

**The Limiting High Temperature Rotational Partition Function of Nonrigid Molecules IV. Ethylene, Propylene, 1Butene, Cis and Trans 2Butene, Isobutene, Trimethylethylene, Tetramethylethylene and Butadiene V. Equilibrium Constants for Reactions of Paraffins, Olefins and Hydrogen**

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## The Limiting High Temperature Rotational Partition Function of Nonrigid Molecules

### IV. Ethylene, Propylene, 1-Butene, *Cis* and *Trans* 2-Butene, Isobutene, Trimethylethylene, Tetramethylethylene and Butadiene

#### V. Equilibrium Constants for Reactions of Paraffins, Olefins and Hydrogen<sup>1</sup>

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IV. Methods previously developed by Eidinoff and Aston and by the writer are used to calculate the limiting high temperature rotational partition function and hence the translation-rotation entropy for the substances named in the title. The results are compared with third law values wherever possible. The agreement is fairly good in most cases, but the calculated values probably yield more accurate structural entropy differences. V. A consistent set of frequencies for methane, ethane, propane and butane is selected, and the corresponding vibrational contributions to  $-F/T$  and  $H/T$  are tabulated. Equilibrium constants for the dehydrogenation reactions of ethane, propane,

normal and isobutane are calculated and compared with experimental values. Systematic deviations are found which would be removed if the experimental equilibrium constants were reduced by a factor of 3, if the experimental hydrogenation heats were reduced by 1500 cal., or if the vibrational contribution to  $-F/T$  at reaction temperatures were 2.5 cal./deg. greater for an olefin (excluding the torsional frequency) than for the corresponding paraffin. Approximate equilibrium constants are calculated for the reactions  $2C_2H_4 = C_4H_8$ ,  $CH_4 + C_2H_4 = C_3H_8$ ,  $CH_4 + C_3H_6 = C_4H_{10}$  and  $C_2H_6 + C_2H_4 = C_4H_{10}$ .

### IV. ETHYLENE, PROPYLENE, 1-BUTENE, *Cis* AND *Trans* 2-BUTENES, ISOBUTENE, TRIMETHYLETHYLENE, TETRAMETHYLETHYLENE AND BUTADIENE

THE method used here to calculate the limiting high temperature rotational partition function of nonrigid molecules has been described in a previous paper.<sup>3</sup> It is sufficient to repeat here that the calculations are based on a model in which all bond distances and bond angles are constant, the lack of rigidity being due only to rotations about single bonds. It is assumed that there is no potential energy associated with these rotations.

As was pointed out in the preceding article, the methyl derivatives of ethylene belong to the class of pseudo-rigid molecules and may be treated by the simplified method developed for that class. The C—C distance is taken as  $1.53 \times 10^{-8}$  cm, C=C as  $1.36 \times 10^{-8}$  cm, C—H as  $1.11 \times 10^{-8}$  cm. It is assumed that the angle

between the two single bonds of an ethylene carbon atom is the normal tetrahedral angle,  $\cos^{-1}(-\frac{1}{3})$ . The reduced moments and translation-rotation entropies are given in Table I.

TABLE I. *Reduced moments and translation-rotation entropies of ethylene derivatives.*

SUBSTANCE	REDUCED MOMENTS $\times 10^{40}$			$S_{t+r}$	$S_{t+r, 298}$
Ethylene	35.380	29.916	5.464	$6.634 + 4R \log T$	51.915
Propylene	106.67	92.780	13.890	$11.725 + 9R/2 \log T$	62.666
<i>Cis</i> 2-Butene	204.94	154.22	50.719	$11.624 + 5R \log T$	68.225
<i>Trans</i> 2-butene	246.41	231.19	15.217	$11.013 + 5R \log T$	67.614
Isobutene	185.19	93.004	92.185	$11.614 + 5R \log T$	68.215
Trimethylethylene	331.39	238.47	92.918	$13.158 + 11R/2 \log T$	75.419
Tetramethylethylene	457.43	278.53	178.91	$10.050 + 6R \log T$	77.971

The calculation for the completely nonrigid molecule 1-butene is of course very much more difficult, but quite straightforward. The *XY* plane is taken parallel to the plane of the parent ethylene molecule, and the *X* axis parallel to the central C—C bond. The angle  $\alpha$  measures the rotation of the  $C_2H_5$  group,  $\alpha=0$  being the position in which all four carbon atoms are in a plane, with the two end atoms on the same side of the two central ones. The angle  $\beta$  measures the rotation of the terminal methyl group. The masses of C and H are  $M$  and  $m$ ; the C—C, C=C and C—H distances are  $D$ ,  $D'$  and  $d$ .

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<sup>3</sup> Kassel, J. Chem. Phys. 4, 276–282 (1936).

