(9)
273.15	88.70(0.11)	317.6(0.10)	256.7(0.05)	16630(15)
298.15	95.18(0.12)	325.7(0.10)	262.2(0.05)	18930(17)
300	95.68(0.12)	326.2(0.11)	262.6(0.05)	19110(18)
400	122.15(0.14)	357.4(0.13)	282.4(0.07)	30010(29)
500	145.88(0.14)	387.3(0.15)	300.4(0.08)	43450(41)
600	165.70(0.13)	415.7(0.17)	317.3(0.09)	59060(53)
700	182.07(0.12)	442.5(0.19)	333.3(0.10)	76470(65)
800	195.79(0.11)	467.8(0.20)	348.5(0.12)	95390(76)
900	207.32(0.10)	491.5(0.21)	363.1(0.12)	115600(85)
1000	217.06(0.09)	513.8(0.22)	377.1(0.13)	136800(94)
1100	225.60(0.09)	535.0(0.22)	390.0(0.14)	159100(102)
1200	232.80(0.08)	555.0(0.23)	403.0(0.15)	181800(109)
1300	239.10(0.08)	574.0(0.23)	416.0(0.15)	205400(116)
1400	244.40(0.07)	592.0(0.24)	428.0(0.16)	229600(122)
1500	249.50(0.07)	609.0(0.24)	439.0(0.16)	254000(128)

[a]Values in parenthesis are estimated uncertainties.

2.9. Miscellaneous Compounds

In this final section, the selection of the the molecular and spectroscopic constants are described for furan, 2,5-dihydrofuran, and tetrahydrofuran, and the calculated thermodyanamic properties are discussed.

2.9.a. Furan

Furan (C_4H_4O) is a five-membered ring compound. Pauling and Schomaker[427] and Beach[428] determined its molecular structure from electron diffraction measurements. The microwave spectrum was observed by Sirvetz,[429] Bak *et al.*,[430,431] and Sorensen,[432] and the rotational and centrifugal distortion constants were reported. Monostori and Weber[433] investigated the pure rotational Raman spectrum and determined one rotational constant (a mean value of A and B) and the centrifugal distortion constant D_J. With a beam maser spectrometer, Tomasevich *et al.*[434] resolved the hyperfine structure in the rotational spectrum. The rotational constants determined from the microwave spectrum by Bak *et al.*[431] were used for calculating the three principal moments of inertia and hence $I_aI_bI_c$ as given in Table A-2. These constants have been confirmed recently by Mata *et al.*[511]

The vibrational spectra of furan have been investigated by numerous researchers. The infrared spectra of this compound were observed by Thompson and Temple,[435] Guthrie *et al.*,[436] Bak *et al.*,[437] and many others.[439–444] Its Raman spectra were studied by Reitz,[438] Guthrie *et al.*,[436] and Rico *et al.*[444]

Complete fundamental vibrational assignments for the furan molecule have been reported by many authors.[80,436,437,445–447] Guthrie *et al.*[436] assigned 18 of the 21 fundamental vibrational frequencies, using the available spectroscopic data.[435,436,438] They selected the remaining three frequencies to give agreement between the calculated and experimentally determined values of vapor heat capacities and third law entropies.

Bak *et al.*[437] used a different set of normal vibrational frequencies obtained from spectral data for calculating the thermodynamic properties. The agreement between the calculated and the experimental C_p° and $\{S^\circ(T)-S^\circ(0)\}$ was worse than that reported by Guthrie *et al.*,[436] especially at higher temperatures.

Based upon a molecular vibrational analysis, Scott[446] established a complete set of vibrational assignments, which was consistent with that given by Shimanouchi.[80] His assignments[446] were adopted in this work.

Using the molecular constants listed in Table A-2, we calculated the thermodynamic properties of furan (g) by the standard statistical mechanical method. The results appear in Table 42. Our calculated C_p° and $\{S^\circ(T)-S^\circ(0)\}$ agree with the experimental data,[436] as indicated in Table A-23. In particular, our calculated third-law entropy of 267.8 J K^{-1} mol^{-1} at 298.15 K agrees well with our statistically calculated value of 267.25 J K^{-1} mol^{-1}, as shown in Table A-26. The thermodynamic properties of furan reported by Guthrie *et al.*[512] were adopted by Stull *et al.*[466]

2.9.b. 2,5-Dihydrofuran

The molecular structure of 2,5-dihydrofuran (C_4H_6O) was determined by Beach[428] from an analysis of electron diffraction results. His results suggested that the nonproton skeleton of 2,5-dihydrofuran was probably planar. This proposed molecular structure was later confirmed by Kowalewski and Kowalewski[447] and Courtieu and Gounelle.[448]

From the proton magnetic resonance spectra of 2,5-dihydrofuran dissolved in a nematic phase, Kowalewski and Kowalewski[447] derived the ratios of the interproton distances in the molecule. Courtieu and Gounelle[448] in-

TABLE 42. Ideal gas thermodynamic properties of furan (C_4H_4O) at 1 bar[a]
$M = 68.0750$

$\frac{T}{\mathrm{K}}$	$\frac{C_p^\circ}{\mathrm{J\ K^{-1}\ mol^{-1}}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\mathrm{J\ K^{-1}\ mol^{-1}}}$	$\frac{-\{G^\circ(T)-H^\circ(0)\}/T}{\mathrm{J\ K^{-1}\ mol^{-1}}}$	$\frac{\{H^\circ(T)-H^\circ(0)\}}{\mathrm{J\ mol^{-1}}}$
0	0	0	0	0
100	33.53(0.01)	220.60(0.11)	187.31(0.11)	3329(0)
150	36.39(0.04)	234.60(0.11)	200.87(0.11)	5060(1)
200	43.60(0.10)	245.96(0.11)	210.75(0.11)	7042(4)
273.15	59.43(0.24)	261.79(0.13)	222.30(0.11)	10786(16)
298.15	65.40(0.29)	267.25(0.15)	225.84(0.11)	12347(22)
300	65.85(0.29)	267.64(0.15)	226.09(0.11)	12468(23)
400	88.80(0.40)	289.81(0.22)	239.25(0.12)	20225(58)
500	107.82(0.42)	311.75(0.31)	251.56(0.14)	30093(99)
600	122.77(0.38)	332.78(0.37)	263.36(0.17)	41653(138)
700	134.59(0.34)	352.63(0.43)	274.71(0.20)	54543(174)
800	144.13(0.29)	371.25(0.47)	285.63(0.23)	68495(205)
900	152.00(0.25)	388.69(0.50)	296.12(0.25)	83314(232)
1000	158.60(0.22)	405.06(0.52)	306.21(0.28)	98853(255)
1100	164.20(0.19)	420.44(0.54)	315.90(0.30)	115001(275)
1200	168.97(0.16)	434.94(0.55)	325.22(0.32)	131665(292)
1300	173.08(0.15)	448.63(0.56)	334.19(0.34)	148773(307)
1400	176.62(0.13)	461.59(0.57)	342.83(0.35)	166262(321)
1500	179.69(0.12)	473.88(0.58)	351.16(0.37)	184081(332)

[a] Values in parenthesis are estimated uncertainties.

vestigated the nuclear magnetic resonance spectrum of 2,5-dihydrofuran in a liquid crystalline phase. These results support the hypothesis that the ring skeleton is planar.

Ueda and Shimanouchi[449] measured the far infrared absorption spectrum in the 500–50 $\mathrm{cm^{-1}}$ region and determined the rotational constants. From their results, we derived the three principal moments of inertia: $I_a = 9.8709 \times 10^{-39}$ g $\mathrm{cm^2}$, $I_b = 1.05002 \times 10^{-38}$ g $\mathrm{cm^2}$, and $I_c = 1.93007 \times 10^{-38}$ g $\mathrm{cm^2}$. These values were used to calculate the product of the three principal moments of inertia given in Table A-2.

The 2,5-dihydrofuran molecule is considered to have a pseudo-four-membered-ring structure. The ring-puckering vibrational spectra of this compound were investigated by Ueda and Shimanouchi[449] and Carreira and Lord.[450] The far-infrared spectrum was originally observed and interpreted by Ueda and Shimanouchi.[449] Carreira and Lord[450] reinvestigated this compound using higher resolution and found a satellite series appearing on the high-frequency side of the main series. For evaluating the thermodynamic properties caused by this ring-puckering motion of the molecule, the ring-puckering vibrational energy levels (0 to 1938.8 $\mathrm{cm^{-1}}$), from the far- infrared results by Carreira and Lord,[450] were employed. The fundamental vibrational frequencies, listed in Table A-2, were obtained from Laane.[451]

Using the selected molecular constants given in Table A-2, the thermodynamic properties of 2,5-dihydrofuran (g) at 1 bar given in Table 43 were calculated.

2.9.c. Tetrahydrofuran

Beach[428] elucidated the molecular structure of tetrahydrofuran (C_4H_8O) by electron diffraction. Using a planar molecular model, he calculated its molecular structural parameters. However, because later investigators found the structures to be non-planar, the results reported by Beach are only of historical interest.

