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The Limiting High Temperature Rotational Partition Function of Nonrigid Molecules

I. General Theory. II. CH_4, C_2H_6, C_3H_8, $CH(CH_3)_3$, $C(CH_3)_4$ and $CH_3(CH_2)_2CH_3$. III. Benzene and Its Eleven Methyl Derivatives[1]

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I. The method given by Eidinoff and Aston for calculating the limiting high temperature rotational partition function has been further simplified. An important special case, comprising molecules which may be represented by a rigid framework to which symmetrical tops are attached in any position is developed. II. The methods of the preceding part are applied to the series of methyl derivatives of methane, and to the completely nonrigid molecule *n*-butane. The calculated entropies at 25°C show the same general variation with chain length and number of branches as has been found experimentally from the third law. III. The entropies of all the isomeric methyl derivatives of benzene are calculated. Comparison with third law values for the liquids is hampered by lack of reliable vapor pressure data and of vibration frequencies, but there are no major discrepancies which must be attributed to either the calculated or the observed entropies.

I. General Theory

In a recent article Eidinoff and Aston[3] have developed a powerful method for calculating the classical rotational partition function for nonrigid molecules. They prove that when the kinetic energy can be written as a positive-definite symmetric quadratic form

$$T=(1/2)\sum_{i=1}^{s}\sum_{j=1}^{s}R_{ij}\dot{q}_i\dot{q}_j \tag{1}$$

and the potential energy is zero, then the classical partition function is

$$Q=(2\pi kT/h^2)^{s/2}\int\cdots\int[R]^{\frac{1}{2}}dq_1\cdots dq_s, \tag{2}$$

where $[R]$ is the determinant formed by the R_{ij}. They did not carry the general theory beyond this point, although they worked out a number of special cases. It is possible, however, to develop a general procedure by which $[R]$ can be obtained without calculating all the terms in T.

Consider any convenient set of three orthogonal axes X, Y, Z fixed in the molecule, with origin at the center of gravity. For a nonrigid molecule, fixed axes mean merely axes which move in some specified unique way as the internal coordinates change. Let the coordinates of the ith atom referred to the X, Y, Z axes be x_i, y_i, z_i, each of which is in general a function of $s-3$ internal angular variables. Then the coordinates of the ith atom referred to U, V, W axes fixed in space and related to the X, Y, Z axes by Eulerian angles θ, φ, χ are

$$\begin{aligned} u_i&=a_{11}x_i+a_{12}y_i+a_{13}z_i,\\ v_i&=a_{21}x_i+a_{22}y_i+a_{23}z_i,\\ w_i&=a_{31}x_i+a_{32}y_i+a_{33}z_i, \end{aligned} \tag{3}$$

where

$$\begin{aligned} a_{11}&=\sin\varphi\cos\chi+\cos\theta\cos\varphi\sin\chi,\\ a_{12}&=-\sin\varphi\sin\chi+\cos\theta\cos\varphi\cos\chi,\\ a_{13}&=\sin\theta\cos\varphi,\\ a_{21}&=-\cos\varphi\cos\chi+\cos\theta\sin\varphi\sin\chi,\\ a_{22}&=\cos\varphi\sin\chi+\cos\theta\sin\varphi\cos\chi,\\ a_{23}&=\sin\theta\sin\varphi,\\ a_{31}&=-\sin\theta\sin\chi,\\ a_{32}&=-\sin\theta\cos\chi,\\ a_{33}&=\cos\theta. \end{aligned} \tag{4}$$

