rapid polymerization of other ketenes have prevented observation of their spectra. In ketene no Raman lines were found in the general range where olefinic frequencies are expected, but above this were lines at 1895 and 2049 cm.$^{-1}$. The two lines of diketene at 1859 and 1896 cm.$^{-1}$ could therefore very conceivably arise from the substituted ketene linkage. There is no evidence that this is actually the case, as acetylketene would be the only known member of its homologous series. At any rate, the authors feel that the Raman spectrum of diketene does not contradict the acetylketene structure.

The spectrum of diketene agrees well with the observations of Kohlrausch and Skrabal. Those investigators did not observe, however, the two weak lines at 1760 and 1791 cm.$^{-1}$ and reported a weak line at 3213 cm.$^{-1}$ which was not found in the present work. The weak lines at 1760 and 1791 cm.$^{-1}$ are probably not caused by a small amount of an impurity, because the intensity of these lines, relative to the intensity of the stronger lines of diketene, did not vary in different fractions when the product was distilled through a 15-plate column. Lines as weak as these two are of little value for the type of structure determination employed here, and their presence is difficult to explain with any of the proposed structures.

Acknowledgment.—The authors wish to express their thanks to Dr. C. D. Hurd and to Dr. F. O. Rice for supplying samples of ketene dimer and β-butyrolactone, respectively.

Summary

1. Raman spectra are reported for diketene, 2,2,4,4-tetramethyl-1,3-cyclobutanedione, β-butyrolactone, vinyl acetate, and dehydroacetic acid. The spectrum of diketene does not resemble that of any of the compounds whose spectra are available.

2. Of the currently discussed structures for diketene it is possible by its Raman spectrum to exclude all except vinylaceto-β-lactone and acetylketene. No definite choice between these two formulas has been made.

CHICAGO, ILL. RECEIVED DECEMBER 29, 1944

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Molecular State of Acetic Acid Vapor

BY H. L. RITTER AND J. H. SIMONS

The phenomenon of association of carboxylic acids in the vapor phase is a familiar one, and the specific linkage through which the association is effected is usually called the hydrogen bond. It has been assumed that dimerization represents the full tendency toward polymerization of these structures, Hammett having mentioned the failure of such compounds to undergo further association.[1] MacDougall's work on propionic acid vapor,[2] however, shows definite evidence of higher order polymerization. His earlier work on acetic acid[3] shows the same evidence, although it is too slight to permit of precision calculations of the concentration of higher order polymer. The data of Ramsay and Young[4] on the density of acetic acid vapor are too sparse for the same calculations.

The present study represents an attempt to procure data on the vapor density of acetic acid over a sufficiently wide range of temperature and pressure and of sufficient precision to determine whether or not acetic acid vapor contains a polymer of higher order than the second and, if so, to establish the identity of this polymer. The equilibrium constants for the polymerization reactions have been calculated as well as the heats of association.

Purification of Material.—Reagent grade acetic acid was fractionally crystallized in an apparatus, a diagram of which is shown in Fig. 1a. About 100 cc. of material was placed in bulb A. It was frozen, allowed to melt all except the last few crystals, and then 90% refrozen with a swirling motion of the container. The 10% liquid was removed by filtration using a vacuum, and the process repeated eleven times. The melting point rose from 15.05° to a final value of 16.56° (cor.),[5] as shown in Fig. 1b. This corresponds to 0.06 mole per cent. impurities, or 0.02 per cent. if water is the sole contaminant. The transfer to sample vials was made by means of a sealed glass manifold system, and contact with foreign gases or water was avoided.

Vapor Pressure.—MacDougall[3] has corroborated the low temperature values given by the "International Critical Tables"[6] and the normal boiling point is accurately known. As this constitutes corroboration of both ends of the vapor pressure curve in which we are interested, the data in these Tables were accepted as correct.

