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Acetic Acid Vapor: 2. A Statistical Mechanical Critique of Vapor Density Experiments

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A statistical mechanical model is used to critique vapor density experiments on acetic acid. The model suggests that the differences in the standard enthalpy of dissociation of acetic acid dimer reported in the literature lie mainly in the interpretation of the data and not in the data itself. If a uniform and plausible interpretative framework is adopted, the discrepancies largely disappear.

1. Introduction

The five most recent vapor density studies of acetic acid vapor put the standard enthalpy of dissociation of the ring dimer between 58 and 69 kJ mol^{-1}. Statistical/quantum mechanical models of the ideal vapor that were developed in the preceding paper[1] are used as critical tools to assess the experimental vapor density studies. The result will be to propose that the studies are all consistent with a standard enthalpy of dissociation at absolute zero of about 65−66 kJ mol^{-1}. The method has a strong empirical component, in which rotational and vibrational parameters are obtained by a combination of empirical and theoretical techniques, and the dissociation energy is regarded as an empirical parameter that can be extracted from reported values of the pressure, density, and temperature. In the process, questions such as the following are addressed: Is the vapor ideal under the conditions of the experiment? Are trimers and tetramers present in significant quantities as some authors claim? Is a data set self-consistent?

Two models of the ideal vapor are employed. As in the preceding paper, they are referred to as the ring-dimer model and the vapor model. The former is used to find the molecular energy of dissociation of the dimer, $D_{2,0}$, zero-point vibrational energy corrected, from experimental vapor density measurements. To use the ring-dimer model to this end, two conditions must be met by the experimental conditions:the vapor must be ideal, and only the cis-monomer and the ring dimer should be present in significant quantities. The vapor model provides guidance for making that judgment.

Section 2 describes conventions. Section 3 is the heart of the paper in which the experimental vapor density studies are reviewed and critiqued. Section 4 briefly reviews the results of nondensity experiments on the vapor. Section 5 presents a summary and conclusions.

2. Conventions

2.1. Standard Enthalpy of Dissociation. It is important to distinguish between three closely related meanings for the term “standard enthalpy of dissociation”. (i) It can be the quantity obtained from the slope of a graph of ln(K) versus 1/T

$$\ln(K) = -\frac{A}{T} + B = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \qquad (1)$$

where A and B are positive constants, and K is the thermodynamic equilibrium constant. (ii) It can be the standard enthalpy change at a specific temperature, calculated from eq 3a in the companion paper to this one.[1] (iii) It can be the standard enthalpy of dissociation at absolute zero, in which case, it is the same as the standard internal energy of dissociation and relates to the molecular energy of dissociation, D_0, by $\Delta H^\circ = \Delta U^\circ = N_A D_0$, where N_A is the Avogadro number.

2.2. Standard Presentation of Results. All numerical results will be presented in a standard format. The stoichiometries will refer to those defined in the preceding paper. Thus, the relationship of dimer and monomer refers to the dissociation $(\mathrm{HOAc})_2 = 2\mathrm{HOAc}$. The thermodynamic equilibrium constant of the ideal vapor is then

$$K_{21} = \frac{P_1^{\,2}}{P_2 P^\circ} = \frac{x_1^{\,2}}{x_2}\frac{P}{P^\circ} = \frac{4\alpha^2}{1-\alpha^2}\frac{P}{P^\circ} \qquad (2)$$

where P_n and x_n are, respectively, the partial pressure and mole fraction of n-mer, α is the degree of dissociation, P is the total pressure, and $P^\circ = 1$ bar $= 750$ Torr. To illustrate what “standard presentation of results” means, consider the following illustrations.

MacDougall[2] uses the above stoichiometry, but omits the factor of P° from eq 2 and reports pressure in units of the Torr. He reports, in his notation, $K_p(313.1) = 2.08$ Torr. His result would appear in this paper as $K_{21}(313.1) = 2.08/750 = 2.77(-3)$.

For Ritter and Simons,[3] the stoichiometry refers to the association reaction $\mathrm{HOAc} = (^1/_2)(\mathrm{HOAc})_2$, and the equilibrium constant is $K_2 = P_2^{1/2}/P_1$. Their equilibrium constant would be reported here as

$$K_{21} = \frac{1}{K_2^{\,2} P^\circ}$$

Their measurement of the enthalpy of association via the linear regression

$$\ln(K_2) = \frac{C}{T} - D$$

where C and D are positive constants would lead to the standard enthalpy and standard entropy of dissociation calculated from $A = 2C$ and $B = 2D - \ln(P^\circ)$; see eq 1.

