The Entropy of Ethyl Alcohol from Molecular Data and the Equilibrium in the Hydration of Ethylene

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The entropy and free energy of ethyl alcohol gas have been calculated from the molecular data at several temperatures on the basis of (*a*) free internal rotation, (*b*) restricted rotation (with potentials; about C−C bond = 3000, C−O bond = 10,000 calories). The latter values are in perfect agreement with those from the third law and from the equilibrium data on the hydration of ethylene.

I. INTRODUCTION

RECENTLY discrepancies have been found between entropies of nonrigid polyatomic molecules, calculated from the molecular data assuming free internal rotations, and those from thermal data down to liquid hydrogen temperatures and the third law of thermodynamics.[1-5] The discrepancy of about 2 e.u., per group capable of internal rotation, might be due to random orientation in the crystal at low temperatures, corresponding to a zero point entropy of 2 e.u., or to a force associated with potential barriers of about 3000 calories restricting the internal rotations.[1, 3] Kemp and Pitzer[3] have shown that restricting potentials are the cause of a discrepancy of 1.51 e.u. in the entropy of ethane at 298°K by considering the equilibrium in the hydrogenation of ethylene, a conclusion in agreement with the infra-red absorption spectrum[6] and the low temperature specific heats of the gas.[7]

Taken together these facts are convincing; but obviously, it is desirable to obtain similar evidence in other cases. The requirements are:

(a) Equilibrium constants for a reaction wherein the number of internally rotating groups is changed.

(b) Complete thermal data *down to liquid hydrogen temperatures.*

(c) Molecular data for each substance.

(d) An accurate value of ΔH close to the temperature of equilibrium.

Such a reaction is that involved in the vapor phase of hydration of ethylene.

$$C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g).$$
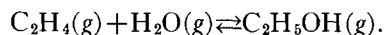
II. THE ENTROPY OF ETHYL ALCOHOL GAS FROM THERMAL DATA

Table I summarizes the calculation of the entropy of the hypothetically perfect gas at the normal boiling point and at 403.2°K from the best available calorimetric data. The entropy increase from 298.16°K was obtained by integration of the equation expressing the heat capacity data of Fiock, Ginnings, and Holton.[9]

TABLE I. *The calorimetric entropy of ethyl alcohol at 351.5°K and 403.2°K.*

	E.U./MOLE
0°K (cryst.)−298.16°K (liq.)[8]	38.4　±.3
Liquid 298.16−351.5°K[9]	4.90±.005
Vaporization 9255/351.5[9]	26.33±.03
Entropy of actual gas at boiling point (351.5°K[11])	69.63±.3
Correction for gas imperfection[10]	.14
Entropy of ideal gas at boiling point	69.8　±.3
0°K (cryst.)−298.16°K (liq.)[8]	38.4　±.3
Liquid 298.16−403.2°K[9]	9.99
Vaporization 8034/403.2[9]	19.93
Entropy of act. gas at 403.2 and 5.682 atmos.	68.32±.3
Correction for gas imperfection[10]	.32
Entropy of ideal gas at 403.2°K and 5.682 atmos.[11]	68.64±.3
$R \ln 5.682$	3.45
Entropy of ideal gas at 403.2°K and 1 atmos.	72.1　±.3

[1] Aston and Messerly (a) J. Chem. Phys. **4**, 391 (1936). (b) J. Am. Chem. Soc. **58**, 2354 (1936).
[2] Kassel, J. Chem. Phys. **4**, 493 (1936).
[3] Kemp and Pitzer (a) J. Chem. Phys. **4**, 749 (1936). (b) J. Am. Chem. Soc. **59**, 276 (1937).
[4] Aston, Siller and Messerly, J. Am. Chem. Soc. **59**, 1743 (1937).
[5] See also Kistiakowsky and Wilson, J. Am. Chem. Soc. **60**, 494 (1938).
[6] Howard, J. Chem. Phys. **5**, 451 (1937).
[7] Kistiakowsky and Nazmi, J. Chem. Phys. **6**, 18 (1938).

