

TABLE VI

HEATS OF VAPORIZATION OF  $C_2F_5Cl$   
Mol. wt. 154.477;  $0^\circ C. = 273.16^\circ K.$ ; 1 cal. = 4.1833 int. joules

Vaporized, mole	Mean temp. of vapor, $^\circ K.$	$\Delta H_v$ , $T, ^\circ K.$ , cal. mole $^{-1}$	$\Delta H$ , real gas 234.04 $^\circ K.$ , cal. mole $^{-1}$
0.019965	233.982	4649	4648
.013234	234.032	4643	4643
.021347	234.359	4624	4627
.021094	234.365	4634	4637

Av. 4639  $\pm$  10

Value calcd. from eq. 1 with  $T_c = 353.1^\circ$

$K.$ ,  $P_c = 30.8$  atm. Berthelot corr. =

-212 cal. mole $^{-1}$  (liq. vol. corr. =

-24 cal. mole $^{-1}$ ) 4634

Value calcd. from eq. 1 and Martin data

of state 4663

furnished by Dr. J. J. Martin to be  $79.28 \pm 0.20$  e.u. (The critical temperature is  $353.1^\circ K.$  and the critical pressure is 30.8 atm.) The potential barrier hindering internal rotation which must be assumed to bring the entropy<sup>5</sup> into agreement with a "spectroscopic" entropy calculated from the Raman and infrared<sup>7</sup> is 5300 cal. mole $^{-1}$ . A doubtful Raman line at  $75$  cm. $^{-1}$ , which is possibly due to the

(7) J. Rud Nielson, E. Y. Liany, R. M. Smith and D. C. Smith, *J. Chem. Phys.*, **21**, 383 (1953).

hindered rotation, has been observed by Professor R. C. Taylor.<sup>8</sup> This corresponds to a barrier of 4500 cal. mole $^{-1}$ . The entropy at  $234.04^\circ K.$  calculated on this basis is 79.47 e.u. The entropy at  $298.16^\circ K.$  calculated from the spectroscopic data using the barrier of 4500 cal. mole $^{-1}$  as derived from the Raman line at  $75$  cm. $^{-1}$  is 85.47 e.u. We prefer this value to that calculated on the basis of the empirical barrier of 5300 cal. mole $^{-1}$ , because assuming the assignment of the  $75$  cm. $^{-1}$  to the torsion to be valid, any errors in the calorimetric data are avoided.

**Acknowledgments.**—We wish to thank the Organic Chemicals Department of E. I. du Pont de Nemours and Company for the extremely pure sample of pentafluorochloroethane and for financial aid with the heat capacity determinations. We wish to thank Professor J. J. Martin of the Engineering Research Institute, University of Michigan, for advance information on the Raman spectrum, critical constants and data of state of this compound. The support of the Office of Naval Research in part of the work is gratefully acknowledged. Dr. J. J. Fritz and Mr. Herbert Segall are responsible for checking the calculations of certain of the heat capacities and helping with many of the others.

(8) Professor R. C. Taylor, Department of Chemistry, University of Michigan, private communication.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY]

## The Vibrational Spectrum, Associative and Thermodynamic Properties of Acetic Acid Vapor

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The infrared spectrum of acetic acid vapor ( $CH_3COOH$  and  $CH_3COOD$ ) has been measured down to  $300$  cm. $^{-1}$  at  $25$  and  $175^\circ$ , and vibrational assignments are made for both the monomer and hydrogen-bonded dimer molecules. Two bands appearing at low frequencies at the higher temperature are attributed to the O-H out-of-plane bending in the *cis* and *trans* forms of the monomer. The heat capacity of the vapor has been measured between  $95$  and  $270^\circ$  and at pressures of approximately  $1/3$ ,  $2/3$  and  $1$  atm. The major contribution to the heat capacity at the lower temperatures in this region is that due to absorption of heat for the dissociation of dimer molecules. It is found, contrary to most other work, that only monomer and dimer molecules (no higher polymers) are present, and the derived dissociation constants are approximately in agreement with those determined by Taylor from low pressure vapor density measurements. At  $100^\circ$  the heat content and entropy change in the dissociation of one mole of dimer are  $15.05$  cal./mole and  $36.3$  cal./mole deg., respectively. The potential barrier hindering internal rotation of the  $CH_3$  group is found to be  $2500 \pm 700$  cal./mole. The thermodynamic properties of the two molecular species are tabulated, but only an inconclusive comparison of the experimental and calculated entropies at  $25^\circ$  can be made, because accurate values of the heat of vaporization at that temperature and of the energy difference between *cis* and *trans* isomers in the monomer are lacking.

The unusual hydrogen-bonded dimer which acetic acid forms has made it the subject of numerous investigations. Several of these investigations have been concerned with the measurement of vapor densities<sup>2-4</sup> and the derivation of the stability of the dimer, and perhaps higher polymers, in the vapor phase. To these may be added measurements of the infrared spectra of the associated and unassociated molecules,<sup>5</sup> low temperature heat capacity measurements,<sup>6</sup> and determina-

tion of the molecular structures by electron diffraction.<sup>7</sup> The resulting data are usually sufficient to establish the vibrational assignment and thermodynamic properties of a molecule. In this case, however, because of the complexity of the vapor state, and also the question of residual entropy, the problem has not been satisfactorily solved.<sup>8</sup>

In this paper there is reported the vapor heat capacity of acetic acid over a range of temperature and pressure. It is found that this physical property is very sensitive to the concentrations of the molecular species present in the vapor and to the equilibria existing between them. In fact, one is able to eliminate those results obtained from vapor density measurements which propose the presence of

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(2) (a) F. M. MacDougall, *THIS JOURNAL*, **58**, 2585 (1936); (b) H. L. Ritter and J. H. Simons, *ibid.*, **67**, 757 (1945).

(3) E. W. Johnson and L. K. Nash, *ibid.*, **72**, 547 (1950).

(4) M. D. Taylor, *ibid.*, **73**, 315 (1951).

(5) R. C. Herman and R. Hofstadter, *J. Chem. Phys.*, **6**, 534 (1938).

(6) G. S. Parks, K. K. Kelley and H. M. Huffman, *THIS JOURNAL*, **51**, 1969 (1929).

(7) J. Karle and L. O. Brockway, *ibid.*, **66**, 574 (1944).

(8) See, however, J. O. Halford, *J. Chem. Phys.*, **9**, 859 (1941); **10**, 582 (1942).

trimers or tetramers in the vapor in addition to the monomer and dimer. These findings, in conjunction with infrared measurements down to 300  $\text{cm}^{-1}$ , have made it possible to evaluate the individual properties of the monomer and hydrogen-bonded dimer and to determine more accurately the equilibrium constant of the association.

### Experimental

**Materials.**—C.P. benzene was distilled from freshly cut sodium through an all-glass column.<sup>9</sup> Only the middle cut was used.

The  $\text{CH}_3\text{COOH}$  was supplied by Dr. Winslow Caughey and had been purified by him in the following manner. Reagent grade acetic acid was refluxed for several hours under prepurified nitrogen and then distilled through a three-foot glass-bead packed column. The first and last quarters of the distillate were discarded. By use of the Karl Fischer method the resulting acetic acid was found to contain less than 0.1% water.

The  $\text{CH}_3\text{COOD}$  was prepared from acetic anhydride and  $\text{D}_2\text{O}$ . The C.P. acetic anhydride (98.4%) used was further purified by recovery of the middle portion in a simple distillation under vacuum. An excess was added to about 12 g. of  $\text{D}_2\text{O}$  (under dry nitrogen), refluxed for six hours and distilled. The 50-ml. portion taken off boiled from 115 to 121°. This was then distilled through an all-glass column<sup>9</sup> and the melting points of the first two cuts determined. The first cut, melting between 15.6 and 15.9°, was used in the infrared measurements. Moisture was excluded during all of the preparative operations.

