Hindered Rotation in Ethyl Alcohol

J. O. HALFORD

Chemistry Department, University of Michigan, Ann Arbor, Michigan

(Received July 15, 1948)

Previous evaluations of the barriers hindering the internal rotations in ethyl alcohol are shown to be unsatisfactory because they fail to produce agreement between molecular and calorimetric entropies over a wide enough temperature range. The principal source of difficulty is found in an inconsistency between the modified Berthelot equation of state and the calorimetric data and vapor pressures used in calculating the third law entropies. Corrections for gas imperfection should be much higher at the temperatures at which the barrier evaluations have been made, but these corrections cannot be determined

accurately with the available data. The larger entropies permit the assignment of lower and more reasonable potential barriers.

For the hydroxyl group rotation, to keep the heat capacity, and therefore the change of entropy with the temperature, within the indicated limits, the simple expression $V = V_0(1-\cos3\theta)/2$ is more suitable than more detailed potential energy functions. With a reasonable assignment of the vibrational frequencies, the sum of the barriers restricting the hydroxyl and methyl group rotations is approximately 6000 cal.

THIS study was originally undertaken to provide an illustration of the approximate method recently proposed by the author[1] for the calculation of the thermodynamic properties of an unsymmetrical internal rotation. The intention was to recalculate the entropy by this new method from the molecular properties assigned by Aston,[2] Isserow, Szasz, and Kennedy to see if the result was appreciably different and if further light might be thrown on the validity of their empirical potential energy function. Unfortunately, their result does not adequately justify their molecular properties, because the entropy calculated by their method from these properties increases too rapidly between the two temperatures which they have chosen for comparison with the calorimetric values. As a consequence, if a third comparison is made at room

temperature, a serious disagreement appears. The situation is not improved by the use of the new entropy evaluation for the hydroxyl group rotation.

The empirical potential energy function gives too much heat capacity to the internal rotations and raises the question as to how to change the barrier assignment in order to lose heat capacity without producing much change in the entropy. This can be done by going to a symmetrical barrier system of the form $V = V_0(1-\cos3\theta)/2$ to eliminate the change of "composition" with the temperature, and by raising one barrier and lowering the other.

This conclusion suggests a further examination of the properties assigned by Schumann[3] and Aston, who used the symmetrical cosine function in conjunction with barriers of 3000 and 10,000 cal. for the methyl and hydroxyl group rotations.

[1] J. O. Halford, J. Chem. Phys. **15**, 645 (1947); **16**, 410 (1948); **16**, 560 (1948).

[2] J. G. Aston, S. Isserow, G. J. Szasz, and R. M. Kennedy, J. Chem. Phys. **12**, 336 (1944).

[3] S. C. Schumann and J. G. Aston, J. Chem. Phys. **6**, 480 (1938).

Their tabulation shows a perfect fit between molecular and calorimetric entropies at 351.5°K and 403.2°K. Recalculation, however, reveals an error of 0.4 unit in the vibrational entropy at 351.5°, with the result that the use of their properties at 298.2° again produces a serious disagreement with the calorimetric value. If they had based their barrier assignment upon the third law value at 298.2°K, rather than 403.2°K, they would have obtained a barrier of 3400 cal. for the hydroxyl group rotation, with no more serious disagreements at other temperatures than those produced by their 10,000-cal. barrier. In a later paper, Aston[4] used the barriers assigned by himself and Schumann to calculate the ethyl alcohol entropy at a series of temperatures, but failed to recognize that his value at 350°K was far enough below the calorimetric one at 351.5°K to bring the barrier assignment into question.

The problem contains three unknowns: the two potential barriers and the mean value of the six rocking (δ) frequencies. In the interpretations by Aston and his collaborators, two of these were assumed or assigned in advance, and the third one was obtained by difference at one or two temperatures. It is possible to reproduce the calorimetric values at two well spaced temperatures with molecular constants, of which one has been assigned. and the other two have been evaluated from the data. The extension to an independent evaluation of the three constants by means of comparisons at three temperatures does not appear to be practical. In the present attempts to find a solution for the unknowns the methyl group barrier is assigned, and a combination of a hydroxyl group barrier with a mean δ-frequency is sought which will produce a numerical fit at 351.5°K and 403.2°K. The result is then tested at 298.2°. In general, for each assumed methyl barrier up to about 5000 cal., one numerically satisfactory combination of the other unknowns is found, but at least one of the two always has an unreasonable value. If the reasonable assumption is made that the frequency must lie below 1100 cm^{-1}, the resulting barriers are extreme. Thus, the properties $V(CH_3) = 500$, $V(OH) = 15,000$, and $\nu(\delta) = 1065$ will come close to fitting the calorimetric data

over the entire temperature range. Lower δ-frequencies require practically free rotation for the methyl group and a high frequency vibration for the hydroxyl group.