Engerholm *et al.*[457] studied the microwave spectrum of tetrahydrofuran and observed complete rotational spectra for the ground and eight excited states. The reported three ground state rotational constants were adopted to calculate the three principal moments of inertia: $I_a = 1.18251 \times 10^{-38}$ g $\mathrm{cm^2}$, $I_b = 1.20300 \times 10^{-38}$ g $\mathrm{cm_2}$, and $I_c = 2.09384 \times 10^{-38}$ g $\mathrm{cm^2}$. From these the value of $I_aI_bI_c$ given in Table A-2 was calculated.

The infrared spectra of tetrahydrofuran have been observed by many researchers.[452–456] The Raman spectra of this compound in the liquid phase were reported by Kohlrausch and Reitz[462] and Luther *et al.*[463] These molecular spectra at room temperature have broad, diffuse bands because of unresolved pseudo-rotational fine structure. Therefore, it was difficult to assign the fundamental vibrational frequencies for this species.

The far infra-red spectrum of tetrahydrofuran was first investigated by Lafferty *et al.*[459] They interpreted their results in terms of a free pseudorotator. Later, Greenhouse and Strauss[460] proposed the existence of hindered pseudorotation in the molecule. They analyzed their results using a separate Hamiltonian but allowing for a small barrier to pseudorotation of 0.60 kJ $\mathrm{mol^{-1}}$. Pseudorotation constants in both the ground and in the first excited radial states were obtained. The spectra showed the effects of a considerable number of complex rotation-vibration interactions.

Engerholm *et al.*[457] studied the microwave spectrum. From the strong vibration rotation interaction, they deduced that this molecule contained a small barrier of about 0.6 kJ $\mathrm{mol^{-1}}$ hindering free pseudorotation. Based upon the variation of the dipole moment, they suggested

TABLE 43. Ideal gas thermodynamic properties of 2,5-dihydrofuran (C_4H_6O) at 1 bar[a]
M = 70.0908

T/K	C_p°/J K^{-1} mol^{-1}	$\{S^\circ(T)-S^\circ(0)\}$/J K^{-1} mol^{-1}	$-\{G^\circ(T)-H^\circ(0)\}/T$/J K^{-1} mol^{-1}	$\{H^\circ(T)-H^\circ(0)\}$/J mol^{-1}
0	0	0	0	0
100	40.54(0.19)	228.01(0.58)	191.17(0.33)	3684(26)
150	45.04(0.12)	245.20(0.63)	206.46(0.42)	5811(33)
200	52.82(0.10)	259.14(0.66)	217.93(0.48)	8243(37)
273.15	69.24(0.11)	277.92(0.67)	231.49(0.53)	12681(42)
298.15	75.60(0.12)	284.25(0.67)	235.65(0.54)	14491(43)
300	76.08(0.12)	284.72(0.67)	235.95(0.54)	14631(44)
400	101.45(0.13)	310.13(0.68)	251.32(0.57)	23523(50)
500	123.50(0.13)	335.21(0.69)	265.60(0.60)	34805(58)
600	141.44(0.12)	359.37(0.70)	279.13(0.61)	48084(67)
700	155.99(0.11)	382.31(0.70)	292.33(0.62)	62980(75)
800	167.99(0.10)	403.94(0.70)	304.95(0.63)	79198(83)
900	178.02(0.10)	424.33(0.71)	317.09(0.64)	96513(90)
1000	186.49(0.09)	443.53(0.71)	328.78(0.65)	114750(98)
1100	193.70(0.09)	461.66(0.71)	340.05(0.65)	133769(104)
1200	199.87(0.08)	478.78(0.71)	350.90(0.66)	153456(111)
1300	205.17(0.08)	494.99(0.71)	361.37(0.66)	173714(117)
1400	209.73(0.08)	510.37(0.71)	371.47(0.66)	194465(123)
1500	213.69(0.07)	524.98(0.71)	381.22(0.67)	215641(128)

[a] Values in parenthesis are estimated uncertainties.

that the twisted configuration had a lower energy than the bent configuration. The results were interpreted in terms of a model of restricted pseudorotation with a potential function of $V = 1/2[0.36(1 - \cos 2\theta) + 0.48(1 - \cos 4\theta)]$ kJ mol^{-1} where θ is the angle of pseudorotation. They compared the observed vibrational intervals with their calculated intervals and calculated with both a factored Hamiltonian and an unfactored Hamiltonian for the ring puckering mode. The calculated intervals with the unfactored Hamiltonian agreed with the observed ones better than those obtained by using the factored Hamiltonian. This conclusion was later confirmed by Davidson and Warsop.[461]

The ring puckering potential function reported by Engerholm *et al.*[457] and a pseudorotation constant F = 3.27 cm^{-1} [459] were employed for generating 132 pseudorotation energy levels (0 to 14200 cm^{-1}) for the calculation of the pseudorotational contributions. The pseudorotation phenomenon was reviewed by Frankiss and Green.[9]

Hossenlopp and Scott[458] assumed a puckered configuration of C_2 point-group symmetry and made a normal coordinate calculation. Their vibrational assignments were adopted in this work for calculating the vibrational contributions. See Table A-2 for the numerical values. Adopting the value of $I_aI_bI_c$ from the work of Engerholm *et al.*[457] and using his own vibrational assignments, Scott calculated the ideal thermodynamic properties.[458] His calculated C_p° values agreed with the experimental vapor heat capacities measured by Finke and Hossenlopp.[464] For evaluation of the pseudorotational contributions to the thermodynamic properties of this compound, he used the first 15 energy levels for pseudorotation observed by Engerholm *et al.*[457] The additional levels needed were estimated to provide a smooth continuation of those listed and to approach the distribution for free pseudorotation with increasing energy. The formula used was: $E(\mathrm{cm}^{-1}) = 3.25n^2 + 5.489 + 9.786/n$ ($n = 7$) where n is an index that numbers the pairs of effectively doubly degenerated levels.

We employed the molecular constants listed in Table A-2, and the 132 pseudorotational energy levels, for the calculation of the thermodynamic properties of tetrahydrofuran (g). The results are presented in Table 44. Our calculated C_p° are compared with the observed vapor heat capacities in Table A-24. Our calculated results are in good agreement with those obtained by Hossenlopp and Scott,[458] although the methods used for calculating the pseudorotational energy levels are different. The calculated ideal gas entropy at 298.15 K, 302.41 J K^{-1} mol^{-1}, agrees with our selected third law value of 299.1 J K^{-1} mol^{-1} given in Table A-26.

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TABLE 44. Ideal gas thermodynamic properties of tetrahydrofuran (C_4H_8O) at 1 bar[a]
$M = 72.1066$

$\frac{T}{\text{K}}$	$\frac{C_p^\circ}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{-\{G^\circ(T)-H^\circ(0)\}/T}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{\{H^\circ(T)-H^\circ(0)\}}{\text{J mol}^{-1}}$
0	0	0	0	0
100	40.61(0.09)	246.46(2.87)	207.30(2.44)	3916(43)
150	44.77(0.08)	263.63(2.88)	223.36(2.58)	6041(45)
200	52.15(0.09)	277.43(2.89)	235.19(2.66)	8448(46)
273.15	69.23(0.14)	296.05(2.89)	249.01(2.72)	12849(49)
298.15	76.25(0.16)	302.41(2.89)	253.22(2.74)	14667(50)
300	76.78(0.16)	302.88(2.89)	253.52(2.74)	14808(50)
400	106.36(0.20)	329.02(2.89)	269.11(2.78)	23965(59)
500	133.58(0.21)	355.75(2.90)	283.76(2.80)	35994(72)
600	156.62(0.19)	382.20(2.90)	297.97(2.82)	50538(87)
700	175.86(0.18)	407.83(2.90)	311.85(2.83)	67191(102)
800	192.02(0.17)	432.40(2.90)	325.39(2.84)	85608(117)
900	205.68(0.16)	455.83(2.91)	338.59(2.84)	105511(130)
1000	217.31(0.15)	478.12(2.91)	351.44(2.85)	126677(143)
1100	227.23(0.15)	499.31(2.91)	363.93(2.85)	148916(155)
1200	235.72(0.14)	519.45(2.91)	376.06(2.86)	172075(166)
1300	243.02(0.13)	538.62(2.91)	387.83(2.86)	196021(177)
1400	249.30(0.12)	556.86(2.91)	399.26(2.87)	220645(187)
1500	254.74(0.12)	574.25(2.91)	410.35(2.87)	245853(197)

[a] Values in parenthesis are estimated uncertainties.

