

Ideal Gas Thermodynamic Properties of Methanoic and Ethanoic Acids

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The thermodynamic properties [$H^\circ - H_0^\circ$, $(G^\circ - H_0^\circ)/T$, $(H^\circ - H_0^\circ)/T$, S° , C_p° , ΔH_f° , ΔG_f° , and $\log K_f$] for methanoic (formic) and ethanoic (acetic) acid monomers and dimers in the ideal gaseous state over the temperature range from 0 to 1500 K at 1 atm have been calculated by the statistical thermodynamic method using the most recent and reliable molecular and spectroscopic constants. The internal rotational contributions of -OH and -CH₃ rotors to the thermodynamic properties were evaluated based on internal rotation partition functions formed by summation of calculated internal rotation energy levels. On an assumption that the vapor contains only monomers and dimers, the thermodynamic properties for the monomer-dimer equilibrium mixture of methanoic and ethanoic acids in ideal gaseous state were derived. The results are in agreement with available experimental data.

Key words: Dimer; enthalpy; entropy; equilibrium constant of formation; ethanoic (acetic) acid; Gibbs energy of formation; heat capacity; ideal gas thermodynamic properties; internal rotational barrier height; methanoic (formic) acid; monomer; torsional frequencies.

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1. Introduction

Methanoic acid (formic acid, HCOOH) and ethanoic acid (acetic acid, CH₃COOH) are the two lowest members of the alkanic acid homologous series. Study of the thermodynamic properties of these two basic key compounds is essential in order to understand and to be able to estimate the properties of the higher members of the alkanic acids (usually called carboxylic acids). The aim of this work is the critical evaluation of the thermodynamic properties of methanoic and ethanoic acids in the temperature range from 0 to 1500 K and at 1 atm (101325.0 Nm⁻²) in the ideal gaseous state. The ideal gas thermodynamic properties were calculated by the standard method of statistical mechanics employing the rigid-rotor and harmonic-oscillator approximations. Contributions to the thermodynamic properties due to internal rotation of -OH and -CH₃ tops in these two molecules were evaluated by use of internal-rotation partition functions formed by summation of calculated internal-rotation energy levels for each rotating top.

It has long been known that carboxylic acid vapors deviate significantly from ideal gas behavior at low temperatures and under high pressures. The presence of dimeric species in formic and acetic acid vapors has been reported by numerous investigators based on experimental measurements of vapor density [1-10]¹ and vapor heat capacity [11, 12]. The nature of hydrogen bonding in these dimeric molecules (HCOOH)₂ and (CH₃COOH)₂ has been studied by many researchers using various spectroscopic methods. For example, infrared spectra of the formic acid dimer have been widely studied [13-21] as a function of temperature from which appropriate enthalpies of dimerization of the reaction 2 HCOOH(g) = (HCOOH)₂(g) were derived. The dissociation energy of dimer to monomer for formic acid has also been determined by Ramsperger and Porter [22] and Su [23] from ultraviolet absorption spectra and from an electron diffraction study of the effect of temperature on molecular structure, respectively. The infrared spectra of hydrogen-bonded acetic acid dimers have been investigated by Herman and Hofstadter [24], Weltner [11], Grenie, Cornut, and Lassegues [26], and others [14-19]. Corsaro and Atkinson [27] measured the ultrasonic absorption in acetic acid-acetone mixtures to determine both the kinetic and the thermodynamic parameters of the rapid acetic acid dimerization reaction.

In view of the above experimental evidence on the existence of dimeric species in the formic and acetic acid vapors, the evaluation of the ideal gas thermodynamic properties of the dimers, (HCOOH)₂ and (CH₃COOH)₂, was also included in this study. Furthermore, since these acid vapors contain both monomers and dimers at room temperature, the ideal gas thermodynamic properties for the monomer-dimer equilibrium mixtures of formic and acetic acids were also derived and compared with available experimental data.

For statistical mechanical calculation of ideal gas thermo-

dynamic properties for simple chemical substances, the following basic information is needed: molecular structural parameters, fundamental vibrational wavenumbers, molecular weight, symmetry number, electronic ground state configuration, electronic energy levels and their quantum weights [28]. However, the formic and acetic acid molecules contain -OH and -CH₃ groups, which rotate around C-O and C-C bonds; thus, the contributions to the thermodynamic properties of the internal rotations need to be evaluated separately. The additional data required for each rotor are the observed internal rotational constant, the empirical potential function and the barrier height for internal rotation. With these input data, the Schrödinger wave equation is solved to obtain the required internal rotation energy levels [60]. The computer generated energy levels (upper limit 15000 cm⁻¹) for each degree of internal rotation are summed to give the internal rotational contributions to the ideal gas thermodynamic properties. The results obtained are added to the corresponding contributions from the other degrees of freedom, i.e., translational, rotational, vibrational, and electronic, for the given compound to yield the final property values.

In the following sections, the method used for selecting the best values of molecular, spectroscopic, and thermal constants is described. These constants were employed for deriving the following ideal gas thermodynamic properties: heat capacity (C_p°), entropy (S°), enthalpy ($H^\circ - H_0^\circ$), the reduced enthalpy function ($(H^\circ - H_0^\circ)/T$), the reduced Gibbs energy function ($(G^\circ - H_0^\circ)/T$), the enthalpy of formation (ΔH_f°), the Gibbs energy of formation (ΔG_f°), and the logarithm of the equilibrium constant of formation ($\log K_f$) in the temperature range 0 to 1500 K at 1 atm, for the following six substances and their mixtures, viz., HCOOH, (HCOOH)₂ and their equilibrium mixture; CH₃COOH, (CH₃COOH)₂ and their equilibrium mixture.

All calculations in this work are based on the 1973 Fundamental Physical Constants recommended by the CODATA Task Group [29] and on the 1973 Atomic Weights: C = 12.011, H = 1.0079, and O = 15.9994. SI units were adopted for presenting the final calculated results. For comparison purposes, the reported values, mostly in calories instead of joules, were used to avoid confusion caused by changing units. For conversion to SI units, the values 1 cal = 4.184 joules and 1 atm = 101325 Nm⁻² should be used.

2. Methanoic Acid

2.1. Monomer

Methanoic acid has two geometric isomers, namely *cis*-form and *trans*-form, as shown in figure 1. The molecular structure of the *cis*-isomer has been studied extensively by numerous researchers during the last several decades by employing microwave [30-42], electron diffraction [43-47], and infrared [49-51] spectroscopy. The existence of *trans*-isomer in the vapor has been mentioned by Coop et al. [52], Williams [49], and Bleakney [53]. Based on in-

¹ Figures in brackets indicate the literature references.

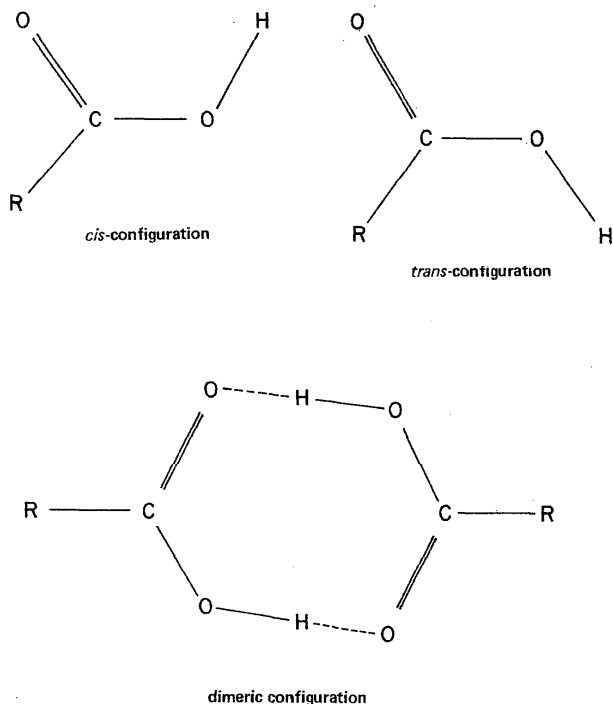


FIGURE 1. Molecular structures of methanoic (R = H) and ethanoic (R = CH₃) acids

frared spectra of four isotopic formic acids, Miyazawa and Pitzer [25] assigned nine fundamental vibrational frequencies, of which four are for *cis*-isomers and two for *trans*-isomer.