The usual parameter  $\mu$  associated with the differing centers of gravity for carbon and hydrogen is in this case

$$\mu = m/(6M + 12m).$$

It is convenient to define a set of secondary parameters

$$\begin{aligned} P &= (2/3 + 8\mu^2)MD^2, & Q &= (1/2 + 8\mu^2)MD^2, \\ R &= (3^{1/2}/36)MDD', & T &= (1/4)MD'^2, \\ p &= (16/9 - 8\mu/3 + 16\mu^2)mD^2, & q &= (23/18 - 8\mu/3 + 16\mu^2)mD^2, \\ r &= (3^{1/2}/6)mDD', & s &= (4/9)mDd, \\ t &= (1/2)mD'^2, & u &= (4/9)3^{1/2}mD'd, \\ v &= (4/9)md^2, \end{aligned}$$

and a further set of tertiary parameters

$$\begin{aligned} A &= P + p + 4s + 22v/3, \\ B &= 4R + 2r, \\ C &= Q + q + 2R + r + s + v/3, \\ D &= 2T + 2t + 2u + 4v, \\ E &= 7R + 3r + T + t + u - v, \\ F &= 7P/2 + 2p - Q/2 + q + 14R + 6r \\ &\quad + 9s + T + t + u + 8v, \\ G &= P + p + 4s + 4v/3. \end{aligned}$$

It is then found that

$$\begin{aligned} K_{\alpha\alpha} &= A + 2v/3, & D_{\alpha} &= A + 2v/3 - B \cos \alpha, \\ K_{\alpha\beta} &= 2v, & D_{\beta} &= 2v, \\ K_{\beta\beta} &= 6v, \\ E_{\alpha} &= 2^{1/2}(C - 4v/3) \cos \alpha, \\ E_{\beta} &= -4 \cdot 2^{1/2}v \cos \alpha, \\ F_{\alpha} &= -2^{1/2}(C - 4v/3) \sin \alpha, \\ F_{\beta} &= 4 \cdot 2^{1/2}v \sin \alpha, \\ \{xx\} + \{yy\} &= D + F - 2B \cos \alpha \\ &\quad - (G - 16v/3) \sin^2 \alpha, \\ \{xx\} + \{zz\} &= F - (G - 16v/3) \cos^2 \alpha, \\ \{yy\} + \{zz\} &= A + 2v/3 + D - 2B \cos \alpha, \\ \{xy\} &= 2^{1/2}[E - (C - 4v/3) \cos \alpha], \\ \{xz\} &= 2^{1/2}(C - 4v/3) \sin \alpha, \\ \{yz\} &= (G - 16v/3) \sin \alpha \cos \alpha - B \sin \alpha. \end{aligned}$$

These are the elements of the determinant in (9) of Part I<sup>2</sup>; by obvious additions and subtractions of rows and columns this determinant is readily reduced from five rows to four. In this process the apparently inept definitions of  $A$ ,  $C$  and  $G$  justify themselves, since the four-rowed determinant does not contain  $v$  explicitly. The complete expansion of the determinant is

$$\begin{aligned} |\mathfrak{D}| &= 6v\{ADF(D+F-G) - 2AE^2(D+F) - 2C^2DF \\ &\quad + \cos \alpha[4ABE^2 - 2ABD(F-G) + 4BC(CD - BE)] \\ &\quad + \cos^2 \alpha[-AD^2G + 4BCE(D+F) - B^2F(D+F-G) - 2C^2D^2] \\ &\quad + \cos^3 \alpha[-4B^2CE + 2B^3(F-G)] + B^2DG \cos^4 \alpha \\ &\quad + \sin^2 \alpha[-AB^2D + 2AE^2G + 4C^2E^2] + B^4 \sin^2 \alpha \cos^2 \alpha\}. \end{aligned}$$

Since this is a function of  $\alpha$  there are no reduced moments. The integral of  $|\mathfrak{D}|^{1/2}$  must be made by quadratures. It is found that the translation-rotation entropy is

$$\begin{aligned} S_{t+r} &= 15.873 + 5R \log T, \\ S_{t+r, 298} &= 72.474. \end{aligned}$$

This value is about 0.5 e.u. lower than the estimate included in a preliminary report on this work;<sup>4</sup> the difference has been definitely traced to errors in making the estimate which it would be useless to discuss here. The translation-rotation entropy of 1-butene is thus about 4.5 e.u. higher than that of the 2-butenes. Only 1.4 e.u. of this difference is due to the fortuitous higher symmetry of the 2-butenes. The remaining 3.1 e.u. has its origin in the fact that 1-butene is formed from butane with the loss of only a low moment methyl-group rotation, while the rotation frozen out in 2-butene has a much higher moment. This difference may be expected to persist for higher olefins. There should be a further, somewhat smaller, decrease for these longer chain olefins as the double bond moves farther toward the center of the molecule.