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5. Appendix

TABLE A-1. Equations for calculating ideal gas thermodynamic properties for polyatomic molecules at a pressure of 1 bar[a,b]

Contribution	Property	Equation
		Linear Molecule
Translation	C_p°	20.786007
	$\{H^\circ(T)-H^\circ(0)\}$	$20.786007T$
	$-\{G^\circ(T)-H^\circ(0)\}/T$	$28.716930 \log M + 47.861550 \log T-30.361772$
	$\{S^\circ(T)-S^\circ(0)\}$	$28.716930 \log M + 47.861550 \log T-9.575765$
Rotation	C_p°	8.314403
	$\{H^\circ(T)-H^\circ(0)\}$	$8.314403T$
	$-\{G^\circ(T)-H^\circ(0)\}/T$	$19.144620 \log [(\mathrm{I}\ T \times 10^{39})/\sigma]-11.583429$
	$\{S^\circ(T)-S^\circ(0)\}$	$19.144620 \log [(\mathrm{I}\ T \times 10^{39})/\sigma]-3.269026$
Vibration	C_p°	$8.314403\Sigma u_i^2 \mathrm{e}^{-u_i}/(1-\mathrm{e}^{-u_i})^2$
	$\{H^\circ(T)-H^\circ(0)\}$	$8.314403T\Sigma u_i \mathrm{e}^{-u_i}/(1-\mathrm{e}^{-u_i})$
	$-\{G^\circ(T)-H^\circ(0)\}/T$	$-19.144620\ \Sigma\log (1-\mathrm{e}^{-u_i})$
	$\{S^\circ(T)-S^\circ(0)\}$	$8.314403\Sigma u_i \mathrm{e}^{-u_i}/(1-\mathrm{e}^{-u_i})-19.144620\ \Sigma\log (1-\mathrm{e}^{-u_i})$
		Nonlinear Molecule
Translation	C_p°	20.786007
	$\{H^\circ(T)-H^\circ(0)\}$	$20.786007T$
	$-\{G^\circ(T)-H^\circ(0)\}/T$	$28.716930 \log M + 47.861550 \log T-30.361772$
	$\{S^\circ(T)-S^\circ(0)\}$	$28.716930 \log M + 47.861550 \log T-9.575765$
Rotation	C_p°	12.471604
	$\{H^\circ(T)-H^\circ(0)\}$	$12.471604T$
	$-\{G^\circ(T)-H^\circ(0)\}/T$	$28.716930 \log T - 19.144620 \log \sigma +$ $9.572310 \log (I_aI_bI_c \times 10^{117})-12.616271$
	$\{S^\circ(T)-S^\circ(0)\}$	$\{H^\circ(T)-H^\circ(0)\}/T - \{G^\circ(T)-H^\circ(0)\}/T$
Vibration	C_p°	$8.314403\Sigma u_i^2 \mathrm{e}^{-u_i}/(1-\mathrm{e}^{-u_i})^2$
	$\{H^\circ(T)-H^\circ(0)\}$	$8.314403\Sigma Tu_i \mathrm{e}^{-u_i}/(1-\mathrm{e}^{-u_i})$
	$-\{G^\circ(T)-H^\circ(0)\}/T$	$-19.144620\ \Sigma\log (1-\mathrm{e}^{-u_i})$
	$\{S^\circ(T)-S^\circ(0)\}$	$8.314403\Sigma u_i \mathrm{e}^{-u_i}/(1-\mathrm{e}^{-u_i})-19.144620\ \Sigma\log (1-\mathrm{e}^{-u_i})$
Internal rotation	C_p°	$\frac{17.211687}{T_2}\left[\frac{\Sigma\epsilon_i^2 g_i w_i}{\Sigma g_i w_i} - \left(\frac{\Sigma\epsilon g_i w_i}{\Sigma g_i w_i}\right)^2\right]$
	$\{H^\circ(T)-H^\circ(0)\}$	$11.962646(\Sigma\epsilon g_i w_i)/\Sigma g_i w_i$
	$-\{G^\circ(T)-H^\circ(0)\}/T$	$19.144620 \log \Sigma g_i w_i$ where $w_i = \exp(-1.438786\epsilon_i/T)$
	$\{S^\circ(T)-S^\circ(0)\}$	$\{H^\circ(T)-H^\circ(0)\}/T - \{G^\circ(T)-H^\circ(0)\}/T$

[a] Units: J mol^{-1} for $\{H^\circ(T)-H^\circ(0)\}$ and J K^{-1} mol^{-1} for the remaining properties, g^3 cm^6 for $I_aI_bI_c$, K for T and cm^{-1} for ϵ_i.

[b] $u_i = 1.4378786\tilde{\nu}_i/T$ where $\tilde{\nu}_i$ = vibrational wavenumber (in cm^{-1}).

TABLE A-2. Molecular weight, product of moments of inertia and vibrational assignments for C_1-C_4 organic oxygen compounds[a]

No.	Compound name	Molecular weight		$\frac{I_aI_bI_c \times 10^{117}}{g^3\ cm^6}$	Fundamental vibrational wave numbers[b] $\frac{}{cm^{-1}}$
1	Methanol	32.0420		7.89719	3681, 3000,2844, 1477, 1455, 1345, 1060, 1033, 2960,1477, 1165
2	Methanol-d_1	33.0482		10.4152	2718, 3000, 2843, 1473, 1456, 864, 1230, 1040,2960, 1473, 1160
3	Methanol-d_3	35.0606		21.8237	3690, 2260, 2077, 1047, 1134, 1297, 858, 988, 2235, 1075, 877
4	Methanol-d_4	36.0668		26.9037	2724, 2260, 2080, 1024, 1135, 1060, 776, 983, 2228, 1080, 892
5	Ethanol	46.0688	*trans*	218.459	3659, 2985, 2939, 2900, 1460, 1430, 1395, 1320, 1245, 1055, 1026, 883, 422, 2887, 2887, 1460, 1270, 1117, 801
			gauche	233.455	3675, 2985, 2939, 2900, 1460, 1430, 1395, 1320, 1245, 1055, 1026, 887, 596, 2887, 2887, 1460, 1270, 1070, 801
6	1-Propanol	60.0956	*trans*	1660.2	3680, 2940(7), 1478, 1463, 1450(2), 1393, 1381, 890, 860,730, 463, 1341, 1299, 1272, 1220, 1103, 1066, 1052, 971, 916
			gauche	1855.1	3705, 2971, 2970, 2941, 2924, 2911, 2903, 2877, 1465, 1462, 1461, 1459, 1394, 1388, 1330, 1255, 1227, 1180, 1075, 1056, 1003, 917, 880, 862, 524, 920, 349
7	2-Propanol	60.0956		1831.0	3650, 2940(6), 2875, 1475(2), 1460(2), 1387, 1367, 1340, 1256(2), 1153, 1130, 1072, 955(2), 940, 818, 488, 427, 373
8	1-Butanol	74.1224		8444.0	3300, 2950(9), 1470, 1450(4), 1294(7). 1250. 1070. 1050. 955(4), 890(3), 446, 392, 350
9	DL-2-Butanol	74.1224		7910.0	3682, 2980(6), 2943(2), 2891, 1450(5), 1394, 1380(2), 1350, 1314, 1290, 1250, 1145, 1110, 1080, 1034, 992, 970, 912, 820, 780, 500, 435, 382, 274
10	2-Methyl-2-propanol	74.1224		5961.7	3643, 2980(6), 2910(2), 2880, 1472(5), 1450, 1395, 1374(2), 1330, 1230, 1215, 1106(2), 1140, 1013(3), 919, 748, 462(2), 424, 356, 344
11	1,2-Ethanediol	62.0682	*TGG'*	1465.3	3638, 2941, 2940, 1470, 1414, 1164, 1265, 1046, 1076, 876, 508, 276, 144, 3671, 2878, 2878, 1465, 1381, 1239, 1358, 862, 1098, 372, 309
			GGG'	1465.3	3623, 2941, 2940, 1471, 1398, 1301, 1179, 1055, 1096, 874, 508, 181, 139, 3671, 2878, 2878, 1465, 1387, 1232, 1342, 864, 1055, 369, 311
			TTT'	1465.3	3656, 2941, 1496, 1403, 1244, 1097, 969, 452, 2941, 1301, 1066, 305, 148, 2878, 1252, 871, 292, 3684, 2878, 1440, 1376, 1174, 1042, 516
			TTG'	1465.3	3656, 3941, 1496, 1396, 1213, 1095, 994, 453, 2941, 1335, 1032, 309, 146, 2878, 1287, 864, 281, 3684, 2878, 1440, 1349, 1174, 1043, 516

TABLE A-2. Molecular weight, product of moments of inertia and vibrational assignments for C_1-C_4 organic oxygen compounds[a] — Continued