Liquid Density.—Available data on the liquid density of acetic acid as a function of temperature[4,7] are discordant and appear unreliable. Accordingly, and inasmuch as the available data do not cover the wide range of temperature we

---

[1] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 35.

[2] F. H. MacDougall, THIS JOURNAL, **63**, 3420 (1941).

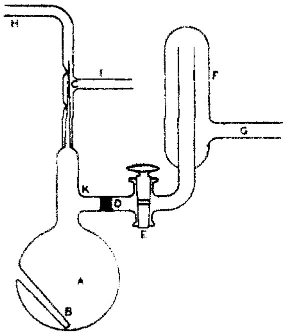
[3] F. H. MacDougall, *ibid.*, **58**, 2585–2591 (1936).

[4] Ramsay and Young, *J. Chem. Soc.*, **49**, 790 (1886).

[5] True melting point assumed to be 16.60°. See W. R. Bousfield and T. M. Lowry, *J. Chem. Soc.*, **99**, 1437 (1911).

[6] "International Critical Tables," Vol. III, p. 217.

[7] D. Tyrer, *J. Chem. Soc.*, **105**, 2534 (1914).



A, Freezing bulb
B, Thermocouple well
C, Capillary tail
D, Glass wool filter
E, Stopcock
F, Trap for impure acid
G, Suction connection
H, Connection to ampules
I, Housing for magnetic breaker
K, To be sealed off

Fig. 1a.—Apparatus for fractional crystallization.

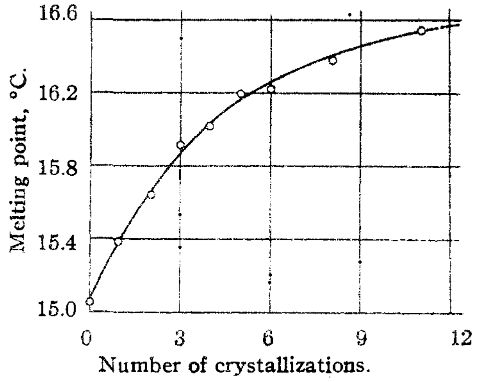


Fig. 1b.—Progress of purification of acetic acid.

require, new data for this function were obtained.

A dilatometer of about 1-cc. capacity was filled with the purified acid by means of an all-glass manifold system and sealed off under vacuum. The instrument was placed in a variable thermostat and liquid heights read off by cathetometer and converted to volumes with the help of the calibration table of the dilatometer, for various temperatures from 25 to 155°. Corrections were made for thermal expansion of the dilatometer, meniscal curvature, and mass of vapor in the dead space. Table I shows the results.

TABLE I

LIQUID DENSITIES OF ACETIC ACID

Density, grams/cc.	Temperature, °C.	Density, grams/cc.	Temperature, °C.
1.0420	26.21	0.9611	97.42
1.0324	34.10	.9506	106.70
1.0246	42.46	.9235	129.86
1.0134	51.68	.9391	117.52
1.0007	63.56	.9119	139.52
0.9875	74.92	.9030	145.60
.9761	85.09	.8889	156.40
.9744	86.31		

The analytical expression of the density–temperature function was determined by least squares, the result being

$$\rho = 1.0718 - 1.162 \times 10^{-3}T + 0.985 \times 10^{-6}T^2 - 5.75 \times 10^{-9}T^3$$

Temperatures were measured by calibrated chromel–alumel thermocouple and a Leeds and Northrup Type K-2 potentiometer; accurate to 0.01°. Volumes were read to 0.001 cc., accurate to 0.0001 cc.; ρ is in grams per cc.

Vapor Density.—The apparatus and technique have been described elsewhere.[8] Two systems were used in parallel to eliminate error due to adsorption on the glass walls of the system. Results are given in Table II and Fig. 2 shows a plot of molecular weight as a function of temperature for the isobars at various pressures. "Molecular weight" for the purpose of this paper is defined by the equation

$$M = dRT/p \qquad (1)$$

where d is the vapor density. This plot also shows a curve of the density of the saturated vapor, indicating the results of several other investigators for the saturated density.