According to the above spectroscopic studies and additional theoretical calculations, the *cis*-isomer is claimed to be a more stable species than the *trans*-isomer. The enthalpy of isomerization has been reported as 1.2–9.46 kcal mol⁻¹ (see table 1 for detailed results). Fukushima, Chao, and Zwolinski [59] calculated the natural formic acid vapor compositions in the temperature range 298.15–1500 K at atmospheric pressure. They found that based on an assumed value of $\Delta H_0^\circ = 2.0$ kcal mol⁻¹ (1 kcal = 4.184 kJ) for the reaction: *cis*-HCOOH(g) = *trans*-HCOOH(g), the concentration of *trans*-isomer in the equilibrium mixture was obtained as 2.8% at 298.15 K and 23.7% at 1000 K. By adopting $\Delta H_0^\circ = 4.0$ kcal mol⁻¹ for the same reaction, the *trans*-isomer concentration in the vapor mixture was calculated to be 0.1% and 9.0% at 298.15 K and 1000 K, respectively. Since the value of ΔH_0° is estimated to be higher than 4.0 kcal mol⁻¹, the change in thermodynamic properties of the formic acid vapor due to the presence of *trans*-isomers is considered to be insignificant. Therefore, for evaluation of the ideal gas thermodynamic properties for HCOOH(g), the *cis*-form molecular structure of this acid was used.

Selection of the molecular structural parameters for the statistical calculation of the ideal gas thermodynamic properties for a popular species such as formic acid was not simple. Even though experimental determinations on molecular structure of formic acid have been reported in the

TABLE 1. Reported enthalpy of isomerization (*cis* → *trans*) for methanoic acid

ΔH_i° , kcal mol ⁻¹	Determination method	Investigator (year)
6.30	M.O. calculation	Radom et al. (1971) ^a
8.1	SCFMO calculation	Schwartz et al. (1970) ^b
9.46	LCAO-MO-SCF Calculation	Hopkinson et al. (1970) ^c
8.1	M.O. calculation	Ros (1968) ^d
≥4.0	Microwave spectrosc.	Lide (1964) ^e
2.0	IR spectrosc.	Miyazawa and Pitzer (1959) ^f
1.2–3.0	Electron impact	Mariner and Bleakney (1947) ^g

^a Reference [54].

^e Reference [58].

^b Reference [55].

^f Reference [25].

^c Reference [56].

^g Reference [53].

^d Reference [57].

1 kcal = 4.184 kJ.

literature, only few results are in accord. For the present work, the structural parameters determined by Bellet et al. [30] from microwave spectrum were adopted. These values are in agreement with those reported by Kwei and Curl [32]. The three principal moments of inertia and their product ($I_A I_B I_C$) were computed as: $I_A = 1.0953 \times 10^{-39}$ g cm², $I_B = 6.9125 \times 10^{-39}$ g cm², $I_C = 8.0078 \times 10^{-39}$ g cm², and $I_A I_B I_C = 6.0631 \times 10^{-116}$ g³ cm⁶. The reduced moment of inertia of -OH rotor in HCOOH molecule and the internal rotation constant were derived to be 1.122×10^{-40} g cm² and 24.96 cm⁻¹, respectively.

Infrared spectra of the formic acid monomer were also studied by many investigators [49, 61–65] with reported fundamental vibrational assignments [62–66]. Together with normal coordinate treatments [25, 59, 67–72], complete sets of fundamental vibrational wavenumbers have been assigned for the HCOOH(g) molecule. In this work, the vibrational assignments of Millikan and Pitzer [66] for $\nu_1 - \nu_6$ and ν_8 and of Miyazawa and Pitzer [25] for $\nu_7 = 625$ cm⁻¹ were used. These values are given in table 2.

The torsional frequency (ν_9) and the internal rotation barrier height (V) of the -OH rotor in the HCOOH molecule have been an interesting subject to research chemists for many years. Table 3 summarizes the reported values of ν_9 and V by numerous investigators to date. The values given by Waring [48] were selected initially so that the calculated statistical entropy would be in reasonable agreement with the third-law entropy. The microwave study of five of the isotopic species of formic acid by Lerner et al. [36] established the torsional frequency of -OH rotor in HCOOH molecule to be 667 ± 41 cm⁻¹ with a minimum of 17 kcal mol⁻¹ for the internal rotation barrier height. The value of $\nu_9 = 658$ cm⁻¹ was obtained by Bonner and Hofstadter [65] from infrared studies. From infrared studies, Miyazawa and Pitzer [25] assigned the band at 638 cm⁻¹ as ν_9 and derived the potential energy function for -OH rotors as $V = \frac{1}{2} [V_1(1 - \cos \theta) + V_2(1 - \cos$

TABLE 2. Molecular constants for methanoic acid monomer and dimer^a

	HCOOH	(HCOOH) ₂
Molecular weight	46.0256	92.0512
Point group	C _s	C _{2h}
Symmetry number	1	2
Ground state configuration	A'	A _g
Product of the three principal moments of inertia, g ² cm ⁶	6.06308 × 10 ⁻¹¹⁶	2.63696 × 10 ⁻¹¹³
Internal rotation constants, cm ⁻¹	24.960	
Torsional frequency (0 → 1), cm ⁻¹	610	
Potential barrier height, kcal mol ⁻¹	12.20	
Vibrational wavenumbers, cm ⁻¹	A': 3570,2943, 1770, 1387, 1229,1105,625; A'': 1033	A _g : 3200,2956,1672, 1395,1350,1204,675, 232,215; B _g : 1063, 677,519; A _u : 1073, 917,164,68; B _u : 3110,2957,1754, 1450,1365,1218, 697,248
Enthalpy of formation at 298.15 K, kcal mol ⁻¹	-90.48	-196.21

^a To convert to SI units: Multiply the listed values in cm⁻¹ by 2.997925 × 10¹⁰ (velocity of light, cm s⁻¹) to give values in hertz; 1 kcal mol⁻¹ = 4.184 kJ mol⁻¹.

2θ) + V₃(1 - cos 3θ)] where θ = internal rotation angle; V₁ = 2.1, V₂ = 9.9, and V₃ = -0.1, all in kcal mol⁻¹. Based on this potential function, they found that the potential maximum was 98° from the *cis* configuration and was 10.9 kcal mol⁻¹ above the *cis* minimum. The value 10.9 kcal mol⁻¹ was later reevaluated to be 13.2 kcal mol⁻¹ by Bernitt et al. [73].

Using ab initio molecular theory to study internal rotation in certain organic molecules, Radom et al. [74] suggested the following potential function: $V = \frac{1}{2}[5.75(1 - \cos \theta) + 8.93(1 - \cos 2\theta) + 0.55(1 - \cos 3\theta)]$ for the OH rotor in HCOOH molecule. The potential energy curve is plotted and shown in figure 2. It indicates that the *cis*-structure is more stable than the *trans*-form by 6.3 kcal mol⁻¹ and the potential maximum is 12.2 kcal mol⁻¹ at θ = 97° from the *cis*-configuration. This barrier height is in reasonable agreement with the experimental estimates [25, 73] given in table 3. Therefore, this potential function was used in this work for the calculation of internal rotation energy levels [60].

TABLE 3. Reported torsional frequency and internal rotational barrier height of -OH rotor in HCOOH molecule^a

Torsional frequency, cm ⁻¹	Barrier height, kcal mol ⁻¹	Investigator (Year)
658		Bonner and Hofstadter (1938) ^b
452	10.0	Waring (1952) ^c
636		Millikan and Pitzer (1957) ^d
667	17.0	Lerner et al. (1957) ^e
638	10.9	Miyazawa and Pitzer (1959) ^f
695	13.2	Bernitt et al. (1965) ^g
610	12.2	This work

^a See table 2 footnote for conversion of listed values to those in SI units.

^b Reference [65].

^c Reference [48].

^d Reference [66].

^e Reference [36].

^f Reference [25].

^g Reference [73]; reevaluation of barrier height using data of reference [25].

These calculated internal rotation energy levels, together with the other molecular constants listed in table 2, were employed for evaluation of the ideal gas thermodynamic properties for formic acid monomer. The results are given in table 4.