**Gaseous Flow Calorimeter.**—The calorimeter and glass vaporizer were constructed along the lines of previous designs.<sup>10</sup> Actually, two calorimeters were constructed; one contained Kovar-glass seals which were replaced by tungsten-glass seals in the later model since acetic acid attacked the Kovar. The performance of the calorimeter used in the acetic acid determinations was checked by making two runs on benzene at 113.6 and 207.8° under 1 atm. pressure. The heat capacities of benzene were found to be 26.65 and 32.35 cal./mole/deg., which agree satisfactorily with the most recent values of the group at the Bureau of Mines which are 26.62 and 32.43 at these temperatures.<sup>11</sup>

The heat of vaporization of benzene under 1 atm. pressure was found to be  $7339 \pm 5$  cal./mole from seven meas-

urements. This agrees well with the most recent value of 7340 cal./mole determined at the Bureau of Mines.<sup>11</sup>

The 13 ohm nichrome heating coil used for the vaporization of acetic acid was enclosed in a coiled length of 6 mm. Pyrex glass tubing with tungsten seals at each end. The space between the wire and the glass was filled with magnesium oxide powder to aid in conduction of heat. The glass tubing was then wrapped with glass cord to promote boiling. The tungsten leads to this heater were also glass covered to several inches above the boiling liquid surface.

**Vapor Heat Capacity of  $\text{CH}_3\text{COOH}$ .**—The heat capacity of acetic acid was measured over a temperature range of 95 to 270° at pressures of 249, 507 and 760 mm. To prevent possible contamination of the acetic acid, a fresh sample was placed in the vaporizer for each point measured. The values obtained are given in Table I. The estimated uncertainty in these values is  $\pm 0.5\%$ . This is higher than usually associated with such measurements, but the deviations from a straight line when the apparent heat capacity was plotted *versus* the inverse rate of flow were also larger than usual due to variations in the rate of boiling. A plot of these values of the heat capacity at all but the highest and lowest temperatures is shown in Fig. 1.

TABLE I  
HEAT CAPACITY (CAL./MOLE DEG.) OF ACETIC ACID VAPOR

T, °K.	Pressure (mm.)		
	249	507	760
368.4	71.8		
396.4		78.3	
397.5			72.2
399.1		79.5	
399.2	87.3		
419.0	77.4		
420.1		81.7	
421.8			79.4
435.8	62.5		
436.0		73.5	
443.7			72.7
470.4		48.1	
470.9			54.9
479.7	33.7		
509.2	28.1		
540.0	25.7		

Heats of vaporization were measured at the temperatures prevailing during the vaporization at the three pressures used. The mean values are given in Table II, along with maximum deviations from these values. Four measurements of the heat of vaporization were made at 249 mm., eight at 507 mm. and sixteen at 760 mm.

TABLE II  
HEATS OF VAPORIZATION (CAL./MOLE) OF ACETIC ACID

T, °C.	P (mm.)	This research	Max. dev.	Ramsay and Young <sup>12</sup>	I.C.T.
85.4	249	5629	8	5597	5680?
105.8	507	5654	10	5648	5760?
118.5	760	5663	11	5656	5810 $\pm 3\%$
140	1414			5622	5670

**Infrared Absorption Measurements.**—The procedure was essentially that described by Herman and Hofstadter<sup>5</sup> except that a model 112 (converted from Model 12B) Perkin-Elmer single-beam, double-pass spectrometer was used. Measurements were made using both a sodium chloride and a cesium bromide prism with a vapor cell of length 7.3 cm. The cell was contained in an oven equipped with the appropriate window material and the temperature of the vapor ranged from 25 to 175°. Clear glyptal worked satisfactorily for sealing the windows to the cell if baked long enough prior to evacuation and filling. The liquid sample was condensed in a side arm (protruding from the oven) and the cell sealed off under vacuum. In order to decrease the intensity of the water and carbon dioxide bands in the so-

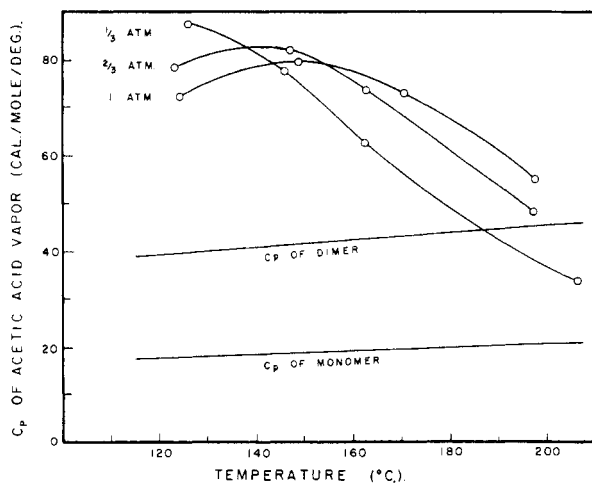


Fig. 1.—Experimental heat capacity of acetic acid vapor at  $1/3$ ,  $2/3$  and 1 atm. pressure. Calculated heat capacities of the monomer and hydrogen-bonded dimer in the ideal gas state are also shown for comparison.

(9) F. Todd, *Ind. Eng. Chem., Anal. Ed.*, **17**, 175 (1945).

(10) G. Waddington, S. S. Todd and H. M. Huffman, *THIS JOURNAL*, **69**, 22 (1947); W. Weltner, Jr. and K. S. Pitzer, *ibid.*, **73**, 2026 (1951).

(11) Private communication of G. Waddington. See an earlier paper by D. W. Scott, G. Waddington, J. C. Smith and H. M. Huffman, *J. Chem. Phys.*, **15**, 565 (1947).

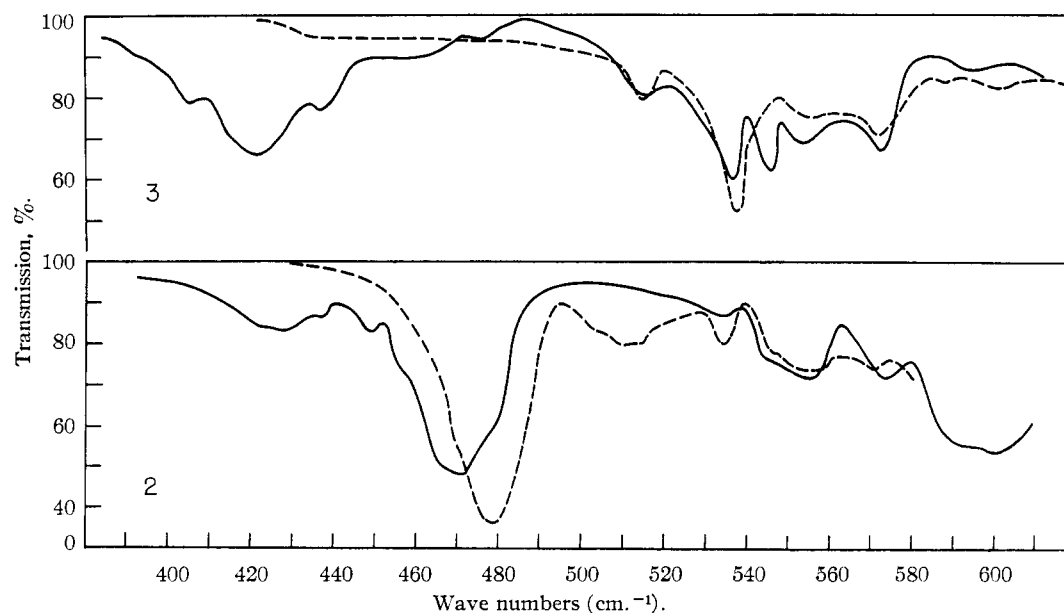


Fig. 2.—(Bottom curve) infrared spectra of acetic acid vapor at 25° and 16 mm. Hg pressure. Solid line indicates spectrum of  $\text{CH}_3\text{COOD}$ , dashed line that of  $\text{CH}_3\text{COOH}$ .

Fig. 3.—(Top curve) infrared spectra of acetic acid vapor at approximately 175° and 18 mm. pressure. Solid line indicates spectrum of  $\text{CH}_3\text{COOD}$ , dashed line that of  $\text{CH}_3\text{COOH}$ .