TABLE II

MOLECULAR WEIGHT CALCULATED FROM OBSERVED DENSITY OF ACETIC ACID AT VARIOUS TEMPERATURES AND PRESSURES

p = 44.5 mm. Mol. wt.	Temp., °C.	p = 92.3 mm. Mol. wt.	Temp., °C.	p = 145.0 mm. Mol. wt.	Temp., °C.	p = 208 mm. Mol. wt.	Temp., °C.
105.7	51.9	104.3	63.3	99.9	77.6	96.5	93.4
96.3	66.2	102.7	67.2	96.6	83.7	95.2	96.1
91.7	74.2	94.3	80.0	86.4	102.0	90.6	104.4
84.8	83.9	90.5	87.1	83.4	109.0	87.6	109.8
81.3	92.0	84.2	98.0	78.6	119.3	81.0	120.2
77.8	97.3	78.2	109.1	75.5	122.8	77.2	129.8
73.9	105.3	74.9	115.6	74.1	130.1	72.4	142.7
67.5	123.6	69.7	127.8	70.5	137.9	69.3	155.0
66.6	127.6	68.8	132.9	67.5	148.2	64.8	185.0
64.1	145.5	65.4	151.1	66.1	160.0	63.3	207.0
64.0	151.5	64.3	160.1	64.3	177.9		
63.5	165.0	63.4	185.0	62.8	191.9		
63.2	171.7						
p = 302 mm.		p = 423 mm.		p = 599 mm.		p = 813 mm.	
99.5	96.9	98.7	105.2	99.0	114.3	95.8	129.4
97.5	99.8	96.2	109.6	96.2	120.0	90.3	141.2
94.4	105.4	90.7	119.3	93.3	124.8	84.5	151.5
91.6	108.8	83.0	134.9	91.1	129.1	80.9	159.4
86.1	119.2	75.6	153.2	87.5	135.7	75.9	171.8
83.4	125.1	73.1	157.7	82.6	146.0	73.2	180.0
79.6	140.4	70.2	169.3	78.2	154.9	69.3	194.8
70.9	158.0	68.2	178.3	72.4	174.1	67.2	203.7
64.3	197.8	66.9	189.5	67.5	193.7		
		64.2	201.2	65.4	205.9		

While the data were experimentally obtained in a series of isobars, it is more convenient to discuss them as isotherms. The family of curves of Fig. 2 was accordingly cross-read at convenient temperatures to yield the plot of Fig. 3, showing the variation of molecular weight with pressure for various temperatures. The presence of a polymer is strikingly evident, and the range of molecular weights from 60 (CH_3COOH = 60.06) at low pressure and high temperature to nearly twice this value at low temperature and high pressure makes probable a high concentration of dimer.

Monomer–Dimer Equilibrium.—Assuming that acetic acid vapor consists of a Dalton's law

---

[8] J. H. Simons and H. L. Ritter, *Rev. Sci. Instruments*, **16**, 23 (1945).

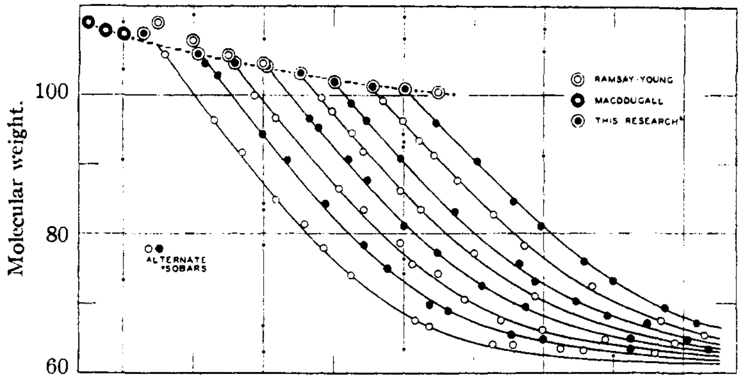


Fig. 2.—Molecular weight of acetic acid vapor as a function of temperature: the isobars are for the pressures, from left to right, listed in order in Table II. The nearly horizontal curve at the top is the saturation line showing the equivalent molecular weights obtained from the work of Ramsay and Young and of MacDougall. In this research, these points were obtained as the intersection of the isobar with the ordinate of the saturation temperature.