[8] Kelley, J. Am. Chem. Soc. **51**, 779 (1929).
[9] Fiock, Ginnings, and Holton, Nat. Bur. Stand. J. Research **6**, 881 (1931).
[10] Calculated from thermodynamics and the modified Berthelot equation: $P_c = 63.1$ atmos., $T_c = 516.3°K$. ("I.C.T.").
[11] *International Critical Tables.*

III. The Entropy of Ethyl Alcohol from Molecular Data

(a) The vibrational entropy

The Raman Spectrum[12a, b] seems to contain lines corresponding to all but one of the nineteen modes of vibration. As only a partial normal coordinate treatment has been made,[12b] comparison with spectra of other molecules was resorted to. On this basis the following frequency assignment has been made

C—C—O skeleton: $\nu(\pi)$, 883; $\nu(\sigma)$, 1096; $\delta(\pi)$ 433:

CH$_3$ (internal): $\nu(\pi)$, 2930; $^2\nu(\sigma)$, 2930; $\delta(\pi)$, 1274; $^2\delta(\sigma)$, 1455:

OH (internal): ν, 3359

CH$_2$ (internal): $\nu(\pi) = \nu(\sigma)$, 2930; $\delta(\pi)$, 1274.

C—O—H (hydrogen angle variation): δ_1, (700).

CH$_3$—CH$_2$—O (hydrogen angle variation): $\delta_2 \sim \delta_3$, 814; $\delta_4 \sim \delta_5$, 1051; δ_6, 1455.

The nomenclature is as usual[13, 2, 4] for the inner frequencies of the groups. The frequencies δ_1, δ_2, δ_3, δ_4, δ_5, and δ_6, correspond to modes of vibration in which the angle of bonds holding hydrogen is changed relative to the whole molecule. At the same time the internal angles of the groups CH$_3$, CH$_2$, and OH are unchanged.[2, 3b]

The frequency δ_1 for OH bending is apparently absent from the Raman spectrum and for this its corresponding value in methyl alcohol has been used.[2] The assignment of the remaining five frequencies is largely a guess. As the result due to all six δ_i frequencies is about what would result if all were at 950 cm^{-1} (the corresponding average for ethane and ethylene),[14] no large error would be expected. The errors due to an extreme misinterpretation will be discussed presently.

Taking hc/k as 1.432 and R as 1.9869, the vibrational entropy and $-((F^0 - E_0^0)/T)_{\text{vib}}$ are then calculated from Nernst's tables.

(b) The translational and rotational entropy

The distances and angles used were: CH = 1.11A; OH = 0.95A; CC = 1.54A; CO = 1.42A: <HCO = <CCO = <HCH = 109° 28'; <COH = 110° 2. For the model in which the methyl and hydroxyl groups are rotating freely, the translational and rotational entropy was calculated by conventional methods.[15, 16]

Kassel has greatly simplified the method of Eidinoff and Aston, particularly in the case where symmetrical tops are attached to a rigid frame (see his Eq. (11)). However his Eq. (11) is obviously valid for any molecule with simple tops attached to a rigid frame, whether these be symmetrical or not. The only limitation is that these tops themselves must be rigid. If the attached rigid tops are not symmetrical the determinant in Eq. (11) of Kassel is a function of the variables α which represent the angular position of these tops. The rotational entropy is then given by

$$Q = (2\pi kT/h^2)^{s/2}(8\pi^2/\sigma)\int_0^{2\pi} \cdots \int_0^{2\pi} [R]^{\frac{1}{2}}d\alpha_1 d\alpha_2 \cdots d\alpha_{s-3}, \tag{1}$$

where

$$[R] = K_1 K_2 \cdots K_{s-3} \begin{vmatrix} (yy)+(zz)-(\lambda\lambda) & -(xy)-(\lambda\mu) & -(xz)-(\lambda\nu) \\ -(xy)-(\lambda\mu) & (xx)+(zz)-(\mu\mu) & -(yz)-(\mu\nu) \\ -(xz)-(\lambda\nu) & -(yz)-(\mu\nu) & (xx)+(yy)-(\nu\nu) \end{vmatrix}.$$

Our choice of axes was dictated by other related problems so as to simplify the total labor. Initially, the y axis was taken to bisect the angle between the C—C bond and one of the CH bonds of the CH$_2$ group. The $x-y$ plane included both of these bonds.

The terms of (1) about parallel axes through the center of gravity$\times 10^{40}$ are:

[12] (a) Bolla, Zeits. f. Physik. **89**, 513 (1934); **90**, 607 (1934). (b) Cross and Van Vleck, J. Chem. Phys. **1**, 350 (1933).