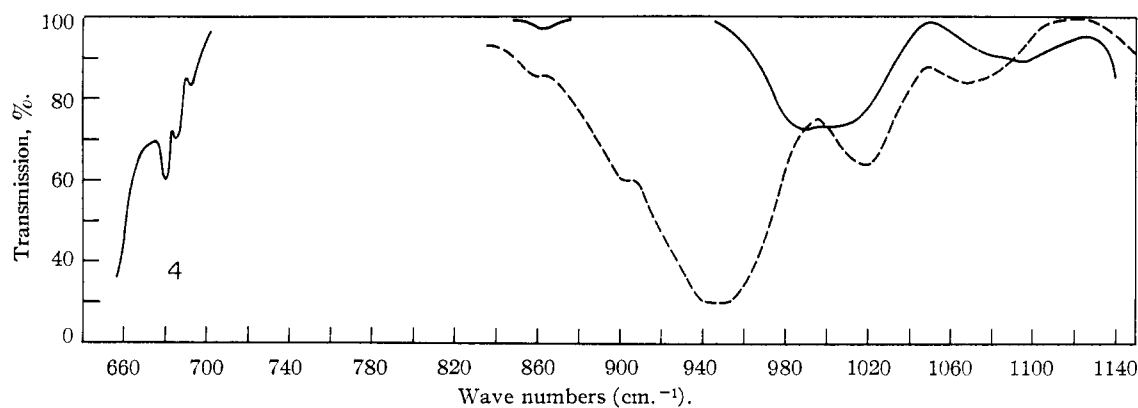


Fig. 4.—Infrared spectra of  $\text{CH}_3\text{COOH}$  vapor. Monomer spectrum indicated by solid line, dimer by dashed line.

dium chloride region, air was passed through silica gel and ascarite and then through the instrument.

The region from 600 to 650  $\text{cm}^{-1}$  was not adequately covered in several of these measurements because of an

TABLE III  
INFRARED BANDS BETWEEN 280 AND 620  $\text{CM}^{-1}$

$\text{CH}_3\text{COOH}$		$\text{CH}_3\text{COOD}$	
High temp.	Low temp.	High temp.	Low temp.
		405 w	
		421 m	426 w
		437 w	
	478 s		449 w
	509 w		471 s
513 w	513 w	514 w	
536 m	534 w	535 m	534 vw
	546 w	546 m	546 w
556 w	556 w	556 w	556 w
572 w	572 w	572 w	574 w
	?	593 vw	597 m
601 vw			

unforeseen difficulty in the use of the instrument. Also, a KBr prism was not available for this work.

The resulting spectra in the CsBr region are shown in Figs. 2 and 3 and the bands appearing there are listed in Table III. The high temperature spectra were determined with the vapor heated to 175° and pressure of about 18 mm. The dimer spectra, containing a small amount of monomer, were determined at a vapor temperature of 25°, vapor pressure = 16 mm. As is usual, the letters, s, m, w, vw stand for strong, medium, weak and very weak intensity bands.

The spectra of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COOD}$  at 25 and 175° were re-examined<sup>5</sup> in the sodium chloride region in order to scrutinize more closely several of the important bands of the dimer and monomer molecules. The region from 1140 to 640  $\text{cm}^{-1}$  (9 to 12  $\mu$ ) is shown in Fig. 4 for  $\text{CH}_3\text{COOH}$  at both temperatures. This was the only portion of the 3 to 15  $\mu$  region in which significant additions were made to the spectra already existing in the literature. Table IV contains a list of the bands found in this region.

#### Heat of Vaporization

The variation of the heat of vaporization, as given in Table II, can be seen to be abnormally small over the temperature range of measurement.

TABLE IV  
INFRARED BANDS BETWEEN 640 AND 1140 CM.<sup>-1</sup>

CH <sub>3</sub> COOH		CH <sub>3</sub> COOD	
High temp.	Low temp.	High temp.	Low temp.
~650 s			
680 m		680 w	
		706 w ?	701 m
			857 w
866 w			
	900 m <sup>a</sup>		893 w <sup>b</sup>
			917 m
			938
	944 s	950 m	
		971 m	
		977	
996 m	1014 m	1010 w	1010 m
1082 w	1066 w	1050 w	1070 m

<sup>a</sup> Shoulder on strong 944 cm.<sup>-1</sup> band. <sup>b</sup> Slight shoulder on medium 930 cm.<sup>-1</sup> band.

This is explained by the fact that the heat of vaporization reaches a flat maximum in the region of the normal boiling point as indicated by the values given in columns 5 and 6 which were taken from the work of Ramsay and Young<sup>12</sup> and the International Critical Tables.<sup>13</sup> The values given by Ramsay and Young were corrected to the presently accurate physical constants.<sup>14</sup> The values measured here are in good agreement with Ramsay and Young at the two higher temperatures but not at 85.4°. These authors did not measure the heat of vaporization but derived it from the exact Clapeyron equation by use of their measured vapor pressures, vapor densities and liquid densities. The sensitivity of the heat of vaporization to slight errors in the measured vapor pressures is well known, so that any discrepancy here is probably attributable to that cause.

### Vibrational Assignments

The infrared spectrum of acetic acid vapor has been measured by Herman and Hofstadter<sup>5</sup> and Giguere and Olmos<sup>15</sup> in the sodium chloride region, and that of the liquid by Hadzi and Sheppard.<sup>16</sup> Herman and Hofstadter have also determined the spectra of CD<sub>3</sub>COOH and CD<sub>3</sub>COOD.<sup>17</sup> The Raman spectrum has been measured by a large number of workers,<sup>18</sup> and the Raman of CH<sub>3</sub>COOD and CD<sub>3</sub>COOD has been determined by Angus, Leckie and Wilson.<sup>19</sup> These measurements, together with those reported here for the region of the spectrum below 600 cm.<sup>-1</sup>, allow a rather definite assignment to be made for both the

(12) W. Ramsay and S. Young, *J. Chem. Soc.*, **49**, 790 (1886).

(13) "International Critical Tables." Vol. V, McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p. 138.

(14) F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling, and G. W. Vinal, *THIS JOURNAL*, **74**, 2699 (1952).

(15) P. A. Giguere and A. W. Olmos, *Can. J. Chem.*, **30**, 821 (1952).

(16) D. Hadzi and N. Sheppard, *Proc. Roy. Soc. (London)*, **A216**, 247 (1953).

(17) R. C. Herman and R. Hofstadter, *J. Chem. Phys.*, **7**, 460 (1950).

(18) See P. Koteswaram, *Z. Physik*, **110**, 118 (1938), for a bibliography of most of the workers. Others are: J. T. Edsall, *J. Chem. Phys.*, **4**, 1 (1936); K. W. F. Kohlrausch, F. Köppl and A. Pongratz, *Z. physik. Chem.*, **B21**, 242 (1933); R. M. Bell and M. A. Jeppesen, *J. Chem. Phys.*, **2**, 711 (1934); J. T. Edsall and E. B. Wilson, Jr., *ibid.*, **6**, 124 (1938).

(19) W. R. Angus, A. H. Leckie and C. Wilson, *Proc. Roy. Soc. (London)*, **A155**, 183 (1936).

monomer and dimer molecules. There are some doubtful frequencies, but for thermodynamic purposes the assignments should be quite satisfactory.

**Acetic Acid Monomer.**—The molecule has, at most, only a plane of symmetry and therefore only two symmetry species, A' and A". Since the Raman spectra are of the liquid they are not of much aid in choosing the vibrational modes due to the monomer except where bands might be expected to undergo only a small change when the dimer is formed. The assignment, not including the CH<sub>3</sub> torsional frequency of A" symmetry type, is given in Table V. The deuterated derivatives are also included in the table to aid in checking the assignment. The Teller-Redlich product rule is of no real help here, however, because so many of the low frequencies are not accurately known. All of the Raman lines are taken from the work of Angus, *et al.*,<sup>19</sup> since they also made measurements on the deuterated acids. An "R" following a band indicates that it was taken from the Raman spectrum.