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TABLE 1: Reported Experimental Standard Enthalpies of Dissociation of the Ring Dimer

method	authors	ΔH°_{21} (kJ mol^{-1})
vapor density	Gibbs (1879)	67.39 ± ?
	Holland et al. (1912; 1916)	62.76 ± ?
	MacDougall (1936)	68.62 ± 3.35
	Ritter and Simons (1945)	60.67 ± 1.67
	Johnson and Nash (1950)	57.82 ± 0.42
	Taylor (1951)	63.89 ± 0.42
	Barton and Hsu (1969)	61.9 ± ?
infrared	Weltner (1955)	62.97 ± 0.21 at 373 K
	Mathews and Sheets (1969)	59.4 ± 2.9
thermal conductivity	Frurip et al. (1980)	61.25 ± 3.3
review article	Chao and Zwolinski (1978)	64.02 ± ? at 0 K

TABLE 2: Five Ring-Dimer Models with $F_2 = 4.5110$ K^{-4} [a]

source	T_{range} (K)	P_{range} (Torr)	$\overline{D_{0,2}}$	$\delta D_{0,2}$	ΔH°	ΔH°(298)	ΔH°(0)
T	324−364	25.98−37.48	1.0809	0.0031	64.10	64.62	65.09
B & H	323−369	33.59−89.26	1.0779	0.0026	63.92	64.44	64.92
J & N	355−365	160.2−182.5	1.0838	0.0037	64.27	64.80	65.27
R & S	325−365	44.5	1.0823	0.0049	64.18	64.71	65.18
M	303−313	3−22	1.0713	0.0003	63.52	64.04	64.52

[a] $\Delta S^\circ = 153.9$ J mol^{-1} K^{-1}. Units of ΔH° are the same as in Table 1. $\overline{D_{0,2}}$ is the average value and $\delta D_{0,2}$ the standard error; both are expressed in units of 10^{-19} J.

TABLE 3: Five Ring-Dimer Models with $F_2 = 4.9414$ K^{-4} [a]

source	T_{range} (K)	P_{range} (Torr)	$\overline{D_{0,2}}$	$\delta D_{0,2}$	ΔH°	ΔH°(298)	ΔH°(0)
T	324−364	25.98−37.48	1.0853	0.0029	64.36	64.89	65.36
B & H	323−369	33.59−89.26	1.0841	0.0027	64.29	64.82	65.29
J & N	355−365	160.2−182.5	1.0883	0.0037	64.54	65.07	65.54
R & S	325−365	44.5	1.0867	0.0048	64.45	64.97	65.44
M	303−313	3−22	1.0752	0.0003	63.76	64.28	64.75

[a] $\Delta S^\circ = 154.6$ J mol^{-1} K^{-1}

3. Critique of Experimental Studies

3.1. Reported Values of ΔH°, the Standard Enthalpy of Dissociation of the Ring Dimer. The values of the standard enthalpy of dissociation reported in Table 1 have been found by their authors by the linear regression method, except for the results of Gibbs,[4] of Holland et al.,[5] and of Chao and Zwolinski,[6] which are the enthalpy of dissociation at absolute zero. The results obtained by infrared analysis and thermal conductivity are included in Table 1 only for the purposes of comparison, the former not lending itself to interpretation with the statistical mechanical model, and the latter not to the model in its present form.

3.2. Experimental Difficulties in Vapor Density Studies. The experimentalists cite two major difficulties: (1) nonideal behavior of the vapor and (2) adsorption of the vapor onto the walls of the container. Mathews and Sheets[7] studied the latter systematically.

The vapor model developed in the preceding paper leads to a third factor, which affects the interpretation of the data. At high temperatures, the dimer population will have a significant fraction of non-ring dimer, which can lead to an underestimation of the equilibrium constant, K_{21}, by as much as 10% at 500 K. This factor, however, has a scant effect on the determination of ΔH° from eq 1. This was indicated by a trial calculation for $T = 300-500$ K at 25 K intervals with the vapor model. In one calculation, it was assumed that all of the isomers described in that paper were present. In a second, only the cis-monomer and the ring dimer were assumed to be present, with the result that ΔH° fell from 64.04 to 63.47 kJ mol^{-1}, a decrease of only 9 ppt.

3.3. Ring-Dimer Models. Tables 2 and 3 give ring-dimer models for the five most recent experimental studies. Temperatures of about 370 K or less were chosen, because the vapor model suggests that the cis-monomer and the ring dimer are the only significant species present at these low temperatures. Low pressures were chosen for ideal behavior. This permits calculation of the molecular dissociation energy, $D_{2,0}$, from the statistical mechanical formula for the equilibrium constant, eq 2b of the preceding paper,[1] using experimental data for a given temperature.

The 5 lowest temperatures were used from the Taylor (T) data set. The 6 lowest-pressure data points were chosen from the 23 in the Barton and Hsu (B & H) data set. The Johnson and Nash (J & N) data set is large, but there are few low-temperature, low-pressure data points, with the consequence that only 3 were used. Ritter and Simons (R & S) collected data isobarically; the 5 lowest temperatures on their lowest-pressure isobar were used. MacDougall (M) collected data along 4 isotherms. However, construction of the ring-dimer model led to the conclusion that the results on one isotherm should be discarded, which is discussed below. This left only 3 isotherms, but 7 or 8 pressure measurements were used for each isotherm.