It is then readily shown that

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

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$$
\begin{aligned}
\dot{u}^2+\dot{v}^2+\dot{w}^2 &= \dot{x}^2+\dot{y}^2+\dot{z}^2+2(\dot{x}y-\dot{y}x)(-\dot{\varphi}\cos\theta \\
&\quad -\dot{\chi})+2(\dot{x}z-\dot{z}x)(\dot{\theta}\sin\chi-\dot{\varphi}\sin\theta\cos\chi) \\
&\quad +2(\dot{y}z-\dot{z}y)(\dot{\theta}\cos\chi+\dot{\varphi}\sin\theta\sin\chi) \\
&\quad +x^2[\dot{\theta}^2\sin^2\chi-2\dot{\theta}\dot{\varphi}\sin\theta\sin\chi\cos\chi \\
&\quad +\dot{\varphi}^2(1-\sin^2\theta\sin^2\chi)+2\dot{\varphi}\dot{\chi}\cos\theta+\dot{\chi}^2] \\
&\quad +y^2[\dot{\theta}^2\cos^2\chi+2\dot{\theta}\dot{\varphi}\sin\theta\sin\chi\cos\chi \\
&\quad +\dot{\varphi}^2(1-\sin^2\theta\cos^2\chi)+2\dot{\varphi}\dot{\chi}\cos\theta+\dot{\chi}^2] \\
&\quad +z^2[\dot{\theta}^2+\dot{\varphi}^2\sin^2\theta]+2xy[\dot{\theta}^2\sin\chi\cos\chi \\
&\quad +\dot{\theta}\dot{\varphi}\sin\theta(\sin^2\chi-\cos^2\chi)-\dot{\varphi}^2\sin^2\theta\sin\chi\cos\chi] \\
&\quad +2xz[\dot{\theta}\dot{\varphi}\cos\theta\cos\chi+\dot{\theta}\dot{\chi}\cos\chi \\
&\quad +\dot{\varphi}^2\sin\theta\cos\theta\sin\chi+\dot{\varphi}\dot{\chi}\sin\theta\sin\chi] \\
&\quad +2yz[-\dot{\theta}\dot{\varphi}\cos\theta\sin\chi-\dot{\theta}\dot{\chi}\sin\theta \\
&\quad +\dot{\varphi}^2\sin\theta\cos\theta\cos\chi+\dot{\varphi}\dot{\chi}\sin\theta\cos\chi]. \qquad (5)
\end{aligned}
$$

Now let

$$\sum_{k=1}^{n} m_k(\dot{x}_k^2+\dot{y}_k^2+\dot{z}_k^2)=\sum_{i=1}^{s-3}\sum_{j=1}^{s-3} K_{ij}\dot{q}_i\dot{q}_j, \qquad (6)$$

$$
\begin{aligned}
\sum_{k=1}^{n} m_k(\dot{y}_k z_k-\dot{z}_k y_k) &= \sum_{i=1}^{s-3} D_i\dot{q}_i, \\
\sum_{k=1}^{n} m_k(\dot{z}_k x_k-\dot{x}_k z_k) &= \sum_{i=1}^{s-3} E_i\dot{q}_i, \qquad (7) \\
\sum_{k=1}^{n} m_k(\dot{x}_k y_k-\dot{y}_k x_k) &= \sum_{i=1}^{s-3} F_i\dot{q}_i,
\end{aligned}
$$

$$
\begin{aligned}
&\sum_{k=1}^{n} m_k x_k^2=\{xx\}, \quad \sum_{k=1}^{n} m_k y_k^2=\{yy\}, \\
&\sum_{k=1}^{n} m_k z_k^2=\{zz\}, \quad \sum_{k=1}^{n} m_k x_k y_k=\{xy\}, \qquad (8) \\
&\sum_{k=1}^{n} m_k x_k z_k=\{xz\}, \quad \sum_{k=1}^{n} m_k y_k z_k=\{yz\}.
\end{aligned}
$$

The determinant of $2T$ can then be written; after simplification by the usual method of addition of rows or columns it becomes

$$
[R]=\sin^2\theta\begin{vmatrix}
K_{11} & \cdots & K_{1,\,s-3} & D_1 & E_1 & F_1 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
K_{s-3,\,1} & \cdots & K_{s-3,\,s-3} & D_{s-3} & E_{s-3} & F_{s-3} \\
D_1 & \cdots & D_{s-3} & \{yy\}+\{zz\} & -\{xy\} & -\{xz\} \\
E_1 & \cdots & E_{s-3} & -\{xy\} & \{xx\}+\{zz\} & -\{yz\} \\
F_1 & \cdots & F_{s-3} & -\{xz\} & -\{yz\} & \{xx\}+\{yy\}
\end{vmatrix}. \qquad (9)
$$

The integral over the external coordinates θ, φ, χ thus is always

$$\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}\int_{\chi=0}^{2\pi}\sin\theta d\theta d\varphi d\chi=8\pi^2. \qquad (10)$$

The elements of the remaining determinant are functions of the internal coordinates $q_1\cdots q_{s-3}$; the completely general theory can be carried no further. The advantage of this method of treatment is that the external rotation is factored out once for all, with the result that the remaining determinant is far easier both to write and to evaluate.