TABLE V

VIBRATIONAL ASSIGNMENT OF		ACETIC ACID MONOMER			
Sym.	Motion	CH <sub>3</sub> -COOH	CH <sub>3</sub> -COOD	CD <sub>3</sub> -COOH	CD <sub>3</sub> -COOD
	C-C-O bending	564	564	?	?
	CH <sub>3</sub> rocking	1184	1184	820	812
	C-C stretching	996	974	926	925
	CH <sub>3</sub> sym. bending	1381	1383	1065	1060
	CH <sub>3</sub> unsym. bending	1403	1403	1065	1060
A'	C=O stretch	1770	1770	1766	1760
	C-O stretch	{1184 1284	1284	{1335 1217	1280
	CH <sub>3</sub> sym. stretching	2935 R	2940 R	(2111)	2111 R
	CH <sub>3</sub> unsym. stretching	3027 R	3021 R	2225	2237 R
	O-C-O bending	680	680	(645)	645
	O-H bending	{1184 1284	950	{1335 1217	1000
	O-H stretch	3546	2653	3640	2660
	CH <sub>3</sub> unsym. bending	1431 R	1434 R	1060	1060
	CH <sub>3</sub> rocking	1082	1050	790	785
A"	CH <sub>3</sub> unsym. stretch	2983 R	2986 R	(2183)	2183 R
	O-H bending <i>trans</i>	538	421	?	?
	<i>cis</i>	650	546	?	?
	C-O bending	536	535	?	?

The only motions requiring explanation are the C-O stretching and bending vibrations, the C-C-O bending, the two O-H bending modes, and perhaps the rocking motion at 1184 cm.<sup>-1</sup>. In spite of the peculiar behavior in the region of the 1184 and 1284 cm.<sup>-1</sup> bands when the spectra of CH<sub>3</sub>COOH and CH<sub>3</sub>COOD are compared, an examination of CD<sub>3</sub>COOD and CH<sub>3</sub>COOD must lead to the conclusion that  $\nu(\text{C-O}) \cong 1280 \text{ cm.}^{-1}$ . An accidental degeneracy is evident in CD<sub>3</sub>COOH at this frequency due to the interaction of the O-H inplane bending and the C-O stretching modes, and this same interaction would be expected in CH<sub>3</sub>COOH. However, the behavior in progressing from CH<sub>3</sub>COOD to CH<sub>3</sub>COOH in this region is not clear and may possibly be due to the presence of *cis* and *trans* forms of the acid which would be expected to have different O-H in-plane bending frequencies. The 1184 cm.<sup>-1</sup> band in CH<sub>3</sub>COOD must be attributed to a CH<sub>3</sub> rocking motion since the O-D motions are now at lower frequencies.

The past work on acetaldehyde<sup>20</sup> and nitrous

(20) K. S. Pitzer and W. Weltner, Jr., *THIS JOURNAL*, **71**, 2842 (1949).

TABLE VI  
 VIBRATIONAL ASSIGNMENT OF THE ACETIC ACID DIMER

Sym.	Motion	CH <sub>3</sub> COOH		CH <sub>3</sub> COOD		CD <sub>3</sub> COOD		CD <sub>3</sub> COOH
		I.R.	Raman	I.R.	Raman	I.R.	Raman	I.R.
A'	C—C—O bending	478	454	471	434		411	
	CH <sub>3</sub> rocking	1066	1112 ?	1070	1094	827		820 <sup>a</sup>
	C—C stretching	(928)	898	928	856	926	800	(926) <sup>b</sup>
	CH <sub>3</sub> sym. bend	1371	1359		1321	1046	1025	1053 <sup>c</sup>
	CH <sub>3</sub> unsym. bend		1431		1434	1075	1093	1075 <sup>c</sup>
	C=O stretch	1739	1683	1725	1655	1740	1657	1730
	C—O stretch	{ 1424 1294	1255	1340		1360	1330 ?	{ 1408 1285
	CH <sub>3</sub> sym. str.	3030	2935	3030	2940	2326	2111	2326
	CH <sub>3</sub> unsym. str.		3027		3021		2237	
	O—C—O bend		623	601	598	645	580	
	O—H bend (i.p.)	{ 1424 1294	1255	1070		1046	1025 ?	{ 1408 1285
	O—H stretch	2990	3193 ?	2260		2299	2275	3106
	CH <sub>3</sub> unsym. bend		1431		1434	1075	1093	1075 <sup>c</sup>
A''	CH <sub>3</sub> rocking	1014	1016	1010	1014	782	713 ?	802
	CH <sub>3</sub> unsym. str.		2983		2986	2326	2183	2326
	O—H bending	944		701		690 <sup>d</sup>	580	939
	C—O bending	509 ?		450 ?				

<sup>a</sup> Weak band taken from Herman and Hofstadter's spectrum.<sup>17</sup> <sup>b</sup> 939 (v.s.) hides the true value. <sup>c</sup> These bands do not appear in trichloroacetic acid spectrum,<sup>16</sup> therefore attributed to CD<sub>3</sub>. <sup>d</sup> A shoulder on Herman and Hofstadter's curve.<sup>17</sup>

acid<sup>21</sup> was of aid in making the remainder of the assignment. The 650 cm.<sup>-1</sup> band is only approximate since, as mentioned above, this region of the spectrum was not properly covered. However, the high frequency side of what looks like a strong band may be seen at 660 cm.<sup>-1</sup> in Fig. 4. Further work in this region, using a potassium bromide prism, should establish its exact position and intensity. Assuming its existence established, then the O—H out-of-plane bending motions are quite clearly analogous to those in the *cis* and *trans* forms of HONO and correspondingly directed O—H groups in the plane of the carboxyl group seems quite certain. The anharmonicity of this vibration is large as may be seen when the O—D and O—H frequencies are compared. The isolated O—D bending at 421 cm.<sup>-1</sup> is interesting since its envelope shows clearly the P, Q and R branches of a type C band. The further identification of these bendings as belonging specifically to *cis* or to *trans* cannot be made, but it seems likely that the *cis* form has the higher frequency.

The so-called "C—O bending" mode is considered the most doubtful frequency.<sup>22</sup> In acetone this vibration occurs at 390 cm.<sup>-1</sup> but in acetic acid it must be assumed to lie much higher since no bands were found in the infrared between 300 and 513 cm.<sup>-1</sup>. 536 cm.<sup>-1</sup> was chosen as the Q branch of this band, which is also not affected by deuteration. The C—C—O bend is also expected to occur near 550 cm.<sup>-1</sup>.<sup>20</sup> The CH<sub>3</sub> torsion is treated below as a hindered internal rotation with a three-fold potential barrier.

**Acetic Acid Dimer.**—The dimer is of C<sub>2h</sub> symmetry and has 42 vibrational modes. If the two monomers making up the dimer were tightly coupled then each fundamental of the monomer

would be split such that each mode of original symmetry A' or A'' would yield two bands of different symmetry: A' → A<sub>g</sub> and B<sub>u</sub>, A'' → A<sub>u</sub> and B<sub>g</sub>. The A<sub>g</sub> and B<sub>g</sub> vibrations are Raman active, and the A<sub>u</sub> and B<sub>u</sub> are infrared active. Besides these, there are six extra modes due to "intermolecular" vibrations which are of low frequency and have not been observed or, if observed, have not been identified as such. Of these six, two are A<sub>g</sub>, two are A<sub>u</sub>, one is B<sub>g</sub> and one is B<sub>u</sub>.

One finds, upon comparing the infrared and Raman spectra of the dimer, that there is essentially no splitting so that only a weak coupling is occurring, as might be expected in a hydrogen-bonded ring. Of course, the O—H vibrations are considerably changed from those in the monomer. The vibrational assignment, excluding the two CH<sub>3</sub> torsions and the six low frequency intermolecular modes, is given in Table VI where the A', A'' symmetry notation is retained.