All of the ring-dimer models employ the same vibrational manifold. The standard entropy of dissociation then will depend only on the choice of rotation parameter, F_2. Ring-dimer models were constructed for two rotation parameters, which represent the full range of rotation parameters found in the ten models constructed in the preceding paper. The entropy and first of the three enthalpy change entries in the tables were obtained by linear regression using eq 1. Although $\overline{D_{0,2}}$ was found from low-temperature data, the semilog graph was made for the temperature range $T = 300-500$ K at 25 K intervals, just as though it were an extensive set of experimental data.

TABLE 4: Thermochemical Data for the Dissociation of *n*-Mers[a]

source	ΔH°_{21}	ΔS°_{21}	ΔH°_{31}	ΔS°_{31}	ΔH°_{41}	ΔS°_{41}
vapor model	57.91	145.5	65.04	223.4	94.14	344.6
J & N	57.82	138.5	94.96	245.8		
R & S	60.67	144.5			112.7	284.5

[a] Units are kilojoules per mole and joules/mole-K. The numerical entries for the vapor model were found from eq 1 for structures (**1**), (**7**), and (**10**) in the preceding paper.

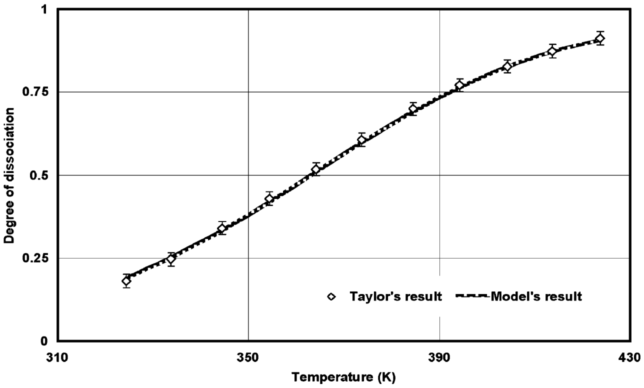

Figure 1. Degree of dissociation vs temperature: Taylor.

The results in Table 2 were calculated with a rotation parameter $F_2 = 4.5110\ \mathrm{K}^{-4}$ but are not sensitive to this choice. Table 4 in the preceding paper shows that the DFT/B3LYP models give somewhat larger values of the parameter than the Hartree−Fock models, the average value for the former being $F_2 = 4.9414\ \mathrm{K}^{-4}$. Table 3 illustrates how using this value of the rotation parameter affects the calculated dissociation energy. The effect is seen to be small.

3.4. Critique of Experimental Results Using the Ring-Dimer Model. *3.4.1. Taylor.*[8] The ring-dimer model is in substantial agreement with the results of Taylor's study, which spans the temperature and pressure ranges of 324.4−423.7 K and 25.98−54.91 Torr. Taylor chose this range of low pressures under the assumption that the vapor would behave ideally. Nash[9] notes that Taylor did not correct for adsorption. Mathews and Sheets argue that uncorrected adsorption results in too high a value of ΔH° and say that it is plausible that this has affected Taylor's result. They also note that the signature of adsorption is the deviation from linearity of an $\ln(K)$ versus $1/T$ plot. However, Taylor's data graphs linearly as shown in his paper and as confirmed by the present author (section 3.6 below). The theoretical model with values of $F_2 = 4.5110\ \mathrm{K}^{-4}$ and $D_{2,0} = 1.0809 \times 10^{-19}$ J fits Taylor's results nicely, as shown in Figure 1, which makes plausible Taylor's claim of ideal behavior. Purely for defining the scale, an "error bar" of full height $\delta\alpha = 0.04$ has been put on each of Taylor's data points. The line, of course, is not a regression line or curve fit but joins the points computed by statistical mechanics for each (P, T) point in Taylor's data set. Pressure increases slowly with temperature in the data set.

3.4.2. Barton and Hsu.[10] These authors report data for three to six pressures on five different isotherms. In Figure 2, their experimental results for three isotherms are compared to those of the B & H ring-dimer model of Table 2. Once again, an "error bar" of full height $\delta\alpha = 0.04$ has been put on the data points purely for the purpose of assessing the degree of agreement between theory and experiment. Note that the pressure range for the 323.11 K isotherm is greater than the entire pressure range in Taylor's study (Tables 2 and 3). The failure of the ring-dimer model at the highest temperature is evident. For a given isotherm, increasingly nonideal behavior is expected as the pressure increases, which is the trend observed in Figure 2 on the two higher isotherms. Barton and Hsu did not correct for vapor adsorption, but they cited work by Nicholls to the effect that adsorption of acetic acid is negligible in the range from 50 to 150 °C.