No.	Compound name	Molecular weight		$\frac{I_aI_bI_c \times 10^{117}}{g^3\ cm^6}$	Fundamental vibrational $\frac{\text{wave numbers}^{b}}{cm^{-1}}$
12	Dimethyl ether	46.0688		170.493	2999(2), 2935, 2920, 2820(2), 1485, 1467, 1463, 1459, 1449, 1432, 1250, 1179, 1178, 1148, 1104, 931, 424
13	Dimethyl ether-d_3	49.0874		285.768	2994, 2932, 2821, 2244, 2189, 2054, 1474, 1457, 1443, 1215, 1165, 1161, 1111, 1075, 1059, 946, 903, 860, 389
14	Dimethyl ether-d_6	52.1060		452.089	2248(2), 2148, 2165, 2054(2), 1162, 1148, 1079, 1063, 1059(2), 1052, 1047, 932, 876, 860, 827, 356
15	Ethyl methyl ether	60.0956	*trans*	1304.52	2989, 2988, 2968, 2962, 2958, 2881, 2864, 2820, 1485, 1472, 1462, 1456(2), 1445, 1392, 1365, 1269, 1208, 1169, 1150, 1120, 1094, 1015, 853, 815, 468, 298
			gauche	1434.5	2989, 2988, 2969, 2962, 2959, 2881, 2864, 2820, 1485, 1472, 1462, 1456(2), 1445, 1383, 1365, 1304, 1208, 1164, 1150, 1120, 1068, 979, 843, 800, 468, 379
16	Diethyl ether	74.1224	*trans-trans*	6978.4	2968(2), 2962(2), 2958(2), 2881(2), 2865, 2864, 1490. 1484. 1456(2). 1443(2), 1414, 1383, 1372, 1351, 1350, 1279, 1237, 1168(2), 1153, 1120, 1077, 1043, 935, 822, 794, 440(2), 208
			trans-gauche	6875.0	2969, 2963, 2962(2), 2959, 2958, 2881(2), 2865, 2864, 1490, 1484, 1456(2), 1443(2), 1393, 1383, 1372(2), 1350, 1297, 1267, 1168(2), 1153, 1120, 1074, 1023, 916, 822, 794, 503, 376, 318
17	Propanone	58.0798		1390.63	3019(2), 2972, 2963, 2937(2), 1731, 1454, 1435, 1426, 1410, 1364(2), 1216, 1091, 1066, 891, 877, 777, 530, 484, 385
18	2-Butanone	72.1066		6268.4	2983(4), 2941, 2910(2), 2884, 1716, 1460(2), 1422, 1413(2), 1373, 1346, 1263(2), 1182, 1108, 1089, 997, 952, 939, 768, 760, 590, 460, 413, 260
19	Methanal	30.0262		1.5874	2843, 2783, 1746, 1500, 1249, 1167
20	Methanal-d_1	31.0324		2.8909	2844, 2121, 1723, 1400, 1074, 1041
21	Methanal-d_2	32.0386		4.9358	2160, 2056, 1700, 1106, 990, 938
22	Ethanal	44.0530		111.80	3005, 2967, 2917, 2822, 1743, 1441, 1420, 1400, 1352, 1113, 919, 867, 763, 509
23	Ethanal-d_1	45.0592		147.20	3028, 2970, 2917, 2071, 1743, 1442, 1420, 1353, 1109, 1043, 849, 802, 668, 500
24	Ethanal-d_4	48.0778		260.79	2265, 2225, 2130, 2060, 1737, 1151, 1045, 1028(2), 938, 747,670, 573, 436 25
	1-Propanal	58.0798	*cis*	1290.0	2993(2), 2927, 2916, 2914, 2759, 1753, 1468(2), 1423, 1398, 1381, 1339, 1093, 1010, 849, 1255, 1129, 896, 672, 658, 271

TABLE A-2. Molecular weight, product of moments of inertia and vibrational assignments for C_1-C_4 organic oxygen compounds[a] — Continued

No.	Compound name	Molecular weight	$\frac{I_aI_bI_c \times 10^{117}}{g^3\ cm^6}$	Fundamental vibrational wave numbers[b] cm^{-1}
			skew 1221.0	2993(2), 2927, 2916, 2914, 2759, 1753, 1468(2), 1423, 1398, 1364, 1339, 1243, 1144, 1129, 998, 907, 873, 672, 508, 325
26	Methanoic acid	46.0256	60.7259	3570, 2943, 1770, 1387, 1229, 1105, 1033, 625
27	Methanoic acid-d_1(HCOOD)	47.0318	76.2477	2948, 2632, 1772, 1360, 1178, 1000, 990, 562
28	Methanoic acid-d_1(DCOOH)	47.0318	85.3306	3570, 2220, 1756, 1220, 1143, 970, 870, 620
29	Methanoic acid-d_2	48.0380	103.740	2632, 2232, 1742, 1171, 980, 945, 873, 558
30	Methanoic acid dimer	92.0512	26369.6	3200, 3110, 2957, 2956, 1754, 1672, 1450, 1395, 1365, 1350, 1218, 1204, 1073, 1063, 917, 697, 677, 675, 519, 248,232, 215, 164, 68
31	Ethanoic acid	60.0524	1033.0	3583, 3051, 2996, 2944, 1788, 1430(2), 1382, 1264, 1182, 1048, 989, 847, 657, 642, 581
32	Ethanoic acid dimer	120.1048	161410.0	3193, 3032, 2949, 1675, 1436, 1436, 1370, 1283, 1018, 886, 624, 448, 196, 110, 3140, 3028, 2956, 1715, 1413, 1413, 1359, 1295, 1013, 886, 624, 480, 188, 2990, 1413, 1050, 934, 635, 67, 47, 3000, 1436, 1112, 912, 623, 115
33	Methyl methanoate	60.0524	806.497	3045, 3012, 2969, 2943, 1754, 1454, 1445, 1443, 1371, 1207, 1168, 1166, 1032, 925, 767, 332, 318
34	Methyl ethanoate	74.0792	4495.80	3035, 3031, 3005, 2994, 2966, 2964, 1771, 1460(2), 1440, 1430(2), 1375, 1248, 1187, 1159, 1060, 1036, 980, 844, 639, 607, 429, 199, 187
35	Ethylene oxide	44.0530	74.4362	3065, 3063, 3018, 3006, 1498, 1472, 1300, 1270, 1151, 1148, 1142, 877, 860, 840, 821
36	Ethylene oxide-d_4	48.0778	162.523	2319, 2250, 2210, 2176, 1309, 1084, 1083, 1012, 968, 903, 896, 809. 752. 581. 577
37	Propylene oxide	58.0798	824.586	3065(2), 3006, 2975, 2929, 2846, 1500, 1456(2), 1406, 1368, 1263, 1166, 1142, 1132, 1102, 1023, 950, 896, 828, 745, 416, 371
38	Furan	68.0750	1448.6	3167, 3161, 3140, 3129, 1556, 1491, 1384, 1267, 1180, 1140, 1066, 1040, 995, 873, 871, 863, 838, 745, 728, 613, 603
39	2,5-Dihydrofuran	70.0908	2000.4	3090(2), 2970(2), 2860(2), 1580, 1480, 1465, 1355, 1345, 1300, 1195, 1165, 1090, 1060, 1030, 1012, 990, 907, 898, 790, 740, 655(2), 384
40	Tetrahydrofuran	72.1066	2978.6	2970(4), 2847(4), 1517(2), 1486, 1452, 1366, 1339, 1289, 1238(2), 1177, 1150(3), 1114, 1076, 1029, 964, 912, 881, 821(2), 654, 596, 278

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[a] Underlined values derived from microwave spectra, others calculated from molecular geometry

[b] Numbers in parenthesis are the degeneracies.

TABLE A-3. Internal rotation molecular constants [a]

No.	Molecule	s	Rotor	σ	N_c	I_r	F	$\tilde{\nu}(0\rightarrow1)$	ϵ_0	V_1	V_2	V_3	V_4	V_6
1	CH_3OH	1	CH_3–OH	3	1	$\underline{0.993}$	$\underline{28.19}$	299.6	0.0			$\underline{4.465}$		$-\underline{0.0062}$
2	CH_3OD	1	CH_3–OD	3	1	1.605	17.44	215.4	0.0			$\underline{4.377}$		
3	CD_3OH	1	CD_3–OH	3	1	1.097	25.52	275.	0.0			$\underline{4.429}$		$-\underline{0.0272}$
4	CD_3OD	1	CD_3–OD	3	1	1.856	15.08	194.	0.0			$\underline{4.333}$		$-\underline{0.0277}$
5	CH_3CH2OH													
	trans	1	CH_3–CH_2OH	3	1	$\underline{4.365}$	6.414	244.1	0.0			$\underline{13.95}$		
		1	CH_3CH_2–OH	1	1	1.329	21.07	205.2	0.0	$\underline{0682}$	$\underline{0.096}$	$\underline{4.725}$		
	gauche	2	CH_3–CH_2OH	3	1	4.363	6.416	261.9	0.444			$\underline{15.92}$		
			CH_3CH_2–OH	1	1	1.337	20.94	248.2	0.494	$\underline{0.682}$	$\underline{0.096}$	$\underline{4.725}$		
6	$CH_3CH_2CH_2OH$													
	trans	1	CH_3–CH_2CH_2OH	3	1	$\underline{4.591}$	6.097	214.2	0.837			$\underline{11.42}$		
			C_2H_5–CH_2OH	1	1	$\underline{14.93}$	1.875	112.4	0.837			$\underline{9.666}$		
			C_3H_7–OH	1	1	$\underline{1.321}$	21.34	226.5	0.837			$\underline{3.347}$		
	gauche	2	CH_3–CH_2CH_2OH	3	1	$\underline{5.050}$	5.543	210.5	0.0			$\underline{12.01}$		
			C_2H_5–CH_2OH	1	1	$\underline{15.635}$	1.791	$\underline{130.0}$	0.0			13.22		
			C_3H_7–OH	1	1	$\underline{1.261}$	22.20	233.2	0.0			$\underline{3.347}$		
7	$(CH_3)_2CHOH$	1												
			CH_3–$CH(CH_3)OH$	3	2	5.036	5.559	251.4				$\underline{16.74}$		
			CH_3H_7–OH	1	1	$\underline{1.281}$	21.853	209.6	0.0	0.364	−1.031	$\underline{4.801}$		
8	$CH_3CH_2CH_2CH_2OH$	1												
			CH_3–C_3H_6OH	3	1	4.85	5.772	229.6	0.0			$\underline{13.64}$		
			C_2H_5–C_2H_4OH	1	1	20.38	1.374	115.6	0.0			$\underline{13.64}$		
			C_3H_7–CH_2OH	1	1	18.35	1.526	121.6	0.0			$\underline{13.64}$		
			C_4H_9–OH	1	1	1.27	22.04	152.3	0.0			$\underline{3.096}$		
9	$CH_3CH_2CH(OH)CH_3$													
	trans	1	CH_3–$C_2H_4(OH)CH_3$	3	1	5.043	5.551	219.4	0.0			$\underline{12.97}$		
			$C_2H_5CH(OH)$–CH_3	3	1	5.043	5.551	251.2	0.0			$\underline{16.74}$		
			C_2H_5–$CH(OH)CH_3$	1	1	30.27	0.925	77.0	0.0			$\underline{9.00}$		
			C_4H_9–OH	1	1	1.320	21.21	224.5	0.0			$\underline{3.347}$		
	gauche	2	CH_3–$C_2H_4(OH)CH_3$	3	1	5.043	5.551	219.4	3.45			$\underline{12.97}$		
			$C_2H_5CH(OH)$–CH_3	3	1	5.043	5.551	251.2	3.45			$\underline{16.74}$		
			C_2H_5–$CH(OH)CH_3$	1	1	30.27	0.925	77.0	3.45			$\underline{9.00}$		
			C_4H_9–OH	1	1	1.320	21.21	224.5	3.45			$\underline{3.347}$		
10	$(CH_3)_3COH$	1												
			CH_3–$C(OH)(CH_3)_2$	3	3	5.145	5.441	242.2	0.0			15.90		
			C_4H_9–OH	3	1	1.291	21.68	236.4	0.0			$\underline{3.766}$		
11	$HOCH_2CH_2OH$													
	TTG'	2	HO–CH_2CH_2OH					$\underline{276,309}$*	0.0					
			$HOCH_2$–CH_2OH					$\underline{144}$*	0.0					
	GGG'	2	HO–CH_2CH_2OH					$\underline{139,311}$*	3.68					
			$HOCH_2$–CH_2OH					$\underline{139}$*	3.68					