Various somewhat specialized types of molecules can be defined for which a further development of the theory is possible. One such type, consisting of two tops spinning freely about an axis which is a principal axis for each, was treated by Eidinoff and Aston. Another type of wide occurrence is the pseudo-rigid molecule, consisting of a rigid framework to which any number of *symmetrical* tops are attached in any positions. This type has the property that the external moments of the molecule are independent of the internal rotations; it includes all the methyl derivatives of methane, ethylene, benzene, water, hydrogen sulfide, ammonia and formaldehyde. Many other equally simple molecules, however, such as n-butane, ethylamine, formic acid and phenol, fall outside the limits of this type. The further development of the general theory for these pseudo-rigid molecules is extremely simple. Take any desired X, Y, Z axes. Let the ith top have moment K_i, and the direction cosines of its axis be λ_i, μ_i, ν_i. Then in the notation already used

$$K_{ii}=K_i \quad K_{ij}=0 \text{ for } i\neq j,$$

$$D_i=\lambda_i K_i \quad E_i=\mu_i K_i \quad F_i=\nu_i K_i.$$

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It follows that

$$[R]=\sin^2\theta\begin{vmatrix} K_1 & \cdots & 0 & \lambda_1K_1 & \mu_1K_1 & \nu_1K_1 \\ \vdots & & \vdots & \vdots & \vdots & \vdots \\ 0 & \cdots & K_{s-3} & \lambda_{s-3}K_{s-3} & \mu_{s-3}K_{s-3} & \nu_{s-3}K_{s-3} \\ \lambda_1K_1 & \cdots & \lambda_{s-3}K_{s-3} & \{yy\}+\{zz\} & -\{xy\} & -\{xz\} \\ \mu_1K_1 & \cdots & \mu_{s-3}K_{s-3} & -\{xy\} & \{xx\}+\{zz\} & -\{yz\} \\ \nu_1K_1 & \cdots & \nu_{s-3}K_{s-3} & -\{xz\} & -\{yz\} & \{xx\}+\{yy\} \end{vmatrix}$$

$$=\sin^2\theta\prod_i K_i\begin{vmatrix} \{yy\}+\{zz\}-\{\lambda\lambda\} & -\{xy\}-\{\lambda\mu\} & -\{xz\}-\{\lambda\nu\} \\ -\{xy\}-\{\lambda\mu\} & \{xx\}+\{zz\}-\{\mu\mu\} & -\{yz\}-\{\mu\nu\} \\ -\{xz\}-\{\lambda\nu\} & -\{yz\}-\{\mu\nu\} & \{xx\}+\{yy\}-\{\nu\nu\} \end{vmatrix}, \quad (11)$$

where

$$\{\lambda\mu\}=\sum_i \lambda_i\mu_iK_i. \quad (12)$$

It is obvious that the determinant is a constant, and therefore that the integration in (2) presents no difficulty. The equation takes a strikingly symmetric form when the invariant ΣK_i is introduced.

$$[R]=\sin^2\theta\prod_i K_i\begin{vmatrix} \begin{matrix}\{yy\}+\{zz\}\\+\{\mu\mu\}+\{\nu\nu\}\\-\Sigma K_i.\end{matrix} & -\{xy\}-\{\lambda\mu\} & -\{xz\}-\{\lambda\nu\} \\ -\{xy\}-\{\lambda\mu\} & \begin{matrix}\{xx\}+\{zz\}\\+\{\lambda\lambda\}+\{\nu\nu\}\\-\Sigma K_i\end{matrix} & -\{yz\}-\{\mu\nu\} \\ -\{xz\}-\{\lambda\nu\} & -\{yz\}-\{\mu\nu\} & \begin{matrix}\{xx\}+\{yy\}\\+\{\lambda\lambda\}+\{\mu\mu\}\\-\Sigma K_i\end{matrix} \end{vmatrix}. \quad (13)$$