The third law values which lead to these extreme results are calculated from excellent data in the usual manner, but they do not provide a rapid enough increase in entropy with the temperature to permit the assignment of reasonable molecular properties. The assumption of a residual entropy at the absolute zero would not take care of the situation, which is concerned almost entirely with the thermal data above room temperature. Neither does the vibrational entropy appear to be at fault. The frequency assignment of Schumann and Aston, except for the missing rocking motions, is a very reasonable one which probably introduces no serious errors. It appears, then, that the source of the difficulty must be in the third law values themselves.

The several terms entering into these values are summarized in Eq. (1),

$$S_T{}^0 = \underset{298.2}{S(1)} + \int_{298.2}^{T} C \, d \ln T + L/T$$

$$+ (27/32) R p T_c{}^3/(p_c T^3) + R \ln p, \quad (1)$$

in which $S_T{}^0$ is the hypothetical perfect gas entropy at one. atmosphere, $\underset{298.2}{S(1)}$ is the entropy of the liquid obtained by Kelley,[5] C is the heat capacity of the liquid at saturation pressure by Fiock, Ginnings, and Holton,[6] L is the heat of vaporization by the same authors, and p_c and T_c are the critical constants, which appear in a term derived from the modified Berthelot equation of state for the correction for gas imperfection.

The quantities introduced into Eq. (1) are interdependent, through the Clapeyron equation, and should be checked for consistency before the results are accepted. It is found that the gas imperfections indicated by the thermal data and vapor pressures are consistently larger than those of the Berthelot equation, and that the gas imperfection correction required at the highest temperature may be as much as five times as high as the one given by the Berthelot equation.

[4] J. G. Aston, Ind. Eng. Chem. 34, 514 (1942).

[5] K. K. Kelley, J. Am. Chem. Soc. 51, 779 (1929).
[6] E. F. Fiock, D. C. Ginnings, and W. B. Holton, J. Research Nat. Bur. Stand. 6, 881 (1931).

TABLE I. The entropy of ethyl alcohol from molecular constants by the method of Aston, Isserow, Szasz, and Kennedy.

		298.2°K			351.5°K			403.2°K	
	Straight		Bent	Straight		Bent	Straight		Bent
$S(T+R)$	59.82		61.20*	61.13		62.51*	62.22		63.60*
S(vib.)		1.76			2.78			3.94	
S(CH₃)	2.79		2.18	3.09		2.53	3.34		2.83
S(OH)	1.41		0.79	1.71		1.05	1.95		1.30
S	65.78		65.93	68.71		68.87	71.45		71.67
% present	91		9	87		13	84		16
Mixing		0.60			0.77			0.87	
$S°(T)$		66.39			69.50			72.36	
$S°$(3rd law)**		67.29			69.71			72.09	

* $S(T+R)$ includes the entropy of mixing of the optical isomers.
** Gas imperfection increment by the modified Berthelot equation.

As the temperature increases, and the vapor pressure rises rapidly, the perfect gas entropy becomes increasingly uncertain. Consequently, conclusions about the molecular properties will be most reliable if they are based upon calculations at the lowest temperatures and pressures. If a mean rocking frequency is assumed, a series of combinations of methyl and hydroxyl group barriers becomes arithmetically possible at each temperature, and, in principle, an acceptable solution is a combination which is valid for two well spaced low temperatures. When the entropy at 298.2° is used in conjunction with the less accurate value at 351.5°, approximate agreement is found only for the highest estimates of the gas imperfection at the higher temperature. The sum of the two barriers is approximately 6000 cal., and the fit is about equally good for methyl barriers between 2500 and 4000 cal. The introduction of the constant probable error of ±0.30 in Kelley's value for the liquid at 298.2° into the calculation serves to make the sum uncertain by about ±1000 cal.