It is believed that the two strong bands in (CH<sub>3</sub>COOH)<sub>2</sub> in the neighborhood of 1300 cm.<sup>-1</sup> are again due to the Fermi resonance of the O—H in-plane bending and the C—O stretching vibrations. The unperturbed C—O mode occurs at about 1340 cm.<sup>-1</sup> as may be seen most clearly by examination of the spectra of (CD<sub>3</sub>COOD)<sub>2</sub><sup>17</sup> and liquid trichloroacetic acid.<sup>16</sup> The strong band at about 1430 cm.<sup>-1</sup> in (CH<sub>3</sub>COOD)<sub>2</sub> is partially attributable to CH<sub>3</sub> bending motions, but since these are not expected to be very strong, the intensity of the band is puzzling. It could be due to the presence of the O—H acid, but there is no other evidence for the existence of this impurity. The C—C stretch occurs at 928 in (CH<sub>3</sub>COOD)<sub>2</sub> but is strongly overlaid by the O—H out-of-plane bending at 944 cm.<sup>-1</sup> in the completely protonated compound. The C—O bending is again a doubtful frequency and no support can be given to the questionable values assigned except that they lie

(21) L. H. Jones, R. M. Badger and G. E. Moore, *J. Chem. Phys.*, **19**, 1599 (1951).

(22) The writer would like to thank Professor Gordon M. Barrow for an enlightening discussion of this phase of the assignment.

in a reasonable region of the spectrum. The potential barrier hindering internal rotation of each  $\text{CH}_3$  in the dimer is assumed the same as that in the monomer and is determined from the measured heat capacity of the vapor.

Since the six intermolecular frequencies are not known exactly, the approximate values of Slutsky and Bauer<sup>23</sup> have been used in order to calculate the contribution of these modes to the vibrational heat capacity. The frequencies calculated by these two authors are 332, 215, 165, 143, 114 and 35  $\text{cm}^{-1}$ . They will make a total contribution of almost  $6R$  to the heat capacity, and in this range the heat capacity contributions are quite insensitive to small errors in frequency. Later on, it will be shown that these frequencies are not completely compatible with the entropy of the dimer and that a better set of frequencies for thermodynamic purposes would be 276, 178, 165, 119, 95 and 29  $\text{cm}^{-1}$ . However, this change has very little effect upon the calculated heat capacities.

It is interesting to note the effect of dimerization upon the O-H bending frequencies. The in-plane O-H bending mode has risen from about 1230 to 1360  $\text{cm}^{-1}$  while the out-of-plane bending has risen from about 590 to 940  $\text{cm}^{-1}$ . This behavior is qualitatively what one would expect and may be compared with the well known decrease in the O-H stretching frequency when a hydrogen bond is formed.

**Acetic Acid (Hypothetical) Trimer and Tetramer.**—For the purpose of calculating the contribution of these species, if they are present, to the heat capacity of the vapor, it is necessary to know their approximate vibrational assignments. One may assume that the coupling between monomeric units is again weak, as in the dimer, and that each monomer in the polymer contributes its characteristic frequencies unchanged. The additional intermolecular modes (12 in the trimer, 18 in the tetramer) may then be taken to be quite low as in the dimer and thus contributing almost  $12R$  and  $18R$  to the heat capacity per mole of trimer or tetramer. Since the contribution of these higher polymers to the heat capacity is small, these assumptions are justified. The  $\text{CH}_3$  torsional modes are again assumed to have the same hindering potential barrier as in the monomer.

### Molecular Species in the Vapor

Vapor density measurements on acetic acid have been made by a large number of workers but the only ones which will be considered here are the three more recent determinations by Johnson and Nash (J and N),<sup>3,24</sup> Ritter and Simons (R and S)<sup>2</sup> and Taylor (T).<sup>4</sup> In the order given, these authors worked at progressively lower pressures and in approximately the same temperature range. The heat of dissociation of the dimer in these determinations shows a trend in the same direction, being 13.8, 14.5 and 15.3 kcal./mole, respectively.

(23) L. Slutsky and S. H. Bauer, *THIS JOURNAL*, **75**, 270 (1953). The similar earlier work of J. O. Halford, *J. Chem. Phys.*, **14**, 395 (1946) also should be mentioned.

(24) There is also recent work by J. Morcillo and A. Pérez-Masia, *Anal. real soc. españ. fis. y quím.*, **48B**, 631 (1952), which agrees with the results of Johnson and Nash.

Johnson and Nash found it necessary to specify the presence of a trimer in the vapor in addition to a dimer in order to account for their experimental results and Ritter and Simons proposed a tetramer. Taylor's values, at a lower pressure, required only a monomer-dimer equilibrium.

One may calculate the heat capacity of acetic acid considering the composition of the vapor to be determined by the concentrations of the various species determined by the equilibrium constants of each of the three sets of authors. The heat capacity per formula weight of acetic acid vapor (60.052 g.) is given by

$$C_p = n_M C_M + n_D C_D + n_T C_T - \frac{\Delta H_2 (\partial n_M / \partial T)}{2} + \frac{(\Delta H_3 - 3 \Delta H_2 / 2) (\partial n_T / \partial T)}{1} \quad (1)$$

where  $n_M$ ,  $n_D$ ,  $n_T$  and  $C_M$ ,  $C_D$ ,  $C_T$  are the number of moles and heat capacities of monomer, dimer and trimer,  $\Delta H_2$  is the heat of association of monomers to dimers,  $\Delta H_3$  the heat of association of monomers to trimers. If tetramers are the higher polymer assumed present, then  $n_T$  and  $C_T$  in this equation stand for the number of moles and heat capacity of tetramer.  $(\Delta H_3 - 3 \Delta H_2 / 2)$  must then be replaced in the last term by  $(\Delta H_4 - 2 \Delta H_2)$  where  $\Delta H_4$  is the heat of association of monomers to tetramers. A more detailed discussion of the algebra involved in calculating  $C_p$  from eq. 1 is given in an appendix to this paper.

In order to determine  $C_M$ ,  $C_D$  and  $C_T$ , and thereby also  $\Delta H_2$  and  $\Delta S_2$  as functions of the temperature (temperature variation of  $\Delta H_3$ ,  $\Delta S_3$  and  $\Delta H_4$ ,  $\Delta S_4$  was neglected), the vibrational assignments of the previous section were utilized. A mean frequency was used for the O-H bending fundamental which was different for the *cis* and *trans* forms of the monomer. The potential barrier hindering internal rotation of the  $\text{CH}_3$  group remains an unknown, it being assumed the same in all molecules. However, the contribution of this internal rotation to the heat capacity then depends only on the reduced moment of inertia<sup>25</sup> of the  $\text{CH}_3$  group in each of the molecular species. Using Karle and Brockway's<sup>7</sup> structures for the monomer and dimer (with the O-C-O angle taken as  $130^\circ$  in both) the reduced moments are very nearly the same, being  $4.98$  and  $5.13 \times 10^{-40}$  g.  $\text{cm}^2/\text{molecule}$ , respectively. Therefore, if the contribution of this degree of freedom to the heat capacity of the monomer is  $C_i$ , the contribution of two methyl groups in the dimer will be very close to  $2C_i$ . This means that, in calculating the  $\Delta C_p$  of the monomer-dimer association reaction as a function of temperature, the internal rotation contribution to each species need not be known. Also, the  $\text{CH}_3$  internal rotation contribution of all the species to the total heat capacity as given in eq. 1 will be  $n_M C_i + n_D (2C_i) + n_T (3C_i) = C_i$ ; since  $n_M + 2n_D + 3n_T = 1$  if the heat capacity is that for one formula weight of acid. The contribution of the  $\text{CH}_3$  torsion would be expected to lie somewhere between about 1 and 2 cal./mole deg. depending upon the height of the barrier hindering internal rotation. Also, for a given barrier,  $C_i$  will vary by only about 10% over the temperature range of observation, being lower at the higher temperatures.

(25) K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942).

Briefly, then, the procedure is to use eq. 1 with  $C_M$ , etc., calculated from the vibrational assignments given above, excluding internal rotation of the  $\text{CH}_3$  groups.  $\Delta C_p$  for the monomer-dimer association may also be calculated and used to account for the temperature variation of the values of  $\Delta H_2$  and  $\Delta S_2$  given by each of the three authors. The internal rotation may then be obtained by difference as is usually done.