Before solving the butadiene problem, it is convenient to develop from the general theory the special case of two rigid groups rotating about a common axis. We take this common axis to be the  $X$  axis and choose  $Y, Z$  axes so that the two groups rotate in opposite directions with equal angular speeds, and so that the center of gravity is in the  $YZ$  plane. Then the instantaneous positions of the atoms are

$$\begin{aligned} x_{i\alpha} &= x_i, \\ y_{i\alpha} &= y_i \cos \alpha + \delta_i z_i \sin \alpha, \\ z_{i\alpha} &= \delta_i y_i \sin \alpha + z_i \cos \alpha, \end{aligned}$$

where  $\delta_i = 1$  for atoms of one group and  $-1$  for those of the other group, and  $\alpha$  measures the rotation of either group with respect to some fixed axis in the  $YZ$  plane. Since the rotating groups are rigid, the  $x_i, y_i, z_i$  are constants. It

<sup>4</sup> L. S. Kassel, J. Chem. Phys. 4, 144 (1936).

is now necessary to define another large group of new parameters.

$$\begin{aligned} \Sigma m_i &= M, & \Sigma m_i y_i &= aM, & \Sigma m_i \delta_i y_i &= bM, \\ \Sigma m_i \delta_i z_i &= cM, & \Sigma m_i z_i &= dM, & \Sigma m_i x_i^2 &= e, \\ \Sigma m_i x_i y_i &= f, & \Sigma m_i \delta_i x_i y_i &= g, & \Sigma m_i x_i z_i &= h, \\ \Sigma m_i \delta_i x_i z_i &= n, & \Sigma m_i y_i^2 &= p, & \Sigma m_i \delta_i y_i^2 &= q, \\ \Sigma m_i y_i z_i &= r, & \Sigma m_i \delta_i y_i z_i &= s, & \Sigma m_i z_i^2 &= t, \\ & & \Sigma m_i \delta_i z_i^2 &= u. \end{aligned}$$

The elements of the determinant are then found to be

$$K = p + t - M[(a \sin \alpha - c \cos \alpha)^2 + (d \sin \alpha + b \cos \alpha)^2],$$

$$D = -(q + u) + M(ab + cd),$$

$$E = g \cos \alpha - h \sin \alpha,$$

$$F = n \cos \alpha + f \sin \alpha,$$

$$\{yy\} + \{zz\} = (p + t) - M[(a \cos \alpha - c \sin \alpha)^2 + (d \cos \alpha + b \sin \alpha)^2],$$

$$\{xx\} + \{zz\} = e + (p - b^2 M) \sin^2 \alpha + 2(s - bdM) \sin \alpha \cos \alpha + (t - d^2 M) \cos^2 \alpha,$$

$$\{xx\} + \{yy\} = e + (p - a^2 M) \cos^2 \alpha - 2(s - acM) \sin \alpha \cos \alpha + (t - c^2 M) \sin^2 \alpha,$$

$$\{xy\} = f \cos \alpha - n \sin \alpha,$$

$$\{xz\} = g \sin \alpha + h \cos \alpha,$$

$$\{yz\} = (r - adM) \cos^2 \alpha + (q - u - abM + cdM) \sin \alpha \cos \alpha - (r - bcM) \sin^2 \alpha.$$

It is always possible to make  $r = s = 0$  by proper choice of the  $Y, Z$  axes, but it may not always be convenient to do so.

When the rotating groups have the  $X$  axis for one principal axis and have their other two principal axes parallel to the  $Y, Z$  axes when  $\alpha = 0$ , this case reduces to one solved by Eidinoff and Aston.<sup>5</sup> Here

$$a = b = c = d = f = g = h = n = r = s = 0$$

and the determinant reduces to

$$\{(p + t)^2 - (q + u)^2\} \{(e + p)(e + t) + (1/4) \sin^2 2\alpha [(p - t)^2 - (q - u)^2]\},$$

which is Eidinoff and Aston's result in a considerably changed notation. When the rotating groups are identical plane structures, as in butadiene,

$$b = c = d = f = h = n = q = r = s = t = u = 0$$

and the determinant reduces to

$$\begin{vmatrix} p - a^2 M \sin^2 \alpha & g \cos \alpha \\ g \cos \alpha & e + p \sin^2 \alpha \end{vmatrix} \times \begin{vmatrix} p - a^2 M \cos^2 \alpha & -g \sin \alpha \\ -g \sin \alpha & e + (p - a^2 M) \cos^2 \alpha \end{vmatrix}.$$

It is then readily found that for butadiene

$$\begin{aligned} S_{t+r} &= 15.883 + (9R/2) \log T, \\ S_{t+r, 298} &= 66.824. \end{aligned}$$

It is interesting to note that the entropy of 1-butene might have been estimated very accurately from the values for butane and butadiene. The butane value is  $S_{t+r} = 13.105 + (11R/2) \log T$ . The value for 1-butene should be  $R \log 2 = 1.377$  higher than the mean of butane and butadiene, on account of the lower symmetry. Hence the predicted first approximation is  $S_{t+r} = 15.871 + 5R \log T$ , only 0.002 lower than that directly calculated. The sign of this difference is that to be expected; expressed in another way, successive additions of hydrogen to butadiene would give entropy increases at 25°C of 4.273 and 4.269 e.u. if the symmetry number varied smoothly. The same trend appears more prominently when methyl groups are substituted successively in the 1, 3 and 5 positions of benzene. The symmetry-free entropy increases are then 5.39, 5.20, 5.02 e.u.

