The Entropy of Acetic Acid

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From third law measurements, vapor pressures and vapor densities, the entropy of the acetic acid monomer at 25° and one atmosphere is 69.4 ± 1.0 e.u. The value 68.7 is calculated from the vapor phase ethyl acetate equilibrium. For a model based upon acetone and approximately representing free rotation the entropy would be 72.7. If there is only a single potential minimum in the hydroxyl group rotational cycle, the large deficiency below the free rotation value is explained without assuming an exceptionally high potential barrier. A brief discussion of the effect of the number of potential minima and their relative depth is appended, and a possible source of error in third law measurements is suggested.

The entropy of the acetic acid monomer as a hypothetical perfect gas can be calculated from the third law entropy of the liquid and the heat of vaporization with the aid of the constants of the reaction

\[(\text{CH}_3\text{COOH})_2 = 2\text{CH}_3\text{COOH}. \]  \hspace{1cm} (1)

This procedure or its equivalent is made necessary by the wide deviations of acetic acid vapor from perfect gas behavior. The significance and accuracy of the result depend upon the completeness with which existing vapor density data may be used to describe the vapor as a mixture of two perfect gases in equilibrium according to Eq. (1). Although it is reasonable to suppose that at low pressures this description should be valid, accurate vapor densities at any one temperature are not available over a wide enough range of pressures to establish the point by experiment. Consequently the entropy requires support from other sources. The calculation has therefore been made at a series of temperatures from 25 to 100° and an average value of the heat capacity between these temperatures has been derived and shown to lie between the heat capacities of the related substances ethyl alcohol and acetone. As a further and more direct confirmation an independent value of the entropy is derived from the results of a recent study of the vapor phase ethyl acetate equilibrium.

In a similar study of the nitrogen dioxide-nitrogen tetroxide case Giauque and Kemp concluded that the entropy of dissociation of the dimer could not be evaluated from equilibrium data within several entropy units. This uncertainty would of course be carried in some measure into the entropy of each component. The acetic acid case appears to be more favorable.

Since the publication by MacDougall of vapor densities measured at low pressures near room temperature, it is possible to evaluate the heat of reaction 1 and the composition of the mixture as a function of temperature with a high probable accuracy. From MacDougall’s results and those of Fenton and Garner, the heat of dissociation of the dimer becomes

\[\Delta H = 18,853 - 9.76T \]  \hspace{1cm} (2)

and, for the dissociation constant,

\[\log k = 25.732 - 4120/T - 4.910 \log T. \]  \hspace{1cm} (3)

Constants calculated by Eq. (3) show an average deviation of 2.0 percent from MacDougall’s mean values. If his point at 25° is left out the deviation decreases to 0.8 percent. Similarly average constants from the Fenton and Garner data are reproduced with a mean deviation of 1.0 percent, or

| TABLE I. Vaporization and association of acetic acid. |
|----------------|----------------|----------------|----------------|----------------|----------------|
| TEMP. DEG. C | ΔH DIS. | k (DIS.) MM | ϕ MM | α | ΔH VAP. |
| 25 | 15,944 | 0.578 | 15.63 | 0.0957 | 10,874 |
| 40 | 15,797 | 2.080 | 34.72 | 0.1215 | 11,011 |
| 60 | 15,602 | 9.48 | 88.96 | 0.1611 | 11,236 |
| 80 | 15,407 | 35.8 | 202.4 | 0.2058 | 11,497 |
| 100 | 15,212 | 115.1 | 417.2 | 0.2540 | 11,779 |

1 The author is indebted to Dr. Donald Brundage for making preliminary calculations.
0.3 percent at three of their four temperatures. Results obtained by Drucker and Ullmann at three temperatures from 80 to 110° are on the average 5 percent above the constants given by Eq. (3). If the weight at higher temperatures were given to the Drucker and Ullmann results it would be impossible to bring Eqs. (2) and (3) into line with the remaining data without an unreasonably large $\Delta C_p$ term expressed in greater detail. The heat of dissociation according to Eq. (2) is 15,944 cal. at 25° as compared with 16,400±800 obtained by MacDougall from his own data alone. Since it seems apparent that his equilibrium constant at 25° is low, and his mean heat of reaction therefore high, the correct value should lie within the lower half of his range of uncertainty. Equation (2) gives heats of dissociation within these limits up to 60°.

