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The Calculation of Thermodynamic Quantities from Spectroscopic Data for Polyatomic Molecules; the Free Energy, Entropy and Heat Capacity of Steam

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The methods already developed by Gordon and Barnes for computing thermodynamic quantities from the band spectrum of a diatomic molecule are extended to deal with the case of the triatomic unsymmetrical rotator. The free energy, entropy and heat capacity of steam are computed for the temperature range 298.1–1500°K from the spectroscopic data of Mecke and his associates. From the free energy so calculated, the known spectroscopic free energies of carbon monoxide, carbon dioxide and hydrogen, and the thermal data of Rossini, revised values of the equilibrium constant for the water-gas reaction are computed. The numbers so obtained are in close agreement with the experimental results of Neumann and Koehler and of Emmett and Schultz.

THE calculation of thermodynamic quantities from the band spectrum of a diatomic molecule has been discussed in detail by various authors[1] and a number of procedures have been developed which avoid the principal difficulties of summation. The corresponding calculation for the polyatomic case has, in general, received scant attention primarily, no doubt, because the requisite experimental data have been lacking. In a recent series of papers, however, Mecke and his associates[2] have presented a reasonably satisfactory analysis of the rotational-vibrational spectrum of steam and although there are still some uncertainties as to the changes in the spectroscopic constants in the higher vibrational states, it is now possible to obtain reliable values of the free energy, entropy and heat capacity for moderate temperatures at least. Moreover, the series which arise in this case are typical of those which will occur in similar calculations for other triatomic unsymmetrical rotators, e.g., SO_2 and H_2S, and it therefore seems justifiable to consider the case of steam in some detail. Indeed, steam provides a particularly good test for any method of approximation, since its rotational-vibrational interaction terms are exceptionally large.

The approximations discussed here are an extension of those developed by Gordon and Barnes[3] for diatomic molecules and the problem is really one of reducing the "state sum" and its derivatives to such a form that the tabulated diatomic functions can be used in their evaluation.

THE EVALUATION OF THE STATE SUM AND THE CALCULATION OF THE FREE ENERGY

The rotational-vibrational energy levels for a triatomic unsymmetrical rotator will, in general, depend on the three fundamental frequencies of the molecule and on its three principal moments of inertia. The frequencies are distinguished by the subscripts δ, π and σ, the corresponding vibrational quantum numbers being v_δ, v_π and v_σ; in the expression for the energy levels, not only will terms occur involving the first and second powers of the vibrational quantum numbers but also "cross terms" of the type $v_\delta \cdot v_\pi$, etc.; moreover, the moments of inertia[4] A, B and C will themselves be

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[1] Mulholland, Proc. Camb. Phil. Soc. **24**, 280 (1928); Sutherland, Proc. Camb. Phil. Soc. **26**, 402 (1930); Giauque and Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932); Gordon and Barnes, J. Chem. Phys. **1**, 297 (1933); Kassel, Phys. Rev. **43**, 364 (1933); J. Chem. Phys. **1**, 576 (1933).

[2] Mecke, Zeits. f. Physik **81**, 313 (1933); Baumann and Mecke, Zeits. f. Physik **81**, 445 (1933); Freudenberg and Mecke, Zeits. f. Physik **81**, 465 (1933).

[3] Gordon and Barnes, J. Chem. Phys. **1**, 297 (1933).

[4] Throughout this paper it is assumed that $A < B < C$.

functions of v_δ, v_π and v_σ.   If the molecule is of the type RXY with non-spinning nuclei, the summation over the rotational levels for a given vibrational state is replaced by its limiting value for high temperatures:

$$Q_R \approx \exp\,(\sigma_{BC}/4)\cdot q_v\cdot(1+\sigma_{BC}/12-\sigma_B\sigma_C/12\sigma_A), \tag{1}$$

where

$$q_v = 8\pi^2 M_v(2\pi kT/h^2)^{\frac{3}{2}} = (\pi/\sigma_A\sigma_B\sigma_C)^{\frac{1}{2}}; \qquad M_v = (A_vB_vC_v)^{\frac{1}{2}};$$

$$\sigma_A,\,\sigma_B,\,\sigma_C = (h^2/8\pi^2kT)\cdot(1/A_v,\,1/B_v,\,1/C_v); \qquad \sigma_{BC} = (\sigma_B\sigma_C)^{\frac{1}{2}}$$

and the subscript v stands for $v_\delta v_\pi v_\sigma$. The error introduced by this approximation is discussed in the note at the end of this paper; it is there shown that the approximation is justifiable in any case likely to occur in practice, provided the temperature is 300°K or more.