The various possible comparisons with third-law entropies are summarized in Table II. Wherever the boiling point is below 298°, comparisons at the boiling point also are shown;

TABLE II. Comparison of calculated and observed entropies.

	ENTROPIES AT 298.1°		Boiling point	ENTROPIES AT b. p.	
	$S_{t+r}$	$S_{obs}$		$S_{t+r}$	$S_{obs}$
Propylene	62.67	63.1	225.3°	60.16	59.2
1-Butene	72.47	(72.5)			
Cis 2-Butene	68.22	73.0	276.8	67.49	71.5
Trans 2-Butene	67.61	71.2	274.1	66.78	69.5
Isobutene	68.21	69.0	266.0	67.08	66.7
Trimethylethylene	75.14	(79.7)			

The experimental values for propylene are taken from Huffman, Parks and Barmore, J. Am. Chem. Soc. **53**, 3876-3888 (1931), and those for the butenes from Todd and Parks, J. Am. Chem. Soc. **58**, 134-137 (1936), 1-butene could not be crystallized and the value of  $S_{obs}$  for it is an estimate made by Todd and Parks. The value for trimethylethylene is obtained by combining the third-law entropy for the liquid determined by Parks and Huffman, J. Am. Chem. Soc. **52**, 4381-4391 (1930), with an estimate of 20.2 e.u. for the entropy of vaporization given by Halford, J. Chem. Phys. **2**, 694-696 (1934).

<sup>5</sup> Eidinoff and Aston, J. Chem. Phys. **3**, 379-383 (1935).

TABLE III. *Relative frequencies of various molecular shapes.*

$\alpha$	BUTADIENE	1-BUTENE	BUTANE	BUTANE, CORRECTED
0°	0.8980	0.8725	0.8425	0.8910
15	.9396	.9243	.9058	.9327
30	1.0207	1.0239	1.0268	1.0098
45	1.0671	1.0812	1.0966	1.0490
60	1.0482	1.0598	1.0731	1.0506
75	0.9935	0.9947	0.9978	1.0150
90	.9644	.9597	.9569	0.9940

at these lower temperatures the vibrational contribution is less, and better agreement might be expected. The differences between calculated and observed values for the 2-butenes are of the right order of magnitude to be overcome by the vibrational contributions omitted from the calculated values. The difference between the experimental values for the two isomers, however, is almost certainly too large. The agreement in the case of trimethylethylene is as good as could be expected when account is taken of the rough estimate used for  $S_{\text{vap}}$ . For propylene and isobutene the experimental values seem to be definitely too low; the estimate for 1-butene is also low. Aside from uncertainties in  $S_{\text{vap}}$ , the principal source of experimental error is probably in the long extrapolation from 90° to 0°K, which contributes 10 to 12 e.u.

These calculations also have bearing on the problem of the average shape of nonrigid molecules, since the integrands of the integrals leading to the partition function are proportional to the probability of finding a molecule with the corresponding angles. Table III contains normalized values of these integrands. The angle  $\alpha$  in this table is that used for the butane and butadiene calculations and is equivalent to  $\alpha/2$  of the 1-butene calculation. That is,  $\alpha=0$  corresponds to the *cis* form of the carbon skeleton and  $\alpha=90^\circ$  to the *trans* form. It has been shown previously<sup>6</sup> that the dependence of vibrational frequencies on  $\alpha$  produces a small pseudopotential energy opposing free rotation. For butane the maximum value of this potential for the lowest vibrational state was estimated as 59 cal. The values in the last column of Table III were obtained by multiplying those of the preceding column by  $e^{-E(\alpha)/298k}$  and renormalizing, where  $E(\alpha)$  is the estimated pseudopotential energy.

<sup>6</sup> L. S. Kassel, J. Chem. Phys. 3, 326-335 (1935).

This procedure, of course, cannot be exactly justified, but it seems clear that at room temperature and higher, in the absence of real potential energy terms greater than 100 cal, the molecular shape will be determined predominantly by free rotation.

#### V. EQUILIBRIUM CONSTANTS FOR REACTIONS OF PARAFFINS, OLEFINS AND HYDROGEN

For the purposes of this section it is necessary to attempt at least a rough treatment of the vibrational contributions to  $H/T$  and  $-F/T$ . The C-C frequencies for the normal hydrocarbons up to butane have been estimated as follows:<sup>6</sup>

Ethane 987  $\text{cm}^{-1}$   
 Propane 403, 937, 1067  $\text{cm}^{-1}$   
 Butane, *cis* 221, 492, 879, 1044, 1106  $\text{cm}^{-1}$   
*trans* 312, 385, 974, 987, 1100  $\text{cm}^{-1}$ .