It is to be hoped that the situation uncovered here is peculiar to ethyl alcohol and related associated substances, and does not mean that similar reconsiderations for other cases in which the Berthelot equation of state has been used are necessary.

I. METHOD OF ASTON, ISSEROW, SZASZ, AND KENNEDY

In this method the potential energies of the internal rotations are obtained from an empirical function based upon the repulsion between hydrogen atoms. The potential energy is taken to be proportional to the inverse nth power of the distance, and the proportionality constant and the exponent n are evaluated from the potential barriers assigned to ethane and neopentane. The barrier for the methyl group is of the form $V = V_0(1 - \cos3\theta)/2$, but V_0 is a function of the angular position of the hydroxyl group. For the hydroxyl group, the potential energy has approximately the form $V = V_1(1 - \cos\theta)/2 + V_2(1 - \cos3\theta)/2$, and contains three minima and three maxima.

The system is regarded as a mixture of isomers for which the entropy of each one can be taken from the tables of Pitzer[7] and Gwinn for the symmetrical rotator. The "composition" is estimated from the free energies of the individuals, and the difference between the minima and the appropriate mixing terms are included to give the required entropy total. Reduced moments of inertia are taken directly from the paper by Aston, Isserow, Szasz, and Kennedy. The barriers and moments are summarized below:

	V(CH₃)	V(OH)
"Straight" form	1800 cal.	2375 cal.
"Bent" form	3000 cal.	4410 cal.

$$I(\text{CH}_3) = 4.83 \cdot 10^{-40} \text{ g cm}^2,$$
$$I(\text{OH}) = 1.40 \cdot 10^{-40} \text{ g cm}^2.$$

The frequency assignment is the same as that of Aston, Isserow, Szasz, and Kennedy, and is taken from Schumann and Aston, except that the average effective value of the six doubtful rocking frequencies is set at 985 cm⁻¹.

Table I contains the recalculated values required for the comparison of molecular and third law entropies at 351.5°K and 403.2°K—the

---

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

TABLE II. Thermodynamic properties of the hydroxyl group rotation in ethyl alcohol calculated by means of mean energy levels from the potential energy function of Aston, Isserow, Szasz, and Kennedy.

$T(°K)$	298.2	351.5	403.2
$-F/T$	0.83±0.03	1.12±0.03	1.39±0.03
H/T	1.60±0.02	1.84±0.01	2.05±0.01
S	2.43±0.05	2.96±0.04	3.44±0.04
C	3.12±0.07	2.96±0.08	2.67±0.07

temperatures chosen by Aston, Isserow, Szasz, and Kennedy. A further comparison at 298.2°K has been added. The table contains several small differences from the original summation by Aston and his collaborators, but the fit obtained at 351.5°K and 403.2°K is not changed in any significant way by the recalculation. The expected large discrepancy at 298.2°K is 0.90 unit, which clearly shows that the molecular properties are not satisfactory. This is also evident from the entropy change between 351.5° and 403.2°K, which is 2.86 units from the molecular properties against 2.38 from the third law values. This corresponds to a difference of nearly 4 units, or approximately 20 percent, in the mean heat capacity for this temperature range.

The method of evaluating the contribution of the rotating hydroxyl group is an unproved approximation which might lead to a serious error. As a check on this possibility, the comparison is repeated with the evaluation for the hydroxyl group carried out with the aid of mean energy levels found by the method recently proposed by the present author. This approximation is also unproved, but it should be more accurate than the earlier one in spite of the fact that its application to ethyl alcohol is a rather severe test because of the low reduced moment of inertia and the presence of shallow valleys in the potential energy curve.