The calculated heat capacity is quite sensitive to the thermodynamic constants of the monomer-dimer reaction, so that, as mentioned above, it was necessary to take account of the temperature dependence of  $\Delta H_2$  and  $\Delta S_2$ . For example, at  $145.8^\circ$  and 0.328 atm. the calculated heat capacity, assuming  $\Delta H_2$  and  $\Delta S_2$  as constant, is 2.2% higher than that calculated allowing variation of these functions with temperature. This example utilized Taylor's<sup>4</sup> equilibrium constant.

The  $C_p$  of the monomer-dimer association over the temperature range of 300 to  $540^\circ\text{K}$ . is found to be (in cal./deg./mole of dimer)

$$\Delta C_p = 2.22 + 0.00328T - 0.185 \times 10^{-5}T^2 \quad (2)$$

Use was made of eq. 2 with the values of  $\Delta H_2$  and  $\Delta S_2$  (at the average temperature over which each set of vapor density measurements was made) and  $K_2$ ,  $K_3$  (or  $K_4$ ) given by each author and  $C_T$  given by

$$C_T (\text{trimer}) = 3(C_M - 7.95) + 7.95 + 12R(0.95)$$

or

$$C_T (\text{tetramer}) = 4(C_M - 7.95) + 7.95 + 18R(0.95)$$

The factor 0.95 in these equations approximately accounts for the fact that the intermolecular frequencies do not contribute  $R$  to the heat capacity.  $C_p$  in eq. 1 may then be calculated excluding  $\text{CH}_3$  torsion contributions. Table VII gives the results at two extremes of experimental conditions. Roman numeral I stands for the terms  $-\Delta H_2(\partial n_M/\partial T)/2$ ; II is either  $(\Delta H_3 - 3\Delta H_2/2)(\partial n_T/\partial T)$  for J and N or  $(\Delta H_4 - 2\Delta H_2)(\partial n_T/\partial T)$  for R and S.

TABLE VII

CONTRIBUTIONS (CAL./MOLE DEG.) TO THE HEAT CAPACITY OF ACETIC ACID (EXCLUDING  $\text{CH}_3$  TORSION) AS CALCULATED FROM THE EQUILIBRIUM CONSTANTS OF THREE SETS OF AUTHORS

Author	$n_{\text{MCM}}$	$n_{\text{DCD}}$	$n_{\text{TCT}}$	I	II	Calc. $C_p$ excl. $\text{CH}_3$ tors.
At $124.3^\circ$ and 1 atm., $C_p$ (obsd.) = 72.2						
J and N	5.07	12.04	1.48	42.70	0.91	62.2
R and S	4.67	12.28	1.69	42.46	-0.53	60.6
T	5.53	12.96	..	52.54	....	71.0
At $266.8^\circ$ and 0.328 atm., $C_p$ (obsd.) = 25.7						
J and N	21.54	0.37	0.00	2.37	0.00	24.3
R and S	21.67	0.23	0.00	1.61	0.00	23.5
T	21.67	0.23	..	1.77	....	23.7

Two things are to be noted from Table VII. The large contribution of term I to the total heat capacity at the lower temperature and, secondly, the large divergence of the observed heat capacities from those calculated using Johnson and Nash's or Ritter and Simon's constants. This divergence is more extensively examined in Table VIII where only Johnson and Nash's constants are

used. The third column of this table gives the mole fraction of monomer present and the last column  $\Delta = C_p(\text{obsd.}) - C_p(\text{calcd.})$ . A corresponding table could also be presented utilizing Ritter and Simon's equilibrium constants and yielding almost the same behavior of  $\Delta$ . Taylor's constants give much better agreement as may be seen from Table IX.  $\Delta$  here goes through a minimum at intermediate values of  $N_M$  but is not greater than about 2 cal./mole deg. over the whole range. Assuming only monomer-dimer equilibrium, one finds that a fit can be made over the complete range of experimental conditions by adjusting  $\Delta H_2$  and  $\Delta S_2$ . Thus if Taylor's values for these quantities are lowered by about 1.5%, the  $\Delta$ 's approach a constant value at all experimental temperatures and pressures (see Table X to be discussed below).

TABLE VIII

HEAT CAPACITY OF ACETIC ACID VAPOR  
(Calculated Using Johnson and Nash's Association Constants)

$t$ ( $^\circ\text{C}$ .)	Pres. (atm.)	$N_M$	Calc. (excl. $\text{CH}_3$ tors.)	Obsd.	$\Delta$
266.8	0.328	0.992	24.3	25.7	1.4
145.8	0.328	.796	71.2	77.4	6.2
162.8	0.667	.786	68.3	73.5	5.2
148.6	1.000	.635	71.9	79.4	7.5
123.2	0.667	.522	68.1	78.3	10.2
124.3	1.000	.460	62.2	72.2	10.0

TABLE IX

HEAT CAPACITY OF ACETIC ACID VAPOR  
(Using Association Constant of Taylor)

$t$ ( $^\circ\text{C}$ .)	Pres. (atm.)	$N_M$	Calc. (excl. $\text{CH}_3$ tors.)	Obsd.	$\Delta$
266.8	0.328	0.995	23.4	25.7	2.3
145.8	0.328	.818	77.7	77.4	-0.3
162.8	0.667	.818	73.4	73.5	0.1
148.6	1.000	.670	79.8	79.4	-0.4
123.2	0.667	.542	77.6	78.3	0.7
124.3	1.000	.483	71.0	72.2	1.2

The important conclusion one reaches from the above calculations is that essential agreement may be obtained with the observed heat capacities over a wide range of conditions if only a monomer-dimer equilibrium is assumed to occur in the vapor. This does not exclude the possibility that a set of equilibrium constants for monomer-dimer plus higher polymer might exist which would also reproduce the measured heat capacities. However, since reasonable agreement<sup>26</sup> with Taylor's thermodynamic constants is obtained and since the low pressure range covered by this author was most likely to yield correct monomer-dimer constants, the evidence points quite strongly toward the exclusion of hydrogen-bonded higher polymers in the vapor over the range of pressure and temperature of this research.

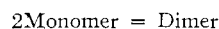
(26) Professor Nash has pointed out that Taylor has neglected any corrections for adsorption in this work. If such a correction is necessary, it is to be noted that Taylor's constants would be shifted in a direction such as to agree more closely with those found in this research.

It should perhaps also be noted that Coolidge<sup>27</sup> had reached these same conclusions for formic acid from vapor density work over the temperature range of 10 to 156° and pressure range of about 3 to 1100 mm.

### The Monomer-Dimer Association Reaction

The variation of  $\Delta H_2$  and  $\Delta S_2$  of the monomer-dimer equilibrium may be carried out until an almost constant difference between the calculated and observed heat capacities is obtained. This difference is then attributed to the  $\text{CH}_3$  torsions, and from it the potential barrier hindering internal rotation of the  $\text{CH}_3$  group, assumed the same in the monomer and dimer, may be calculated. This barrier height will be strongly dependent upon the accuracy of the experimental heat capacities at the highest temperatures since the calculated values at these temperatures are insensitive, as one might expect, to the monomer-dimer reaction constants. This may be seen by reference to the lower part of Table VII where even the very large differences in the constants of the three sets of authors yield  $\Delta$ 's of 1.4, 2.2 and 2.0 cal./mole deg. There is not a very large variation even in this extreme case. Thus, because the potential barrier is not really evaluated from data over a wide range of temperature, it is considered accurate to  $\pm 700$  cal./mole.

