of the melting point was used, as the heat of fusion has been corrected for the effect of premelting. Thus very little uncertainty is introduced in the calculation of the entropy by the premelting effect.

The expression, $\Delta S = R(27T_c^3P/32T^3P_c)$, obtained by using Berthelot's equation in connection with the thermodynamic equation $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$, was used to correct the entropy for gas imperfection at the boiling point. The critical pressure and temperature were taken as $P_c = 48.8$ atm and $T_c = 305.2$°K.[14]

The discussion of Kemp and Pitzer in the following paper shows that it is correct to use the third law value of the entropy of ethane in thermodynamic calculations.

Summary

The heat capacity of solid and liquid ethane has been measured from 15°K. to the boiling point.

The melting point of ethane has been determined to be 89.87 ± 0.1°K. The heat of fusion of ethane has been found to be 682.9 cal./mole.

The heat of vaporization of ethane at the boiling point has been found to be 3514 cal./mole.

The entropy of ethane gas at the boiling point calculated from the above data is 49.54 e.u. The entropy at 298.1°K. is 54.85 e.u.

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[14] Pickering, *J. Phys. Chem.*, **28**, 97 (1924).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Entropy of Ethane and the Third Law of Thermodynamics. Hindered Rotation of Methyl Groups

BY J. D. KEMP AND KENNETH S. PITZER[1]

Since the development of methods of calculating entropy from spectroscopic and molecular structure data, it has become possible to investigate the practical applicability of the third law of thermodynamics in a larger number of cases than previously. For many molecules, there is no question about the correctness of directly applying the third law to low temperature heat capacity measurements in obtaining entropies to be used in thermodynamic calculations. However, in certain cases, false equilibrium, encountered in obtaining low temperature calorimetric measurements, has complicated the use of the third law. The reasons for the complications in the several known cases are understood, and the immediate problem is to gather more information as to which molecules will be affected in order to increase the general usefulness of the third law.

The discrepancy found in hydrogen was first explained correctly by Giauque and Johnston,[2] who suggested the possibility of similar discrepancies in other molecules containing symmetrically placed hydrogens. Later investigations of the entropies of ammonia,[3] hydrogen sulfide[4] and methane[5] have shown that there is no persistence of rotation in the crystal lattices of these molecules which contain symmetrically placed hydrogens. A discrepancy has been found to exist in the case of water, but it has been explained by Pauling[6] as due to the formation of hydrogen bonds in the crystal. In all of these cases, there is no reason to doubt that the calculation of the entropies from molecular structure data is correct.

As attempts are made to deal with larger and more complicated molecules, it becomes more difficult to obtain sufficient molecular data to make even approximately correct calculations of thermodynamic quantities. An increased knowledge as to which molecules the third law may be applied unambiguously will thus be very valuable.

It is of interest therefore to consider the correlation between the third law value of the entropy of ethane obtained by Witt and Kemp[7] and the various possible values of the entropy which may be calculated assuming different molecular models.

In this paper, a comparison of the third law value for the entropy of ethane with one derived

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[1] Shell Research Fellow, academic year 1936–1937.

[2] Giauque and Johnston, THIS JOURNAL, **50**, 3221 (1928). See also Giauque, *ibid.*, **52**, 4816 (1930).

[3] Overstreet and Giauque, *ibid.*, **59**, 254 (1937).

[4] Giauque and Blue, *ibid.*, **58**, 831 (1936).

[5] Giauque, Blue and Overstreet, *Phys. Rev.*, **38**, 196 (1931).

[6] Pauling, THIS JOURNAL, **57**, 2680 (1935).

[7] Witt and Kemp, *ibid.*, **59**, 273 (1937).

from reliable data on the heat and free energy of hydrogenation of ethylene will be found to prove definitely that no false equilibrium exists in ethane. This, of course, means that it is correct to use the third law value in thermodynamic calculations.

In order to make a statistical mechanical calculation of the entropy of ethane, it will be necessary to consider the energy levels of the restricted rotator.

The Energy Levels of Ethane.—Since the spectroscopic interpretation of ethane is uncertain, it was necessary to make certain assumptions with regard to the potential barrier hindering the internal rotation of the methyl groups. A potential function, $^1/_2\ V_0\ (1 - \cos 3\phi)$, which gives three humps of height V_0, was assumed to modify the relative rotation of the methyl groups. Although this form of the potential function is entirely arbitrary, it is a reasonable one and is the only form for which solutions of the wave equation are available.