II. MOLECULAR CONSTANTS FROM ASTON, ISSEROW, SZASZ, AND KENNEDY; HYDROXYL GROUP CONTRIBUTION FROM MEAN ENERGY LEVELS

The potential energy curve for the hydroxyl group rotation is replaced by a series of linked sections of cosine function, and a set of mean energy levels is found for each region of the energy—rotational coordinate surface, thus per-

mitting a direct evaluation of the partition function and its derivatives. To find the mean energy levels, a quantum number index is set up in terms of E/V_1, where V_1 is one of the potential barriers, according to the equation,

$$\Re = \sum (\rho_i/a_i)(V_i/V_1)^{\frac{1}{2}}/2. \qquad (2)$$

The index ρ is obtained from Table II of reference 1b, and the quantities V_i and a_i are taken from the text and the published potential energy curve of Aston, Isserow, Szasz, and Kennedy as follows:

	1	2	3
V	2375	815	4410
$1/a$	0.3518	0.2259	0.4222

The potential barriers, and the quantity a_3, as well as the sum $1/a_1+1/a_2$, can be taken from values given in their paper, but the individual quantities a_1 and a_2 depend upon the rotational coordinates of the lower maxima, which are not given in the text. It is accurate enough for the present purpose to estimate these coordinates from the printed potential energy curve. The reduced moment of inertia is the same as in Section I.

When values of the index $\Re$ for the mean energy levels are assigned as described in earlier papers, the following ratios E/V_1 are obtained: 0.212, 0.597, and 0.909 within the lower valley and belonging to the "straight" form; 0.864 or 0.801, two states at the same level, one for each valley corresponding to a "bent" form, with the alternatives given because the low barrier V_2 leaves the accurate position in doubt; 1.030, 1.247 (2), 1.552 (2), 1.860, 1.887, 2.180, 2.232, 2.484, 2.548, 2.787, 2.904, 3.158, 3.338, 3.586, 3.830, 4.065, 4.371, 4.595, 4.962, 5.168, vibrational and rotational states at energies above the lower potential maxima. It is interesting that for each "bent" form only one uniquely characteristic level appears.

From these mean energy ratios the thermodynamic properties of the hydroxyl group rotation are calculated at three temperatures as shown in Table II. The indicated uncertainty is solely that due to the alternative positions of the states in the shallow valleys for the "bent" forms. There is no basis for estimating other uncertainties inherent in the approximation.

Each entropy is higher by about 0.4 unit than the corresponding one obtained by the method of Aston and his collaborators. The heat capacity is in agreement at 403.2°K and is higher by 0.4 unit at 298.2°K. In Table II the entropy is higher than in Table I because here the mixing terms are automatically included, while in Table I they were listed separately.

In Table III, the entropy summations obtained with this new treatment of the hydroxyl group rotation are compared with the calorimetric values. With two potential barriers for the methyl group, according to the angular position of the hydroxyl group, there is no clear way to evaluate the contribution of the methyl group rotation. It is evident, however, from Table I, that this quantity is not sensitive to the calculated "composition." Consequently, no significant error will be made if the contribution is taken from Table I and used in the new summation.

With all three temperatures considered, the new approximation does not materially change the character of the fit shown in Table I. The situation is improved in the lower part of the temperature range but is worse at higher temperatures because of the general upward revision of the entropies from molecular constants. The heat capacity is still much too high for the rate of change of the entropy with the temperature.

A comparison of Tables I and II shows that the mean heat capacity obtained by two distinctly different approximations is very nearly the same, and is therefore probably near to the correct value for the chosen potential energy function. To obtain a better agreement with the calculated third law values it will be necessary to adopt a potential energy function which leads to lower heat capacities. The symmetrical function of the form $V = V_0(1 - \cos 3\theta)/2$, which, according to the tables of Pitzer and Gwinn, has maximum heat capacities of about 2.35, fulfills this requirement.

These considerations suggest that a description of the type originally proposed by Schumann and Aston should be more successful. Because their tabulations show agreement at 351.5°K and 403.2°K, it appears possible that their potential barriers will be satisfactory at 298.2°K.

TABLE III. The entropy of ethyl alcohol from molecular data, evaluated from the constants of Aston, Isserow, Szasz, and Kennedy with the aid of mean energy levels for the hydroxyl group rotation.

$T(°K)$	298.2	351.5	403.2
$S(T+R)$	59.82	61.13	62.22
S(vib.)	1.76	2.78	3.94
S(CH₃)	2.74	3.02	3.26
S(OH)	2.43	2.96	3.44
$S^0(T)$	66.75	69.89	72.86
S^*(3rd law)	67.26	69.71	72.09

* Gas imperfection increment by the modified Berthelot equation.