There is thus an *ellipsoid of moment of inertia* which has a high formal similarity to the ellipsoid of inertia. The elements of the determinant in (13) may be called reduced moments and products of inertia, and the determinant may be considered as defining a reduced ellipsoid of inertia. Since λ, μ, ν transform under rotation of axes in exactly the same way as x, y, z, a principal axes transformation may be made here exactly as for the rigid body. For the purpose of locating the principal axes, each top of mass m_i, radius of gyration r_i, and axial direction cosines λ_i, μ_i, ν_i introduces two extra virtual mass points $m_i/2$ with coordinates λ_ir_i, μ_ir_i, ν_ir_i and $-\lambda_ir_i$, $-\mu_ir_i$, $-\nu_ir_i$. The contribution $-K_i$, that is, $-m_ir_i^2$ to each moment of inertia does not affect the location of the principal axes, but may be included in the model as a mass of $-m_i$ distributed symmetrically over the surface of a sphere of radius $(1/3)\sqrt{6}r_i$. This rigid configuration of positive and negative masses, plus the $s-3$ separate tops with axes fixed in space is thermodynamically equivalent (at high temperatures) to the pseudo-rigid molecule from which it is derived.

For most molecules of interest the symmetry is such that the principal axes of inertia coincide with the principal axes of moment of inertia and may be determined by inspection. The determinant may then be written directly in the diagonal form, with the principal reduced moments immediately apparent. For such molecules as $CH_3CH_2CD_3$ and 1,2,4-trimethylbenzene, however, this is not the case, and it might not be

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obvious that there is any physically significant transformation to a diagonal determinant, or any reduced moments. The foregoing argument shows that reduced moments exist for every pseudo-rigid molecule, and thus gives a veneer of elegance to the calculation. As a matter of practical convenience, however, when at least one of the principal axes is not obvious, it is usually easier to evaluate the nondiagonal determinant in (11) than to make the frequently very cumbersome principal axes transformation of the more symmetric form (13).

It is possible that the reduced rigid molecule plus independent tops may form a useful zeroth approximation for a perturbation theory calculation of the actual energy levels of pseudo-rigid molecules. No attempt has been made to do this, however, since no application for the results is evident.

II. CH_4, C_2H_6, C_3H_8, $CH(CH_3)_3$, $C(CH_3)_4$ AND $CH_3(CH_2)_2CH_3$

Formal theory

The entire series of methylated methanes satisfy the requirements of (11), and have principal axes obvious on inspection. Ethane and tetramethylmethane have been treated previously but are included here for comparative purposes.

For ethane it must be remembered that only one methyl group is a top, the other being the rigid framework. Then, if the molecular axis is taken as the X axis, $\{yy\}=\{zz\}=K$, the moment of a methyl group, and $\lambda=1$, $\mu=\nu=0$. Hence

$$[R]=\sin^2\theta K^2(\{xx\}+K)^2.$$

The symmetry number is 18 and the rotational partition function is

$$Q_{\text{rot}}=(1/18\pi)(8\pi^3kT/h^2)^2K(\{xx\}+K),$$

as has been found previously by more laborious methods.

For propane, take the XY-plane to be that of the carbon atoms, with the Y axis bisecting the central angle. Then $\lambda_1=\sqrt{6}/3$, $\mu_1=\sqrt{3}/3$, $\nu_1=0$, $\lambda_2=-\sqrt{6}/3$, $\mu_2=\sqrt{3}/3$, $\nu_2=0$ and

$$[R]=\sin^2\theta K^2(\{xx\}+\{yy\})(\{xx\}+\{zz\}-2K/3)(\{yy\}+\{zz\}-4K/3).$$

The symmetry number is again 18 and

$$Q_{\text{rot}}=(1/18\pi)(8\pi^3kT/h^2)^{5/2}K(\{xx\}+\{yy\})^{1/2}(\{xx\}+\{zz\}-2K/3)^{1/2}\times(\{yy\}+\{zz\}-4K/3)^{1/2}.$$