The enthalpy of combustion, ΔH_c^o (298.15 K), of liquid formic acid was determined to be -60.86 ± 0.06 and -60.67 ± 0.07 kcal mol⁻¹ by Sinke [75] and Lebedeva [76], respectively. From these values the enthalpies of formation, ΔH_f^o (1, 298.15 K), were derived as -101.52 and -101.70 kcal mol⁻¹. Combining the experimental data with appropriate enthalpy of vaporization, Wagman et al. [77] obtained the value ΔH_f^o (HCOOH, g, 298.15 K)

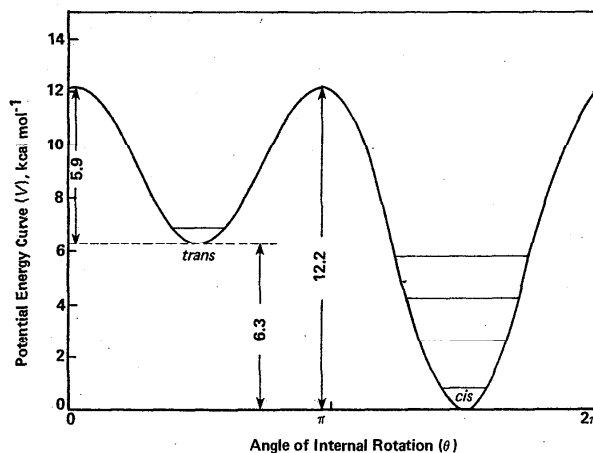


FIGURE 2. Internal rotation potential energy curve for -OH rotor in methanoic acid molecule

TABLE 4. Ideal gas thermodynamic properties for methanoic acid monomer

T	$H^\circ - H_0^\circ$	$-\frac{(G^\circ - H_0^\circ)}{T}$	$\frac{H^\circ - H_0^\circ}{T}$	S°	C_p°	ΔH_f°	ΔG_f°	$\log K_f$
K	J mol ⁻¹	J K ⁻¹ mol ⁻¹			kJ mol ⁻¹			
0	0	0	0	0	0	-371.30	-371.30	infinite
50	1662.9	151.84	33.258	185.10	33.258	-373.19	-370.42	386.969
100	3327.8	174.89	33.278	208.17	33.441	-374.11	-367.31	191.859
150	5029.6	188.42	33.530	221.95	34.909	-375.18	-363.68	126.643
200	6843.3	198.15	34.216	232.37	37.830	-376.35	-359.67	93.934
273.15	9812.4	209.05	35.923	244.97	43.538	-378.04	-353.31	67.563
298.15	10928.	212.23	36.651	248.88	45.679	-378.57	-351.00	61.494
300	11012.	212.45	36.707	249.16	45.839	-378.61	-350.83	61.084
400	16032.	223.46	40.080	263.54	54.523	-380.50	-341.26	44.564
500	21897.	232.80	43.793	276.59	62.631	-381.95	-331.29	34.609
600	28527.	241.12	47.545	288.66	69.813	-382.99	-321.05	27.950
700	35827.	248.72	51.182	299.90	76.037	-383.65	-310.66	23.182
800	43704.	255.78	54.630	310.41	81.339	-383.99	-300.21	19.601
900	52066.	262.41	57.851	320.26	85.770	-384.04	-289.73	16.815
1000	60831.	268.86	60.831	329.49	89.402	-383.86	-279.24	14.586
1100	69923.	274.59	63.566	338.15	92.328	-383.50	-268.85	12.766
1200	79276.	280.23	66.064	346.29	94.653	-383.02	-258.41	11.248
1300	88837.	285.61	68.336	353.94	96.482	-382.46	-248.05	9.967
1400	98559.	290.75	70.400	361.15	97.911	-381.86	-237.69	8.868
1500	108410.	295.67	72.272	367.94	99.025	-381.24	-227.43	7.920

= -90.48 kcal mol⁻¹ which was adopted here. Based on this selected value and the thermodynamic functions for C (graphite), H₂(g), O₂(g) from [78] and those for HCOOH(g) from this work, the values of ΔH_f° , ΔG_f° , and $\log K_f$ in the temperature range from 0 to 1500 K and at 1 atm were calculated. They are given in table 4.

2.2. Dimer

The molecular structure and vibrational frequencies of the formic acid dimer has been investigated by researchers for several decades. The planar ring structure of this molecule has been originally determined by Pauling and Brockway [80] by electron diffraction in 1934. From resonance considerations, they also proposed that the dimeric molecule had a D_{2h} symmetry with four equivalent oxygen atoms. This symmetric molecular model was rejected by later electron diffraction studies [44, 47, 79] and instead, a molecular model of C_{2h} symmetry with conventional double and single carbon-oxygen bonds, as shown in figure 1, was favored.

In this work, the molecular parameters employed for statistical mechanical calculations were those determined by Almenningen et al. [44]. Using their structural data, the three principal moments of inertia and the product of the three principal moments of inertia for formic acid dimeric molecule were calculated as: $I_A = 1.3615 \times 10^{-38}$ g cm², $I_B = 3.7724 \times 10^{-38}$ g cm², $I_C = 5.1340 \times 10^{-38}$ g cm² and $I_A I_B I_C = 2.6370 \times 10^{-113}$ g³ cm⁶.

The fundamental vibrational wavenumbers for formic acid dimer have been reported sporadically by numerous

investigators by studying the infrared [13-15, 65, 81-93] and Raman [94, 95] spectra of this compound. Because of the planar structure with point group C_{2h}, the twenty-four vibrational degrees of freedom of the dimeric molecule can be grouped into 9 a_g, 8 b_u, 4 a_u and 3 b_g vibrations. Miyazawa and Pitzer [96], using a rigid monomer model, made a normal coordinate treatment of the low frequency vibrations of formic acid dimer. In this treatment, they correlated 7 a_g, 7 b_u, 2 b_g and 2 a_u vibrations with the corresponding internal vibrations of the two monomer units; while the remaining 2 a_g, 1 b_u, 1 b_g and 2 a_u vibrations were considered as the translational and rotational vibrations of two monomer units against each other. Based on incomplete spectral data, normal coordinate analysis, and entropy calculations, they assigned six low frequency vibrations for the dimer. A normal coordinate treatment of out-of-plane vibrations of formic acid dimer was performed by Miyazawa and Pitzer [25] from the infrared spectra of four isotopic species of formic acid measured in the vapor phase as well as in the solid nitrogen matrix in the region 400-800 cm⁻¹.

Kishida and Nakamoto [97] made a normal coordinate analysis of dimeric formic acid and calculated all the in-plane vibrations, i.e. 9 a_g and 8 b_u vibrations, using reported experimental spectral data [13, 95]. Recently, Alfheim et al. [98] employed the best available assignments of fundamental vibrational frequencies and performed a complete normal coordinate analysis of formic acid dimer. Their calculated values were in good agreement with the experimentally observed ones [13, 14, 94-96]. Thus, the complete set of fundamental vibrational wavenumbers proposed by Alfheim et al., (see table 2) was adopted for

evaluation of the vibrational contributions to ideal gas thermodynamic properties for the formic acid dimer.

The value of ΔH_f° (g, 298.15 K) for $(\text{HCOOH})_2$, $-196.21 \text{ kcal mol}^{-1}$, was calculated from ΔH_f° (HCOOH , g, 298.15 K) = $-90.48 \text{ kcal mol}^{-1}$ [77] and ΔH_r° (298.15 K) = $-15.25 \text{ kcal mol}^{-1}$ for the following reaction: $2 \text{HCOOH}(g) = (\text{HCOOH})_2(g)$. This ΔH_r° was obtained by trial and error in order that the derived equilibrium constants for this reaction yielded the calculated vapor densities of the monomer-dimer equilibrium mixture to be consistent with the observed ones [1, 2, 3].

Coolidge [1] determined the densities of formic acid vapor at temperatures between 10 and 156 °C and at pressures favorable to partial dissociation. His sample of 99.99% purity was prepared by vacuum sublimation. A correction for wall adsorption had been applied to the measurements. On the assumption that the formic acid vapor contained only monomers and dimers, he derived the equilibrium constants for the dimerization reaction at different temperatures and calculated the enthalpy change of this dimerization reaction to be $-14.12 \text{ kcal mol}^{-1}$, as shown in table 5. The P - V - T measurements of Coolidge were confirmed by later experimental determinations of Dawson and Haydon [2] and also Taylor and Bruton [3], and were selected as the most reliable data.

Mathews and Sheets [17] have observed the fundamental OH stretching adsorption band at various temperatures for $\text{HCOOH}(g)$ molecule and derived an equation which included the ratio of surface area/volume of the reaction vessel for evaluating the enthalpy of dimerization.