III. POTENTIAL BARRIERS ACCORDING TO SCHUMANN AND ASTON

Schumann and Aston assigned individual frequencies to the rocking motions equivalent, in effect, to a mean value of about 905 cm⁻¹. They assumed 3000 cal. for the barrier to the methyl group rotation and obtained 10,000 cal. by difference, at 403.2°K, for the hydroxyl group rotation. In Table IV the entropy calculated with their molecular constants is compared with the third law values calculated with the aid of the modified Berthelot equation.

The difference between Table IV and the original summation by Schumann and Aston is in the vibrational entropy at 351.5°K. Although the fit is somewhat better than that of Tables I and III, it is still unsatisfactory for similar reasons. The totals from molecular constants are in good agreement with the calculations of Aston.[4]

IV

A closer numerical interpretation is now sought with the type of potential energy function used by Schumann and Aston. The entire region of possible values of the three unknowns can be scanned in the manner described in the introductory section. For the first combination found in which the numerical fit is close and the mean

TABLE IV. The entropy of ethyl alcohol from the molecular constants assigned by Schumann and Aston.

$T(°K)$	298.2	351.5	403.2
$S(T+R)$	59.82	61.13	62.22
S(vib.)	2.03	3.13	4.32
S(CH₃)	2.18	2.53	2.83
S(OH)	2.45	2.60	2.75
$S^0(T)$	66.48	69.39	72.11
S^0(3rd law)**	67.26	69.71	72.09

** Gas imperfection increment by the modified Berthelot equation.

TABLE V. Molal volumes of ethyl alcohol vapor at saturation pressures (liters).

$T(°K)$	$V^0 = RT/p$	V(Berthelot)	V(thermal)	V(direct)
298.2	317.42	316.63	316.69	
313.2	146.37	145.66	144.22	
333.2	59.34	58.72	57.42	
353.2	27.14	26.59	25.79	
373.2	13.75	13.27	12.78	13.30
403.2	5.82	5.41	5.17	5.21

TABLE VI. Estimated entropy increments for gas imperfection in ethyl alcohol at saturation pressures.

$T°K$ Increments	298.2	351.5	403.2
Source of a and b:			
Critical constants	0.01	0.08	0.32
Volume at 298 and 353	0.03	0.22	0.82
Volume at 353 and 403	0.05	0.42	1.61
Minimum entropy	67.26	69.71	72.09
Maximum entropy	67.30	70.05	73.38

rocking frequency falls below 1100 cm^{-1}, the constants are $V_{CH_3} = 500$, $V_{OH} = 15,000$, and $\nu(\delta) = 1065$.

It can be concluded with confidence, if not with certainty, that the only acceptable numerical interpretations will involve properties close to those just listed. As a result, it is evident not only that the interpretation of Aston, Isserow, Szasz, and Kennedy is inadequate, but also that the hydroxyl group barrier consistent with an acceptable frequency assignment is even more extreme than the one proposed by Schumann and Aston. This barrier is now so far out of line with other barrier evaluations as to be almost certainly wrong, but the indications are that such a barrier is necessary to produce an acceptable numerical agreement with the third law values over the entire temperature range.

V. REVISION OF THE THIRD LAW ENTROPY

It is this situation which has led to an inquiry into the validity of the modified Berthelot equation of state for ethyl alcohol vapor. For this purpose, as shown in Table V, molal volumes of the vapor, calculated in several ways, are compared. The first column shows the absolute temperature, the second the perfect gas volume, the third the Berthelot volume, the fourth the volume calculated from the specific volumes obtained by Fiock, Ginnings, and Holton from the vapor pressure, the heat of vaporization, and the density of the liquid, and the fifth column gives two estimates obtained by interpolation from vapor density data found in the International Critical Tables.

The volume from the thermal data and the vapor pressures is consistent with the modified Berthelot equation only at the lowest temperature. At all other temperatures the consistent gas imperfections are appreciably larger than those given by the Berthelot equation. No

conclusion can be drawn from the last column, for which one entry checks the Berthelot equation and the other is consistent with the thermal data.