TABLE A-3. Internal rotation molecular constants[a] — Continued

No.	Molecule	s	Rotor	σ	N_c	I_r	F	$\tilde{\nu}(0\rightarrow 1)$	ϵ_0	V_1	V_2	V_3	V_4	V_6
	TTT'	2	$HO-CH_2CH_2OH$					305.292*	10.66					
			$HOCH_2-CH_2OH$					148[d]	10.66					
	TTG'	2	$HO-CH_2CH_2OH$					309.281*	13.35					
			$HOCH_2-CH_2OH$					146[d]	13.35					
12	CH_3OCH_3	1	CH_3-OCH_3	3	2	4.291	6.524	214.5	0.0			10.807		
13	CH_3OCD_3	1												
			CH_3-OCD_3	3	1	4.529	6.181	223.9	0.0			12.26		
			CH_3O-CD_3	3	1	7.248	3.862	162.0	0.0			10.09		
14	CD_3OCD_3	1	CD_3-OCD_3	3	2	7.697	3.637	166.0	0.0			11.14		
15	$CH_3CH_2OCH_3$													
	trans	1	$CH_3-CH_2OCH_3$	3	1	5.276	5.306	248.	0.0			17.01		
			$CH_3CH_2O-CH_3$	3	1	3.558	7.867	202.	0.0			8.31		
			$CH_3CH_2-OCH_3$	1	1	18.72	1.495	115.	0.0			12.48		
	gauche	2	$CH_3-CH_2OCH_3$	3	1	4.994	5.605	239.	6.28			15.04		
			$CH_3CH_2O-CH_3$	3	1	5.046	5.548	192.	6.28			9.57		
			$CH_3CH_2-OCH_3$	1	1	18.54	1.510	126.	6.28			14.76		
16	$CH_3CH_2OCH_2CH_3$													
	TT	1	$CH_3-CH_2OC_2H_5$	3	2	4.168	6.715	238.	0.0			12.79		
			$CH_3CH_2-OC_2H_5$	1	2	19.46	1.439	120.	0.0			14.05		
	TG	4	$CH_3-CH_2OC_2H_5$	3	2	4.718	5.933	227.	5.73			13.01		
			$CH_3CH_2-OC_2H_5$	1	2	22.56	1.240	107.	5.73			13.05		
17	CH_3COCH_3	1	CH_3-COCH_3	3	2	4.888	5.727	104.3	0.0			3.255		
18	$CH_3CH_2COCH_3$	1												
			$C_2H_5CO-CH_3$	3	1	5.071	5.520	83.3	0.0			2.17		
			$CH_3-CH_2COCH_3$	3	1	5.119	5.468	199.6	0.0			11.00		
			$C_2H_5-COCH_3$	1	1	26.21	1.068	60.6	0.0	7.991		4.00		
22	CH_3CHO	1	CH_3-CHO	3	1	3.648	7.673	150.	0.0			4.92		
23	CH_3CDO	1	CH_3-CDO	3	1	3.982	7.030	145.	0.0			5.067		
24	CD_3CDO	1	CD_3-CDO	3	1	6.406	4.370	116.	0.0			4.858		
25	CH_3CH_2CHO													
	cis	1	CH_3-CH_2CHO	3	1	4.664	6.002		0.0			9.540		
			C_2H_5-CHO	1	1	7.135	3.923	133.	0.0	1.799	3.965	13.94	0.051	
	skew	2	CH_3-CH_2CHO	3	1	4.621	6.058		0.0			13.2		
			C_2H_5-CHO	1	1	10.815	2.588	74.	0.0	1.799	3.965	13.94	0.051	
26	HCOOH	1	HCO–OH	1	1	1.122	24.96	609.6	0.0	24.06	37.36	2.301		
27	HCOOD	1	HCO–OD	1	1	1.824	15.35	483.	0.0	24.06	37.36	2.301		
28	DCOOH	1	DCO–OH	1	1	1.178	23.76	595.	0.0	24.06	37.36	2.301		
29	DCOOD	1	DCO–OD	1	1	1.978	14.15	464.	0.0	24.06	37.36	2.301		
31	CH_3COOH	1												
			CH_3-COOH	3	1	4.955	5.649	75.	0.0			2.013		
			CH_3CO-OH	1	1	1.317	21.26	565.	0.0	24.06	37.36	2.301		

TABLE A-3. Internal rotation molecular constants[a] — Continued

No.	Molecule	s	Rotor	σ	N_c	I_r	F	$\tilde{\nu}(0 \rightarrow 1)$	ϵ_0	V_1	V_2	V_3	V_4	V_6
32	$(CH_3COOH)_2$	1	CH_3-$C_3H_5O_4$	3	2	5.222	5.361	74	0.0			2.013		
33	$HCOOCH_3$													
	cis	1	HCOO-CH_3	3	1	4.894	5.720	130	0.0			4.86		
			HCO-OCH_3					332*						
34	CH_3COOCH_3	1												
	cis		CH_3-$COOCH_3$	3	1	5.009	5.589	65	0.0			1.191		
			CH_3COO-CH_3	3	1	4.936	5.671	133.3	0.0			5.084		
			CH_3CO-OCH_3					187*						
37	C_3H_6O	1	CH_3-C_2H_3O	3	1	4.793	5.841	200	0.0			10.68		−0.084

[a] s = number of identical species of type identified; σ = symmetry number for internal rotation; N_c = number of contributions; I_r = reduced moment of inertia; F = internal rotational constant (eq. 11); $\tilde{\nu}(0 \rightarrow 1)$ = wavenumber of 0 – 1 transition for torsional mode, ϵ_0 = energy of lowest state relative to ground state, V_n = coefficient of potential function (eq. 12). Units of ϵ and V_n are kJ mol^{-1}.

The underlined values of I_r and F have been derived from microwave spectra and reported in the literature. Those not underlined have been calculated from molecular geometry.
The underlined values of V_N and $\tilde{\nu}$ have been reported in the literature. Others have been calculated from the relations among V_n, F, and $\tilde{\nu}$ as described in section 1.3 of the introduction.