A summary of the reported enthalpies of dimerization for methanoic acid is presented in table 5. The temperature ranges for the ΔH values obtained by spectroscopic methods were unavailable. Our recommended ΔH° value is consistent with those of [16], [17], and [99].

Employing the molecular constants listed in table 2 for $(\text{HCOOH})_2$ and following the same calculation procedures as mentioned in section 2.1, the ideal gas thermodynamic properties for methanoic acid dimer were evaluated. The results are presented in table 6.

2.3. Equilibrium Mixture

Based on the selected enthalpy of dimerization $\Delta H^\circ = -14.72 \text{ kcal mol}^{-1}$ and the calculated $H^\circ - H_0^\circ$, S° , and C_p° for $\text{HCOOH}(g)$ and $(\text{HCOOH})_2$, the ideal gas thermodynamic properties: $H^\circ - H_0^\circ$ ($H^\circ - H_0^\circ$)/ T , C_p° , S° , and $(G^\circ - H_0^\circ)/T$ for the monomer-dimer equilibrium mixture over the temperature range 50 to 1000 K and at 1 atm were computed and are given in table 7. The equilibrium constants of the dimer \rightarrow monomer reaction in the temperature range from 100 to 800 K and the concentration of dimers in the gaseous mixture at 0.1, 1.0, and 5.0 atm in the same temperature range are derived and presented in table 8. The vapor heat capacities of the equilibrium mixture are plotted in figure 3. The values in table 7 and figure 3 were evaluated based on one mole of methanoic acid monomer [112].

TABLE 5. Reported enthalpies of dimerization for methanoic acid*

ΔH° , kcal mol ⁻¹	Determination method and temperature	Investigator (year)
-14.8 ± 0.5	Spectroscopic (IR)	Clague and Bernstein (1969) ^b
-14.4 ± 0.1	P - V - T ; 283–353 K	Halford (1942) ^c
-14.12	P - V - T ; 283–429 K	Coolidge (1928) ^d
-14.11 ± 0.40	P - V - T ; 323–423 K	Taylor and Bruton (1952) ^e
-14.1 ± 1.5	Spectroscopic (IR); 300–423 K	Mathews and Sheets (1969) ^f
-13.9	P - V - T ; 323–398 K	Barton and Hsu (1969) ^g
-13.9	Spectroscopic (UV)	Ramsperger and Porter (1926) ^h
-12.4 ± 1.0	Spectroscopic (ED); 298–448 K	Su (1967) ⁱ
-12.4 ± 0.7	Spectroscopic (IR)	Herman (1940) ^j
-11	Theoretical calc.	Excoffon and Marechal (1972) ^k

* Selected as the best value: ΔH° (298.15 K) = $15.25 \text{ kcal mol}^{-1}$ or ΔH° (0 K) = $-14.72 \text{ kcal mol}^{-1}$.

^b Reference [16].

^c Reference [99].

^d Reference [1].

^e Reference [3].

^f Reference [17].

^g Reference [4].

^h Reference [22].

ⁱ Reference [23].

^j Reference [100].

^k Reference [18].

3. Ethanoic Acid

3.1. Monomer

The molecular structure of ethanoic acid (CH_3COOH) has been determined by electron diffraction [47, 101, 102] and microwave spectroscopy [103, 104, 105]. Figure 1 indicates the two isomeric forms of this molecule. The *cis*-form isomer of ethanoic acid is more stable than the *trans*-form as is also true for methanoic acid. The ethanoic acid molecule, however, has two rotating tops, namely the $-\text{OH}$ and $-\text{CH}_3$ groups. In evaluating the ideal gas thermodynamic properties for this compound, the internal rotational contributions of these two rotors to the thermodynamic properties are assumed to be additive and the same procedure was followed as for formic acid, described in section 2.1.

Krisner and Saegbarth [105] have recently studied the microwave spectra of the molecules CH_3COOH and CD_3COOH . Using the principal axis method and a computer program extended to include terms through $n = 6$ in the perturbation series [108], they identified 30 new E -type transitions. The rigid-rotational constants were derived as: $A = 11335.50 \text{ MHz}$, $B = 9478.64 \text{ MHz}$, and

TABLE 6. Ideal gas thermodynamic properties for methanoic acid dimer

T	$H^\circ - H_0^\circ$	$-\frac{(G^\circ - H_0^\circ)}{T}$	$\frac{(H^\circ - H_0^\circ)}{T}$	S°	C_p°	ΔH_f°	ΔG_f°	log K_f
K	J mol ⁻¹	J K ⁻¹ mol ⁻¹			kJ mol ⁻¹			
0	0	0	0	0	0	-804.18	-804.18	infinite
50	1825.6	181.35	36.512	217.86	42.505	-809.46	-796.30	831.883
100	4335.8	208.70	43.358	252.06	57.327	-812.12	-782.09	408.516
150	7481.4	227.55	49.876	277.42	68.030	-814.53	-766.55	266.932
200	11119.	242.69	55.595	298.29	77.429	-816.85	-750.20	195.929
273.15	17288.	261.17	63.292	324.47	91.320	-819.99	-725.34	138.705
298.15	19632.	266.83	65.844	332.67	96.140	-820.94	-716.59	125.543
300	19810.	267.23	66.032	333.27	96.496	-821.01	-715.94	124.654
400	30408.	287.61	76.020	363.63	115.226	-824.23	-680.38	88.848
500	42781.	305.61	85.562	391.17	131.801	-826.49	-644.16	67.294
600	56679.	322.00	94.464	416.47	145.720	-827.93	-607.54	52.891
700	71846.	337.19	102.64	439.83	157.280	-828.69	-570.73	42.588
800	88071.	351.39	110.09	461.48	166.927	-828.90	-533.86	34.857
900	105180.	364.75	116.87	481.62	175.041	-828.62	-496.99	28.844
1000	123040.	377.39	123.04	500.43	181.911	-827.92	-460.13	24.034
1100	141530.	389.38	128.66	518.05	187.758	-826.89	-423.51	20.111
1200	160560.	400.80	133.80	534.60	192.757	-825.61	-386.82	16.838
1300	180060.	411.70	138.51	550.21	197.046	-824.12	-350.33	14.076
1400	199950.	422.13	142.82	564.95	200.742	-822.47	-313.84	11.709
1500	220190.	432.12	146.79	578.91	203.939	-820.69	-277.61	9.667

TABLE 7. Ideal gas thermodynamic properties of methanoic acid monomer-dimer equilibrium mixture

T	$H^\circ - H_0^\circ$	$-\frac{(G^\circ - H_0^\circ)}{T}$	$\frac{(H^\circ - H_0^\circ)}{T}$	S°	C_p°
K	J mol ⁻¹	J K ⁻¹ mol ⁻¹			
50	912.7	90.676	18.255	108.93	21.253
100	2167.3	104.36	21.673	126.03	28.665
150	3740.5	113.78	24.937	138.71	34.016
200	5562.0	121.34	27.810	149.15	38.858
273.15	8902.9	130.65	32.593	163.25	58.955
298.15	10655.	133.63	35.737	169.37	84.151
300	10814.	133.85	36.047	169.90	86.810
400	33099.	149.16	82.747	231.91	343.168
500	51800.	171.31	103.600	274.91	83.721
600	58997.	189.80	98.328	288.13	71.469
700	66239.	204.73	94.628	299.36	76.795
800	74000.	217.29	92.500	309.79	82.192
900	82227.	228.19	91.364	319.56	86.827
1000	90851.	237.86	90.851	328.72	90.679

 TABLE 8. Equilibrium constants and concentration of (HCOOH)₂ in HCOOH-(HCOOH)₂ equilibrium mixture

T	K_{eq}	Mole fraction of dimer		
		$P = 0.1$ atm	$P = 1.0$ atm	$P = 5.0$ atm
100	6.33×10^{24}	1.000	1.000	1.000
200	1.15×10^8	1.000	1.000	1.000
298.15	3.60×10^6	0.847	0.949	0.977
300	3.07×10^6	0.835	0.944	0.975
400	5.25×10^{-1}	0.048	0.276	0.545
500	1.19×10^{-2}	0.001	0.012	0.054
600	9.82×10^{-4}	0.000	0.001	0.005
700	1.68×10^{-4}	0.000	0.000	0.001
800	4.51×10^{-5}	0.000	0.000	0.000

