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An attempt has been made to correlate several data on this system by a statistical calculation of the equilibrium constants in the temperature range of 400 to 700°C. The data are in good agreement but the calculated values of the K's are smaller than the experimental by a factor of two. It is thought that the principal reason for this discrepancy lies in the calculation of the entropy of free rotation in ethane, although other factors may contribute.

THERE are in existence two fairly recent determinations of the equilibrium constants of the ethane-ethylene-hydrogen system. The first is that of Pease and Durgan,[1] who, using a static system and approaching the equilibrium from both sides, found K's at 600°, 650° and 700°C. The other, which is the work of Frey and Huppke,[2] was carried out in a flow system by catalytic dehydrogenation of ethane at one atmosphere pressure in the temperature range from 400–500°C. The results of these two researches are in good agreement.[3] The purpose of this paper is to attempt to correlate by means of statistical calculations the figures obtained from these experiments with the recent accurate measurement of the heat of hydrogenation of ethylene at 82°C as determined by Kistiakowsky et al.[3]

For the present calculation the values of the entropy (excluding nuclear spin) and of the heat content of hydrogen at the desired temperatures have been taken by direct graphical interpolation of the data of Davis and Johnston.[4]

There are in the literature several recent discussions of the computation of the entropy of polyatomic molecules such as ethylene and ethane.[5] It suffices for the present paper to give briefly the specific values and assumptions actually used.

The calculation of the translational entropies of ethane and ethylene requires no discussion; the values obtained are given in Table II. The estimation of the magnitude of the vibrational entropies is, however, a somewhat more difficult matter. Neither of these molecules has been completely analyzed. In the case of ethylene Kassel[4a] has lumped Mecke's[6] eleven frequencies in the following manner: 950 cm⁻¹ (triple); 1100 (single); 1400 (double); 1620 (single); and 3090 (quadruple). Kassel assumes for the frequency of the torsion about the double bond the value of 950 cm⁻¹. Penney,[7] however, gives 750 cm⁻¹ (a figure quoted to him verbally by Sutherland). In view of the uncertainty of this frequency it was decided to select 790 cm⁻¹ which gives the best agreement with the accurate experimental values of Cp for ethylene as determined by Eucken and Parts,[8] as shown by Table Ia. It is seen that the figures deviate but slightly and in a random manner over quite a

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[1] Pease and Durgan, J. Am. Chem. Soc. **50**, 2715 (1928).
[2] Frey and Huppke, Ind. Eng. Chem. **25**, 54 (1933).
[3] Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan, J. Am. Chem. Soc. **57**, 65 (1935).
[4] Davis and Johnston, J. Am. Chem. Soc. **56**, 1045 (1934).
[5] See for example (a) Kassel, J. Am. Chem. Soc. **55**, 1361 (1933); (b) Mayer, Brunauer and Mayer, J. Am. Chem. Soc. **55**, 37 (1933); (c) Halford, J. Chem. Phys. **2**, 694 (1934). This latter paper gives the formulae quite explicitly.

TABLE I.

	(a) Ethylene: vibrational heat capacity (12 degrees of freedom)						
T	143	160	196	245	280	373.5	464
$\Sigma C_{vib.}$(calc.)	0.092	0.183	0.540	1.347	2.078	4.164	5.914
$C_{vib.}$(E. & P.)*	0.08	0.21	0.53	1.30	2.03	3.96	6.20
Deviation	+0.01	−0.03	+0.01	+0.05	+0.05	+0.20	−0.29

* $8R/2$ has been deducted from the Cp values of Eucken and Parts.

	(b) Ethane: vibrational heat capacity (17 degrees of freedom)					
T	143	160	196	245	280	373.5
$\Sigma C_{vib.}$(calc.)	0.242	0.434	1.043	2.224	3.211	6.068
$C_{vib.}$(E. & P.)*	0.32	0.50	1.16	2.13	3.18	5.89
Deviation	−0.08	−0.07	−0.12	+0.09	+.03	+0.18

* $9R/2$ has been deducted from the Cp values of Eucken and Parts.