A barrier height of 2500 cal./mole and the following values of  $\Delta H_2$ ,  $\Delta S_2$  and  $K_2$  for the reaction



yield heat capacities in agreement with the experimental ones to within the estimated error at almost all points. This is shown in Table X under the columns entitled "perfect gases."

$$\Delta H_2 \text{ (cal./mole)} = -16,075 + 2.22T + 0.00164T^2 - 6.17 \times 10^{-7} T^3 \quad (2a)$$

$$\Delta S_2 \text{ (cal./mole deg.)} = -50.542 + 5.112 \log T + 0.00328T - 9.26 \times 10^{-7} T^2 \quad (2b)$$

$$\log K_2 \text{ (atm.}^{-1}\text{)} = -11.53093 + \frac{3513.10}{T} + 1.11716 \log T + 3.582 \times 10^{-4} T - 6.75 \times 10^{-8} T^2 \quad (2c)$$

These equations give at 100° (mean temperature of Taylor's work):  $\Delta H_2 = -15.050$  kcal./mole and  $\Delta S_2 = -36.30$  cal./mole deg. as compared to  $\Delta H_2 = -15.270$  kcal./mole and  $\Delta S_2 = -36.84$  cal./mole deg. given by Taylor. The uncertainty in the  $\Delta H_2$  of this research is estimated as about  $\pm 0.05$  kcal./mole and in  $\Delta S_2$  as about  $\pm 0.1$  cal./mole deg.

**Gas Imperfection.**—In order to account for this small effect upon the heat capacity, but correspondingly large effect upon the vapor densities, the second virial coefficients of the monomer and dimer have been arbitrarily assumed to be given by the Berthelot equation. The equation of state of the monomer was thus specified by taking the critical temperature and pressure in Berthelot's equation as those for acetic acid ( $T_c = 321.6^\circ$ ,  $P_c = 57.2$  atm.). The dimer was assumed to behave similarly to isobutyl acetate which has the critical constants,  $T_c = 288^\circ$ ,  $P_c = 31$  atm. Then

(27) A. S. Coolidge, *THIS JOURNAL*, **50**, 2166 (1928).

TABLE X

A COMPARISON OF THE CALCULATED AND EXPERIMENTAL HEAT CAPACITY<sup>a</sup> OF ACETIC ACID VAPOR (CAL./MOLE DEG.)

$T$ (°K.)	Pres. (atm.)	Perfect gases		Imperfect gases		
		$C_p$ (calcd.)	$\Delta$	$C_p$ (imp.)	$C_p$ (calcd.)	$\Delta$
368.4	0.328	71.9	-0.1	0.10	72.0	-0.2
396.4	0.667	78.0	.3	.16	78.2	.1
397.5	1.000	71.7	.5	.25	72.0	.2
399.1	0.667	79.3	.2	.16	79.5	.0
399.2	0.328	87.4	-.1	.08	87.5	-.2
419.0	0.328	78.1	-.7	.07	78.2	-.8
420.1	0.667	81.8	-.1	.14	81.9	-.2
421.8	1.000	80.0	-.6	.22	80.2	-.8
435.8	0.328	62.5	.0	.07	62.6	-.1
436.0	0.667	74.0	-.5	.14	74.1	-.6
443.7	1.000	73.4	-.7	.21	73.6	-.9
470.4	0.667	48.1	.0	.12	48.2	-.1
470.9	1.000	54.5	.4	.17	54.7	.2
479.7	0.328	33.6	.1	.05	33.7	.0
509.2	0.328	27.5	.6	.05	27.5	.6
540.0	0.328	25.5	.2	.04	25.6	.1

<sup>a</sup>  $\Delta = C_p(\text{obsd.}) - C_p(\text{calcd.})$ ;  $C_p(\text{obsd.})$  is from Table I,  $C_p(\text{imp.})$  is calculated from eq. 4.

the second virial coefficients for the monomer and dimer, respectively, are given by

$$B_{MM} = 60.0 (1 - 2.12 \times 10^6/T^2) \text{ cc./mole}$$

$$B_{DD} = 104.4 (1 - 1.89 \times 10^6/T^2) \text{ cc./mole}$$

Assuming that the equation of state of the mixture may be written<sup>28</sup>

$$PV = (n_M + n_D)RT + (n_M B_{MM} + n_D B_{DD})P \quad (3)$$

the contribution of gas imperfection to the heat capacity is

$$C_p(\text{imp.}) = n_M(1.85 \times 10^7 P/T^3) + n_D(2.87 \times 10^7 P/T^3) \quad (4)$$

The results of the application of eq. 4 are given in column 5 of Table X. The correction is, as expected, quite small.

The vapor density may be calculated from eq. 3 and compared with that determined from the equations of other authors. For example, at the arbitrary temperature and pressure of 397.5°K. and 1 atm., the equations of Ritter and Simons yield a vapor density of 3.001 g./l., Johnson and Nash's equations give 2.908, and the above relation gives 2.875, where about 3% is due to gas imperfection.

### Thermodynamic Properties of the Monomer and Dimer

From the foregoing vibrational assignments, the molecular structures, and the  $\text{CH}_3$  barrier of 2500 cal./mole, the entropy change in the monomer-dimer equilibrium at 100° can be calculated and compared with the value of  $-36.3$  determined from the heat capacity measurements. Here, however, the unknown proportion of *cis* and *trans* isomers in the monomeric vapor is of importance, which was not the case in the heat capacity calculations. The energy difference between these isomers in formic acid has been approximately determined by

(28) See, for example, R. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Cambridge University Press, New York, N. Y., 1949, p. 297.



Mariner and Bleakney,<sup>29</sup> and Williams.<sup>30</sup> If it may be assumed that the isomers are similar in the two acids, which seems very likely, a value of  $\Delta E = 1500$  cal./mole may be taken as a rough average from their measurements. This energy difference and the Boltzmann equation yield an entropy of mixing of 0.85 cal./mole deg. for each mole of monomer, and  $\Delta S_2$  becomes  $-39.8$  cal./mole deg. at  $100^\circ$ .

The calculated entropy is very sensitive to the values of the low frequencies (whereas the heat capacity is not) and the intermolecular frequencies of the dimer taken from the approximate calculations of Slutsky and Bauer are undoubtedly the cause of the major portion of the 3.5 e.u. discrepancy. (Of course, any error in the assignment of the C-O bending frequency would also be reflected here.) In order to correct this error, some or all of the six frequencies must be lowered a sufficient amount so that the entropy of the dimer is increased by 1.8 e.u. This may be done by adjusting Slutsky and Bauer's force constants, and we have chosen arbitrarily to decrease the two force constants determining the five bending frequencies. It is found that lowering each force constant by 31 per cent. will raise the entropy of the dimer by the prescribed amount. The five intermolecular modes which were formerly at 332, 215, 143, 114 and 35 cm.<sup>-1</sup> now lie at 276, 178, 119, 95 and 29 cm.<sup>-1</sup>, respectively.

The thermodynamic functions (to the harmonic oscillator-rigid rotator approximation) of the monomer and dimer may now be calculated over the temperature range of  $298.16^\circ$  to  $1500^\circ\text{K}.$ ; the results are given in Tables XI and XII. The entropy of mixing of *cis* and *trans* forms in the monomer (assuming that  $\Delta E = 1500$  cal./mole) varies from 0.62 e.u. at  $298.16^\circ\text{K}.$  up to  $R \ln 2$  at about  $1000^\circ\text{K}.$  The heat and free energy of formation are obtained from the heat of combustion of liquid acetic acid,<sup>31</sup> the heat of vaporization at  $25^\circ$  (see the next section entitled "Experimental Entropy") and the corresponding functions for water and carbon dioxide.<sup>32</sup> The thermodynamic functions for hydrogen, graphite and oxygen were also taken from the API tables. The concentrations of monomer and dimer, and  $\Delta H_2$  at  $25^\circ$  were also necessary:  $n_M = 0.0959$ ,  $n_D = 0.4520$ ,  $\Delta H_2 = -15.28$  kcal./mole of dimer. The accuracy of the monomer functions is considered to be better than those of the dimer for the various reasons discussed above.  $\Delta H_0$  of the monomer-dimer reaction calculated by use of these tables is found to vary considerably, probably because of inaccuracies in the dimer functions. The second decimal place throughout the tables is carried only to aid the user to maintain higher accuracy when values at intermediate temperatures are considered. The heat and free energy of formation are uncertain to several tenths of a kcal./mole for the monomer and

probably uncertain to several kcal./mole for the dimer.