The contributions to  $H/T$  and  $-F/T$  for butane may reasonably be taken as the mean of the not greatly different *cis* and *trans* contributions. Each hydrogen atom introduces one C-H stretching frequency near 3000  $\text{cm}^{-1}$ ; these frequencies make an almost negligible contribution to the thermodynamic functions except at very high temperatures. The C-H bending frequencies are far more important. In methane<sup>7</sup> they are 1306 (triple) and 1536 (double). There are ten C-H bending frequencies in ethane which have been assigned by Eucken and Parts<sup>8</sup> as follows: 712 (double), 826 (double), 1460 (double), 1465 (double), 1499 (double). A single methyl group has three bending frequencies; thus four of the ten C-H bending frequencies in ethane must depend upon bond angles C-C-H, while six may be determined largely by angles H-C-H. This is a very crude analysis, but it suggests that the former type is to be associated with frequencies near 770  $\text{cm}^{-1}$ , the latter with frequencies near 1440  $\text{cm}^{-1}$ . Each methylene group in the molecule should then contribute one frequency near 1440  $\text{cm}^{-1}$  and three near 770  $\text{cm}^{-1}$ ; in paraffins with branched chains each CH group contributes two frequencies near 770  $\text{cm}^{-1}$ . On this basis the

<sup>7</sup> Childs, Proc. Roy. Soc. A153, 555-557 (1936).

<sup>8</sup> Eucken and Parts, Zeits. f. physik. Chemie B20, 184-194 (1933).

distribution of C-H frequencies in the simpler paraffins is

	770 cm <sup>-1</sup>	1440 cm <sup>-1</sup>	3000 cm <sup>-1</sup>
Methane	0	5	4
Ethane	4	6	6
Propane	7	7	8
Butane	10	8	10
Isobutane	8	9	10

These frequencies have been used to calculate the total vibrational contributions to  $-F/T$  and to  $H/T$  for methane, ethane, propane and butane given in Table IV. In view of the uncertainty attached to these values, the subsequent calculations will be made so as to defer as long as possible the introduction of vibrational contributions, and to indicate explicitly the net magnitude of those quantities.

The only possible extensive direct comparison with experimental results is for the dehydrogenation reactions; the method of calculation used for these reactions is given in detail for the dehydrogenation of propane. The translation-rotation entropies of Part IV may be combined to give

TABLE IV. *Vibrational  $-F/T$  and  $H/T$  for hydrocarbons.*

<i>T</i> , °K	METH- ANE	ETH- ANE	PRO- PANE	BU- TANE	790 cm <sup>-1</sup>	572 cm <sup>-1</sup>	244 cm <sup>-1</sup>
<i>-F/T</i>							
100	0.000	0.000	0.006	0.057	0.000	0.000	0.055
200	.000	.029	.164	.508	.006	.032	.358
298.1	.005	.219	.691	1.484	.045	.131	.704
300	.005	.223	.703	1.506	.046	.134	.711
355	.025	.426	1.171	2.283	.083	.207	.892
400	.055	.645	1.637	3.023	.121	.274	1.036
500	.160	1.237	2.830	4.862	.218	.429	1.321
600	.323	1.962	4.205	6.917	.326	.586	1.578
673	.479	2.549	5.282	8.498	.409	.697	1.743
700	.548	2.788	5.706	9.117	.440	.739	1.809
800	.820	3.674	7.258	11.359	.554	.882	2.023
900	1.119	4.582	8.818	13.596	.664	1.024	2.203
1000	1.455	5.536	10.431	15.873	.774	1.159	2.376
1100	1.805	6.487	12.016	18.106	.876	1.279	2.531
1200	2.183	7.467	13.630	20.348	.985	1.379	2.680
1300	2.570	8.456	15.244	22.594	1.084	1.507	2.812
1400	2.961	9.414	16.790	24.734	1.173	1.616	2.943
1500	3.359	10.341	18.261	26.769	1.264	1.713	3.069
<i>H/T</i>							
100	0.000	0.002	0.039	0.222	0.000	0.004	0.200
200	.003	.190	.676	1.446	.040	.137	.707
298.1	.070	.911	2.209	3.778	.173	.374	1.022
300	.070	.929	2.247	3.834	.177	.384	1.027
355	.175	1.516	3.352	5.435	.273	.507	1.146
400	.297	2.052	4.311	6.804	.353	.603	1.224
500	.688	3.355	6.517	9.880	.537	.785	1.356
600	1.179	4.683	8.659	12.803	.670	.930	1.449
673	1.570	5.629	10.137	14.801	.764	1.017	1.501
700	1.730	5.987	10.685	15.532	.796	1.046	1.519
800	2.305	7.238	12.582	18.058	.902	1.147	1.572
900	2.888	8.429	14.354	20.398	.993	1.218	1.616
1000	3.456	9.547	15.996	22.552	1.070	1.283	1.651
1100	4.012	10.599	17.521	24.540	1.137	1.338	1.679
1200	4.545	11.587	18.946	26.392	1.196	1.386	1.704
1300	5.050	12.506	20.259	28.095	1.249	1.426	1.724
1400	5.538	13.375	21.494	29.689	1.291	1.462	1.745
1500	6.002	14.192	22.645	31.172	1.331	1.493	1.757