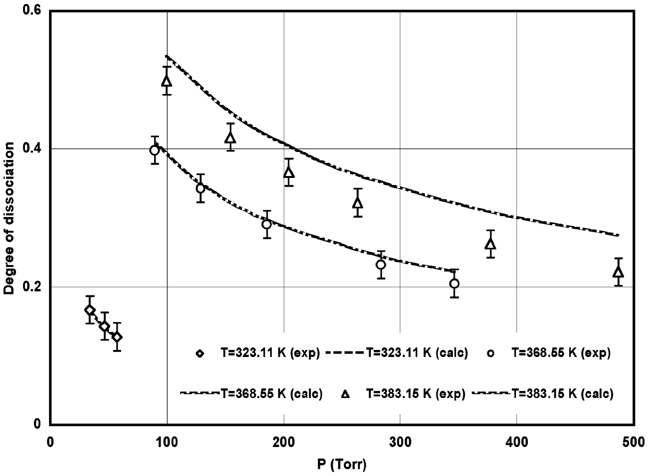

Figure 2. Degree of dissociation vs pressure: Barton and Hsu.

TABLE 5: Johnson & Nash Data Point, $T = 355.1$ K, $P = 160.2$ Torr[a]

source	K_{21}	K_{31}	x_1	x_2	x_3	d	M
J & N	5.419(−2)	8.910(−2)	0.385	0.585	0.029	0.714	98.7
vapor	8.853(−2)	1.333(+2)	0.469	0.531	3.53(−5)	0.665	91.9
ring-dimer	3.853(−2)	∞	0.344	0.656	0	0.719	99.4

[a] Density d is in grams/liter and molar mass M in grams/mole.

3.4.3. Ritter and Simons,[11] *and Johnson and Nash.*[12] It is convenient to discuss the results of these pairs of investigators together because of the similarity of their approach and conclusions. Both pairs argued that their data could be understood by assuming either a nonideal vapor of monomer and dimer or an ideal vapor of monomer, dimer, and higher oligomer. Both pairs of authors concluded that the latter option was better, with Johnson and Nash concluding that the higher oligomer was the trimer, while Ritter and Simons concluded that it was the tetramer. Johnson and Nash discuss the relationship between deviations from ideality and clustering of gas molecules.

Table 4 summarizes the thermochemical results of both pairs of investigators and those from Table 1 of the preceding paper for the vapor model. The present theoretical study does not support the presence of either trimer or tetramer in significant amounts for three reasons.

Reason 1. According to the vapor model, the trimer and tetramer populations will always be small under the conditions studied by Ritter and Simons and by Johnson and Nash. Figure 2 in the preceding paper illustrates that assertion, and the following discussion amplifies it.

Table 5 compares Johnson and Nash's conclusions for one of their data points with conclusions from the two models employed here. K_{31} for the vapor model is for isomer (**7**) in the preceding paper. K_{21} for the ring-dimer model follows from the J & N line in Table 2 above. The striking difference in results is that Johnson and Nash believe that the vapor is about 3% trimer, whereas in the vapor model, it is 35 ppm, a discrepancy that is reflected in the values for the equilibrium constants, K_{31}. If Johnson and Nash are correct, then the vapor model is badly in error for the trimer, but that inference is hard to accept, since the model does well for the dimer.

Is it possible that what Johnson and Nash "observed" in the vapor is a mix of trimers and not just one trimer? The model is at odds with that possibility. The argument is by contradiction. Suppose that the model agrees with the conclusion of Johnson and Nash about the trimer mole fraction. The starting point in the population analysis is to find the mole fraction of monomer by solving the trinomial equation

$$\sum_{k=1}^{3} A_k x_1^k = 1$$

where the important term for this analysis is

$$A_3 = \frac{1}{K_{31}}\left(\frac{P}{P^\circ}\right)^2 (1 + \sum_n K_{33}^{(n)}) \tag{3}$$

The sum is over all less-stable trimers, for example, trimers (**8**) and (**9**) in the preceding paper. Johnson and Nash suppose that there is only one trimer, so

$$K_{31}(\text{expt}) = \frac{1}{A_3}\left(\frac{P}{P^\circ}\right)^2$$

and thus, eq 3 becomes

$$K_{31}(\text{theory}) = K_{31}(\text{expt})(1 + \sum_n K_{33}^{(n)})$$

The fact that K_{31}(theory) > K_{31}(expt) means that Johnson and Nash attribute the high trimer population to one trimer that resists dissociation, whereas theory attributes it to many trimers that readily dissociate. It is easy to put a lower bound on how many trimers there must be to reconcile the two interpretations. Let

$$\sum_{n=1}^{N} K_{33}^{(n)} = N\langle K_{33}\rangle$$

where $N + 1$ is the total number of trimers and $\langle K_{33}\rangle$ is the average value of the equilibrium constant for trimer isomerization. Solving for N gives

$$N = \frac{1}{\langle K_{33}\rangle}\left[\frac{K_{31}(\text{theory})}{K_{31}(\text{expt})} - 1\right]$$

Using the values of K_{31} from Table 5 gives (since $\langle K_{33}\rangle \le 1$) $N + 1 \ge 1.50 \times 10^3$, which is absurd.

Thus, either the model is wildly wrong or Johnson and Nash are wrong about the presence of trimer. The only remaining possibility for reconciliation is the existence of a trimer or trimers far more stable than the three that have been identified.