* harmonic oscillator assumed

TABLE A-4. Comparison of observed and calculated heat capacities of methanol(g)

$\frac{T}{K}$	$\frac{C_p^\circ}{\text{J K}^{-1}\text{ mol}^{-1}}$				$\frac{C_p^\circ}{\text{J K}^{-1}\text{ mol}^{-1}}$
	Exptl.	Correlation[a]	W-P[b]	K-W[c]	This work
349.65	72.68[d]		46.07	47.28	47.66
358.15	59.79[d]		46.74	45.48	48.33
358.85	60.58[d]		48.20	46.86	48.28
359.85	60.33[d]		48.83	47.40	48.45
368.15	56.99[d]		50.29	48.66	49.08
382.15	54.81[d]		51.30	50.04	50.17
401.15	54.43[d]		52.34	51.59	51.71
420.15	54.68[d]		53.22	52.80	53.26
442.65	56.99[d]		55.90	55.73	55.10
341	112.97[d]		51.42	62.05	46.99
363	58.58[d]		49.37	47.74	48.66
405	54.52[d]		52.59	51.92	52.01
345.6	50.96±0.8[e]		47.86[f]	46.86[f]	47.36
403.2	52.63±0.2[e]		52.01[g]	51.76[g]	51.88
464.0	57.49±0.4[e]		57.20[g]	57.20[g]	56.82
521.2	60.58±0.8[e]		60.42[f]	60.46[f]	61.34
347.35	86.86[h]	46.82	52.72	55.61	47.49
356.55	66.61[h]	47.57	51.34	50.33	48.16
373.35	56.19[h]	48.99	51.00	49.41	49.50
398.95	52.97[h]	51.13	50.75	49.96	51.55
401.15	54.02[h]	51.34	51.92	51.13	51.71
401.35	54.14[h]	51.34	52.05	51.30	51.71
431.45	55.77[h]	53.89	54.52	54.22	54.18
442.15	56.02[h]	54.77	54.94	54.73	55.06
457.35	56.99[h]	56.02	56.11	55.98	56.27
477.75	57.24[h]	57.74	56.52	56.48	57.91
485.05	56.57[h]	58.37	55.90	55.90	58.49
498.95	60.12[h]	59.54	59.58	59.58	59.62
521.35	61.55[h]	61.42	61.09	61.13	61.34
555.95	63.93[h]	64.31	63.60	63.64	63.97
581.35	66.36[h]	66.44	66.11	55.15	65.86
585.35	66.82[h]	66.78	66.57	66.61	66.15

[a] $C_p^\circ/\text{J K}^{-1}\text{ mol}^{-1} = 10.226(1.73 + 8.20 \times 10^{-3}\ T)$ with the average deviation of ± 1.34 J K^{-1} mol^{-1}

[b] Virial coefficients B and D of Ref. 55 were used for gas imperfection corrections.

[c] Virial coefficients B and D of Ref. 56 were used for gas imperfection corrections.

[d] Observed at 750 mm Hg with the uncertainty of about 1 percent.[52,53]

[e] Observed at 260 mm Hg[55].

[f] With the estimated error of ± 1.3 J K^{-1} mol^{-1}.

[g] With the estimated error of ± 0.4 J K^{-1} mol^{-1}.

[h] Observed at 1 atm.[54]

TABLE A-5. Comparison of observed and calculated entropies of methanol(g)

$\frac{T}{K}$	$\frac{\{S(T)-S^\circ(0)\}\text{ (Experimental)}}{\text{J K}^{-1}\text{ mol}^{-1}}$			$\frac{\{S^\circ(T)-S^\circ(0)\}\text{ (Calculated)}}{\text{J K}^{-1}\text{ mol}^{-1}}$
	Real gas at saturation	Ideal gas at 1 bar W–P[a]	K–W[b]	This work
313.1	248.56[c]	242.10	241.59	241.99
327.9	244.79[c]	244.31	243.94	244.08
337.8	242.53[c]	245.95	245.65	245.46
323.15	245.95[d]	243.69	243.23	243.41
337.85	242.91[d]	245.90	245.61	245.46
363.15	237.01[d]	249.13	249.21	248.93
383.15	233.33[d]	251.55	251.97	251.57

[a] Weltner-Pitzer[55] virial coefficients, B and D, were applied to corrections for gas imperfection.

[b] Kretschmer-Wiebe[56] virial coefficients, B and D, were applied to corrections for gas imperfection.

[c] Derived from enthalpy of vaporization[55] and C_l[83] with the estimated error of ± 1.26 J K^{-1} mol^{-1}

[d] Derived from enthalpy of vaporization[58] and C_l[83] with presumably the same uncertainty as in footnote *c*.

TABLE A-6. Comparison of observed and calculated heat capacities of ethanol (g)

$\frac{T}{\mathrm{K}}$	$\frac{C_p^\circ}{\mathrm{J\ K^{-1}\ mol^{-1}}}$		$\frac{T}{\mathrm{K}}$	$\frac{C_p^\circ}{\mathrm{J\ K^{-1}\ mol^{-1}}}$	
	Exptl.[a]	this work		Exptl.[b]	this work
350.01	73.05	73.35	200	51.38	52.02
360.00	74.56	74.94	297	62.30	62.32
370.01	76.02	76.52	280	62.09	62.47
380.00	77.49	78.10	367.9	75.52	76.19
400.08	80.42	81.24	410.16	82.01	82.79
425.06	84.06	85.06	422	83.39	84.59
450.06	87.65	88.76	437	87.99	86.84
475.10	91.25	98.32	476	91.21	92.48

[b] Ref. 91.

[b] Ref. 59.

TABLE A-7. Comparison of observed and calculated entropies of ethanol (g)

$\frac{T}{\mathrm{K}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\mathrm{J\ K^{-1}\ mol^{-1}}}$				
	Exptl.[a]	Brickwedde[b]	Barrow[c]	Green[d]	this work
298.15	282.86	278.14	282.86	282.80	280.64
351.5	293.66	290.56	294.08	294.20	292.04
403.15	305.33	302.53	304.91	304.20	302.68

[a] Calculated from low temperature thermal measurements. The average uncertainty is ±1.67 J $\mathrm{K^{-1}\ mol^{-1}}$.

[b] Ref. 92.

[c] Ref. 57.

[d] Ref. 59.

TABLE A-8. Comparison of observed and calculated C_p° and $\{S^\circ(T)-S^\circ(0)\}$ of 1-propanal (g)

$\frac{T}{\mathrm{K}}$	$\frac{C_p^\circ}{\mathrm{J\ K^{-1}\ mol^{-1}}}$		$\frac{T}{\mathrm{K}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\mathrm{J\ K^{-1}\ mol^{-1}}}$	
	Exptl.[a]	Calc.		Exptl.[a]	Calc.
371.2	102.26	101.75	298.15	322.49[b]	322.58
391.2	106.44	106.12	298.15	323.20[c]	
411.2	110.42	110.42			
431.2	114.35	114.62			
451.2	118.62	118.71			

[a] Ref. 60.

[b] Based on low temperature thermal measurements of Parks *et al.*;[105] and vapor pressure, enthalpy of vaporization, and gas imperfection correction of Ref. 60. The uncertainty was ±2.93 J $\mathrm{K^{-1}\ mol^{-1}}$.

[c] Based on S(298.15 K) = 193.59 J $\mathrm{K^{-1}\ mol^{-1}}$ for 1-propanol (liq), a reevaluated value, instead of the reported value of 192.88 J $\mathrm{K^{-1}\ mol^{-1}}$.

TABLE A-9. Comparison of observed and calculated C_p° and $\{S^\circ(T) - S^\circ(0)\}$ of 2-propanol (g)

$\frac{T}{\mathrm{K}}$	$\frac{C_p^\circ}{\mathrm{J\ K^{-1}\ mol^{-1}}}$		$\frac{T}{\mathrm{K}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\mathrm{J\ K^{-1}\ mol^{-1}}}$	
	Exptl.[a]	Calc.		Exptl.[a]	Calc.
358.72	103.53	103.05	298.15	310.14[b]	309.20
373.15	106.28	106.27		310.65[c]	
398.15	111.63	111.75	324.56	317.42	316.94
423.15	117.03	117.03	339.25	321.69	321.21
448.15	122.09	122.13	355.39	326.59	325.89
473.15	127.03	126.99			

[a] Ref. 115.

[b] Based on low temperature thermal data of Andon *et al.*;[116] vapor pressure of Biddiscombe *et al.*;[117] enthalpy of vaporization of Hales *et al.*;[115] and gas imperfection correction of Green.[111] The uncertainty was ±0.8 J $\mathrm{K^{-1}\ mol^{-1}}$.

[c] Use the same data as those given in note b, except a value of $S(l, 298.15\ \mathrm{K}) = 181.08\ \mathrm{J\ K^{-1}\ mol^{-1}}$ is employed to replace the reported value of 180.58 $\mathrm{J\ K^{-1}\ mol^{-1}}$ for calculation. The uncertainty is ±1.26 J $\mathrm{K^{-1}\ mol^{-1}}$.

TABLE A-10. Comparison of observed and calculated C_p° and $\{S^\circ(T)-S^\circ(0)\}$ of 1-butanol (g)

$\frac{T}{\mathrm{K}}$	$\frac{C_p^\circ}{\mathrm{J\ K^{-1}\ mol^{-1}}}$		$\frac{T}{\mathrm{K}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\mathrm{J\ K^{-1}\ mol^{-1}}}$	
	Exptl.[a]	Calc.		Exptl.[a]	Calc.
398.15	137.884	137.65	298.15	363.28[a]	361.83[b]
413.15	142.064	141.88		362.44±4.2[b]	363.70[c]
433.15	147.419	147.36		360.19[d]	361.61[e]
453.15	152.657	152.67			

[a] Ref. 120.

[b] Ref. 63, interpolated values.

[c] Ref. 64.

[d] Recalculated value, based on $S(\mathrm{l}, 298.15\ \mathrm{K}) = 225.77\ \mathrm{J\ K^{-1}\ mol^{-1}}$ instead of 228.03 $\mathrm{J\ K^{-1}\ mol^{-1}}$.[63]

[e] Recalculated in this work.