The quantum mechanical problem as set up in the preceding paragraph has been solved by Nielsen[8] and by Teller and Weigert,[9] who found that the wave equation separates into two parts. One of these is the usual equation for the rotation of a symmetric top with energies

$$W_{J,K} = \left(\frac{h^2}{8\pi^2}\right)\left[\frac{J(J+1)}{I_x} + K^2\left(\frac{1}{I_z} - \frac{1}{I_x}\right)\right]$$

while the second may be transformed easily into Mathieu's differential equation. Of the acceptable solutions for the latter, some are the ordinary Mathieu functions for which the characteristic values and thereby the energies are given by Ince.[10] The energies for the remaining solutions were obtained easily with sufficient accuracy for the present purpose by approximate means.

Nuclear spin was neglected in all calculations, and the molecules were assumed to be equally divided between states with odd and even values of the quantum number K. A symmetry number of 18 was used.

For vibrational frequencies we have used the assignment of Teller and Topley[11] except for one frequency $^2\nu_\alpha{}^M$ which they fixed only from specific heat data assuming free internal rotation. We have fixed $^2\nu_\alpha{}^M$ by the same method, obtaining different values depending on the restricting potential, V_0. The order of magnitude has been restricted to about 1000 cm.$^{-1}$ as indicated by the analogous frequencies in ethylene.

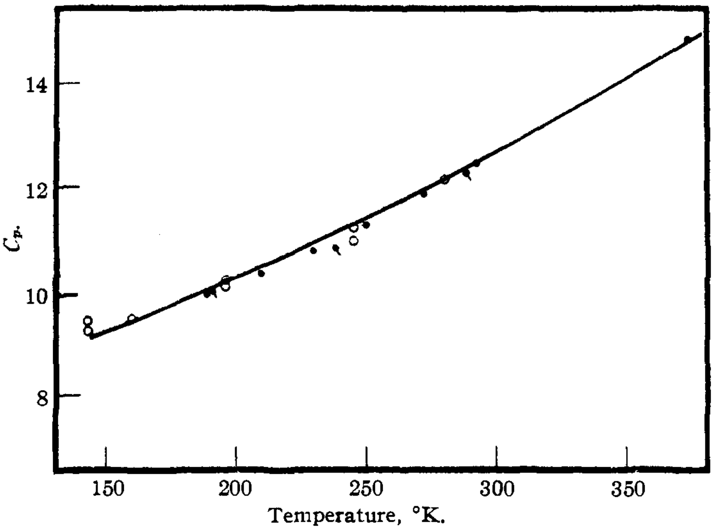

Fig. 1.—Heat capacity of ethane gas in calories per mole per degree: ● Eucken and Parts; ♦ Heuse; ○ Eucken and Weigert; the smooth curve represents the theoretical calculation.

It has been assumed that each methyl group has the same configuration as in methane and that the carbon–carbon distance is 1.52Å. One thus obtains $I_z = 40.1 \times 10^{-40}$ g. cm.^{2} and $I_{CH_3} = I_x/2 = 5.4 \times 10^{-40}$ g. cm.^{2}.

The Heat Capacity of Ethane Gas.—The heat capacity of ethane gas has been measured recently by Eucken and Parts[12] and by Eucken and Weigert.[13] Their results agree very well with the earlier measurements of Heuse.[14] Eucken and Parts, whose measurements extend down to the boiling point, find that their data may be fitted either by the assumption of free rotation with the unknown frequency $^2\nu_\alpha{}^M = 712$ cm.$^{-1}$ or with a torsional vibration of frequency 298 cm.$^{-1}$ and $^2\nu_\alpha{}^M = 920$ cm.$^{-1}$. Eucken and Weigert compared the thermal conductivity of ethane and ethylene and, assuming the same accommodation coefficient for both, calculated the heat capacity for ethane down to 140°K. Using the calculations of Teller and Weigert,[9] they found

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(8) Nielsen, *Phys. Rev.*, **40**, 445 (1932).

(9) Teller and Weigert, *Nachr. Ges. Wiss. Göttingen. Math. physik. Klasse*, 218 (1933).

(10) Ince, *Proc. Roy. Soc. Edinburgh*, **46**, 316 (1925–26).

(11) Teller and Topley, *J. Chem. Soc.*, 876 (1935).

(12) Eucken and Parts, *Z. physik. Chem.*, **B20**, 184 (1933).

(13) Eucken and Weigert, *ibid.*, **B23**, 265 (1933).