mixture of monomer and dimer, the total pressure

$$p = p_1 + p_2 \qquad (2)$$

where p_1 is the partial pressure of $(AcOH)_1$ in the mixture. If monomer and dimer are in equilibrium according to the reaction

$$AcOH \longrightarrow \frac{1}{2}(AcOH)_2$$

the equilibrium constant K_2 may be defined by

$$p_2 = K_2^2 p_1^2$$

Placing this expression in (2), dividing through by p, and writing $X_1 = p_1/p$ for the mole fraction of monomer

$$X_1 + K_2^2 X_1^2 p = 1 \qquad (3)$$

If of one mole of monomer, α moles associate to $\alpha/2$ moles of dimer, then the mixture will contain $1 - (\alpha/2)$ total moles, and the mole fraction of monomer

$$X_1 = 2(1 - \alpha)/(2 - \alpha) \qquad (4)$$

Further, the molecular weight of the mixture, equal to the total mass divided by the number of moles is

$$M = 2M_0/(2 - \alpha) \qquad (5)$$

Elimination of α and X_1 from (3), (4), and (5) gives for K_2

$$K_2^2 = \frac{M_0(M - M_0)}{(2M_0 - M)^2 p} \qquad (6')$$

From the coördinated values of p and M furnished by Fig. 3, K_2 may be calculated. This has been done for temperatures from 80 to 170°. The values were not constant for a given temperature, but were found to vary monotonically with pressure. Figure 4 shows a plot of this calculated equilibrium "constant" as a function of pressure for various temperatures. Whether the cause of the inconstancy is the imperfection of the gas (assumed to be perfect according to our definition of molecular weight) or the presence of a higher polymer, the true values of K_2 should be obtainable by extrapolating the point-sequences of Fig. 4 to zero pressure. Accordingly we rewrite (6′), redefining K_2 by

$$K_2^2 = \lim_{p \to 0} \frac{M_0(M - M_0)}{(2M_0 - M)^2 p} \qquad (6)$$

using Fig. 4 as sufficient evidence of the existence of the limit.

One test of the validity of (6) is the applicability of van't Hoff's law. Figure 5 shows a plot of ln K_2 against $1/T$ for the ten values obtained in this research (tabulated in Table III) and the four values obtained by MacDougall at lower temperatures.[3] The linearity of this plot and the agreement between MacDougall and the present work is satisfactory. The equation of the line (assuming linearity: it was not felt that the slight curvature warranted non-linear treatment considering the precision of the data) was found by least squares to be

$$\ln K_2 = (3645/T) - 11.997$$

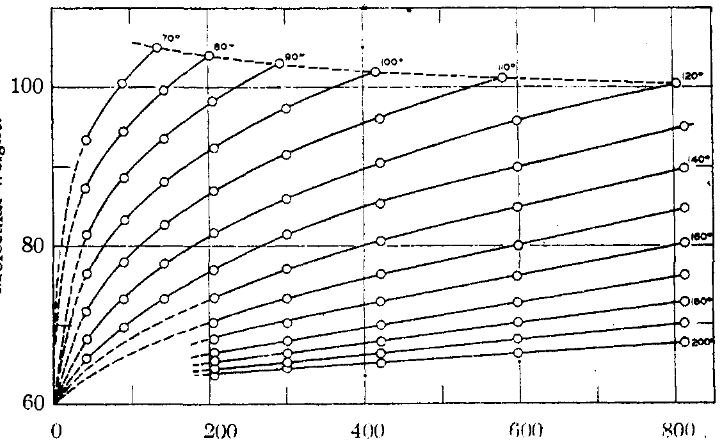


Fig. 3.—Molecular weight of acetic acid vapor as a function of pressure: the dotted portions to the left and the incompleted curves at the bottom represent the missing low pressure data and the unreliable portion of Fig. 2 at the extreme right. The nearly horizontal curve at the top is the saturation curve.