The heat of vaporization is evaluated from the vapor pressures in the International Critical Tables,6 which are reproduced with an average deviation of 0.1 percent from 20 to 100° by the equation

$$ \log p = 18.8302 - 2630/T - 3.562 \log T. $$  

For the vaporization of 120 grams of the acid

$$ \Delta H = (1+a)(12035-7.08T). $$  

Table I contains the heat of dissociation, the degree of dissociation $\alpha$, the dissociation constant, the vapor pressure and the heat of vaporization calculated from the above equations at five temperatures. The heats of vaporization listed in the International Critical Tables7 and marked as questionable are as much as 320 cal. lower than those appearing in Table I. MacDougall’s values, 11,000 at 25° and 11,270 at 40° are correspondingly high. They cannot be taken as more reliable, however, because they are based upon low pressures measured over a range of only 20°. If gas imperfections have been adequately accounted for in the factor $1+\alpha$, the heats of vaporization derived from Eq. (5) should not be in error by more than 100 calories.

The entropies of vaporization of the monomer and dimer are most readily obtained with the aid of individual heats of vaporization calculated from the equations

$$ \Delta H_1 (\text{vap.}) = \Delta H (\text{vap.})/2 + (1-\alpha)\Delta H (\text{dis.})/2 $$  

and

$$ \Delta H_2 (\text{vap.}) = \Delta H (\text{vap.}) - \alpha\Delta H (\text{dis.}). $$

For 60 grams of liquid the entropy at 25° is 38.2 according to Parks, Kelley and Huffman.8 The added liquid entropy for higher temperatures is calculated from the heat capacity given in the International Critical Tables.9 After conversion to calories this becomes $C_p=12.9+0.056T$ in the appropriate temperature range. The results of the entropy calculation are shown in Table II for the monomer and in Table III for the dimer. The mean heat capacity of the monomer and dimer vapors is now derived from the entropy by means of the equation $dS/dT = C_p/T$. For the monomer, $C_p$ is 17.4 and for the dimer it is 44.1. Because of structural similarity it is reasonable to assume that the monomer value should be near the mean of the heat capacities of ethyl alcohol and acetone. From Table IV these are, respectively, 16.8 and 19.9 at the mean temperature of 62°. For reaction 1, $\Delta C_p$ is $-9.3$ as compared with $-9.76$ shown in Eq. (2). This discrepancy is probably due to an oversimplification of Eq. (5), for which the true heat capacity, there represented as $-7.08(1+\alpha)$, should have the more

<table>
<thead>
<tr>
<th>TEMP. DEG. C</th>
<th>$S$ (60 g H, 0°C)</th>
<th>$\Delta H_1$</th>
<th>$\Delta H_2$</th>
<th>$p$</th>
<th>$R \ln p$ (208)</th>
<th>$S$ GAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>38.2°</td>
<td>12,646</td>
<td>42.4°</td>
<td>4.2°</td>
<td>11.2°</td>
<td>69.3°</td>
</tr>
<tr>
<td>40</td>
<td>39.6°</td>
<td>12,445</td>
<td>39.7°</td>
<td>7.5°</td>
<td>9.1°</td>
<td>70.2°</td>
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<tr>
<td>60</td>
<td>41.5°</td>
<td>12,162</td>
<td>36.5°</td>
<td>24.6°</td>
<td>6.8°</td>
<td>71.2°</td>
</tr>
<tr>
<td>80</td>
<td>43.4°</td>
<td>11,867</td>
<td>33.6°</td>
<td>69.0°</td>
<td>4.7°</td>
<td>72.2°</td>
</tr>
<tr>
<td>100</td>
<td>45.2°</td>
<td>11,564</td>
<td>30.9°</td>
<td>169.0</td>
<td>2.9°</td>
<td>73.2°</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>TEMP. DEG. C</th>
<th>$\Delta H_1$</th>
<th>$\Delta H_2$</th>
<th>$p$</th>
<th>$R \ln p$ (208)</th>
<th>$S$ GAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>9349</td>
<td>31.3°</td>
<td>12.90</td>
<td>8.1°</td>
<td>99.6°</td>
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<tr>
<td>40</td>
<td>9092</td>
<td>29.0°</td>
<td>27.20</td>
<td>6.6°</td>
<td>101.7°</td>
</tr>
<tr>
<td>60</td>
<td>8722</td>
<td>26.1°</td>
<td>64.27</td>
<td>4.9°</td>
<td>104.4°</td>
</tr>
<tr>
<td>80</td>
<td>8326</td>
<td>23.5°</td>
<td>133.3</td>
<td>3.4°</td>
<td>107.0°</td>
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<tr>
<td>100</td>
<td>7916</td>
<td>21.2°</td>
<td>248.2</td>
<td>2.2°</td>
<td>109.5°</td>
</tr>
</tbody>
</table>