Next, consider the conclusion of Ritter and Simons about the existence of a tetramer. Figure 3 shows how the ring-dimer model with $F_2 = 4.5110$ K^{-4} and $D_{2,0} = 1.0823 \times 10^{-19}$ J fits a subset of their data. The "error bars" on the data points have been arbitrarily set at a full height of δM = 2 g mol^{-1} as assistance in assaying the agreement between model and experiment. In Figure 3 on the 44.5 Torr isobar, the first nine points show good agreement between model and experiment. It seems odd that the remaining four plateau instead of falling to the molar mass of monomer, so they have not been used in the subsequent analysis. The temperature range and the pressure on this isobar are comparable to the conditions in Taylor's experiments.

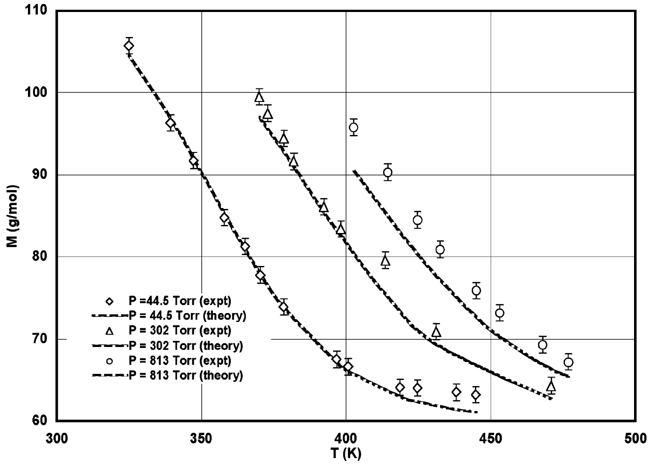

Figure 3. Molar mass vs temperature: Ritter and Simons.

TABLE 6: Experiment and Models for P = 44.5 Torr and T = 370.5[a] K

source	K_{21}	K_{41}	x_1	x_2	x_4	d	M
R & S	1.000(−1)	9.260(−2)	0.705	0.295	5.5(−4)	0.150	77.8
models	9.821(−2)	8.771(+4)	0.701	0.299	6.0(−10)	0.150	78.0

[a] Units of molar mass, M, are grams/mole and of density, d, grams/liter.

TABLE 7: Experiment and Models for P = 800 Torr and T = 393.2 K

source	K_{21}	K_{41}	x_1	x_2	x_4	d	M
R & S	3.115(−1)	7.661(−1)	0.403	0.555	0.042	3.29	101
models	3.270(−1)	4.470(+5)	0.421	0.579	8.5(−8)	3.09	94.8

Table 6 shows the agreement between the statistical mechanical models and experiment for one temperature on the isobar. The "models" line is a mix of results from the two models: K_{21} was found for the R & S ring-dimer model from Table 2, and K_{41} was found for the vapor model's tetramer (**10**) in the preceding paper. Although the dissociation constants for the tetramer differ by 6 orders of magnitude, the compositions and molar masses are in substantial agreement, because the pressure is so low that the amount of tetramer is negligible.

Figure 3 shows that theory and experiment do not agree at the high-pressure 800 Torr isobar. Table 7, which shows the difference in results for one temperature on that isobar, brings the difference into sharp focus between the interpretation of Ritter and Simons and that suggested by the models. As before, K_{21} is for the ring-dimer model and K_{41} for the vapor model.

Ritter and Simons measured P, T, and d, then found M from the ideal gas equation, $M = dRT/P$. With the presence of tetramer inferred, the value of K_{41} was chosen to correctly generate the calculated molar mass, which is the one on the R & S line. They conclude that the vapor is 4.2% tetramer. The 800 Torr isobar for the statistical model in Figure 3 represents ideal behavior. The discrepancy between it and the experimental data points is due to nonideality. Having used the ideal gas law to find the molar mass, Ritter and Simons must ascribe the discrepancy to the presence of the tetramer. Thus, the deviation from ideality is a manifestation of clustering.

The models lead to two challenges to this interpretation: (1) Clustering does not necessarily lead to nonideal behavior. This is shown by the 44.5 Torr isobar of Figure 3 and the data of Table 6; Figure 1 also shows it. The dimeric cluster behaves ideally if the pressure is low enough. (2) There is essentially

TABLE 8: Thermochemistry of Oligomerization[a]

source	ΔH°_{23}	ΔS°_{23}	ΔH°_{24}	ΔS°_{24}
vapor model	21.82	−5.2	21.68	−53.6
J & N	−8.23	−38.0		
R & S			8.6	4.5

[a] Units are kilojoules/mole and joules/mole−K.

TABLE 9: Molecular Dissociation Energy Found from Four Isotherms[a]

T (°C)	25	30	35	40
$D_{2,0}$	1.0748 ± 0.0014	1.0715 ± 0.0003	1.0714 ± 0.0002	1.0709 ± 0.0009

[a] $F_2 = 4.5110\ K^{-4}$. $D_{2,0}$ is in units of 10^{-19} joules.

no tetramer present at 800 Torr. The statistical mechanical values of K_{41} doubtless are approximate, but it seems unlikely that they are in error by 6 orders of magnitude. This point is strengthened by considering the HF/6-31G(d) values for K_{21}, which are 0.2007 and 0.5945, respectively, at 370.5 and 393.2 K, which are high by a factor of 2−3 but not 6 orders of magnitude.