The resulting heat of formation of a single hydrogen bond is $H_2 = -7250$ cal./mole.

The 120° Isotherm.—Curve 1 of Fig. 6 is a reproduction of the 120° isotherm of Fig. 2. The ordinate of this curve is the molecular weight calculated from the perfect gas law (1). To

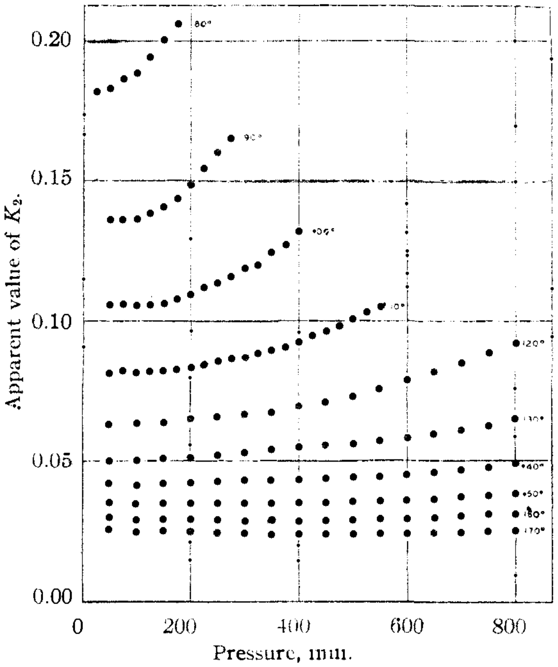


Fig. 4.—Apparent value of K_2 as a function of pressure.

examine how far this curve falls short of the truth, equation (6′) was plotted using the extrapolated value of K_2 at 120°, calculating M as a function of p. This curve is curve 4 of Fig. 6. To test the suggestion that curves 1 and 4 do not agree because of the assumption of the perfect gas law, molecular weights were recalculated from van der Waals equation

$$(pd^2 + aM^2)(M - bd) = d_3RT$$

in which a and b are the usual van der Waals constants and d is the vapor density, using the experimental values of p, d, and T. The values of a and b were assumed by proportionating between those for butyl acetate (mol. wt. 116) and methyl ethyl ether (mol. wt. 60) according to the approximate value of the molecular weight previously calculated. The results for 120° are plotted as curve 2 in Fig. 6. While the proper constants a and b are unknown for acetic acid monomer and dimer, the deviations from imperfection as calculated from the constants for methyl ethyl ether and for butyl acetate are surely of the correct order of magnitude. Moreover, equilibrium constants were calculated for various total pressures using fugacities as calculated from the van der Waals constants. The results duplicate within 1% at 800 mm. the values for the 120° curve of Fig. 4. The extrapolated K_2 is, of course, identical, whence it follows that curve 4 is the same whether the perfect gas assumption is made or not; and that, if the discrepancy between curves 1 and 4 may be explained in part by an improper assumption of the perfect gas law, the discrepancy between curves 2 and 4 remains unexplained.