(14) Heuse, *Ann. Physik*, **59**, 86 (1919).

that the best fit is obtained with a potential barrier of 315 cal.

We have also calculated the heat capacity of ethane in the range 140 to 400°K. and find that in addition to the combination $V_0 = 315$ cal., ${}^2\nu_\alpha{}^M = 750$ cm.$^{-1}$,[15] a fit may also be obtained for V_0 near 3150 cal. and ${}^2\nu_\alpha{}^M = 1160$ cm.$^{-1}$ as is seen in Fig. 1. The latter is, of course, essentially the second alternative of Eucken and Parts, but is based on a restricted rotator model rather than an oscillator. Since no other reasonable combinations of V_0 and ${}^2\nu_\alpha{}^M$ even approximate the specific heat curve, we need consider only these two in later calculations.

The Entropy of Ethane.—We have calculated the entropy of ethane from molecular structure data using the familiar expression for the rotational entropy of a rigid symmetric top and adding to it the entropy due to the hindered internal rotation of the methyl groups and the ordinary vibrational and translational contributions. A symmetry number of 18 was used.

It has been shown that in order to explain the observed heat capacity of ethane gas, a potential barrier of about 3150 cal. or one near 315 cal. must be assumed. Table I gives a comparison of the entropy of ethane, calculated from molecular structure data, assuming various potential barriers, with the calorimetric entropy obtained by Witt and Kemp.[7]

TABLE I

THE ENTROPY OF ETHANE CALCULATED FROM MOLECULAR STRUCTURE DATA COMPARED WITH THE ENTROPY OBTAINED CALORIMETRICALLY FROM THE THIRD LAW[16]

T, °K.	Potential barrier V_0, cal./mole	Statistical mechanical entropy, cal./deg./mole	Third law entropy, (exptl.) cal./deg./mole
184.1	0	51.09	
184.1	315	50.98	
184.1	3150	49.30	49.54 ± 0.15
298.1	0	56.36	
298.1	315	56.26	
298.1	3150	54.62	54.85 ± 0.2

It may be seen from Table I that there is agreement between the calorimetric and calculated entropies, within the limits of uncertainty, when a potential barrier of 3150 cal. is assumed.

A further comparison may be obtained between the third law entropy and entropies calculated from the heat and free energy of hydrogenation of ethylene. The heat of hydrogenation of ethylene has been measured accurately by Kistiakowsky and co-workers.[17] A preliminary value calculated from heats of combustion by Rossini[18] is in very good agreement with the direct determination of Kistiakowsky. The equilibrium data have been summarized by Teller and Topley[11] and the value they select as the most reliable (log $K_p = 1.613$ at 863°K.) was used in our calculations. The entropy change in the reaction $C_2H_4 + H_2 = C_2H_6$ may then be obtained at 355°K., provided that the heat capacities of the various gases are known from 355 to 863°K. It is given by the expression

$$\Delta S^\circ_{355} = \frac{\Delta H^\circ_{355} - \Delta F^\circ_{863}}{863} - \int_{355}^{863} \Delta C_p \left(\frac{1}{T} - \frac{1}{863}\right) \mathrm{d}T$$

Since no experimental data are available on the heat capacity of ethane above 400°K., it was necessary to calculate that quantity, using the various molecular models found to give satisfactory heat capacities below 400°K. Fortunately, as can be seen in the expression above, the effect of the heat capacity is small, particularly at the higher temperatures. In calculating the entropy of ethane from the heat and free energy of the hydrogenation of ethylene, the assignment of frequencies of ethylene given by Bonner[19] and the moments of inertia given by Badger[20] were used. The entropy of ethylene at 355°K. obtained by using these values is 54.43 e.u. The thermodynamic constants for hydrogen were taken from the tables given by Davis and Johnston.[21] The values of the entropy of ethane so obtained depend chiefly upon the ΔF and ΔH of hydrogenation of ethylene and only to a small extent upon the assumption made regarding the potential barrier.

Table II gives a comparison between the third law value of the entropy of ethane and the value obtained from the ΔH and ΔF of hydrogenation of ethylene. For further comparison, values of the entropy obtained from a statistical mechanical calculation are also included.

The comparison of the entropies obtained from ΔF and ΔH with the entropy obtained from the third law shows that, regardless of the

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[15] The difference between Teller and Topley's assignment of the remaining vibration frequencies and that of Eucken and co-workers leads to the difference in ${}^2\nu_\alpha{}^M$.