[13] Bartholomé and Sachsse, Zeits. f. physik. Chemie **B30**, 40 (1935).

[14] Pitzer, J. Chem. Phys. **5**, 473 (1937).

[15] Eidinoff and Aston, J. Chem. Phys. **3**, 379 (1935).

[16] Kassel, J. Chem. Phys. **4**, 276 (1936).

TABLE II. *The entropy of ethyl alcohol from molecular data.*

	FREE ROTATION		RESTRICTED ROTATION	
$T°K$	351.5	403.2	351.5	403.2°K
S_{t+r}	69.44	70.80	61.13	62.30
S_v	3.53	4.29	3.53	4.29
$S_{rr}(CH_3)$ (3000 cal.)			2.5	2.8
$S_{rr}(OH)$ (10,000 cal.)			2.6	2.7
Total (less nuclear spin)	73.0	75.1	69.8	72.1
Calorimetric corrected to ideal gas state	69.8	72.1	69.8	
Discrepancy	3.2	3.0	0.0	—

$(xx) = 32.54 - 1.18 \sin \alpha + 1.29 \sin^2 \alpha$,
$(yy) = 43.67 + 1.97 \cos \alpha + 0.86 \cos^2 \alpha$,
$(zz) = 29.17 - 1.31 \cos \alpha + 0.42 \cos^2 \alpha$,
$(xz) = 12.63 - 1.12 \sin \alpha - 0.35 \cos \alpha$
$\qquad\qquad\qquad + 0.72 \sin \alpha \cos \alpha$,
$(yz) = 25.76 - 0.20 \cos \alpha + 0.59 \cos^2 \alpha$,
$(xy) = -28.14 - 0.49 \cos \alpha + 1.22 \sin \alpha$
$\qquad\qquad\qquad + 1.03 \sin \alpha \cos \alpha$

(where α is the angle orienting the OH group),

$(\lambda\lambda) = 3.65 \times 10^{-40}$, $(\mu\mu) = 2.26 \times 10^{-40}$,

$(\nu\nu) = 0.89 \times 10^{-40}$, $(\lambda\mu) = -2.58 \times 10^{-40}$,

$(\lambda\nu) = 0$, $(\mu\nu) = -0.63 \times 10^{-40}$,

$K_{OH} = 1.32 \times 10^{-40}$, $K_{CH_3} = 5.46 \times 10^{-40}$.

The symmetry number is three.

It is necessary to integrate Eq. (1) graphically to obtain the partition function.

The rotational and translational entropy is

$$S_{t+r} = 10/2 \, R \ln T + 11.194 \qquad (2)$$

and the "free energy"

$$-((F^0 - E_0^0)/T)_{t+r} = 10/2 \, R \ln T + 1.260. \qquad (3)$$

Table II (columns 1 and 2) summarizes the calculations of the total entropy (S_{t+r+v}) at the boiling point and at 403.2°K (130°C) on the basis of free rotation.

The discrepancy of 3.2 e.u. at 351.5°K and of 3.0 e.u. at 403.2°K will later be shown *not* to be due to random orientation in the crystal.

On the basis that the discrepancy is due to the incorrect assumption of free internal rotation, the potential hindering the rotation of the hydroxyl group was chosen to fit the data at 403.2°K. The method of Pitzer[17] was used, and

[17] Pitzer, J. Chem. Phys. **5**, 469 (1937).

from his work, the potential hindering the methyl group was taken as 3000 cal. For this calculation "s" in the first factor of Eq. (1) was taken as 3. The terms $\lambda\lambda$, $\lambda\mu$, etc. and the factors K_1 and K_2 were omitted from $[R]$. The integral of $[R \text{ (new)}]^{\frac{1}{2}}$ was evaluated as before but divided by $(2\pi)^2$ to obtain an average. As the entropy of the rigid molecule changes by only 0.02 e.u. over the range of α this method is obviously sufficiently accurate. The symmetry number for the rigid case is unity but there is a symmetry number of three in the contribution of the methyl group. The expressions for the rotational and translational entropy and free energy were then

$$S_{t+r} = 10/2 \, R \ln T + 11.209 - \sum S_f - S, \qquad (4)$$

$$-\left(\frac{F^0 - E_0^0}{T}\right)_{t+r} = 10/2 \, R \ln T + 1.275 - \sum \frac{F - F_f}{T}. \qquad (5)$$

The last terms in (4) and (5) are the sums of the effects of the potentials restricting the rotation of the OH and CH_3 groups (three minima in each case), which are to reduce the S and F as calculated on the basis of free rotation. They are obtained directly from Pitzer's tables.[17]

The potential hindering the rotation of the hydroxyl group to give the best fit was 10,000 cal. The results of columns three and four (Table II) were obtained using these potentials.