If there is no tetramer present, then the deviation from ideality is due to other causes, which this paper does not address. This leads to additional inferences. Using the formula $M = dRT/P$ to find the molar mass is justified at the lower isobar but not at the higher. This assertion is supported by the theory of clustering in nonideal vapors developed by Coolidge,[13] who, utilizing the virial equation of state, showed that the mole fractions depend on the virial coefficients. If this is correct, then neither molar mass reported in Table 7 should be seen as reliable. The crucial inference is that computing the molar mass by the ideal gas law and finding a dissociation constant, K_{41}, compatible with that value, led Ritter and Simons to underestimate the strength of hydrogen bonding in the dimer. In fact, their own data is consistent with other estimates, as the entries in Tables, 2, 3, and 10 show.

Reason 2. All three entropies of dimer dissociation, ΔS°_{21}, shown in Table 4 are lower than for the ring-dimer models as given in Tables 2 and 3. If the ring-dimer models' vibrational manifolds are a good representation of the actual vibrational manifolds of the cis-monomer and the ring dimer, then a simple calculation shows that, for example, the Johnson and Nash value of the entropy of dissociation implies $F_2 \approx 0.67\ \mathrm{K}^{-4}$. Neither the ten models listed in Table 4 of the preceding paper nor the principal moments of inertia data cited in the Chao and Zwolinski review article suggest that such a small value of the rotation parameter is plausible.

Reason 3. A test for the plausibility of the experimental results can be obtained by considering the hypothetical oligomerization of $^{n}/_{2}$ mol of dimer into an n-mer, $n = 3, 4$

$$\frac{n}{2}(\mathrm{HOAc})_2 = (\mathrm{HOAc})_n$$

From the definition of ΔH°_{n1}, it follows that the enthalpy of oligomerization is given by

$$\Delta H^\circ_{2n} = \frac{n}{2}\,\Delta H^\circ_{21} - \Delta H^\circ_{n1}$$

with an analogous equation holding for entropy changes. The results in Table 4 lead to those in Table 8.

As noted in section 4.2 of the preceding paper, the vapor model leads to simple rules of thumb for understanding the oligomerization quantitatively. In going, for example, from 1.5 mol of dimer to trimer, three structural units of the type shown by structure (**12**) are broken, whereas one type (**12**) and one type (**15**) are formed, so $\Delta H^\circ_{23} \approx 3(29) - (29 + 34) = 24$ kJ mol^{-1}. The reaction is endothermic, because there is no way to compensate energetically for the net breaking of the optimal type of hydrogen bond. Even though the model is an approximate one, it is hard to understand how the reaction can be exothermic as implied by Johnson and Nash's results. Whatever the structure of the tetramer, it seems implausible that the conversion of two moles of dimer to one of tetramer should involve an entropy increase as the results of Ritter and Simons imply. Thus, there seems to be some element of implausibility in both pairs of experimental results.

3.4.4. MacDougall.[14] Mathews and Sheets attribute MacDougall's high value of the enthalpy of dissociation (Table 1) to the low temperatures (25−40 °C, every 5 °C) of his experiments, which lead to excessive errors due to adsorption. The ring-dimer model suggests another cause. It permits a probe of subsets of measurements and, in this instance, singles out a data point that may be faulty. For each isotherm, MacDougall reports the degree of dissociation, α, for a number of low pressures. The model allows the calculation of the molecular dissociation energy, $D_{2,0}$, for each data point. For each isotherm, $D_{2,0}$ was calculated for seven or eight values of the pressure and their corresponding degrees of dissociation. The results are summarized in Table 9 for $F_2 = 4.5110\ \mathrm{K}^{-4}$. Clearly, the first result is an outlier, which is rejected on the basis of a simple Q-test. The remaining three have been averaged, entered into Table 2, and used to find the enthalpy of dissociation by the method outlined above. The drop from 68.62 (Table 1) to 63.52 kJ mol^{-1} (Table 2) is a dramatic one. A linear regression on MacDougall's reported equilibrium constants for the three remaining temperatures leads to yet another value for the enthalpy of dimer dissociation, 65.3 kJ mol^{-1}. Since the remaining three data points span only 10 °C, and given the variability of result with this method, perhaps these results should be regarded with some caution. Using the other value of the rotation parameter again leads to rejection of the first data point and to the results in Table 3.