For *iso*butane, take the Z axis that of the unique CH, and the XZ plane containing one CC. Then $\lambda_1=2\sqrt{2}/3$, $\mu_1=0$, $\nu_1=1/3$, $\lambda_2=-\sqrt{2}/3$, $\mu_2=\sqrt{6}/3$, $\nu_2=1/3$, $\lambda_3=\sqrt{2}/3$, $\mu_3=-\sqrt{6}/3$, $\nu_3=1/3$. Since $\{xx\}=\{yy\}$

$$[R]=\sin^2\theta K^3(\{xx\}+\{zz\}-4K/3)^2(2\{xx\}-K/3).$$

The symmetry number is 81 and

$$Q_{\text{rot}}=(1/81\pi)(8\pi^3kT/h^2)^3K^{3/2}(\{xx\}+\{zz\}-4K/3)(2\{xx\}-K/3)^{1/2}.$$

Finally, for tetramethylmethane it is merely necessary to add $\lambda_4=0$, $\mu_4=0$, $\nu_4=-1$ to the preceding case and to note that here $\{xx\}=\{yy\}=\{zz\}$. The symmetry number is $12\times81=972$. Then

$$[R]=\sin^2\theta K^4(2\{xx\}-4K/3)^3$$

and

$$Q=(1/972\pi)(8\pi^3kT/h^2)^{7/2}K^2(2\{xx\}-4K/3)^{3/2}.$$

This result is identical with that previously derived by the writer and by Eidinoff and Aston by more difficult methods.

The technique which has been developed for these calculations is thus so powerful that the longest part of the computation is the determination of the external moments, which would still be necessary if the internal rotations were frozen. If D, d are the CH and CC distances, and M, m the masses of C and H, straightforward calculation gives the following results.

Ethane $\{xx\}=MD^2/2+3mD^2/2+2mDd+2md^2/3.$

Propane $\{xx\}=4MD^2/3+4mD^2+8mD/3+4md^2/3$

$$\{yy\}=(2/9+4\mu^2/9)MD^2+(1/27)(14-8\mu+32\mu^2)mD^2+4mDd/3+8md^2/3$$

$$\{zz\}=4md^2,$$

where $\mu=m/(3M+8m)$.

Isobutane $\{xx\}=4MD^2/3+4mD^2+8mDd/3+8md^2/3,$

$$\{zz\}=(1/12+\mu^2/4)MD^2+(1/8)(1-2\mu+5\mu^2)mD^2+2mDd/3+14md^2/3,$$

where $\mu=m/(2M+5m)$.

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Tetramethylmethane $\{xx\}=4MD^2/3+4mD^2+8mDd/3+4md^2.$

In all cases $K=8md^2/3.$

For n-butane the X, Y, Z axes are taken the same as in previous work on the vibrational frequencies.[4] The angle there designated φ is here called α. The angles describing the rotations of the two end methyl groups are β, γ. Then

$$\{xx\}=17MD^2/9+31mD^2/6+22mDd/9+26md^2/9,$$

$$\{yy\}=(1/9)[8(1+\mu^2)MD^2+(20-8\mu+20\mu^2)mD^2+32mDd+16md^2]\cos^2\alpha+(16/3)md^2\sin^2\alpha,$$

$$\{zz\}=(1/9)(16MD^2+48mD^2+32mDd+16md^2)\sin^2\alpha+(16/3)md^2\cos^2\alpha,$$

$$\{xy\}=0,\quad \{yz\}=0,$$

$$\{xz\}=(\sqrt{2}/9)(10MD^2+30mD^2+8mDd-8md^2)\sin\alpha,$$

$$\Sigma m(\dot{x}y-\dot{y}x)=(16\sqrt{2}/9)md^2\sin\alpha(\dot{\beta}+\dot{\gamma})=F(\dot{\beta}+\dot{\gamma}),$$

$$\Sigma m(\dot{z}x-\dot{x}z)=(\sqrt{2}/9)[(10MD^2+30mD^2+8mDd-8md^2)\dot{\alpha}-16md^2(\dot{\beta}-\dot{\gamma})]\cos\alpha=E_1\dot{\alpha}+E_2(\dot{\beta}-\dot{\gamma}),$$

$$\Sigma m(\dot{y}z-\dot{z}y)=(8/9)md^2(\dot{\beta}+\dot{\gamma})=D(\dot{\beta}+\dot{\gamma}),$$