TABLE A-11. Comparison of observed and calculated C_p° and $\{S^\circ(T)-S^\circ(0)\}$ of DL-2-butanol (g)

$\frac{T}{\mathrm{K}}$	$\frac{C_p^\circ}{\mathrm{J\ K^{-1}\ mol^{-1}}}$		$\frac{T}{\mathrm{K}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\mathrm{J\ K^{-1}\ mol^{-1}}}$	
	Exptl.[a]	Calc.		Exptl.[a]	Calc.
365.15	131.10	131.30	298.15	359.14[a]	359.53[b]
383.15	136.52	136.21		355.37[c]	
401.15	141.46	141.04			
419.15	146.23	145.78			
437.15	150.96	150.41			
455.15	155.64	154.92			

[a] All data taken from Ref. 61.

[b] Recalculated in this work.

[c] Taken from Table A-26.

TABLE A-12. Comparison of observed and calculated C_p° and $\{S^\circ(T) - S^\circ(0)\}$ of 2-methyl-2-propanol (g)

$\frac{T}{\mathrm{K}}$	$\frac{C_p^\circ}{\mathrm{J\,K^{-1}\,mol^{-1}}}$		$\frac{T}{\mathrm{K}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	
	Exptl.[a]	Calc.		Exptl.[a]	Calc.
365.15	132.63	133.22	330.15	338.28	338.76
383.15	137.95	138.32	339.65	342.16	342.28
401.15	142.88	143.30	345.65	344.62	344.50
419.15	148.07	148.20			
437.15	153.55	152.93			

[a] All data taken from Ref. 62.

TABLE A-13. Comparison of observed and calculated C_p° and $\{S^\circ(T)-S^\circ(0)\}$ of dimethyl ether (g)

$\frac{T}{\mathrm{K}}$	$\frac{C_p^\circ}{\mathrm{J\,K^{-1}\,mol^{-1}}}$		$\frac{T}{\mathrm{K}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	
	Exptl.[a]	Calc.		Exptl.[a]	Calc.
272.20	62.01	62.47	298.15	267.09 ±0.84	267.34
300.76	65.90	65.90			
333.25	70.33	70.00			
370.42	75.14	74.81			

[a] Ref. 158.

[b] Evaluated from the low temperature thermal measurements of Kennedy *et al.*[159]

TABLE A-14. Comparison of observed and calculated C_p° and $\{S^\circ(T)-S^\circ(0)\}$ of diethyl ether (g)

$\frac{T}{\mathrm{K}}$	$\frac{C_p^\circ}{\mathrm{J\,K^{-1}\,mol^{-1}}}$		$\frac{T}{\mathrm{K}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	
	Exptl.[a]	Calc.		Exptl.[a]	Calc.
309.98	121.91[a]	122.01	298.15	342.31[a]	342.67
329.98	126.56	126.46		342.55[d]	
350.00	131.32	131.05		342.71[e]	
375.00	137.35	136.90			
400.01	143.27	142.82			
424.99	149.10	148.70			
450.04	155.11	154.52			
308.15	116.32[b]	121.61			
341.15	132.63	129.00			
370.25	144.77	135.78			
373.15	147.28	136.47			
376.15	143.09	137.17			
407.15	145.18	144.50			
419.15	148.95	147.33			
458.15	169.45	156.39			
473.15	171.54	159.80			
523.15	165.27	170.77			
573.15	184.10	181.09			
623.15	186.19	190.74			
400	131.38[c]	142.81			
450	144.77	154.52			
500	158.58	165.77			

[a] Ref. 160.

[b] Ref. 161.

[c] Ref. 162.

[d] Evaluated based on low temperature thermal data and other related quantities reported by Counsell *et al.*[160].

[e] See table A-26.

TABLE A-15. Comparison of observed and calculated heat capacities of propanone (g)

$\frac{T}{\text{K}}$	$\frac{C_p^\circ}{\text{J K}^{-1}\text{ mol}^{-1}}$		$\frac{T}{\text{K}}$	$\frac{C_p^\circ}{\text{J K}^{-1}\text{ mol}^{-1}}$	
	Exptl.[a]	this work		Exptl.	this work
334	80.96	80.92	338.2	81.50[b]	81.63
348	83.38	83.30	371.2	87.19[b]	87.19
363	87.03	85.81	405.2	92.93[b]	92.93
378	89.24	88.37	439.2	98.66[b]	98.53
393	91.84	90.88	410.02	94.14[c]	93.76
408	94.18	93.39			
428	99.04	96.70			
438	100.50	98.32			
332.6	80.58	80.71			
347.8	83.35	83.26			
372.3	87.53	87.40			
422.6	96.78	95.81			

[a] Ref. 222; the first 8 data points were measured using reverse-flow calorimeter and the remaining 4 data points were measured using direct flow calorimeter.

[b] Ref. 189.

[c] Ref. 106.

TABLE A-16. Comparison of observed and calculated entropies of propanone(g)

$\frac{T}{\text{K}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\text{J K}^{-1}\text{ mol}^{-1}}$			
	Exptl.[a]	P.-K.(1957)[b]	S.-A.(1938)[c]	this work
298.15	294.96±1.05	295.04±1.26		297.62
329.3			304.29±2.09	305.33

[a] Calculated from low temperature thermal measurements.[194]

[b] Ref. 189.

[c] Ref. 108.

TABLE A-17. Comparison of observed and calculated C_p° and $\{S^\circ(T)-S^\circ(0)\}$ of 2-butanone (g)

$\frac{T}{\text{K}}$	$\frac{C_p^\circ}{\text{J K}^{-1}\text{ mol}^{-1}}$		$\frac{T}{\text{K}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\text{J K}^{-1}\text{ mol}^{-1}}$	
	Exptl.[a]	this work		Exptl.	this work
347.15	113.43[a]	112.97	298.15	338.64±2.51[a]	339.90±0.66
372.15	119.03	118.11		338.72±0.84[c]	
397.15	124.39	123.80		338.30±0.84[d]	
432.15	131.71	131.21		338.22±0.84[e]	
467.15	138.62	138.41			
410.2	124.68[b]	126.65			

[a] Ref. 193; the reported S(298.15 K) value was incorrect[192] due to some mathematical errors involved in calculation, the correct value should be 338.64 J K^{-1} mol^{-1}.

[b] Ref. 106.

[c] The value was calculated from low temperature thermal measurements,[192,236] based on S(l, 298.15 K) = (239.07 ± 0.63) J K^{-1} mol^{-1}.[194]

[d] Calculated value, based on S(l, 320 K) = 250.29 J K^{-1} mol^{-1}.[236]

[e] Ref. 192.

TABLE A-18. Comparison of observed and calculated heat capacities of ethanal (g)

$\frac{T}{\mathrm{K}}$	$\frac{C_p^\circ}{\mathrm{J\,K^{-1}\,mol^{-1}}}$			
	Exptl.[a]	Exptl.[b]	Exptl.[c]	Calc.
298.1	61.92	54.81	54.98	55.31
322.9	61.92	58.66	58.03	57.91
372.7	63.60	62.34	62.43	63.30
422.4	68.20	67.57	67.45	68.70

[a] Ref. 134; the values refer to real gas at 1 atm.

[b] Used second virial coefficient data from Ref. 135 for conversion to C_p°.

[c] Used second virial coefficient data from Ref. 136 for conversion to C_p°.

TABLE A-19. Comparison of observed and calculated C_p° and $\{S^\circ(T)-S^\circ(0)\}$ of 1-propanal (g)

$\frac{T}{\mathrm{K}}$	$\frac{C_p^\circ}{\mathrm{J\,K^{-1}\,mol^{-1}}}$		$\frac{T}{\mathrm{K}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	
	Exptl.[a]	Calc.		Exptl.[b]	Calc.
325.0	84.53	84.55	298.15	304.51	304.51
350.1	88.39	88.33			
347.5	92.22	92.23			

[a] Ref. 148.

[b] Ref. 149, recalculated value using C_p° from Table 25.

TABLE A-20. Comparison of observed and calculated heat capacities of ethanoic acid (g)[a]

$\frac{P}{\mathrm{torr}}$	$\frac{T}{\mathrm{K}}$	$\frac{C_p^\circ}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	
		Exptl.[b]	Calc.
249	368.4	300.41	291.62
	399.2	365.26	357.73
	419.0	323.84	323.42
	435.8	261.50	261.50
	479.7	141.00	141.42
	509.2	117.57	115.06
	540.0	107.53	107.11
507	396.4	327.61	317.57
	399.1	332.63	323.00
	420.1	341.83	335.98
	436.0	307.52	307.52
	470.4	201.25	202.09
760	397.5	302.08	291.21
	421.8	332.21	318.82
	443.7	305.01	304.60
	470.9	229.70	229.28

[a] 1 torr = 133.322 $\mathrm{Nm^{-2}}$.

[b] Ref. 248.

TABLE A-21. Comparison of observed and calculated heat capacities of methyl ethanoate (g)

$\frac{T}{\mathrm{K}}$	$\frac{C_p^\circ}{\mathrm{J\ K^{-1}\ mol^{-1}}}$	
	Exptl.[a]	Calc.
335	92.58	92.35
350	95.46	95.25
375	100.39	100.09
400	105.31	104.90
435	109.98	109.64
450	114.63	114.27

[a] Ref. 362.