3.5. Comments on Older Studies. *3.5.1. Holland; Nernst and von Wartenberg.* Nernst and von Wartenberg corrected the results reported by Holland. The equation used for fitting vapor density measurements is

$$\log_{10}(K_{21}) = -\frac{\Delta U}{2.303RT} + A\log_{10}(T) + B \qquad (4)$$

Gibbs[15] gives an instructive derivation of this equation from the formulas for the internal energy and entropy of an ideal gas, along with the requirement that d$U = 0$ in an isolated system and d$S = 0$ in an isolated system at equilibrium. It is clear from the derivation that ΔU is the internal energy of dissociation of the dimer at absolute zero. The equation also can be regarded as the indefinite integral of the van't Hoff equation in conjunction with Kirchhoff's Law, in which case $A = \Delta C_\mathrm{P}/R$ and $\Delta C_\mathrm{P} = C_{\mathrm{P},2} - 2C_{\mathrm{P},1}$, where the quantities on the right-hand side are the constant-pressure heat capacities of the n-mers. Nernst et al. obtained their value of the enthalpy of dissociation at absolute zero by setting $A = 1.75$. Moewlyn-Hughes remarks[16] that equations such as eq 4 were "constructed on fragmentary specific heat data, and in a form committed to a numerical value of 1.75 as the coefficient of $\log_{10} T$, according to the early version of Nernst's heat theorem". Rather than revisit this superseded method of finding the enthalpy of dissociation, the data supplied by Nernst and von Wartenberg was fit to eq 1 (see section 3.6 below). Their high ranges of temperatures

TABLE 10: Linear Regressions on Selected Experimental Data[a]

authors	T_{range} (K)	P_{range} (Torr)	ΔH°_{21}	ΔS°_{21}	N	-r
T	324−424	26−55	65.01	156.6	11	0.9998
R & S	325−401	44.5	64.14	153.6	9	0.9984
J & N	355−377	160−199	65.89	158.5	5	0.9953
M	303−313	3−22	65.34	159.7	3	1.0000
H, N, & W	413−485	410−1482	65.89	170.0	7	0.9987
B	292−403	2.6−59.7	67.32	161.9	10	1.0000
N	351−423	66−103	65.98	163.5	7	0.9940

[a] Authors: Taylor; Ritter and Simons; Johnson and Nash; MacDougall; Holland, Nernst, and von Wartenberg; Bineau; and Naumann. Units are SI. *N* is the number of data points, and *r* is the linear regression coefficient.

and pressures ($T = 413-485$ K, $P = 409.8-1482$ Torr) do not lend themselves to the construction of a ring-dimer model.

3.5.2. Gibbs. Gibbs writes a variant of eq 4 as

$$\log_{10}\left[\frac{(4.146 - D)^2}{2.073(D - 2.073)}\right] = -\frac{3520}{T} - \log_{10} P + 11.349 \quad (5)$$

He has dropped the $A \log_{10} T$ term as negligible and factored the pressure out of the equilibrium constant, although nowhere does he use the term “equilibrium constant” or its symbol. The symbol *D* is for acetic acid vapor density, but in his words, “in the sense in which the term is usually employed in chemical treatises, i.e., its density taken relatively to air at the same temperature and pressure”.[17] On this scale, the vapor density of monomer is 2.073, the ratio of the molar mass of monomer to the average molar mass of air.

In the section of his paper on acetic acid, Gibbs reviews eight experimental data sets by nine investigators. In 1879, eq 5 was an innovation in theory, and his goals were to test it as an equation of state for the mixed vapor of monomer and dimer by comparing calculated densities, *D*, to experimental ones and to judge the experiments in light of theory. The two constants on the right-hand side of eq 5 were fixed by using the experimental studies of Cahours (1845) and of Bineau (1846). The number 3520 K has been used to obtain the entry for Gibbs in Table 1.

3.6. Linear Regression of Experimental Data. Linear regressions on selected experimental data were carried out for the purposes of comparison to other determinations of the enthalpy and entropy of dimer dissociation. The results are shown in Table 10. From the data provided in each paper, the lowest-pressure data were chosen to get the best possible approximation to ideal behavior. In all instances, a straight line fit the data well.

Taylor’s entire data set was used; the enthalpy change found is about 2% greater than the one that he reported (Table 1). The Ritter and Simons data is an isobar; the result agrees closely with that of the ring-dimer models (Tables 2 and 3) but is about 5% higher than the value reported by them (Table 1). Most of the Johnson and Nash data was for pressures in excess of 200 Torr; the result is 14% higher than their reported result relative to that value. The MacDougall data spans only 10 °C. The Holland data set whose results were corrected by Nernst and von Wartenberg is all at relatively high pressure. Gibbs gives evidence that the Bineau samples of acetic acid contained water vapor. He also notes that the Naumann pressure data was obtained without aid of a cathetometer, in which case, the resulting errors in measurement will be largest for the lowest pressures, precisely the ones employed here; his comparison of densities calculated from eq 5 and those reported by Naumann show a sharp discrepancy.