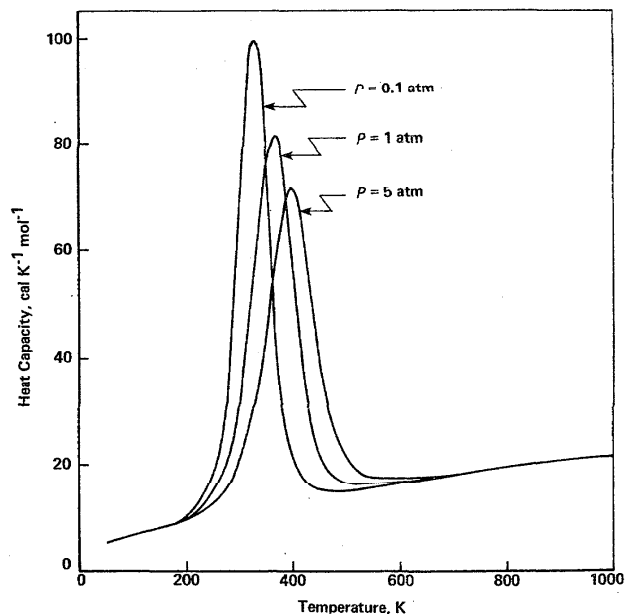


FIGURE 3. Vapor heat capacity of methanoic acid at different temperatures and pressures

$C = 5325.01$ MHz. These three constants were adopted to calculate the three principal moments of inertia as: $I_A = 7.40342 \times 10^{-39}$ g cm², $I_B = 8.85376 \times 10^{-39}$ g cm², and $I_C = 1.57599 \times 10^{-38}$ g cm². The product of the three principal moments of inertia $I_A I_B I_C$, as shown in table 9, was used for evaluating the rotational contributions to thermodynamic properties for ethanoic acid in the ideal gaseous state at 1 atm.

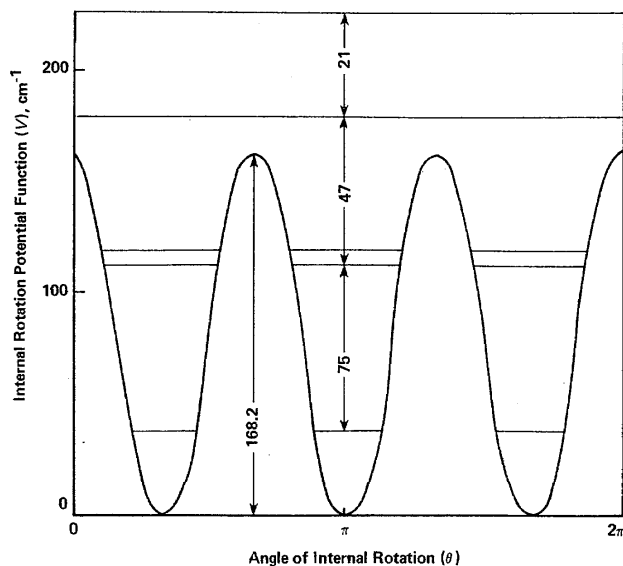
In the theoretical treatments of Killb, Lin, and Wilson [106] and Herschbach [107], the internal rotation of the methyl group in CH₃COOH was classified as an "inter-

TABLE 9. Molecular constants for ethanoic acid monomer and dimer^a

	CH ₃ COOH	(CH ₃ COOH) ₂
Molecular weight	60.0524	120.1048
Point group	C _s	C _{2h}
Symmetry number	1	2
Ground state configuration	A'	A _g
Product of the three principal moments of inertia, g ² cm ⁴	1.0330 × 10 ⁻¹¹⁴	1.6141 × 10 ⁻¹¹²
For -CH ₃ rotor:		
Internal rotation constant, cm ⁻¹	5.6488	5.3613
Torsional frequency (0 → 1), cm ⁻¹	75	74
Potential barrier height, kcal mol ⁻¹	0.481	0.481
For -OH rotor:		
Internal rotation constant, cm ⁻¹	21.255	
Torsional frequency (0 → 1), cm ⁻¹	565	
Potential barrier height, kcal mol ⁻¹	12.2	
Vibrational wave numbers, cm ⁻¹	A': 3583, 3051, 2944, 1788, 1430, 1382, 1264, 1182, 989, 847, 657, 581; A'': 2996, 1430, 1048, 642	A _g : 3193, 3032, 2949, 1675, 1436, 1436, 1370, 1283, 1018, 886, 624, 448, 196, 110; B _u : 3140, 3028, 2956, 1715, 1413, 1413, 1359, 1295, 1013, 886, 624, 480, 188; A _u : 2990, 1413, 1050, 934, 635, 67, 47; B _g : 3000, 1436, 1112, 912, 623, 115
Enthalpy of formation at 298.15 K, kcal mol ⁻¹	-103.31	-222.04

^a See table 2 footnote for conversion of the given values to SI units.

mediate barrier." Table 10 summarizes the reported internal rotation barrier heights (V_3) of CH₃ rotor in CH₃COOH molecule. The values of Tabor [104], Krisher and Saegebarth [105], and Chadwick and Katrib [109] are in good agreement and appear to be more reliable than the other values. From analysis of the microwave data, Krisher and Saegebarth found an excellent fit of observed *A-E* splittings (within ±0.1 MHz) for the CH₃ rotor using the values of $I_a = 3.216 \pm 0.002 \text{ u}\text{\AA}^2$ ($5.34 \times 10^{-40} \text{ g cm}^2$) for the reduced moment of inertia, $\theta = 4^\circ 30' \pm 15'$ for the angle between the CH₃ axis and the principal axis, α , and a value for $S = 13.232 \pm 0.002$. Using their internal rotation constant (F) and barrier height (V_3) as listed in table 9, and $V = (\frac{1}{2})V_3(1 - \cos 3\theta)$ as the internal rotation potential function, 108 internal rotational energy levels (0 to 16500 cm⁻¹) were generated [60] for calculating the internal rotation contributions from CH₃ rotor to the ideal gas thermodynamic properties for CH₃COOH. The torsional frequency (0 → 1) of CH₃ group was derived to be $75 \pm 1 \text{ cm}^{-1}$, as shown in figure 4.

FIGURE 4. Potential function and energy levels for CH₃ rotor internal rotation in ethanoic acid molecule

It should be mentioned that in table 10 the uncertainty of 0.001 kcal mol⁻¹, assigned to the barrier height of 0.481 kcal mol⁻¹ for the CH₃ rotor in CH₃COOH by Krisher and Saegebarth [105], is not an absolute error limit. The uncertainty in a barrier height determined by microwave techniques is usually based on an assumed molecular model for the internal rotational dynamics, which contains the assumed shape of the potential energy function and parameters of the molecular structure. For acetic acid, the sixth-order calculation used afforded some adjustable parameters beyond the height of the barrier, which were selected as the moment of inertia, I_a , and the orientation angle of the rotating CH₃ top. This combination of parameters was "best-fitted" to the very large observed splittings for many transitions in a consistent fashion, which provided prediction of further transition frequencies

TABLE 10. Reported internal rotation barrier height of CH₃ rotor in CH₃COOH molecule

Barrier height ^a kcal mol ⁻¹	Method of determination	Investigator (year)
0.400	theoretical calc.	Eijck (1966) ^b
0.480		Chadwick and Katrib (1974) ^c
0.481 ± 0.001	microwave	Krisher and Saegebarth (1971) ^d
0.483 ± 0.025	microwave	Tabor (1957) ^e
0.640 ± 0.800	electron dif- fraction	Derissen (1971) ^f
0.690 to 0.880	theoretical calc.	Meyer et al. (1975) ^g

^a 1 kcal = 4.184 KJ.

^b Reference [110].

^c Reference [109].

^d Reference [105]; the reported value used in this work.

^e Reference [104].

^f Reference [102].

^g Reference [111].

not used in the calculation as checks for reliability of the fit. All of the above results required the indicated limit of precision, $0.001 \text{ kcal mol}^{-1}$, for the parameter V_3 which is the internal rotation barrier height. However, the "absolute accuracy" on the barrier is probably $\pm 0.02 \text{ kcal mol}^{-1}$, when the approximate nature of the model is taken into consideration.