Table III

Temperature Variation of K_2 and K_4

Temp., °C.	K_2 For pressures in mm.	K_4
80	0.1806	0.0214
90	.1358	.0145
100	.1050	.0110
110	.0812	.0088
120	.0630	.0073
130	.0500	.0063
140	.0415	.0053
150	.0350	
160	.0290	
170	.0248	

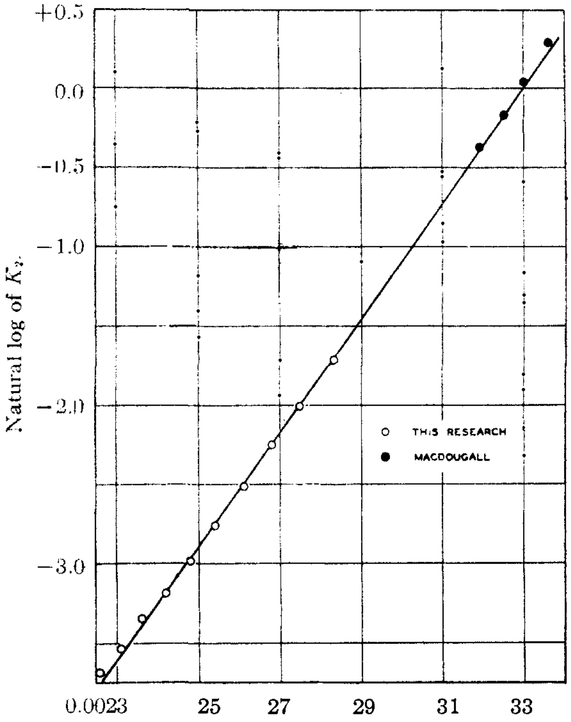


Fig. 5.—Variation of K_2 with temperature.

Monomer–Trimer Equilibrium.—Let K_3 be the equilibrium constant for the reaction

$$\text{AcOH} \longrightarrow {}^1/_3(\text{AcOH})_3$$

Of one mole of monomer, let the equilibrium mixture contain the fraction α_i of monomer converted to i-mer. The mixture will consist of α_1 moles of monomer, $\alpha_2/2$ moles of dimer, and $\alpha_3/3$ moles of trimer. Since the mass of this mixture is M_0, the effective molecular weight is

$$M = \frac{6M_0}{6\alpha_1 + 3\alpha_2 + 2\alpha_3} \tag{7}$$

and the mole fraction of i-mer is

$$X_i = M\alpha_i/iM_0 \quad (i = 1,2,3)$$

Substituting this into the expressions for K_2 and K_3 gives

$$K_2^2 = \frac{X_2}{PX_1^2} = \frac{M_0\alpha_2}{2pM\alpha_1^2} \tag{8}$$

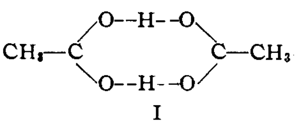
$$K_3^3 = \frac{X_3}{P^2X_1^3} = \frac{M_0^2\alpha_3}{3p^2M^2\alpha_1^3} \tag{9}$$

From equations (7) and (8) and $\Sigma\alpha_1 = 1$, α_2 and α_3 may be eliminated to give

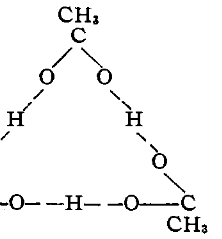
$$\alpha_1 = \frac{M_0}{PMK_2^2}\left[\left\{1 + pK_2^2\left(3 - \frac{M}{M_0}\right)\right\}^{1/2} - 1\right] \tag{10}$$

From the coördinated values of p and M available from Fig. 3 and the extrapolated values of K_2, α_1 may be calculated; and from α_1 using the appropriate equations above, α_2, α_3 and K_3. Values of K_3 have been calculated for the 120° isotherm. Again there is a clear monotonic dependence on pressure, values ranging from 0.0126 to 0.0081. An average value of 0.010 was selected and the whole process of computation reversed, calculating M as a function of p. Curve 3 of Fig. 6 results. There remains a discrepancy between curves 1 and 3, a discrepancy which would have been greater if an extrapolated value had been taken for K_3 rather than average.