TABLE XI

THERMODYNAMIC PROPERTIES OF ACETIC ACID MONOMER  
(Cal./Mole Deg.) and (Kcal./Mole)

$T(^{\circ}\text{K.})$	$C_p$	$S^\circ$	$-\frac{(F^\circ - H_0^\circ)}{T}$	$\frac{(H^\circ - H_0^\circ)}{T}$	$-\Delta H_f^\circ$	$-\Delta F_f^\circ$
0	0	0	0	0	101.20	101.20
298.16	15.90	67.52	56.50	11.02	104.53	75.41
300	15.97	67.63	56.58	11.05	104.55	75.23
400	19.52	72.86	60.29	12.57	105.43	65.10
600	25.15	82.17	66.19	15.98	106.54	44.40
800	29.08	90.23	71.44	18.79	107.26	23.82
1000	31.99	97.08	75.92	21.16	107.61	3.33
1200	34.14	103.11	79.96	23.15	107.72	-16.91
1500	36.46	110.95	85.35	25.59	107.60	-46.74

TABLE XII

THERMODYNAMIC PROPERTIES OF ACETIC ACID DIMER  
(Cal./Mole Deg.) and (Kcal./Mole)

$T(^{\circ}\text{K.})$	$C_p$	$S^\circ$	$-\frac{(F^\circ - H_0^\circ)}{T}$	$\frac{(H^\circ - H_0^\circ)}{T}$	$-\Delta H_f^\circ$	$-\Delta F_f^\circ$
0	0	0	0	0	217.74	217.74
298.16	34.99	96.44	73.91	22.53	224.26	154.51
300	35.13	96.66	74.05	22.61	224.29	154.06
400	42.32	107.76	81.12	26.64	225.60	129.76
600	53.89	127.20	93.33	33.87	227.29	80.71
800	62.45	143.90	103.95	39.95	227.97	31.84
1000	68.06	158.42	113.40	45.02	227.88	-16.45
1200	72.47	171.25	122.01	49.24	227.25	-63.96
1500	77.11	187.97	133.57	54.40	225.73	-133.86

**Experimental Entropy.**—The entropy of liquid acetic acid at  $25^\circ$  has been measured by Parks, Kelley and Huffman<sup>6</sup> as 38.2 cal./mole deg. It seems likely that there is no residual entropy in the solid at  $0^\circ\text{K}.$  since the homolog of acetic acid, formic acid, exists as long chains in the solid<sup>33</sup> at low temperatures and an analogous structure might be expected for the heavier acid. If the value for the liquid is combined<sup>8</sup> with the heat of vaporization and association, the entropy of monomer and dimer vapor at this temperature can be determined. From eq. 2a  $\Delta H_2 = -15.28$  kcal./mole at  $25^\circ$ , but the heat of vaporization at this temperature is not accurately known. The value (corrected) of 5183 cal./mole given by Ramsay and Young<sup>12</sup> yields an entropy of 67.6 cal./mole deg. for the monomer and 98.2 for the dimer. However, if Halford's<sup>8</sup> equation for Ramsay and Young's vapor pressure measurements, which is of more nearly correct theoretical form, is used in conjunction with Ramsay and Young's other data, the heat of vaporization becomes 4820 cal./mole at  $25^\circ$ . Neither value can be considered very reliable. A value of 5000 cal./mole yields values of 66.9 and 96.9 cal./mole deg. for the "experimental" entropies of the monomer and dimer, and this average value has been used in the previous section for the conversion of the heat of combustion of liquid acetic acid to that of vapor at  $25^\circ$ . In view of the uncertainty in this value and in the *cis-trans* energy difference in the monomer, a comparison of the theoretical and experimental entropies does not seem warranted.

(29) T. Mariner and W. Bleakney, *Phys. Rev.*, **72**, 792 (1947).

(30) V. Z. Williams, *J. Chem. Phys.*, **15**, 243 (1947).

(31) "International Critical Tables," Vol. V, McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p. 165. An average value of 208.3 kcal./mole was used here.

(32) "Selected Values of Properties of Hydrocarbons," American Petroleum Institute Project 44, National Bureau of Standards.

(33) F. Holtzberg, B. Post and I. Fankuchen, *Acta Cryst.*, **6**, 127 (1953).

### Conclusion

One must conclude from this research that it is very probable that acetic acid vapor is composed only of a mixture of monomer and hydrogen-bonded dimer molecules at pressures up to one atmosphere and in the temperature range of 90 to 270°. It is reassuring that the constants of the association reaction as determined by Taylor<sup>4</sup> at low pressures, where only the monomer-dimer equilibrium would be important, also come closest to those determined here. It is unnecessary to point out the difficulty of making correct vapor density measurements on a substance such as acetic acid when the large number of varying heats of dimerization in the literature attest so well to this fact. Since this is not the case with vapor heat capacities, one can feel quite confident of the results obtained here.

A careful infrared investigation of the temperature variation of the intensities of *cis* and *trans* bands of the monomer should allow a more definite value of the energy difference between these isomers to be obtained. An accurate determination of the heat of vaporization at 25° is also needed to make possible a more reliable comparison of calculated and experimental entropies.

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### Appendix

If only monomers and dimers are present then

$$n_M^0 + 2n_D^0 = 1 \quad (1)$$

and

$$K_2 = (n_M^0 + n_D^0)n_D^0/(n_M^0)^2P$$

where the superscript 0 indicates that no higher polymers are considered present and  $n_M^0$ ,  $n_D^0$  are the number of moles of monomer and dimer.  $K_2$  is the equilibrium constant for the monomer-dimer

association reaction and  $P$  the pressure. Then

$$n_M^0 = (4K_2P + 1)^{-1/2} \quad (2)$$

and

$$(\partial n_M^0 / \partial T) = -2(n_M^0)K_2P\Delta H_2/RT^2 \quad (3)$$

$$(\partial n_D^0 / \partial T) = -(\partial n_M^0 / \partial T)/2$$

where  $\Delta H_2$  is the change in heat content in the association reaction.

If trimers are also present then three equations result

$$n_M + 2n_D + 3n_T = 1 \quad (4)$$

$$K_2 = (n_M + n_D + n_T)n_D/n_M^2P \quad (5)$$

$$K_3 = (n_M + n_D + n_T)^2n_T/n_M^3P^2 \quad (6)$$

Since  $n_T$  is small, these equations may be solved for  $n_M$  and  $n_T$  by successive approximations. Equation 5 is best written in terms of  $n_M^0$ . Combining eqs. 2, 4 and 5

$$n_M = -n_T(n_M^0)^2 + n_M^0[n_T^2(n_M^0)^2 + (1 - 4n_T + 3n_T^2)]^{1/2} \quad (7)$$

and eq. 6 may be written

$$n_T = 4K_3n_M^3P^2/(1 + n_M - n_T)^2 \quad (8)$$

The starting approximation may be made by neglecting  $n_T$  in the denominator on the right side and letting  $n_M = n_M^0$ .

Having found  $n_M$  and  $n_T$ , then  $n_D$ ,  $(\partial n_M / \partial T)$ , and  $(\partial n_T / \partial T)$  may be found from eq. 4 and the following

$$\begin{aligned} (\partial n_M / \partial T) &= (\partial n_T / \partial T)[-(n_M^0)^2 + (n_M^0)^2(n_T(n_M^0)^2 - \\ &\quad 2 + 3n_T)/(n_M + n_T(n_M^0)^2)] + (\partial n_M^0 / \partial T)[-2n_M^0n_T + \\ &\quad (n_M + n_T(n_M^0)^2)/n_M^0 + n_T^2(n_M^0)^2/(n_M + n_T(n_M^0)^2)] \\ (\partial n_T / \partial T) &= n_T/(N - n_T)[N\Delta H_3/RT^2 + \\ &\quad (\partial n_M / \partial T)(3N/n_M - 1)] \end{aligned}$$

where

$$N = n_M + n_D + n_T$$

If the expression for the total heat content is differentiated and eq. 4 is also used, the heat capacity can be shown to be given by

$$C_p = n_M C_M + n_D C_D + n_T C_T - \Delta H_2(\partial n_M / \partial T)/2 + (\Delta H_3 - 3\Delta H_2/2)(\partial n_T / \partial T)$$

If tetramers are present instead of trimers an analogous set of equations may be derived.

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