IV. TOTAL ENTROPY AND FREE ENERGY TABLES

The values of the total entropy and free energy are given in Table III at several temperatures on the basis of free and hindered rotation with the above potentials.

TABLE III.

$T°K$	FREE ROTATION S	RESTRICTED ROTATION		S FROM EQUILIBRIUM DATA	
		S	$\frac{(F^0 - E_0^0)}{T}$	C_p's F.R.	C_p's R.R.
400	74.93	71.92	58.97	71.15	71.87
450	77.33	74.53	60.58	73.88	74.54
500	79.67	77.02	62.10	76.48	77.08
550	81.93	79.43	63.58	78.97	79.62
600	84.13	81.76	65.04	81.32	82.07

V. COMPARISON WITH THE EQUILIBRIUM DATA

The remarkably accurate equilibrium data[18-20] for the reaction

$$C_2H_4 \ (g) + H_2O \ (g) = C_2H_5OH \ (g)$$
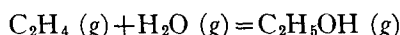
are plotted in Fig. 1 (on the basis of fugacities). To calculate the entropy of ethyl alcohol from these data it is necessary to know the heat of reaction and the entropies of the reactants. The entropy of water vapor was obtained from the results of Gordon,[21] that of ethylene was calculated using the data and method given by Egan and Kemp.[22] In both cases the values used were from the molecular data. These are in complete agreement with experiment.[22, 23]

The heat of reaction at 25° in the standard state can be calculated to well within 400 calories from the heats of formation of the components with a correction to the ideal gas state. Table IV

TABLE IV. Heats of formation of ideal gases in calories for all P and 298.2°K.

	ETHYLENE	WATER	ETHYL ALCOHOL
Liquid at 298.2	—	−68,313[24]	−66,750[25]
Vaporization at 298.2	—	10,499[26]	10,120[9]
Saturated vapor at 298.2	—	−57,814	−56,630
Real gas at 1 atmos.	12,140[27]	—	—
Berthelot correction	+12	+1	+5
Ideal gas at 1 atmos.	12,152	−57,813	−56,625
Limit of error ±	210	13	220

summarizes the calculation.

The correction to the ideal gas state was made on the basis of the modified Berthelot equation and the thermodynamic equation of state. It is

$$-\left[\frac{9T_cRP}{128P_c} - \frac{81}{64} \frac{RT_c^3P}{P_cT^2} \right].$$

The "I.C.T." critical constants were used in all cases.

[18] Stanley, Youell, Dymock, J. Soc. Chem. Ind. **53**, 205T (1934).

[19] Applebey, Glass, Horsley, J. Soc. Chem. Ind. **56**, 279T (1937).

[20] Dodge and Bliss, Ind. Eng. Chem. **29**, 19 (1937).

[21] Gordon, J. Chem. Phys. **2**, 65 (1934).

[22] Egan and Kemp, J. Am. Chem. Soc. **59**, 1264 (1937).

[23] Giauque and Archibald, J. Am. Chem. Soc. **59**, 561 (1937).

[24] Rossini, Nat. Bur. Stand. J. Research **6**, 1 (1931).

[25] Rossini, Nat. Bur. Stand. J. Research **13**, 189 (1934).

[26] Giauque and Stout, J. Am. Chem. Soc. **58**, 1144 (1936).