4. Other Experimental Studies of the Vapor

In their infrared studies of the vapor, Mathews and Sheets argued that only monomer and dimer were present. In his infrared study, Weltner[18] showed that the vapor’s heat capacity could be accounted for quantitatively by assuming the presence of only monomer and dimer. Frurip et al.[19] in their thermal conductivity measurements on the vapor report that they found no evidence of significant amounts of *n*-mers higher than the dimer. Sievert et al.[20] carried out mass spectral and electric deflection studies of acetic acid clusters and found an upper limit of 3% for preexisting acetic acid trimers, but no evidence of higher clusters. Mori and Kitagawa[21] produced acetic acid dimers and trimers in molecular beams by supersonic expansions, but the vapor in such expansions need not be in an equilibrium state.

5. Summary and Conclusions

1. Acetic acid vapor behaves ideally at low pressures such as 26−55 Torr (Taylor) and 44.5 Torr (Ritter and Simons) as indicated by the agreement of the ring-dimer model, which is a statistical mechanical model for an ideal vapor, and experimental measurements (Figures 1 and 3).

2. Acetic acid vapor at temperatures less than about 370 K and at the low pressures cited is almost exclusively a cis-monomer and a ring dimer. Since the vapor is ideal, the statistical mechanical formula for the equilibrium constant can be solved for the molecular dissociation energy, $D_{2,0}$, and thus for the standard enthalpy of dissociation at absolute zero, $\Delta H^\circ_{21}(0) = N_A D_{2,0}$ (companion paper,[1] eqs 2a−2b).

3. The values of the dissociation energy obtained by this procedure are not sensitive to the choice of rotation parameter, F_2 (Tables 2 and 3). The plausible range of values of the rotation parameter is small (companion paper,[1] Table 4).

4. ΔH°_{21} obtained by linear regression is about 1 kJ mol^{-1} less than $\Delta H^\circ_{21}(0)$ (Tables 2 and 3).

5. The ring-dimer and vapor models do not support the claim that the vapor may contain up to 3−5% trimer or tetramer. They also suggest that the claims are inconsistent or implausible on other grounds (Tables 4−8 and accompanying discussion).

6. The ring-dimer model suggests that there may be a faulty isotherm in MacDougall’s data set of four (Table 9). If so, his data set spans only 10 °C.

7. The five most recent vapor density studies give dimer standard dissociation enthalpies of 58−69 kJ mol^{-1}. If the inferences drawn in Summary points 1−6 are correct, then the discrepancies largely disappear (Tables 2, 3, and 10).

8. The best estimate of ΔH°_{21} from this work is 64.0−65.0 kJ mol^{-1} and of $\Delta H^\circ_{21}(0)$ is 65.0−66.0 kJ mol^{-1}. The best estimate of the standard entropy of dissociation is 154−157 J mol^{-1} K^{-1}.

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References and Notes

(1) Lofgren, S. M.; Mahling, P. R.; Togeas, J. B. *J. Phys. Chem. A* **2005**, *109*, 5430.

(2) MacDougall, F. H. *J. Am. Chem. Soc.* **1936**, *58*, 2585.

(3) Ritter, H. L.; Simons, J. H. *J. Am. Chem. Soc.* **1945**, *67*, 757.

(4) Gibbs, J. W. *Am. J. Sci. Ser. 3* **1879**, *18*. Reprinted in *The Scientific Papers of J. Willard Gibbs*; Longman, Greens: London, New York, 1906; Ox Bow Press Reprint; Vol. 1, Thermodynamics; p 372.

(5) Holland, C. *Z. Elektrochem.* **1912**, *18*, 234. Nernst, W.; von Wartenberg, H. *Z. Elektrochem.* **1916**, *22*, 37.

(6) Chao, J.; Zwolinski, B. J. *J. Phys. Chem. Ref. Data* **1978**, *7*, 363.

(7) Mathews, D. M.; Sheets, R. W. *J. Chem. Soc. A* **1969**, 2203.

(8) Taylor, M. D. *J. Am. Chem. Soc.* **1951**, *73*, 315.

(9) Reported by Weltner, no. 26 of ref 18 below.

(10) Barton, J. R.; Hsu, C. C. *J. Chem. Eng. Data* **1969**, *14*, 184.

(11) See ref 3.

(12) Johnson, E. W.; Nash, L. K. *J. Am. Chem. Soc.* **1950**, *72*, 547.

(13) Coolidge, A. S. *J. Am. Chem. Soc*. **1928**, *50*, 2166.

(14) See ref 2.

(15) See ref 4. Ox Bow edition, 374.

(16) Moelwyn-Hughes, E. A. *Physical Chemistry*, 2nd rev. ed.; Pergamon: Oxford, 1964; page 1000.

(17) See ref 4. Ox Bow edition, 372.

(18) Weltner, W. *J. Am. Chem. Soc.* **1955**, *77*, 3941.

(19) Frurip, D. J.; Curtiss, L. A.; Blander, M. *J. Am. Chem. Soc.* **1980**, *102*, 2610.

(20) Sievert, R.; Cadez, I.; Van Doren, J.; Castleman, A. W., Jr. *J. Phys. Chem.* **1984**, *88*, 4502.

(21) Mori, Y.; Kitagawa, T. *Int. J. Mass Spectrosc. Ion Processes* **1988**, *84*, 305.