$$\begin{aligned} \Delta(F^\circ - E_0^\circ)/T &= -0.876 + 5R \log T \\ &+ (-F_v/T)_{\text{propane}} - 2.784 - (9R/2) \log T \\ &- (-F_{vt}/T)_{\text{propylene}} - (-F/T)_{\text{hydrogen}}, \end{aligned}$$

where a subscript  $v$  indicates a vibrational contribution excluding torsional vibrations, and a subscript  $vt$  indicates vibration including torsion. Values of  $(-F/T)_{\text{hydrogen}}$  have been tabulated by Giaque.<sup>9</sup> Then at 673°K,

$$\begin{aligned} \Delta(F^\circ - E_0^\circ)/T &= -27.200 \\ &+ (-F_v, 673/T)_{\text{propane}} - (-F_{vt}, 673/T)_{\text{propylene}}. \end{aligned}$$

The hydrogenation heat determined by Kistiakowsky, Ruhoff, Smith and Vaughan<sup>10</sup> is

$$\Delta H_{355} = 30,115$$

$$\begin{aligned} \text{or } \Delta E_0^\circ &= 27,998 + (H_v, 355)_{\text{propane}} \\ &- (H_{vt}, 355)_{\text{propylene}}. \end{aligned}$$

Hence at 673°K,

$$\begin{aligned} \Delta F^\circ/T &= 14.396 + (-F_v, 673/T + H_v, 355/T)_{\text{propane}} \\ &- (-F_{vt}, 673/T + H_{vt}, 355/T)_{\text{propylene}}. \end{aligned}$$

The experimental value of Frey and Huppke<sup>11</sup> at this temperature is

$$-R \log K = 12.158.$$

These two theoretically identical expressions will agree if

$$\begin{aligned} (-F_{vt}, 673/T + H_{vt}, 355/T)_{\text{propylene}} \\ - (-F_v, 673/T + H_v, 355/T)_{\text{propane}} = 2.238. \end{aligned}$$

Smith and Vaughan<sup>12</sup> have given 790 cm<sup>-1</sup> for the torsion frequency in ethylene. If the force constant remains the same, simple reduced mass considerations indicate a value of 572 cm<sup>-1</sup> for propylene, isobutene and 1-butene, and of 244 cm<sup>-1</sup> for both 2-butenes. For convenience values of  $-F/T$  and of  $H/T$  for these frequencies have been included in Table IV. If

<sup>9</sup> Giaque, J. Am. Chem. Soc. **52**, 4816-4831 (1930).

<sup>10</sup> Kistiakowsky, Ruhoff, Smith and Vaughan, J. Am. Chem. Soc. **57**, 876-883 (1935).

<sup>11</sup> Frey and Huppke, Ind. Eng. Chem. **25**, 54-59 (1933).

<sup>12</sup> Smith and Vaughan, J. Chem. Phys. **3**, 341-343 (1935).

this value of  $572\text{ cm}^{-1}$  is used for the torsion frequency, the preceding equation becomes

$$(-F_v, 673/T + H_v, 355/T)_{\text{propylene}} - (-F_v, 673/T + H_v, 355/T)_{\text{propane}} = 1.273.$$

Since the olefin, excluding the torsion frequency, has six fewer vibrations than the paraffin, and since there is no reason to expect that any force constants are lowered by the dehydrogenation (it is definitely known that the stretching constant for  $\text{C}=\text{C}$  is greater than that for  $\text{C}-\text{C}$ ), one would expect a negative value for the above function. The loss of four  $\text{CH}$  bending vibrations at  $1440\text{ cm}^{-1}$  would make a contribution of  $-0.49$ , and consideration of the  $\text{CC}$  vibrations might easily increase this to  $-1.0$ . In order to obtain even a zero value it would be necessary to reduce the experimental equilibrium constant by a factor of 1.90, or to reduce the heat of hydrogenation by  $857\text{ cal}$ , or to use a torsion frequency of  $250\text{ cm}^{-1}$ .

The results of similar calculations for the other olefins are summarized in Table V. Vibrational functions analogous to those of the preceding two equations are designated  $\delta_{vt}$  and  $\delta_v$ , respectively. It will be noted that the various  $\delta_v$  show a consistency that would be entirely lacking if any constant paraffin-olefin entropy difference had been assumed rather than the actual calculated translation-rotation differences ranging from 3.034 for isobutane to 8.752 for *trans* 2-butene. This consistency was noted in a preliminary report<sup>4</sup> where it was fortuitously somewhat improved by the erroneous estimate there used for 1-butene.