[16] The values in this table differ slightly from the preliminary survey by Kemp and Pitzer, *J. Chem. Phys.*, **4**, 749 (1936).

[17] Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan, THIS JOURNAL, **57**, 65 (1935). See also Kistiakowsky, Ruhoff, Smith and Vaughan, *ibid.*, **58**, 137 (1936).

[18] Kassel, *J. Chem. Phys.*, **4**, 435 (1936). A personal communication from F. D. Rossini.

[19] Bonner, THIS JOURNAL, **58**, 34 (1936).

[20] Badger, *Phys. Rev.*, **45**, 648 (1934).

[21] Davis and Johnston, THIS JOURNAL, **56**, 1045 (1934).

TABLE II

A SUMMARY OF THE ENTROPY OF ETHANE AT 355 °K.

Potential barrier, V_0, cal./mole	0	315	3150
S_{355} from molecular structure data, cal./deg./mole	58.74	58.64	57.06
S_{355} from ΔH°_{355} and ΔF°_{863}, cal./deg./mole (exptl.)	56.61	56.61	57.34
S_{355} from the third law, cal./deg./mole (exptl.)		57.20 ± 0.2	

height of the potential barrier assumed, no residual entropy, such as would be left if there were false equilibrium in the crystal at very low temperatures, remains after the ordinary extrapolation of the heat capacity data to absolute zero. Indeed, for barriers lower than 3150 cal., the impossible situation of obtaining too much entropy from the third law arises. As the correctness of the third law value for the entropy of ethane is now established, the values calculated assuming potential barriers of 315 cal. or less must be in error. It is strong evidence for the existence of a potential barrier of the order of 3000 cal. per mole, which has heretofore been considered improbable.[10,22]

Unfortunately, numerous statistical mechanical calculations have been published with respect to molecules allowing similar rotations for which no potential barrier was assumed. The results for ethane suggest that the entropies so calculated may be in error by as much as 1.5 cal./deg./mole for each internal rotation.[23] Several authors have obtained such disagreements. Kassel[18] was unable to correlate the ΔF and ΔH for the hydrogenation of some higher olefins, finding entropy differences of from 2 to 3 cal./mole/deg. Since one single bond has been formed and the restricting potentials for others probably have been changed by the reaction, the apparent disagreement may well be due to the assumption of completely free rotation in the calculations. Aston and Messerly[24] in the case of tetramethylmethane obtained a disagreement of about 8 cal./deg./mole between the third law entropy and a calculated value of the entropy, while Kassel[25] obtained a similar difference of 3.76 cal./deg./mole for *n*-butane. They suggested that the calorimetric rather than the calculated entropies (assuming free rotation) are in error and ascribe the disagreement to a lack of equilibrium in the crystal at very low temperatures. The work on ethane indicates that this view is probably erroneous and that the entropies of simple hydrocarbons obtained from the application of the third law of thermodynamics to calorimetric data extending to hydrogen temperatures are the correct entropies to use in thermodynamic calculations. As we now know that the calorimetric entropies of ammonia, hydrogen sulfide, methane and ethane are the correct ones to use in thermodynamic calculations, an even more general statement may be made. That is: very probably no molecules other than hydrogen and deuterium retain any entropy due to the persistence of rotation in the crystal below 10°K.

Summary

The entropy of ethane has been calculated from the heat and free energy of hydrogenation of ethylene considering ethane as a restricted internal rotator. A comparison of the values so obtained, with the entropy obtained from calorimetric measurements extending to low temperatures by use of the third law of thermodynamics, proves the correctness of the third law value.

Very strong evidence has been presented for the existence of a potential barrier of about 3150 cal./mole restricting the internal rotation of the methyl groups in ethane by the comparison of the experimental values of the entropy of ethane with values obtained from statistical mechanical calculations. It is believed that the discrepancies noted by some authors in the cases of other hydrocarbons are due to the assumption of incorrect molecular models involving free internal rotation of the methyl groups. From a knowledge of the correctness of the third law entropies in the cases of ammonia, hydrogen sulfide, methane and ethane, it may be stated that very probably no molecules other than deuterium and hydrogen will have any residual entropy due to the persistence of rotation in the crystal at temperatures below 10°K.

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[22] (a) Eyring, THIS JOURNAL, **54**, 3191 (1932).

[23] Where six rather than three potential humps would be present it is quite possible that free rotation may be good approximation.

[24] Aston and Messerly, *J. Chem. Phys.*, **4**, 391 (1936).

[25] Kassel, *ibid.*, **4**, 276 (1936).