[6] Mecke, Zeits. f. physik. Chemie **B17**, 1 (1932).
[7] Penney, Proc. Roy. Soc. **A144**, 166 (1934).
[8] Eucken and Parts, Zeits. f. physik. Chemie **B20**, 190 (1933).

TABLE II.

T	298°	355	673	773	873	973
(a) Entropy of ethylene						
Translational	35.968	36.833	40.018	40.706	41.307	41.848
Vibrational	0.671	1.233	5.761	7.305	8.831	10.320
Rotational	15.909	16.439	18.349	18.759	19.119	19.439
Total	52.548	54.505	64.128	66.770	69.257	71.607
(b) Entropy of ethane						
Translational	36.175	37.040	40.225	40.913	41.514	42.055
Vibrational	1.149	1.950	8.106	10.220	12.320	14.390
Rotational	18.903	19.602	22.146	22.694	23.180	23.611
Total	56.227	58.592	70.477	73.827	77.014	80.056
(c) Entropy of hydrogen						
Total	31.230	32.420	36.905	37.873	38.473	39.517
(d)						
ΔS for $H_2+C_2H_4 \rightarrow C_2H_6$	−27.551	−28.333	−30.556	−30.816	−30.986	−31.068
(e) Heat content						
H_2	2023	2417	4642	5348	6057	6775
C_2H_4	2534	3171	8062	9976	12,025	14,197
C_2H_6	2939	3713	9768	12,195	14,822	17,625
(f) ΔH for $C_2H_4+H_2 \rightarrow C_2H_6$	−32,567	−32,824 ±50	−33,885	−34,078	−34,209	−34,296
(g) ΔF for $C_2H_4+H_2 \rightarrow C_2H_6$	−24,358	−22,767	−13,322	−10,255	−7157	−4069
(h) K calc.	$7.08(10^{19})$	$1.01(10^{14})$	$2.10(10^4)$	$7.89(10^2)$	61.7	8.19
(i) $1/K$ (calc.)*			0.000048	0.0013	0.016	0.122
(j) K of $C_2H_6 \rightarrow C_2H_4+H_2$ (obs.)			0.00015[2]	0.0032[2]	0.031[1]	0.20[1]
(k) K of $C_2H_6 \rightarrow C_2H_4+H_2$ (recalc.)†			0.000083	0.0024	0.031	0.17

* or K for the reaction written $C_2H_6 \rightarrow C_2H_4+H_2$.
† as done by Kistiakowsky *et al.*; see reference 3.

large temperature range. Ethane has been treated in similar fashion using the assignments of Eucken and Parts; namely, 712 cm^{-1} (double); 826 (double); 990 (single); 1460 double; 1465 (double); 1499 (double); and 2975 (sixfold); a total of seventeen vibrational degrees of freedom. The results obtained with these assignments are given in Table Ib. Use of these two sets of frequencies gives the values for $S_{vib.}$ to be found in Table II. The entropy of nuclear spin has been omitted in all calculations.

After a consideration of the various interatomic distances given by different authors, the following values were chosen for the calculation of the moments of inertia of the two hydrocarbons: $C-C$, 1.53A; $C=C$, 1.36; $C-H$, 1.08. The tetrahedral angle was assumed in the case of ethane, and the angle between the two carbon-hydrogen linkages on either end of the ethylene molecule was taken to be 110 degrees. This latter value is probably incorrect, but is sufficiently accurate for the present work. The moments of inertia found for ethylene were 5.205 (10^{-40}), 29.53 (10^{-40}) and 34.71 (10^{-40}). Those used in the case of ethane were 10.27 (10^{-40}) and 35.98 (10^{-40}) (double). A symmetry number of

four was used in obtaining the values for $S_{rot.}$ of ethylene as given in Table IIa.

The free rotation of the two methyl groups in ethane complicates the statistical computation of its entropy of rotation. Eucken and Weigert[9] found their values of Cp for ethane to be in accord with the quantum-mechanical treatment of this problem as analyzed by Teller and Weigert.[10] The latter showed that this contribution to the rotational heat capacity becomes classical at 298°K, going through a slight "hump" in approaching this temperature. If one calculates the rotational entropy assuming free rotation to lowest temperatures (using two pairs of moments of inertia; namely, 5.14 (10^{-40}) and 35.98 (10^{-40}), and a symmetry number of 18), he obtains the data given in Table IIb.