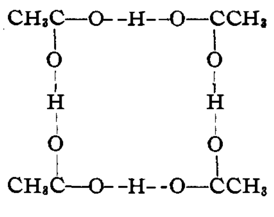
Monomer–Tetramer Equilibrium.—Since the assumption of a trimer does not alone give agreement with experiment, there are two possible means of going one step further. One is to assume that there is also a tetramer present; the other that there is a tetramer in place of the trimer. In some ways, indeed, the formation of a tetramer rather than a trimer is to be expected. One may expect the trimer to have a structure diagrammatically like configuration II, a reasonable extension of the generally accepted "picture" of the dimer, I. Such a structure would be formed on collision of a molecule of monomer and one of dimer by the breakage of one hydrogen bond and the formation of two new ones. Since the bond breakage must take place first and is endothermic, there is a barrier equal to the heat of formation of one hydrogen bond to be overcome in the formation of the trimer (neglecting the possibility of a three-body collision). Similarly, configuration III for the tetramer involves a barrier of twice the energy of a hydrogen bond.



I



II



III

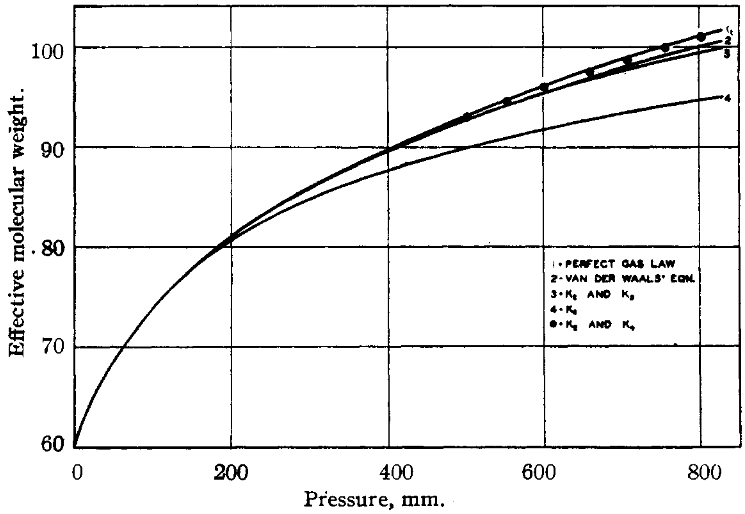
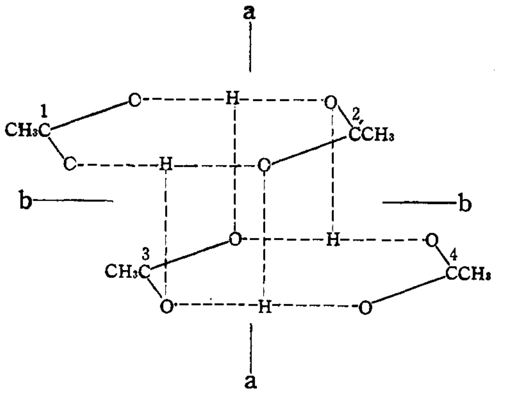


Fig. 6.—Isotherm at 120°.

There is, however, a configuration for the tetramer which does not require the hurdling of a potential barrier. Thus it may be possible for two of the dimeric structures to associate as in IV without the breaking of any exothermic bonds. This configuration, moreover, would seem to possess two resonant forms, in which the dimeric structures may be either 12 and 34 or 13 and 24, the tetramer splitting either horizontally at *bb* or vertically at *aa*.



IV

Tetramer configuration

The facts that the trimer of II requires the breaking of an exothermic bond and the tetramer IV does not and that the tetramer has resonant structures not available to the trimer are reasonable *a priori* arguments in favor of the tetramer. Moreover, since the formation of one-quarter mole of tetramer from one mole of monomer requires the formation of exactly the same number of hydrogen bonds as the formation of one-half mole of dimer, one may expect that the energies of dimerization and tetramerization would be nearly equal, the latter somewhat less (in absolute value) because of the resonance.