$$\Sigma m(\dot{x}^2+\dot{y}^2+\dot{z}^2)=(1/9)\dot{\alpha}^2\{8MD^2[(1+\mu^2)+(1-\mu^2)\cos^2\alpha]+48mD^2\cos^2\alpha+mD^2(20-8\mu+20\mu^2)\sin^2\alpha+32mDd+64md^2\}+(16/9)md^2(\dot{\alpha}\dot{\beta}-\dot{\alpha}\dot{\gamma})+(8/3)md^2(\dot{\beta}^2+\dot{\gamma}^2)=K_1\dot{\alpha}^2+K_2\dot{\beta}^2+K_2\dot{\gamma}^2+2K_3(\dot{\alpha}\dot{\beta}-\dot{\alpha}\dot{\gamma}),$$

where

$$\mu=m/(2M+5m).$$

Then the determinant of $2T$ is easily written and factored, giving

$$[R]=\sin^2\theta\begin{vmatrix}K_2 & D & F\\ 2D & \{yy\}+\{zz\} & -\{xz\}\\ 2F & -\{xz\} & \{xx\}+\{yy\}\end{vmatrix}\begin{vmatrix}K_1 & K_3 & E_1\\ 2K_3 & K_2 & 2E_2\\ E_1 & E_2 & \{xx\}+\{zz\}\end{vmatrix}.$$

When advantage is taken of simple relationships between D, E_2, F and K_2 and between $\{xz\}$ and E_1, a further reduction is possible.

$$[R]=\sin^2\theta K_2^2[AC-(2/9)K_2C-\{(16/9)K_2A+S^2\}\sin^2\alpha]\times[K_1B-(2/9)K_2B-\{(16/9)K_2K_1+S^2\}\cos^2\alpha],\quad(14)$$

where

$$\{xx\}+\{yy\}=C,\ \{xx\}+\{zz\}=B,\ \{yy\}+\{zz\}=A,$$

$$S^2=(2/81)(10MD^2+30mD^2+8mDd-8md^2)\times(10MD^2+30mD^2+8mDd+40md^2/3).$$

Evidently $[R]$ is a function of α; hence there are no reduced moments for n-butane. The integration in (2) must be made by quadratures. The range of integration for each of the angles α, β, γ is 0 to 2π. The configurations α and $\alpha+\pi$ differ only in external orientation, however, and for this cause a factor 2 appears in the symmetry number. Two factors of 3 arise from the two terminal methyl groups. The end-over-end symmetry of ethane and propane is present in butane also for all values of α. The total symmetry number is therefore 36, and

$$Q_{\text{rot}}=(1/36\pi)(8\pi^3kT/h^2)^3(1/2\pi)\int_0^{2\pi}K_2(D_1D_2)^{\frac{1}{2}}d\alpha,$$

where D_1, D_2 are the two bracketed functions in (14).

Numerical values

The best values for the interatomic distances probably are $D=1.53\times10^{-8}$ cm, $d=1.11\times10^{-8}$ cm. The numerical values of the reduced moments$\times10^{40}$ are then as follows:

Methane	5.46,	5.46,	5.46,				
Ethane	41.5,	41.5,	5.46,	5.46,			
Propane	109.2,	92.2,	22.44,	5.46,	5.46,		
Isobutane	178.9,	98.8,	98.8,	5.46,	5.46,	5.46,	
Tetramethylmethane	178.9,	178.9,	178.9,	5.46,	5.46,	5.46,	5.46.

For n-butane

$$(1/2\pi)\int_0^{2\pi}K_2(D_1D_2)^{\frac{1}{2}}\,d\alpha=5.957\times10^{-116}.$$

This is the effective square root of the product of the moments; it may be compared with 1.686×10^{-116} for isobutane.

[4] Kassel, J. Chem. Phys. 3, 326 (1935).