That the assumption of free rotation to lowest temperatures is permissible may be shown in the following manner. If C (of internal rotation) as obtained from the paper of Teller and Weigert is plotted against ln T, graphical integration

[9] Eucken and Weigert, Zeits. f. physik. Chemie **B24**, 277 (1934).
[10] Teller and Weigert, Nachr. d. Ges. d. Wiss. zu Göttingen, 218 (1933).

gives the contribution to the rotational entropy at any temperature. This area was found to correspond to 7.241 e. u. at 298°K. The classical calculation of this portion of $S_{rot.}$ (setting $\sigma = 9$) gives the value of 7.160 e. u. These values are in reasonable agreement.

The heat contents of Table IIc were arrived at by use of the vibrational frequencies already mentioned, together with the assumption that rotation has already become classical at these temperatures. The value of ΔH for the reaction

$$H_2 + C_2H_4 \rightarrow C_2H_6$$
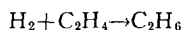
on which the final data are based is $-32,824 \pm 50$ cal. at 355°K.[3] The summary of the calculations is shown in the last few lines of the listing.

It is immediately apparent that the three researches are essentially in agreement. However, the calculated values of $1/K$ are fairly uniformly one-half as large as the experimental figures for the equilibrium constant. This discrepancy presents a real problem. To decrease the $K_{calc.}$ (line h) by a factor of two would necessitate a change of ΔH beyond probability. At 298°K such an alteration would involve a change in ΔS of 1.376 e. u., and so would decrease the original difference in the entropy of ethane and ethylene from 3.7 to 2.3 e. u. This latter figure agrees well with the empirical rule of Parks and Huffman[11] that the entropy difference between a saturated hydrocarbon and its corresponding olefine is 2.7 e. u. at 298°K.

An attempt to localize this difference of 1.38 e. u. in some part of the entropy calculation results in the elimination of $S_{trans.}$. It likewise seems improbable that there is any large error in the estimation of $S_{vib.}$ for the two hydrocarbons; indeed the contributions from this type of motion are small at 298°K and are undoubtedly of correct relative magnitudes. It is possible, however, that at higher temperatures this calculation

may be in error. However, the inconsistency may more probably be attributed to $S_{rot.}$. The configuration given ethylene in these calculations is certainly open to question. In fact Dieke and Kistiakowsky[12] from an analysis of band spectra of formaldehyde found 2.941 (10^{-40}) as the moment of inertia of the top. The value 2 $(2.941)10^{-40}$ is larger than the one here calculated, $(5.205)10^{-40}$, as might be expected because of the attraction of the oxygen for the two hydrogen atoms. If one still uses 1.08A for the $C-H$ distance, this experimental moment corresponds to an angle of 121° between the $C-H$ bonds. But in the case of ethylene this spreading effect should be less, and hence the value 5.88 (10^{-40}) might be taken as an upper limit. In fact Badger[13] has determined the moments of inertia of ethylene from spectroscopic data, and finds for the three moments the values of 33.2, 27.5 and 5.7 (10^{-40}). These give a product of 5200 (10^{-120}), while the value actually used was 5330 (10^{-120}). This discrepancy is quite negligible.

The model of ethane is, perhaps, less doubtful; the interatomic distances are quite well established, and the tetrahedral angle must be a good approximation. The former factor should be sufficiently accurate to allow no errors greater than a few tenths of an entropy unit, and regarding the latter, elimination of the discrepancy would require the assignment of fantastic values. Were the entire fault in the moments of inertia, the product of the four principal moments (assuming classical free rotation) would have to be reduced from 34,210 (10^{-160}) to 24,660 (10^{-160}); this is obviously too radical.

Thus, although other factors may be contributory, most of the uncertainty would appear to lie in the treatment of the problem of the free rotation of the two methyl groups of ethane.

[11] Parks and Huffman, *Free Energies of Some Organic Compounds*, Chem. Cat. Co., N. Y., 1932, p. 79.

[12] Dieke and Kistiakowsky, Phys. Rev. **45**, 4 (1934).
[13] Badger, Phys. Rev. **45**, 648 (1934).