To obtain reliable gas imperfection corrections would require accurate knowledge of the volumes or vapor densities as a function of the pressure from high attenuation to the saturation pressure at each temperature. Such data are not available, and, consequently, it is not possible to calculate accurate third law entropies, corrected for gas imperfection, at the higher temperatures and pressures. It is possible, however, if the form of the equation of state is assumed, to evaluate the constants in the assumed equation and use them to make rough estimates of the corrections for gas imperfection. For this purpose, it is convenient to use the form of the modified Berthelot equation:

$$pV/RT = 1 + (p/T)(a - b/T^2). \qquad (3)$$

For this equation the gas imperfection increment is

$$S^0 - S = 2bRp/T^3. \qquad (4)$$

When the constants are evaluated from the volumes from thermal data at 353.2°K and 403.2°K, b is 4.61×10^6, and, when the temperatures used are 298.2 and 353.2°K, b is 2.35×10^6. In the ordinary form of the modified Berthelot equation b is 0.90×10^6. The corresponding estimates of the correction for gas imperfection are shown in Table VI. In addition to the above estimates a three constant equation with a term in $(p/T)(1/T)$ was fitted and tried, but it did not reproduce the volumes as well as the two constant equation based upon the volumes at 353 and 403°. The correction calculated from the three constant equation was higher at 351.5° and lower at 403.2°K.

The selection of molecular properties should be based upon the entropy at 298.2°, which is essentially independent of the gas imperfection problem. In making a barrier assignment, the minimum entropy at 298.2°K in conjunction with the maximum value at 351.5°K has been chosen. This arbitrary choice is made principally because it leads to a nearly consistent result. It is justified by the calculated volumes in Table V. The highest temperature (403.2°K) is left out of consideration.

VI. NEW APPROXIMATION TO THE MOLECULAR CONSTANTS

Except for the OH (δ) frequency, the vibrational assignment of Schumann and Aston has been adopted. If for this quantity (700 cm⁻¹) the more probable value[8] of 1100 cm⁻¹ is substituted, the mean frequency is close to that of Aston, Isserow, Szasz, and Kennedy at 985 cm⁻¹. Vibrational entropy contributions are therefore taken from Tables I and III. For the simple cosine potential function, with equal stability for the straight and bent forms, the barriers at 298.2°K and 351.5°K may be found as summarized in Table VII, which shows for each temperature the selected total entropy and a series of consistent barrier combinations.

The combinations shown in Table VII are not in exact agreement at the two temperatures. To produce a closer agreement would require a set of properties in the direction of those listed in Section IV, but a more detailed treatment along these lines would not be justified because of the uncertainty in the gas imperfection correction at the higher temperature. It can be concluded that a fit at 298.2°K is not inconsistent with the data at 351.5°K, and that for an assumed mean

---

[8] J. O. Halford, L. C. Anderson, and G. H. Kissin, J. Chem. Phys. **5**, 927 (1937).

TABLE VII. Potential barriers in ethyl alcohol.

T(°K)	298.2		351.5	
S^0(total)	67.26		70.05	
$\nu(\delta)$	985 cm⁻¹		985 cm⁻¹	
Barriers	$V(CH_3)$	$V(OH)$	$V(CH_3)$	$V(OH)$
	2000	4200	2000	4800
	2500	3200	2500	3800
	3000	2700	3000	3100
	3500	2200	3500	2600
	4000	1800	4000	2200

δ-frequency of 985 cm⁻¹ the sum of the methyl and hydroxyl group barriers is about 6000 cal.

The uncertainty of ±0.3 in Kelley's calorimetric entropy of the liquid at 298.2°K must be applied to all the entropies in exactly the same manner, and has no effect upon the difference between the entropies at two temperatures. Its application to the values in Table VII will make the barrier sum for the two rotations uncertain by about ±1000 cal., and will have little effect upon the relative value of this sum at the two temperatures.

A further interesting result of the new approximations to the third law entropy is that the empirical potential energy function of Aston, Isserow, Szasz, and Kennedy is not eliminated from consideration. It is still possible that a mean δ-frequency and new methyl group barriers could be found which would lead to satisfactory agreement with the new entropy estimates.

The barrier combinations presented in Table VII are proposed only as a set of tentative solutions to the problem. They should be regarded as subject to revision whenever more extensive and accurate vapor densities are made available to permit better evaluations of the hypothetical perfect gas entropy. If, at the same time, the results can be made consistent with accurate vapor heat capacities over an extended temperature range, it will become possible to assign reliable molecular constants.