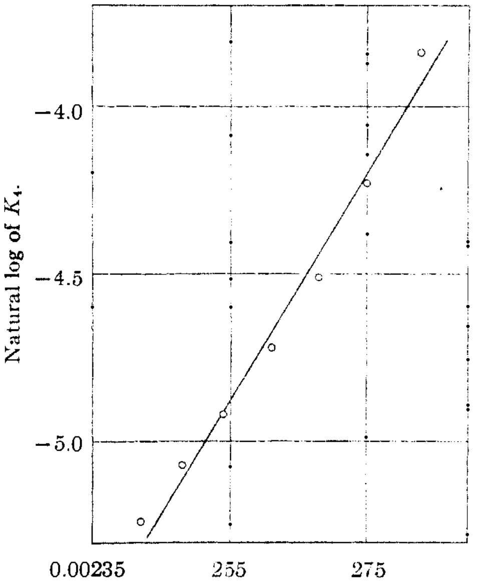


Fig. 7.—Variation of K_4 with temperature.

An analysis similar to that carried out for the monomer–dimer–trimer equilibrium was carried out for the tetramer case. These equations may be derived in the same way as above

$$K_4^4 = \frac{\alpha_4 M_0^3}{4P^2M^3\alpha_1^4} \tag{11}$$

and

$$\alpha_1 = \frac{3M_0}{4MpK_2^2}\left[\left\{1 + \frac{8}{9}pK_2^2\left(4 - \frac{M}{M_0}\right)\right\}^{1/2} - 1\right] \tag{12}$$

With these equations, equation (8), and $\Sigma\alpha_i = 1$, K_4 may be calculated from the original p and M data. The monotonic decrease in K with pressure is no longer apparent. Typical of the data are those given in Table IV, the 120° isotherm. The fractions of monomer which exist in the three states are also given.

The average value of K_4 thus obtained was taken as the true equilibrium constant. The value of K_4 for 120° was used to calculate M from p using the above equation in reverse. The circles in Fig. 6 are the points so calculated. The agreement with curve 1 is good. Values of K_4 for seven temperatures are given in Table III, the values for the higher temperatures being too erratic to allow meaning to be attached to them. Figure 7 shows a plot of ln K_4 against $1/T$ for these data. The points may probably be regarded as forming a straight line within the precision of our measurements, the least squares equation of the line being

TABLE IV

EQUILIBRIUM VALUES OF MOLECULAR SPECIES OF ACETIC ACID AT 120°

p, mm.	α_1	α_2	α_4	K_4
800	0.245	0.639	0.116	0.0076
700	.264	.637	.099	.0076
600	.289	.636	.075	.0074
500	.319	.625	.056	.0073
400	.358	.608	.034	.0070
300	.408	.569	.023	.0071
200	.483	.503	.014	.0075
100	.623	.379	[a]	[a]

[a] Experimental error causes $\alpha_1 + \alpha_2 > 1$, for $p = 100$ mm., hence α_4 and K_4 have been omitted at this pressure.

$$\ln K_4 = 3390/T - 13.52$$

The corresponding heat of reaction is $H_4 = -6750$ cal./mole.

Summary

1. Data for the effective molecular weight (equivalent to vapor density) for acetic acid vapor have been obtained over the range from 50 to 800 mm. pressure and from saturation temperature to about 170°.

2. It has been shown that in this region acetic acid vapor shows the presence of at least one polymer of order higher than the dimer, and evidence has been adduced in support of the theory that the next higher polymer is the tetramer.

3. The equilibrium constants K_i for the reactions AcOH = $(1/i$ (AcOH)$_i)$ have been calculated for $i = 2$ and 4. They are given by ln $K_2 = (3645/T) - 11.997$, ln $K_4 = (3390/T) - 13.52$ for pressures in mm.

4. The calculated heats of reaction are: $H_2 = -7250$ cal./mole ± 200 cal./mole, $H_4 = -6750$ cal./mole ± 600 cal./mole.

STATE COLLEGE, PA. RECEIVED JANUARY 8, 1945