Due to the unavailability of appropriate function (V) for the OH rotor internal rotation in ethanoic acid molecule, the internal rotation potential function for OH group in HCOOH molecule was tentatively adopted here as an approximation. For evaluation of I_a for OH rotor in CH_3COOH molecule, the molecular structural parameters determined by Derissen [102] were employed. The values of I_a and F were derived to be $0.7931 \text{ u}\text{\AA}^2$ ($1.317 \times 10^{-40} \text{ g cm}^2$) and 21.255 cm^{-1} , respectively. Based on the adopted V and F , sixty internal rotation energy levels (0 to 21500 cm^{-1}) were generated. The OH torsional frequency ($0 \rightarrow 1$) was obtained as 565 cm^{-1} . The potential maximum was at 97° from the *cis* configuration and was $12.2 \text{ kcal mol}^{-1}$ above the *cis* minimum. The energy difference (ΔE) between *trans*- and *cis*-isomers was $6.3 \text{ kcal mol}^{-1}$. Recently Meyer et al. [111] obtained from a theoretical calculation the values $V_{\text{max}} = 12.7 - 14.8 \text{ kcal mol}^{-1}$ for the OH potential function and $\Delta E = 8.3 - 10.9 \text{ kcal mol}^{-1}$ for the difference in stability of the *cis*- and *trans*-isomers.

The infrared vibrational spectra of acetic acid vapor have been observed by Sverdlov [94], Weltner [11], Wilmshurst [113], and Haurie and Novak [114]. Shimanoichi [115] critically reviewed the reported vibrational data and assigned a complete set of fundamental vibrational wavenumbers for acetic acid. His assignments were selected for calculating the vibrational contributions to the thermo-

dynamic properties, except for the two torsional frequencies; i.e. $\nu_{17} = 534 \text{ cm}^{-1}$ for $-\text{OH}$, and $\nu_{18} = 93 \text{ cm}^{-1}$ for $-\text{CH}_3$ tops. The numerical values for these selected fundamental frequencies are tabulated in table 9. In the same table the selected value for ΔH_f° (CH_3COOH , g, 298.15 K) was taken from NBS Technical Note 270-3 [77].

Employing the derived internal rotation energy levels for OH and CH_3 tops, and the selected molecular data presented in table 9, the ideal gas thermodynamic properties for ethanoic acid listed in table 11 were calculated for the temperature range 0-1500 K and at 1 atm.

3.2 Dimer

The molecular structure of ethanoic acid dimer has been elucidated by Derissen [102] and Karle and Brockway [47] by the electron diffraction method. The general structure of this planar molecule is shown in figure 1. It should be noted that this molecule has two hydrogen bonds, similar to the methanoic acid dimer, with two methyl rotors. In the calculation of the internal rotation contribution of the two CH_3 rotors to the ideal gas thermodynamic properties of $(\text{CH}_3\text{COOH})_2$ molecule, the value of $I_a = 3.144 \text{ u}\text{\AA}^2$ ($5.221 \times 10^{-40} \text{ g cm}^2$) and $F = 5.361 \text{ cm}^{-1}$ were evaluated based on the molecular structural parameters determined by Derissen [102]. The potential function used was $V = \frac{1}{2}V_3(1 - \cos 3\theta)$ where $V_3 = 481 \text{ cal mol}^{-1}$, the same as that for the CH_3 rotor in the CH_3COOH monomer. The product of the three principal moments of inertia was calculated to be $3.52528 \times 10^7 \text{ u}^3 \text{\AA}^6$ ($1.6141 \times 10^{-112} \text{ g}^3 \text{ cm}^6$).

The vibrational spectra of ethanoic acid dimer have been analyzed by numerous investigators using infrared [11,

TABLE 11. Ideal gas thermodynamic properties for ethanoic acid monomer

T	$H^\circ - H_0^\circ$	$-\frac{(G^\circ - H_0^\circ)}{T}$	$\frac{(H^\circ - H_0^\circ)}{T}$	S°	C_p°	ΔH_f°	ΔG_f°	$\log K_f$
K	J mol^{-1}	$\text{J K}^{-1} \text{mol}^{-1}$			kJ mol^{-1}			
0	0	0	0	0	0	-418.13	-418.13	infinite
50	1791.3	167.94	35.826	203.76	39.535	-422.01	-415.79	434.370
100	3803.5	193.59	38.035	231.63	40.424	-423.70	-408.95	213.610
150	5866.8	209.22	39.112	248.33	42.740	-425.74	-401.14	139.689
200	8133.4	220.67	40.667	261.33	48.344	-427.98	-392.60	102.536
273.15	12062.	233.83	44.159	277.98	59.385	-431.22	-379.17	72.508
298.15	13597.	237.75	45.605	283.36	63.438	-432.25	-374.33	65.579
300	13715.	238.04	45.716	283.75	63.739	-432.32	-373.96	65.111
400	20894.	252.06	52.235	304.30	79.665	-435.99	-353.92	46.216
500	29590.	264.46	59.181	323.64	93.926	-438.87	-333.06	34.794
600	39612.	275.86	66.020	341.88	106.181	-441.02	-311.69	27.135
700	50766.	286.53	72.534	359.05	116.627	-442.54	-289.99	21.639
800	62885.	296.62	78.606	375.22	125.501	-443.52	-268.13	17.507
900	75820.	306.21	84.245	390.45	132.989	-444.01	-246.17	14.287
1000	89442.	315.35	89.442	404.80	139.257	-444.09	-224.13	11.707
1100	103640.	324.11	94.215	418.32	144.462	-443.84	-202.26	9.604
1200	118300.	332.49	98.587	431.08	148.760	-443.37	-180.24	7.845
1300	133360.	340.55	102.59	443.13	152.302	-442.74	-158.34	6.362
1400	148740.	348.28	106.25	454.53	155.220	-441.99	-136.40	5.089
1500	164390.	355.73	109.59	465.32	157.631	-441.16	-114.64	3.992

13, 90, 91, 113, 117, 118, 121], far infrared [14, 119], near-infrared [120], and Raman [116] spectroscopy. Incomplete vibrational assignments were reported. Normal-coordinate treatment of ethanoic acid dimer has been performed by Fukushima and Zwolinski [122] and Kishida and Nakamoto [97]. The experimental vibrational assignments of Haurie and Novak [121] and Weltner [11] were adopted in this work. Seven missing fundamental vibrational wavenumbers were taken from Fukushima and Zwolinski [122]. The numerical values of the selected 40 fundamental assignments are given in table 9. The two reported torsional frequencies: $\nu_{33} = \nu_{42} = 100 \text{ cm}^{-1}$ for methyl rotors were not used. According to our internal rotation energy level calculation, the torsional transition ($0 \rightarrow 1$) for CH_3 rotor was 74 cm^{-1} . One hundred and eight (108) internal rotation energy levels (0 to 15700 cm^{-1}) for each CH_3 rotor were generated and employed for calculating the thermodynamic functions for this dimeric species.

The enthalpy of formation, ΔH_f° (g, 298.15 K) = $-221.72 \text{ kcal mol}^{-1}$ was derived from $\Delta H_0^\circ = -15.30 \text{ kcal mol}^{-1}$ for the dimerization reaction: $2 \text{ CH}_3\text{COOH}(\text{g}) = (\text{CH}_3\text{COOH})_2(\text{g})$ and the adopted value ΔH_f° (CH_3COOH , g, 298.15 K) = $-103.31 \text{ kcal mol}^{-1}$. The ΔH_0° value was selected by trial and error method such that the adopted one yielded the calculated vapor heat capacity of the ethanoic acid monomer-dimer equilibrium mixture to be consistent with the experimental data.

By use of the above molecular data, the ideal gas thermodynamic properties for ethanoic acid dimer were evaluated and the results are reported in table 12.

3.3 Equilibrium Mixture

Based on the vapor density measurements and infrared

spectra of ethanoic acid in the gaseous state, it has been proposed that ethanoic acid vapor contains polymeric species at low temperatures and high pressures. In order to better fit the experimental data, many investigators suggested the presence of dimers [3, 4, 6, 11, 16, 17, 123], trimers [8], and tetramers [7] in the vapor state.

In this study a molecular model assuming the vapor to contain monomers and dimers only was used for calculating the thermodynamic properties of ethanoic acid in the ideal gaseous state. The necessary ideal gas enthalpy, entropy, and heat capacity data for ethanoic acid monomer and dimer were obtained from tables 11 and 12, respectively. The values for the enthalpy of dimerization (ΔHd) was selected to provide calculated C_p° values for the monomer-dimer equilibrium mixture in reasonable agreement with the experimental heat capacity data as a function of temperature.