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The translational plus rotational entropies, taking account of the symmetry but omitting nuclear spin contributions are therefore

Methane	$S=-0.754+4R\log T$	$S_{298.1}=44.527,$
Ethane	$S=4.498+(9/2)R\log T$	$S_{298.1}=55.439,$
Propane	$S=9.058+5R\log T$	$S_{298.1}=65.659,$
Isobutane	$S=8.988+(11/2)R\log T$	$S_{298.1}=71.249,$
Tetramethylmethane	$S=6.036+6R\log T$	$S_{298.1}=73.957,$
n-Butane	$S=13.105+(11/2)R\log T$	$S_{298.1}=75.366.$

The estimated vibrational entropy for n-butane at 298.1° is 2.79 e. u.; the value for isobutane will not differ greatly from this, so that approximate cancellation of vibrational contributions will occur. n-Butane is thus favored over isobutane by a ΔS of approximately 4.117 for all moderate temperatures. Heats of combustion determined by Rossini[5] indicate a ΔH of 1630 cal. favoring isobutane. An approximate value for the free energy change is then

$$n\text{-}C_4H_{10}=iso\text{-}C_4H_{10},\quad \Delta F/T=4.117-1630/T.$$

The corresponding values of the equilibrium constant $[iso\text{-}C_4H_{10}]/[n\text{-}C_4H_{10}]$ are 1.97 at 298.1°, 0.98 at 400° and 0.65 at 500°K. The effect of the vibrational contribution is probably in the direction of still smaller equilibrium constants, especially at the higher temperatures. It is interesting to note in passing the very fair agreement of this ΔS value with the statistical third law value of 4.5 e. u. decrease per methyl group side-chain found by Parks for the liquid state.

The relatively small vibrational contributions to the entropy have been estimated on a consistent basis[6] for the four normal hydrocarbons. Table I gives these estimates, the resulting total $S_{298.1}$ values (omitting the nuclear spin contribution) and the increment per CH_2 group added in the chain. The only direct comparison with third law results is for n-butane, where the calculated value is 3.76 e. u. $=R\log 6.6$ higher than the experimental value of Huffman, Parks and Barmore.[7] This difference is well beyond any reasonable error in the calculation, and is presumably due either to an error in the 11.7 e. u. extrapolation from 90°K, to 0°, or to a zero-point entropy of the crystals caused by lack of equilibrium at the lower temperatures. The nearly linear increase in entropy with length of the carbon chain is of interest. The data of Parks and his associates give an increase of 7.7 e. u. per CH_2 group in the liquid state. For the hypothetical perfect gas at atmospheric pressure this would be approximately 9.3 e. u. The calculated values for longer chains will probably increase by at least 10.0 e. u. per CH_2 group.

TABLE I.
Entropies of normal hydrocarbons.

SUBSTANCE	S_{vib}	S_{total}	Δ per CH_2
Methane	0.11	44.64	
Ethane	0.52	55.96	11.32
Propane	1.74	67.40	11.44
n-Butane	2.79	78.16	10.76

III. Benzene and its Eleven Methyl Derivatives

All these molecules consist of symmetrical tops on a rigid framework. For all except 1,2,4-trimethylbenzene the principal axes are obvious; in this one case it is readily found that the principal axes of the reduced ellipsoid of inertia make angles of 43.10° and 46.90° with the axis of the 2-methyl group. The calculations are extremely simple, requiring only a few hours for all twelve compounds. Table II gives the three reduced moments, the symmetry number, the calculated rotational plus translational entropy for the gas at 298.1°K, the experimental third law entropy for the liquid at the same temperature, and wherever possible for the gas. The interatomic distances used are[8] $d_{CC}=1.40\times10^{-8}$ cm in the benzene ring and 1.50×10^{-8} cm from the ring to the attached methyl group; $d_{CH}=1.14\times10^{-8}$ cm for hydrogen attached to the ring and 1.11×10^{-8} cm for methyl group hydrogen atoms. The third law entropies for the gaseous state are very uncertain beyond the xylenes. Even for these compounds the vapor pressure data in *International Critical Tables* are totally wrong, and the low temperature measurements of

[5] Rossini, J. Chem. Phys. **3**, 438 (1935).
[6] Using frequencies calculated by Kassel, J. Chem. Phys. **3**, 326 (1935).
[7] Huffman, Parks and Barmore, J. Am. Chem. Soc. **53**, 3876 (1931).
[8] Jones, Trans. Faraday Soc. **31**, 1036 (1935).