If, as in the case of steam, there are two equivalent atoms in the molecule each possessing j_S units of nuclear spin, the rotational state sum becomes

$$Q_R \approx \exp\,(\sigma_{BC}/4)\cdot q_v\cdot(1+\sigma_{BC}/12-\sigma_B\sigma_C/12\sigma_A)\cdot(2j_S+1)^2/2. \tag{2}$$

The vibrational terms in the expression for the energy levels will be of the type

$$\epsilon_v = (\epsilon_v)_\delta+(\epsilon_v)_\pi+(\epsilon_v)_\sigma+\epsilon_i, \tag{3}$$

where

$$(\epsilon_v)_\delta = (v_\delta+\tfrac{1}{2})\omega_\delta-(v_\delta+\tfrac{1}{2})^2\omega_\delta\chi_\delta, \tag{4}$$

$$\epsilon_i = -y_{\delta\pi}\cdot v_\delta v_\pi-y_{\pi\sigma}\cdot v_\pi v_\sigma-y_{\sigma\delta}\cdot v_\sigma v_\delta \tag{5}$$

with definitions similar to (4) for $(\epsilon_v)_\pi$ and $(\epsilon_v)_\sigma$.   Thus the rotational-vibrational state sum, Q_{RV}, may be written

$$Q_{RV} = \Sigma \exp\,[-\epsilon_v/kT]\cdot\exp\,(\sigma_{BC}/4)\cdot q_v\times(1+\sigma_{BC}/12-\sigma_B\sigma_C/12\sigma_A)\cdot(2j_S+1)^2/2, \tag{6}$$

where the summation is to run over all values of v_δ, v_π and v_σ.

Since A_v, B_v and C_v can all be expressed in terms of their values in the lowest vibrational state plus certain linear and quadratic terms in the vibrational quantum numbers, it follows that q_v can be replaced by an expression of the type

$$q_v = q_0(1+a_\delta v_\delta+a_\pi v_\pi+a_\sigma v_\sigma+b_\delta v_\delta^2+\cdots+c_{\delta\pi}\cdot v_\delta v_\pi+\cdots), \tag{7}$$

where q_0 is the value of q_v for $v_\delta = v_\pi = v_\sigma = 0$, the a's, b's and c's are numerical constants and the dots after a plus sign indicate two terms obtained by permuting δ, π and σ in the term immediately preceding it.

Since ϵ_i/kT is in general small, $\exp\,[\epsilon_i/kT]$ can be expanded in a power series and by an obvious rearrangement the logarithm of the state sum can then be written

$$\ln Q_{RV}+E_0/RT = (\ln Q_V+\epsilon_0/kT)_\delta+(\ln Q_v+\epsilon_0/kT)_\pi+(\ln Q_v+\epsilon_0/kT)_\sigma$$
$$+\sigma_{BC}/4+\ln\,(2j_S+1)^2q_0/2+\ln\,(1+r_i), \tag{8}$$

where

$$r_i = (y_{\delta\pi}/kT)\cdot(\bar{v})_\delta(\bar{v})_\pi+\cdots+\tfrac{1}{2}(y_{\delta\pi}/kT)^2\cdot(\overline{v^2})_\delta\cdot(\overline{v^2})_\pi+\cdots+\tfrac{1}{2}(y_{\delta\pi}/kT)\cdot(y_{\pi\sigma}/kT)\cdot(\bar{v})_\delta(\overline{v^2})_\pi(\bar{v})_\sigma$$
$$+\cdots+a_\delta(\bar{v})_\delta+\cdots+b_\delta(\overline{v^2})_\delta+\cdots+c_{\delta\pi}(\bar{v})_\delta\cdot(\bar{v}_\pi)+\cdots+\sigma_{BC}/12-\sigma_B\sigma_C/12\sigma_A, \tag{9}$$

$$(\ln Q_V+\epsilon_0/kT)_\delta = \ln\Sigma \exp\,[-(v_\delta\omega_\delta-(v_\delta^2+v_\delta)\omega_\delta\chi_\delta)/kT], \tag{10}$$

$$(\bar{v})_\delta = (\Sigma v_\delta\cdot\exp\,[-(\epsilon_v)_\delta/kT])/(Q_V)_\delta, \tag{11}$$

$$(\overline{v^2})_\delta = (\Sigma v_\delta^2\cdot\exp\,[-(\epsilon_v)_\delta/kT])/(Q_V)_\delta, \tag{12}$$

with similar definitions for symbols involving π and σ. Since numerical values of $(\ln Q_V + \epsilon_0/kT)$, $\bar{v}$ and $\overline{v^2}$ can be found from Gordon and Barnes'[3] Tables I, II, V and IX or by means of the approximations discussed in their Example 4, for given values of $w = \omega/kT$ and χ, it follows that the numerical value of the expression on the right of Eq. (8) can be found at once. If r_i is small in comparison with unity, Eq. (8) can be still further simplified, giving

$$\ln Q_{RV} + E_0/RT \approx (\ln Q_V + \epsilon_0/kT)_\delta + \cdots + \ln (2j_S+1)^2 q_0/2$$

$$+ (y_{\delta\pi}/kT) \cdot (\bar{v})_\delta \cdot (\bar{v})_\pi + \cdots + a_\delta(\bar{v})_\delta + \cdots + b_\delta(\overline{v^2})_\delta + \sigma_{BC}/3 - \sigma_B\sigma_C/12\sigma_A. \quad (13)$$