It will be observed that if  $\delta_v$  is to be made zero by changing the torsion frequencies, the three frequencies estimated at  $572\text{ cm}^{-1}$  are changed to an average value of  $240\text{ cm}^{-1}$ , and the two estimated at  $244\text{ cm}^{-1}$  to an average of 87

$\text{cm}^{-1}$ . These are reductions by factors of 0.42 and 0.36. If a mean of 0.39 is applied to the estimate of  $790\text{ cm}^{-1}$  for ethylene, the result is  $308\text{ cm}^{-1}$ . If the lower dissociation constant for ethane recalculated by Smith and Vaughan from Frey and Huppke's data is used, the result is  $\delta_{vt} = 0.280$ ; then  $790\text{ cm}^{-1}$  gives  $\delta_v = -0.273$  and  $308\text{ cm}^{-1}$  gives  $\delta_v = -1.699$ . This latter value is in fact about what would be calculated from the vibrational frequencies used by Smith and Vaughan. It is utterly impossible, however, to accept such a value for the torsion frequency in ethylene, since it would make a contribution of  $0.95\text{ cal./deg.}$  to the heat capacity at  $143^\circ\text{K}$ , where Eucken and Parts found a total vibrational heat capacity of only  $0.08\text{ cal./deg.}$  Reduction of the  $\delta_v$  values by manipulation of the assumed torsion frequency is thus out of the question for ethylene, and presumably for the higher olefins as well.

The ethane figures become more consistent with those for the higher hydrocarbons if the original equilibrium constant of Frey and Huppke is used. This gives  $\delta_{vt} = 1.456$ , and with a torsion frequency of  $790\text{ cm}^{-1}$ ,  $\delta_v = 0.903$ . To make  $\delta_v = 0$  it would be necessary to reduce  $K$  by a factor of 1.65 or to reduce  $\Delta H$  by  $608\text{ cal.}$  Comparison with experiment may also be made at higher temperatures. Teller and Topley<sup>13</sup> have selected  $R \log K = -7.379$  at  $863^\circ\text{K}$  as the best value based on all experimental work. This value gives  $\delta_{vt} = 1.533$ , and with a torsion frequency of  $790\text{ cm}^{-1}$ ,  $\delta_v = 0.797$ .

Thus all these comparisons have given values of  $\delta_v$  between 0.8 and 2.0, while the value to be expected is in the neighborhood of  $-1.0$ . There are five possible interpretations of this discrepancy. The equilibrium constants determined experimentally may be too large by a factor of 3. The hydrogenation heats may be too high by  $1500\text{ cal.}$  These seem to be the most reasonable explanations, but it is also conceivable that the low temperature specific heat of ethylene is too low by  $1\text{ cal./deg.}$  and hence that the torsion frequencies are much lower than they could otherwise be; or that the other vibrational frequency assignments are quite wrong, so that the only serious error is in the expected value of  $\delta_v$ ; or finally that the paraffin-olefin translation-

TABLE V. Comparison of calculated and observed dissociation constants for dehydrogenation reactions.

OLEFIN	$\delta_{vt}$ (cal./deg.)	$\delta_v$ (cal./deg.)	TO MAKE $\delta_v = 0$		
			Reduce $K$ by factor of	Reduce $\Delta H$ by, (cal.)	Use torsion frequency of, ( $\text{cm}^{-1}$ )
Propylene	2.238	1.273	1.90	857	250
1-Butene	2.471	1.506	2.13	1014	260
<i>Cis</i> 2-Butene	4.343	1.923	2.63	1294	89
<i>Trans</i> 2-Butene	4.427	2.007	2.75	1352	85
Isobutene	2.721	1.756	2.42	1182	210

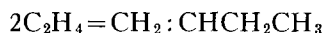
<sup>13</sup> Teller and Topley, J. Chem. Soc., July, 876-885 (1935).

rotation entropy differences which have been calculated are 2.5 e.u. too great.

*Added in proof, May 29.* Dr. F. D. Rossini has kindly given me his preliminary value for the heat of hydrogenation of ethylene, calculated from heats of combustion. The agreement with the direct determination of Kistiakowsky *et al.* is very good. Interpretation of the discrepancy as due to an error in the hydrogenation heats is thus definitely eliminated for ethylene, and rendered unlikely for the higher hydrocarbons.

Although the cause of this disagreement between theoretical and experimental dehydrogenation constants cannot be definitely assigned, it is certainly possible to calculate reliable approximate values for other equilibrium constants. In doing this we shall assume that for any olefin  $H_v/T$  and  $-F_v/T$  are the same as for the corresponding paraffin as given in Table IV; the torsion contribution from the appropriate frequency, 790, 572 or 244  $\text{cm}^{-1}$  must be added to these values. This assumption, which is certainly not literally correct, amounts to assuming a true  $K$  value for the dehydrogenations which is smaller than that observed, but larger than that calculated with plausible olefin frequencies.