7 Vol. 5, p. 138.
9 Vol. 5, p. 114.
The detailed form

\[
\Delta C_p = 2\alpha C_{p1} + (1 - \alpha) C_{p2} + \Delta H (\text{dis.}) \, d\alpha/dT - 2C_p(1). \tag{8}
\]

Since the discrepancy involves only a fraction of an entropy unit, the second approximation required to produce consistency would not be justified by the data used.

The above calculation using individual heats of vaporization is different in form from the method outlined by Giauque and Kemp. Their approach leads to two equations, one expressing the two unknowns in terms of the entropy of dissociation of the dimer, the other relating them to the entropy of the mixture and the entropy of mixing. The two methods can readily be shown to be equivalent, either by algebraic proof or by numerical substitution.

If the entropy calculation is made from MacDougall's data alone the results for \( S_1 \) and \( S_2 \) at 25° are 70.3 and 100.0, which represent practical maximum values and show that the entropies are not highly sensitive to the interpretation of the data.

A further estimate of the monomer entropy can be made from the result of a recent study of the vapor phase ethyl acetate equilibrium by Halford and Brundage. For the reaction

\[
\text{CH}_3\text{COOH}(g) + \text{C}_2\text{H}_5\text{OH}(g) = \text{CH}_3\text{COOC}_2\text{H}_5(g) + \text{H}_2\text{O}(g), \tag{9}
\]

the minimum mean value of the entropy reasonably derivable from existing equilibrium data between 40 and 230° is -3.3 units. To derive the value at 25° requires knowledge of the heat capacities of the reactants. Table IV shows estimated values together with references to the data upon which they are based. In the absence of direct data, acetic acid is assumed to have the

| \text{TABLE IV. Heat capacity of gases, 25 to 150°, } C_p = A + BT. |
|-------------------|---|---|---|
| \text{A} | \text{B} | \text{REFERENCES} |
| \text{H}_2\text{O} | 7.47 | 0.0017 | (a) |
| \text{C}_2\text{H}_5\text{OH} | 3.4 | 0.040 | (b) |
| \text{CH}_3\text{COOC}_2\text{H}_5 | 8.9 | 0.060 | (b), (c) |
| \text{CH}_3\text{COOH} | 5.1 | 0.037 | Estimate |
| \text{CH}_3\text{COCH}_3 | 8.3 | 0.034 | (b), (c) |

The mean temperature dependence of ethyl alcohol and acetone at 25° and one atmosphere is estimated to be 68.7. Although this estimate in itself is subject to considerable error, it nevertheless contributes

\[\text{B. Bennewitz and Rossner, Zeits. f. physik. Chemie 339, 134 (1938).}\]
\[\text{International Critical Tables, Vol. 5, p. 79.}\]
\[\text{J. O. Halford and D. Brundage, in press.}\]
Table VI. Acetic acid entropy from the entropy of acetone.

<table>
<thead>
<tr>
<th></th>
<th>Acetone</th>
<th>Acetic Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M$</td>
<td>58.08</td>
<td>60.05</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>1.48</td>
<td>1.20, 1.23</td>
</tr>
<tr>
<td>$I_{CH_{3}}$</td>
<td>0.0527</td>
<td>0.0527</td>
</tr>
<tr>
<td>$I_{OH}$</td>
<td>0.0131</td>
<td></td>
</tr>
<tr>
<td>$S$(vib.)</td>
<td>2.4</td>
<td>2.4</td>
</tr>
<tr>
<td>$S_{298}$</td>
<td>70.6</td>
<td>72.7</td>
</tr>
</tbody>
</table>

strongly to the high probability already established that the entropy of the acid monomer lies within the limits 69.4±1.0.