By the method of trial and error, we found that the value $\Delta Hd = -15.30 \text{ kcal mol}^{-1}$ at 0 K was the best one. The calculated heat capacities were in agreement with those measured by Weltner [11], which was the only piece of work available for comparison. The results are listed in table 13. At $P = 249$ torr, the average deviation (Δ) was 1.0%; $P = 507$ torr, $\Delta = 1.5\%$; and $P = 760$ torr, $\Delta = 1.9\%$. The agreement between calculated and observed heat capacities improves with higher temperatures and lower pressures as to be expected.

Table 14 summarizes the reported ΔHd values for ethanoic acid by several investigators using different experimental methods. Our selected value $\Delta Hd = -15.10 \text{ kcal mol}^{-1}$ at 298.15 K was in excellent agreement with that reported by Weltner.

Following the same procedure as described in section 2.3, the ideal gas thermodynamic properties of ethanoic

TABLE 12. Ideal gas thermodynamic properties for ethanoic acid dimer

T	$H^\circ - H_0^\circ$	$-\frac{(G^\circ - H_0^\circ)}{T}$	$\frac{(H^\circ - H_0^\circ)}{T}$	S°	C_p°	ΔH_f°	ΔG_f°	$\log K_f$
K	J mol ⁻¹	J K ⁻¹ mol ⁻¹				kJ mol ⁻¹		
0	0	0	0	0	0	-900.30	-900.30	infinite
50	2388.0	197.46	47.759	245.22	68.841	-909.24	-888.70	926.408
100	6355.8	235.98	63.558	299.54	86.379	-912.69	-866.81	452.770
150	10923.	263.62	72.823	336.45	96.441	-916.32	-843.10	293.590
200	16035.	285.60	80.176	365.78	108.432	-920.22	-818.10	213.662
273.15	24718.	312.11	90.494	402.61	129.503	-925.88	-779.90	149.138
298.15	28052.	320.19	94.089	414.28	137.250	-927.68	-766.38	134.265
300	28307.	320.77	94.356	415.13	137.828	-927.81	-765.36	133.260
400	43648.	349.93	109.120	459.05	168.730	-934.16	-710.19	92.740
500	61944.	375.87	123.888	499.76	196.487	-939.02	-653.63	68.284
600	82801.	399.72	138.002	537.72	219.962	-942.51	-596.22	51.905
700	105810.	422.00	151.155	573.15	239.621	-944.85	-538.27	40.166
800	130620.	442.98	163.278	606.26	256.190	-946.22	-480.09	31.346
900	156960.	462.87	174.404	637.27	270.266	-946.74	-421.78	24.479
1000	184610.	481.78	184.608	666.38	282.293	-946.49	-363.37	18.980
1100	213370.	499.82	193.969	693.79	292.609	-945.62	-305.31	14.498
1200	243080.	517.07	202.568	719.64	301.485	-944.31	-247.00	10.752
1300	273620.	533.60	210.478	744.08	309.142	-942.62	-188.99	7.594
1400	304880.	549.47	217.768	767.24	315.768	-940.62	-130.90	4.884
1500	336750.	564.72	224.498	789.22	321.519	-938.38	-73.22	2.550

TABLE 13. Comparison of measured and calculated vapor heat capacity for ethanoic acid

P torr	T K	C_p° , cal mol ⁻¹		C_p° (meas.) - C_p° (calc.)	
		measured ^a	calculated	cal mol ⁻¹	%
249	368.4	71.8	69.7	2.1	2.9
	399.2	87.3	85.5	1.8	2.1
	419.0	77.4	77.3	0.1	0.1
	435.8	62.5	62.5	0.0	0.0
	479.7	33.7	33.8	-0.1	-0.3
	509.2	28.1	27.5	0.6	2.1
	540.0	25.7	25.6	0.1	0.4
					1.0
507	396.4	78.3	75.9	2.4	3.1
	399.1	79.5	77.2	2.3	2.9
	420.1	81.7	80.3	1.4	1.7
	436.0	73.5	73.5	0.0	0.0
	470.4	48.1	48.3	-0.2	-0.4
					1.5
760	397.5	72.2	69.6	2.6	3.6
	421.8	79.4	76.2	3.2	4.0
	443.7	72.9	72.8	-0.1	-0.1
	470.9	54.9	54.8	0.1	0.2

^a Reported by Weltner [11].

TABLE 14. Reported enthalpies of dimerization for ethanoic acid

$-\Delta H_d$ kcal mol ⁻¹	T K	P torr	Investigators (year)
<i>Vapor density measurements</i>			
13.8 ± 0.1	355 - 473	160 - 1150	Johnson and Nash (1950) ^b
14.5 ± 0.4	353 - 483	45 - 813	Ritter and Simons (1945) ^c
14.6 ^a	383 - 457	120 - 290	Fenton and Garner (1930) ^d
14.8	323 - 398	30 - 700	Barton and Hsu (1969) ^e
15.27 ± 0.07	323 - 423	13 - 34	Taylor (1951) ^f
16.4 ± 0.8	298 - 313	5 - 25	MacDougall (1936) ^g
<i>Infrared spectroscopic method</i>			
11.4			Excoffon and Marechal (1972) ^h
14.2 ± 0.7			Mathews and Sheets (1969) ⁱ
14.6 ± 0.5			Clague and Bernstein (1969) ^j
15.9			Herman and Hofstadter (1938) ^k
17.0 ± 0.8			Pross and Zeggeren (1960) ^l
<i>Derived from calculation</i>			
15.05 ± 0.05	373		Weltner (1955) ^m
15.10	298.15		This work

^a Calculated from $Q_v = 13.79$ kcal mol⁻¹ determined experimentally by the formula $\Delta H = Q + \Delta n RT$, T taken at 420 K.

^b Reference [8].

^c Reference [3].

^d Reference [16].

^e Reference [7].

^f Reference [6].

^g Reference [24].

^h Reference [123].

ⁱ Reference [18].

^j Reference [124].

^k Reference [4].

^l Reference [17].

^m Reference [11].

acid monomer-dimer equilibrium mixture in the temperature range from 50 to 1000 K at 1 atm were evaluated and presented in table 15. In table 16 the equilibrium constants of the gaseous reaction: $(\text{CH}_3\text{COOH})_2 \rightarrow 2 \text{CH}_3\text{COOH}$ and the mole fraction of dimers in the vapor

mixture over the temperature range from 100 to 900 K and at three different pressures: 0.1 atm, 1.0 atm, and 5.0 atm are presented. The values listed in tables 13, 15, and 16 were evaluated based on one mole of ethanoic acid monomer.

TABLE 15. Ideal gas thermodynamic properties of ethanoic acid monomer-dimer equilibrium mixture

T	$(H^\circ - H_0^\circ)$	$-\frac{(G^\circ - H_0^\circ)}{T}$	$\frac{(H^\circ - H_0^\circ)}{T}$	S°	C_p°
K	J mol ⁻¹	J K ⁻¹ mol ⁻¹			
50	1193.9	98.734	23.878	122.61	34.420
100	3178.0	117.99	31.780	149.77	43.189
150	5461.8	131.81	36.412	168.22	48.221
200	8018.4	142.80	40.092	182.89	54.295
273.15	12498.	156.09	45.754	201.85	71.811
298.15	14470.	160.21	48.533	208.74	87.516
300	14634.	160.51	48.779	209.29	89.087
400	32138.	177.83	80.346	258.18	297.22
500	58959.	200.83	117.92	318.75	162.30
600	71363.	222.55	118.94	341.49	111.33
700	82728.	240.81	118.18	359.00	117.30
800	94881.	256.60	118.60	375.21	125.64
900	107820.	270.64	119.80	390.45	133.03
1000	121450.	283.35	121.45	404.80	139.27

TABLE 16. Equilibrium constants and concentration of $(\text{CH}_3\text{COOH})_2$ in $\text{CH}_3\text{COOH}-(\text{CH}_3\text{COOH})_2$ equilibrium mixture

T K	K_{eq}	Mole fraction of dimer		
		$P = 0.1 \text{ atm}$	$P = 1.0 \text{ atm}$	$P = 5.0 \text{ atm}$
100	3.46×10^{25}	1.000	1.000	1.000
200	3.84×10^8	1.000	1.000	1.000
298.15	1.26×10^3	0.915	0.972	0.988
300	1.08×10^3	0.908	0.970	0.986
400	2.02	0.147	0.502	0.731
500	4.94×10^{-2}	0.005	0.045	0.170
600	4.30×10^{-3}	0.000	0.004	0.021
700	7.69×10^{-4}	0.000	0.001	0.004
800	2.15×10^{-4}	0.000	0.000	0.001
900	8.01×10^{-5}	0.000	0.000	0.000

4. Discussion

The thermodynamic properties of methanoic and ethanoic acids in the gaseous state have interested chemists and chemical engineers for decades due to the industrial importance of these two compounds. The presence of polymeric species in the vapor makes their experimental measurements difficult. Without reliable thermodynamic properties for the monomers and dimers of these two alkanic acids, it is impossible to extend the limited amount of experimentally determined thermodynamic properties to wider ranges of conditions which are usually necessary in industrial applications.