For the reaction



we can calculate

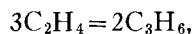
$$\Delta H_{298} = -24,307 \text{ cal.}$$

by combining Rossini's values for the heats of combustion of hydrogen,<sup>14</sup> ethane<sup>15</sup> and butane<sup>15</sup> with the heat of hydrogenation of ethylene determined by Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan<sup>16</sup> and the heat of hydrogenation of 1-butene.<sup>10</sup> Use of Table IV in the manner stated in the preceding paragraph then gives  $\Delta E_0^\circ = -23,122 \text{ cal.}$  Then

$$R \log K = 8.565 - 3R \log T + 23,124/T$$

$$+ (-F_{vt}/T)_{\text{butane}} - 2(-F_{vt}/T)_{\text{ethylene}}.$$

In a similar way one finds



$$\Delta H_{298} = -26,877 \text{ cal.}, \quad \Delta E_0^\circ = -25,354 \text{ cal.},$$

<sup>14</sup> Rossini, Bur. Standards J. Research **6**, 1-35 (1931).

<sup>15</sup> Rossini, Bur. Standards J. Research **12**, 735-750 (1934).

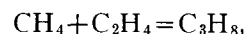
<sup>16</sup> Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan, J. Am. Chem. Soc. **57**, 65-75 (1935).

TABLE VI. Values of  $\log_{10} K$  for several hydrocarbon reactions.

$T$	$K_1$	$K_2$	$K_3$	$K_4$	$K_5$	$K_6$
500	4.405	5.536	1.901	3.099	0.708	6.581
600	2.602	3.574	.457	1.472	-0.570	4.269
700	1.301	2.160	-0.591	.296	-1.501	2.577
800	.308	1.082	-1.395	-0.602	-2.215	1.278
900	-0.472	.235	-2.032	-1.312	-2.784	.243
1000	-1.109	-0.451	-2.553	-1.892	-3.252	-0.605
1100	-1.639	-1.024	-2.988	-2.375	-3.643	-1.313
1200	-2.099	-1.522	-3.363	-2.791	-3.978	-1.913
$K_1 = (1 - \text{C}_4\text{H}_8)/(\text{C}_2\text{H}_4)^2$ $K_4 = (\text{C}_4\text{H}_{10})/(\text{C}_2\text{H}_6)(\text{C}_2\text{H}_4)$ $K_2 = (\text{C}_3\text{H}_6)^2/(\text{C}_2\text{H}_4)^3$ $K_5 = (\text{C}_4\text{H}_{10})/(\text{CH}_4)(\text{C}_3\text{H}_8)$ $K_3 = (\text{C}_3\text{H}_8)/(\text{CH}_4)(\text{C}_2\text{H}_4)$ $K_6 = (\text{C}_4\text{H}_{10})/(\text{H}_2)(1 - \text{C}_4\text{H}_8)$						

$$R \log K = 9.507 - 3R \log T + 25,354/T$$

$$- 3(-F_{vt}/T)_{\text{ethylene}} + 2(-F_{vt}/T)_{\text{propylene}},$$



$$\Delta H_{298} = -19,155 \text{ cal.}, \quad \Delta E_0^\circ = -17,692 \text{ cal.},$$

$$R \log K = 9.139 - 3R \log T + 17,692/T$$

$$+ (-F_v/T)_{\text{propane}} - (-F_v/T)_{\text{methane}}$$

$$- (-F_{vt}/T)_{\text{ethylene}},$$

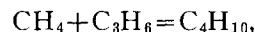


$$\Delta H_{298} = -21,805 \text{ cal.}, \quad \Delta E_0^\circ = -20,559 \text{ cal.},$$

$$R \log K = 7.933 - 3R \log T + 20,559/T$$

$$+ (-F_v/T)_{\text{butane}} - (-F_v/T)_{\text{ethane}}$$

$$- (-F_{vt}/T)_{\text{ethylene}},$$



$$\Delta H_{298} = -16,814 \text{ cal.}, \quad \Delta E_0^\circ = -15,373 \text{ cal.},$$

$$R \log K = 8.095 - 3R \log T + 15,373/T$$

$$+ (-F_v/T)_{\text{butane}} - (-F_v/T)_{\text{methane}}$$

$$- (-F_{vt}/T)_{\text{propylene}},$$



$$\Delta H_{298} = -29,931 \text{ cal.}, \quad \Delta E_0^\circ = -28,044 \text{ cal.},$$

$$R \log K = -3.762 + (R/2) \log T + 28,044/T$$

$$- (-F/T)_{\text{hydrogen}} - (-F/T)_{572 \text{ cm}^{-1}}.$$

Equilibrium constants calculated from these equations are shown in Table VI.

No entirely convincing estimate of the accuracy of these values is possible, but it would require a highly unfortunate set of cumulative errors to make any of them wrong by a factor greater than 2. Table VI should therefore be useful in the study of cracking reactions, and of the newer polymerization processes for gasoline production.