For comparison, a theoretical value is calculated from the entropy of acetone with the aid of the equation

$$S_{298} = 23.730 + (3/2)R \ln M + 8.712n + (1/2)R \ln (A^B \cdot \cdot \cdot G^r) - R \ln \sigma + S \text{ (vib.)} \quad (10)$$

in which $M$ is the molecular weight in grams, $A$, $B$, etc., are moments of inertia, external and internal, in c.g.s. units times 10$^{38}$, $a + b + \cdots + g = n$, is the number of rotational degrees of freedom and $\sigma$ is the symmetry number. Equation (10), for the entropy with free internal rotation, differs only negligibly from the theoretically correct form derived by Kassel.$^{17}$ It is assumed in its application to acetic acid that the hydroxyl group may be described closely enough as a symmetrical internal rotator. The vibrational entropy of acetone is derived from the total entropy in Table V by the use of the above equation, and should therefore be low by an amount representing the restriction of internal rotation. For acetone the restricting barrier is probably small,$^{18}$ corresponding almost to free rotation. Acetic acid is then assumed to have the same vibrational entropy, and its total entropy, shown in Table VI, should therefore be only a little lower than the free rotation value.

This approach, rather than the customary one involving a questionable independent estimate of the vibrational contribution, is of special interest because it can be used to calculate the entropy of methyl alcohol from that of ethane or of ethyl alcohol from propane within a small fraction of an entropy unit. Consequently the result of Table VI is the entropy which acetic acid would have if the substitution of the hydroxyl group for a methyl group produced the same changes in all three molecules, ethane, propane and acetone.

In calculating the external moment product $ABC$ and the moments of inertia $I$ of the internal rotators, all angles between single bonds were assigned the tetrahedral value, and interatomic distances were taken as $c-c = 1.54$, $c-h = 1.09$, $c-o = 1.43$, $c-o = 1.24$ and $o-h = 0.97$. For acetic acid the two tabulated moment products were calculated for models with the acid hydroxyl in the cis- and trans-positions relative to the carbonyl oxygen. The hydroxyl group was assumed to rotate as if its center of gravity were on the C–O bond.

It appears from the above results that restricted rotation of the acid hydroxyl group causes an entropy decrease below the free rotation value which exceeds the corresponding effect in methyl or ethyl alcohol by nearly three units. This large deficiency can be readily explained in a way that indicates that the experimental entropy of 69.4 is not far from correct. It is reasonable to assume that in the entire rotational cycle there is only a single potential minimum of sufficient depth to trap the hydroxyl group. For such a model, with vibration restricted to the ground state, the entropy would be 68.3 plus a small increment entering through the use of the acetone vibrational entropy. The experimental value thus allows 1.1 e.u. to be divided between this increment and the actual entropy of the torsional motion.

Although Pitzer's$^{19}$ method of finding the restricting potential barrier was developed for $n$ equal sinusoidal potential valleys each covering one $n$th of the cycle, his table can be used for the single minimum model postulated for acetic acid. The case is similar to his treatment of the individual forms of $n$-butane.$^{20}$ It is assumed that the single minimum occupies one-third of the cycle. For an imaginary model with two more minima equal in depth to the first the entropy would be 69.4 plus a mixing term $R \ln 3$, giving $S_{j} - S = 1.1$ for use in the table. The resulting potential barrier is about 3000 cal., a value which

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is subject to an error, probably negligible, because
the table applies only when the rotational states
are symmetrically disturbed in \( \pi \) regions of the
cycle, rather than unsymmetrically as they would
be in the single minimum case.

In general, for the hydroxyl group in torsional
motion against an unsymmetrical radical, it will
be necessary to add a mixing term to the experi­
tmental entropy before a potential barrier can be
estimated by means of Pitzer's table or the
equivalent functions. This term has a maximum
value \( R \ln n \), but may be near zero if the potential
valleys approach equality in depth. With ethyl
alcohol, for example, there are probably three
minima of which two are equal but different from
the third, and a mixing term between zero and
\( R \ln 3 \) should be added to the experimental
entropy before the barrier is estimated. If the

correction is not made the barrier will be high.

An interesting possibility occurs for substances
which have stable torsional vibrations resulting
in optically isomeric configurations. The mole­
cules might remain asymmetric after crystal­
lization and might produce crystals of the
racemic compound type which would remain
unchanged upon cooling toward the absolute
zero. Consequently the entropy at the absolute
zero would not be zero but \( R \ln 2 \), and the third
law entropy would be in error by this amount.
How probable this situation is depends upon the
relative magnitude of intramolecular and inter­
molecular forces in the solid state.