Based on a monomer-dimer molecular model, our calculations show that at room temperature and atmospheric pressure the methanoic acid vapor contains 95% dimers and ethanoic acid vapor, 97%. Thus, for reliable thermodynamic calculations, accurate thermodynamic properties for both the monomers and dimers are needed.

Unfortunately, no vapor heat capacity data were avail-

able on methanoic acid for comparison with our calculated C_p° values for the methanoic acid ideal gas equilibrium mixture. The enthalpy of formation, ΔH_f° (g, 298.15 K) = $-196.21 \text{ kcal mol}^{-1}$, for methanoic acid dimer was derived based on $\Delta Hd = -15.25 \text{ kcal mol}^{-1}$, which was selected such that the derived vapor densities of the equilibrium mixture at various temperatures to be consistent with the experimental values given by Coolidge [1]. The calculated equilibrium constants for the dimer dissociation reaction over the temperature range 100–800 K are listed in table 8. The uncertainty of our selected ΔHd value is estimated to be $\pm 0.15 \text{ kcal mol}^{-1}$.

Thermodynamic properties of methanoic acid in the ideal gaseous state have been evaluated by Waring [48] and more recently by Green [125]. Their calculated values are somewhat inconsistent with the more reliable values reported by us. For comparison, the C_p° and S° values of Green are smaller than ours by 0.11 and 0.03 cal K⁻¹ mol⁻¹ at 298.15 K and 1.42 and 0.74 cal K⁻¹ mol⁻¹ at 1000 K. The C_p° values calculated by Waring are higher

than ours at temperatures below 600 K and lower than ours at temperatures above 600 K. For example, the difference at 298.15 K and 1500 K are 0.72 and $-1.14 \text{ cal K}^{-1} \text{ mol}^{-1}$, respectively.

The third law S° (HCOOH, g, 298.15 K) was obtained as $59.44 \text{ cal K}^{-1} \text{ mol}^{-1}$ by Waring [48]. Assuming there was random orientation in the crystal, he added $(\frac{1}{2}) R \ln 2 = 0.689 \text{ cal K}^{-1} \text{ mol}^{-1}$ to this value, yielding S° (HCOOH, g, 298.15 K) = $60.133 \text{ cal K}^{-1} \text{ mol}^{-1}$. Using the molecular data available then, he calculated the statistical entropy to be $59.342 \text{ cal K}^{-1} \text{ mol}^{-1}$, excluding the entropy from the torsional vibration of the OH group. Thus the entropy of the OH vibrations was assumed to be $0.791 \text{ cal K}^{-1} \text{ mol}^{-1}$, corresponding to an estimated frequency of 452 cm^{-1} . Since methanoic acid has an infinite-chain type crystalline structure [126], the entropy should not contain the additional term $(\frac{1}{2}) R \ln 2$ arising from random orientation. His reported values for HCOOH(g) are in error with or without the 0 K additional correction term. Our calculated entropy value S° (HCOOH, g 298.15 K) = $59.483 \text{ cal K}^{-1} \text{ mol}^{-1}$ is in agreement with the reported third law values, $59.44 \pm 0.1 \text{ cal K}^{-1} \text{ mol}^{-1}$ by Waring [48] and also $59.30 \pm 0.3 \text{ cal K}^{-1} \text{ mol}^{-1}$ by Halford [99]. The statistical entropy for methanoic acid dimer (g) has been reported as $83.35 \text{ cal K}^{-1} \text{ mol}^{-1}$ [48] and $82.89 \text{ cal K}^{-1} \text{ mol}^{-1}$ [125], respectively, while our recommended value is $79.51 \text{ cal K}^{-1} \text{ mol}^{-1}$.

Acetic acid dimerization has been investigated extensively by Weltner [11] and Ramsey and Young [127]. In view of the lack of definitive experimental evidence for the existence of higher polymers than dimers, we tentatively adopted the monomer-dimer ideal gas equilibrium mixture as our molecular model for evaluating the thermodynamic properties for ethanoic acid in the gaseous state. Based on this molecular model, the calculated heat capacities were in reasonable agreement with those measured by Weltner, as indicated in table 13. In this table the calculated values at lower temperatures and higher pressures deviate more from the experimental data than the ones at higher temperatures and lower pressures. Due to the fact that experimental measurements at lower temperatures and higher pressures may involve unexpected experimental difficulties, e.g. surface adsorption effects, etc., the accuracy of the data point obtained at these conditions is perhaps lower than that of the other points. There may be a possibility that the differences in C_p° between the calculated and experimental values are caused by neglecting the presence of higher polymeric forms than dimeric in the vapor phase; however, this speculation needs to be confirmed by future experimental observation.

Ideal gas thermodynamic properties for ethanoic acid monomers and dimers were evaluated by Weltner [11], employing the then available molecular data on these species. In comparison with our values, his calculated heat capacities for ethanoic acid monomer are higher at temperatures below 600 K and lower at temperatures above 600 K. For ethanoic acid dimer, his calculated heat capacities

are higher than our calculated ones by $2.2 \text{ cal K}^{-1} \text{ mol}^{-1}$ at 298.15 K and $0.3 \text{ cal K}^{-1} \text{ mol}^{-1}$ at 1500 K.

The third law S° (g, 298.15 K) for ethanoic acid monomer and dimer were reported as $67.6 \text{ cal K}^{-1} \text{ mol}^{-1}$ and $98.2 \text{ cal K}^{-1} \text{ mol}^{-1}$, respectively by Weltner [11]. The statistical entropy for the monomer at 298.15 K was obtained as $69.4 \pm 1 \text{ cal K}^{-1} \text{ mol}^{-1}$ by Halford [128], $67.52 \text{ cal K}^{-1} \text{ mol}^{-1}$ by Weltner, and $67.72 \text{ cal K}^{-1} \text{ mol}^{-1}$ by the authors. The statistical S° (g, 298.15 K) for the ethanoic dimer was calculated to be $99.6 \text{ cal K}^{-1} \text{ mol}^{-1}$ by Halford [128] and $96.44 \text{ cal K}^{-1} \text{ mol}^{-1}$ by Weltner, while our calculated value was $99.02 \text{ cal K}^{-1} \text{ mol}^{-1}$. Based on our calculated values of S° (g, 400 K) for ethanoic acid monomers and dimers, the entropy of dimerization was derived to be $-35.74 \text{ cal K}^{-1} \text{ mol}^{-1}$ which is consistent with the reported experimental value $-36.77 \pm 1.5 \text{ cal K}^{-1} \text{ mol}^{-1}$ by Slutsky and Bauer [129] and Taylor [9].

It is important to note that Mathews and Sheets [17] have found that repeated determinations with different surface areas resulted in marked changes in apparent enthalpies of dimerization from vapor density measurements as well as from infrared absorbance measurements. Therefore, the ΔHd values listed in table 5 and 14 are inaccurate unless the corrections for the surface absorption effect are uniformly applied by the investigators, as did Coolidge [1].

Finally, it should be emphasized that although our statistical calculations include some simplified assumptions, e.g., use of OH internal rotation potential function in HCOOH molecule for that in CH_3COOH molecule, etc., the evaluated thermodynamic properties for equilibrium mixtures of methanoic and ethanoic acid are in good agreement with the experimental data. This confirms the fact that the use of monomer-dimer molecular model to calculate the thermodynamic properties of methanoic and ethanoic acids is adequate and the evaluated property values are reliable for most applications.

5. Acknowledgement

This study was supported by the NBS Office of Standard Reference Data under contract number 5-35794 with the Thermodynamics Research Center of the Texas Engineering Experiment Station, Texas A&M University. The authors are grateful for the valuable comments and suggestions offered by the editor and referees of this paper.

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