[27] Rossini and Knowlton, Nat. Bur. Stand. J. Research **19**, 339 (1937).
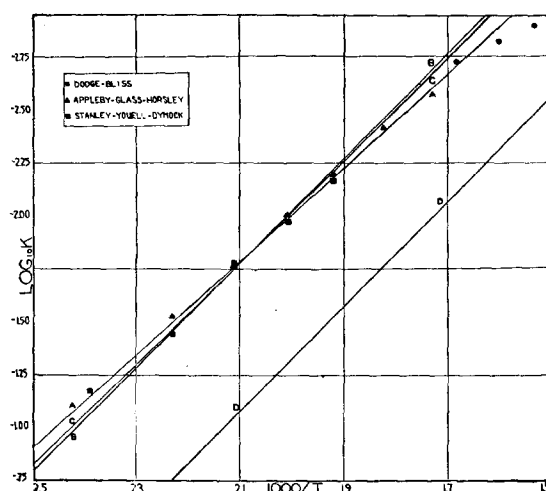
FIG. 1. Equilibrium constants for the reaction $C_2H_4(g) + H_2O(g) = C_2H_5OH(g)$.

The entropies in columns five and six of Table III were calculated from the best curve through the equilibrium data (Fig. 1). The ΔH^0 value, used to get the results in column five, was calculated from that at 25° using heat capacities obtained from the molecular data on the assumption of free rotation. For column six, heat capacities, obtained on the basis of restricted rotation with the potentials already given, were used to extrapolate $\Delta H^0_{298.2}$.

VI. ACCURACY

If the frequencies δ_1, δ_2 and δ_3 are all taken at 1050, the entropy from molecular data is decreased 0.7 e.u. at 351.5°K, 0.8 e.u. at 403.2°K, and 1.3 e.u. at 600°K. The $-(F-E_0^0)/T$ value at 400 is decreased by 0.3 e.u. that at 600 by 0.5 e.u. The error in the third law entropies might be 0.3 e.u. This seems an upper limit to the error. The maximum error in $\Delta H_{298.2}$ would introduce 1 e.u. at 400°K and 0.7 e.u. at 600°K. The maximum error in ΔS from the equilibrium measurements would be the error in ΔH at 298.2 plus that in extrapolation to the temperature T. The error in the equilibrium constants themselves produces a negligible error as is evident from Fig. 1. At 400 and 600°K, respectively the limits of error due to extrapolation are 0.2 e.u. and 0.4 e.u. (i.e. if $\delta_1 = \delta_2 = \delta_3 = 1050$).

The comparison of the calorimetric entropies with those from the molecular data on the basis

of free rotation could thus be in error by 1.0 e.u. (0.7+0.3) at 351.5°K and 1.1 e.u. (0.8+0.3) at 403.2. The empirical potentials partly absorb the error in the calculation using restricting potentials.

The error in the comparison of the entropies from the equilibrium data with those from free rotation could be that in $\Delta H^0_{298.2}$ plus that in the entropy from molecular data minus that in the extrapolation of ΔH as both use the same frequencies. The maximum errors at 400°K and 600°K are thus 1.6 e.u.

The arbitrary choice of potentials for the same comparison on the basis of restricted rotation partly absorbs this error.

VII. DISCUSSION

From the previous discussion it is at once evident that no reasonable assumption as to error can reconcile the discrepancy (about 3.0 e.u.) between the entropies calculated on the basis of free rotation and the experimental ones either from the third law or the equilibrium data. An assumption of random orientation in the crystal would reconcile the third law values, but not those from the equilibrium measurements. On the other hand, the remarkable check of the entropy values calculated with the above restricting potentials, both with the experimental results from the third law and from the equilibrium data at all temperatures, practically amounts to proof, not only of the existence of such potentials, but that the values are essentially correct (i.e., that the vibrational frequency assignment has been properly made).

The practical significance of the results is shown graphically in Fig. 1. Curve A is the best curve through the equilibrium data. Curve B represents equilibrium constants obtained from the third law data using heat capacities calculated assuming free rotation, to extrapolate above 403.2°K. The equilibrium constants plotted on curve C were evaluated using heat capacities, calculated on the basis of restricted rotation, to extrapolate the third law entropies and $\Delta H^0_{298.2}$. The small extrapolation is noteworthy.[28] Curve D was obtained using entropies from the molecular data assuming free rotation. The curve using entropies from molecular data with restricting potentials coincides with curve C because the potentials were solved for from the third law data at 403.2°. It is thus evident that *the thermodynamic values in Table III calculated on the basis of restricted rotation (columns 3 and 4) can be looked upon as values in best accord with all experimental facts.*

[28] Parks, Ind. Eng. Chem. **29**, 845 (1937), has also used this reaction for a third law check with a long extrapolation of which he was in doubt.