TABLE A-22. Comparison of observed and calculated C_p° and $\{S^\circ(T)-S^\circ(0)\}$ of epoxyethane (g)

$\frac{T}{\mathrm{K}}$	$\frac{C_p^\circ}{\mathrm{J\ K^{-1}\ mol^{-1}}}$		$\frac{T}{\mathrm{K}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\mathrm{J\ K^{-1}\ mol^{-1}}}$	
	Exptl.[a]	this work		Exptl.[a]	this work
307.18	49.37	49.12	283.66	240.77	240.65
337.04	53.51	53.39	298.15	243.11	242.99
371.23	58.41	58.28			

[a] Ref. 158.

[b] Evaluated based upon the low temperature thermal data reported by Ref. 405.

TABLE A-23. Comparison of observed and calculated C_p° and $\{S^\circ(T)-S^\circ(0)\}$ of furan (g)

$\frac{T}{\mathrm{K}}$	$\frac{C_p^\circ}{\mathrm{J\ K^{-1}\ mol^{-1}}}$		$\frac{T}{\mathrm{K}}$	$\frac{\{S^\circ(T)-S^\circ(0)\}}{\mathrm{J\ K^{-1}\ mol^{-1}}}$	
	Exptl.[a]	this work		Exptl.[a]	this work
317.25	70.29	70.00	279.16	263.16	263.12
358.20	80.12	79.58	293.16	266.21	266.17
402.20	90.00	89.29	304.52	268.64	268.64
449.20	99.58	98.70			
487.20	106.48	105.65			

[a] Ref. 436.

TABLE A-24. Comparison of observed and calculated heat capacities of tetrahydrofuran (g)

$\frac{T}{\mathrm{K}}$	$\frac{C_p^\circ}{\mathrm{J\ K^{-1}\ mol^{-1}}}$	
	Exptl.[a]	Calc.
328.2	85.10	85.06
349.2	91.42	91.34
399.2	106.15	106.11
449.2	120.46	120.25
500.2	133.72	133.64

[a] Ref. 458.

TABLE A-25. Calculated ideal gas thermodynamic properties at 298.15 K and 1 bar

Compound	$\{H^\circ(T)-H^\circ(0)\}$ / J mol^{-1}	$-\{G^\circ(T)-H^\circ(0)\}/T$ / J K^{-1} mol^{-1}	$\{S^\circ(T)-S^\circ(0)\}$ / J K^{-1} mol^{-1}	C_p° / J K^{-1} mol^{-1}
Methanol	11435	201.46	239.81	44.04
Methanol-d_1	11703	204.38	243.63	45.61
Methanol-d_3	11849	207.39	247.13	49.41
Methanol-d_4	12146	210.15	250.90	51.00
Ethanol	14250	232.85	280.64	65.20
1-Propanol	17462	264.02	322.58	85.56
2-Propanol	17266	251.29	309.20	89.32
1-Butanol	20633	292.39	361.59	108.03
DL-2-Butanol	21526	287.33	359.53	112.74
2-Methyl-2-propanol	20656	257.42	326.70	113.63
1,2-Ethanediol	16560	248.2	303.8	82.7
Dimethyl ether	14344	219.23	267.34	65.57
Dimethyl ether-d_3	14993	229.73	280.01	71.49
Dimethyl ether-d_6	15703	226.70	279.37	77.45
Ethyl methyl ether	18473	247.30	309.25	93.30
Diethyl ether	23459	263.99	342.67	119.46
Propanone	16486	242.32	297.62	75.02
2-Butanone	20312	271.78	339.90	101.68
Methanal	10020	185.16	218.76	35.39
Methanal-d_1	10096	193.88	227.74	36.54
Methanal-d_2	10210	190.83	225.07	38.14
Ethanal	12896	220.69	263.95	55.32
Ethanal-d_1	13192	222.57	266.82	58.11
Ethanal-d_4	14041	228.21	275.30	64.64
1-Propanal	17490	245.81	304.51	80.73
1-Butanal	22046	269.78	343.67	103.36
Methanoic acid monomer	10927	212.34	248.99	45.68
Methanoic acid dimer	19632	266.94	332.78	96.14
Methanoic acid, equil.mixt.	10655	133.74	169.48	84.15
Methanoic acid-d_1(HCOOD)	11301	214.17	252.07	48.25
Methanoic acid-d_1(DCOOH)	11110	214.20	251.46	47.87
Methanoic acid-d_2	11510	215.94	254.55	50.58
Ethanoic acid monomer	13597	237.86	283.47	63.44
Ethanoic acid dimer	28052	320.30	414.39	137.25
Ethanoic acid, equil. mixt.	14470	160.32	208.85	87.52
Methyl methanoate	14465	236.76	285.28	64.38
Methyl ethanoate	18362	262.79	324.38	86.03
Epoxyethane	10856	206.58	242.99	47.86
Epoxyethane-d_4	11919	212.12	252.09	58.58
DL–1,2–Epoxypropane	14375	238.70	286.91	72.55
DL–1,2–Epoxybutane	18930	262.2	325.7	95.18
Furan	12347	225.84	267.25	65.40
2,5-Dihydrofuran	14491	235.65	284.25	75.60
Tetrahydrofuran	14667	253.22	302.41	76.25

TABLE A-26. Comparison of ideal-gas, third-law entropy values based on Part I and Part III with the ideal gas values calculated from the Partition Function.

Compound	T/K	$S(l)^a$/J K^{-1} mol^{-1}	P^c/bar	$R\ln\left(\frac{P}{p^{st}}\right)$	$\Delta_v H^d$/kJ mol^{-1}	$\Delta_v S$/J K^{-1} mol^{-1}	$\{S°(g)-S_r(g)\}$/J K^{-1} mol^{-1}	$\{S°(T)-S°(0)\}$	
								3rd law	this work
Methanol	298.15	127.27±0.21	0.1694	−14.76	37.97	127.35	1.92 [l]	241.78	239.81
Ethanol	298.15	160.1	0.0788	−21.13	42.56	142.75	0.80 [l]	282.52	280.64
1-Propanol	298.15	193.60	0.0255	−30.51	47.50	159.32	0.21 [l]	322.62	322.58
2-Propanol	298.15	181.07	0.0602	−23.36	45.50	152.61	0.54 [l]	310.86	309.20
1-Butanol	298.15	225.78	0.0085	−39.56	52.39	175.72	0.04 [l]	361.98	361.59
DL-2-Butanol	298.15	218.99±0.3 [b]	0.0244	−30.87	49.79	167.00	0.25 [l]	355.37	359.53
2-Methyl-2-Propanol	298.15	193.1±0.7	0.0560	−23.97	46.83	157.70	1.13 [l]	327.00	326.70
1,2-Ethanediol	298.15	163.2±2.2	1.189×10^{-4} [e]	−75.14	66.72 [e]	223.78	0.00	311.84	303.8
Diethyl Ether	298.15	253.76±0.2	0.7123	−2.82	27.10	90.89	0.88 [k]	342.71	342.67
Propanone	298.15	199.8±1	0.3066	−9.83	30.99	103.94	0.74 [k]	294.6	297.62
2-Butanone	298.15	239.06±0.4	0.1263	−17.20	34.79	116.69	0.36 [k]	338.91	339.90
Methanoic Acid	298.15	129.59±0.5	0.0567	−23.86	20.10	67.42	81.8 [o]	254.9	248.99
Ethanoic Acid	298.15	157.2±2	0.0207	−32.24	23.36	78.35	81.2 [o]	284.5	283.47
Epoxyethane	83.71	149.34±0.25	1.01325	+0.11	25.53 [j]	89.99	0.55 [m]	239.99	242.99
DL–Epoxypropane	298.15	196.5±0.5	0.764 [f]	−2.24	27.89	93.54	0.58 [m]	288.4	286.91
DL–1,2–Epoxybutane	298.15	230.87±0.1	0.2126 [g]	−12.87	31.52	105.72	0.31 [m]	324.03	325.7
Furan	298.15	177.0±0.5	0.8015 [h]	−1.84	27.45	92.07	0.52 [k]	267.8	267.25
Tetrahydrofuran	298.15	204.3±0.7	0.2164 [i]	−12.73	31.99	107.29	0.28 [n]	299.1	302.41

[a] Thermodynamic properties of key organic oxygen compounds in the carbon range C_1 to C_4, Part I.

[b] Value for D-2-Butanol + Rln2

[c] TRC k-table except as noted.

[d] Thermodynamic properties of key organic oxygen compounds in the carbon range C_1 to C_4, Part III (in preparation), the values are those selected by Majer except as noted.

[e] Ref. 514

[f] Ref. 516, 517

[g] Ref. 518

[h] Ref. 519

[i] Ref. 520

[j] Ref. 521

[k] Calculated from second virial coeff. TRC h-table

[l] Ref. 522

[m] Average as calculated from second virial coeff. for analogous ether, and from the Tsonopoulos correlation.

[n] Ref. 515

[o] Calculated from TRC ideal gas tables $\Delta_f G$ for monomer and dimer of acids. (This correction and its uncertainty are large. Only dimers are assumed and there is a large uncertainty in the enthalpy of dimerization.)