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TABLE II. *Entropies of the methyl benzenes.*

SUBSTANCE	MOMENTS $\times 10^{40}$			σ' [a]	S_{t+r}	THIRD LAW S_{liq}	S_{gas}
Benzene	297.22	148.61	148.61	12	59.77	41.9[b]	65.1
Toluene	477.27	328.66	148.61	2	68.72	52.4[e]	77.3
o-Xylene	638.13	383.59	254.53	2	73.76	59.3[b]	83.6
m-Xylene	693.34	466.40	226.93	2	73.92	60.3[b]	85.5
p-Xylene	720.94	572.33	148.61	4	72.37	60.5[b]	86.5
1,2,3-Trimethylbenzene	835.27	466.40	368.87	2	78.60	—	—
1,2,4-Trimethylbenzene	908.42	638.09	270.33	1	80.06	67.7[c]	94.1
1,3,5-Trimethylbenzene	932.80	466.40	466.40	6	76.76	—	—
1,2,3,4-Tetramethylbenzene	1079.2	678.26	400.90	2	83.28	69.5[c]	—
1,2,3,5-Tetramethylbenzene	1122.8	656.43	466.40	2	83.43	74.1[c]	—
1,2,4,5-Tetramethylbenzene	1144.7	784.19	360.47	4	82.00	71.8[c]	97.3
Pentamethylbenzene	1336.7	784.19	552.56	2	87.89	80.0[d]	—
Hexamethylbenzene	1568.4	784.19	784.19	12	88.74	85.5[d]	—

[a] The total symmetry number is $\sigma = 3^n\sigma'$ where n is the number of methyl groups.
[b] Huffman, Parks and Daniels, J. Am. Chem. Soc. **52**, 1547 (1930).
[c] Huffman, Parks and Barmore, J. Am. Chem. Soc. **53**, 3876 (1931).
[d] Parks, Ind. Eng. Chem. **25**, 887 (1933).
[e] Kelley, J. Am. Chem. Soc. **51**, 2740 (1929)

Linder[9] also seem to be inaccurate. The entropies of vaporization used for the xylenes in Table II have been calculated from new vapor pressure measurements which will shortly be published elsewhere. Comparison of third law gas values with theoretical translation-rotation entropies gives an indicated vibrational entropy of 9.8 e. u. for *o*-xylene and 14.1 e. u. for *p*-xylene. Either of these values might be considered plausible, but it does not seem possible that there could be such a large difference between the isomers. The vapor pressure of 1,3,5-trimethylbenzene has been measured, and the calculated entropy of vaporization has been assumed to apply to 1,2,4-trimethylbenzene. Linder's vapor pressures for 1,2,4,5-tetramethylbenzene, which presumably are for the solid, have been corrected to the liquid state by means of the same data used by Parks to estimate the entropy of fusion. For the pentamethyl and hexamethyl compounds even the liquid entropies are quite uncertain, and no attempt has been made to estimate values for the gases.

Parks concluded that the entropies of the liquid methylbenzenes could be represented by

$$S_{298.1} = 44.5 + 7.7n.$$

[9] Linder, J. Phys. Chem. **35**, 531 (1931).

The gaseous translation-rotation entropies follow a similar linear relationship considerably more closely than the experimental liquid figures do. The chief deviations arise from the varying symmetry number. The irregular part of this variation can be eliminated by adding $R \log\sigma'$. It is then found that

$$S_{t+r} + R \log \sigma' = 65.244 + 4.814n$$

represents the calculated values with a maximum deviation of 0.64 e. u. The variation is definitely nonlinear, however, and a much better representation is

$$S_{t+r} + R \log \sigma' = 64.751 + 5.406n - 0.0987n^2$$

with a maximum deviation of 0.24 e. u., and a maximum deviation of 0.066 e. u. from the average for all isomers with the same n. The maximum spread between isomers is 0.343 e. u. for the trimethylbenzenes.

The excesses of the third law values for the gases over the calculated translation-rotation entropies are of magnitudes compatible with interpretation as vibrational entropies. Any calculation of the theoretical vibrational entropies for these compounds would be premature, however, and is deferred until more complete vibrational analyses are available.

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