The Calculation of the Rotational-Vibrational Entropy and Heat Capacity

Since $S_{RV} = R \ln Q_{RV} + RT\partial \ln Q_{RV}/\partial T$ and $C_{RV} = T\partial S_{RV}/\partial T$ it follows from Eq. (8) that

$$S_{RV}/R = (S_V/R)_\delta + (S_V/R_V)_\pi + (S_V/R)_\sigma + \ln (2j_S+1)^2 q_0/2 + 3/2 + \ln (1+r_i) + (T\partial r_i/\partial T)/(1+r_i), \quad (14)$$

$$C_{RV}/R = (C_V/R)_\delta + (C_V/R)_\pi + (C_V/R)_\sigma + 3/2$$

$$+ \{T\partial(T\partial r_i/\partial T)/\partial T\}/(1+r_i) + (T\partial r_i/\partial T)/(1+r_i) - (T\partial r_i/\partial T)^2/(1+r_i)^2, \quad (15)$$

where $(S_V)_\delta$ and $(C_V)_\delta$ stand for the entropy and heat capacity of an anharmonic oscillator whose energy levels are given by Eq. (4), with similar definitions for symbols involving π and σ. The expressions for $T\partial r_i/\partial T$ and $T\partial(T\partial r_i/\partial T)/\partial T$ can be readily written down by means of the typical relations,

$$T\partial\bar{v}/\partial T = s_1 - \bar{v}, \quad (16)$$

$$T\partial\overline{v^2}/\partial T = s_2 - \overline{v^2}, \quad (17)$$

$$T\partial s_1/\partial T = c_1, \quad (18)$$

$$T\partial s_2/\partial T = c_2, \quad (19)$$

$$T\partial(\bar{v})_\delta \cdot (\bar{v})_\pi/\partial T = (s_1)_\delta \cdot (\bar{v})_\pi + (\bar{v})_\delta \cdot (s_1)_\pi - 2(\bar{v})_\delta \cdot (\bar{v})_\pi, \quad (20)$$

$$T\partial\{(\bar{v})_\delta \cdot (\bar{v})_\pi/T\}\partial T = \{(s_1)_\delta \cdot (\bar{v})_\pi + (\bar{v})_\delta \cdot (s_1)_\pi - 3(\bar{v})_\delta \cdot (\bar{v})_\pi\}/T, \quad (21)$$

$$T\partial(s_1)_\delta \cdot (\bar{v})_\pi/\partial T = (c_1)_\delta \cdot (\bar{v})_\pi + (s_1)_\delta \cdot (s_1)_\pi - (s_1)_\delta \cdot (\bar{v})_\pi, \quad (22)$$

$$T\partial\{(s_1)_\delta \cdot (\bar{v})_\pi/T\}/\partial T = \{(c_1)_\delta(\bar{v})_\pi + (s_1)_\delta \cdot (s_1)_\pi - 2(s_1)_\delta \cdot (\bar{v})_\pi\}/T. \quad (23)$$

Since numerical values of S_V/R, C_V/R, s_1, s_2, c_1 and c_2 can be found from Gordon and Barnes' tables for given values of ω/kT and χ, Eqs. (14) and (15) may be used to find an approximate value of the rotational-vibrational entropy and heat capacity. Alternatively and to a somewhat poorer approximation, from Eq. (13)

$$S_{RV}/R = (S_V/R)_\delta + (S_V/R)_\pi + (S_V/R)_\sigma + \ln (2j_S+1)^2 q_0/2 + 3/2$$

$$+ (y_{\delta\pi}/kT) \cdot \{(s_1)_\delta \cdot (\bar{v})_\pi + (\bar{v})_\delta \cdot (s_1)_\pi - 2(\bar{v})_\delta \cdot (\bar{v})_\pi\} + \cdots$$

$$+ a_\delta(s_1)_\delta + a_\pi(s_1)_\pi + a_\sigma(s_1)_\sigma + b_\delta(s_2)_\delta + \cdots \quad (24)$$

$$C_{RV}/R = (C_V/R)_\delta + (C_V/R)_\pi + (C_V/R)_\sigma + 3/2$$

$$+ (y_{\delta\pi}/kT) \cdot \{(c_1)_\delta \cdot (\bar{v})_\pi + (\bar{v})_\delta \cdot (c_1)_\pi + 2(s_1)_\delta \cdot (s_1)_\pi - 4(s_1)_\delta \cdot (\bar{v})_\pi - 4(\bar{v})_\delta \cdot (s_1)_\pi + 6(\bar{v})_\delta \cdot (\bar{v})_\pi\}$$

$$+ \cdots + a_\delta(c_1)_\delta + a_\pi(c_1)_\pi + a_\sigma(c_1)_\sigma + b_\delta(c_2)_\delta + \cdots. \quad (25)$$

TABLE I. $T = 1500°K$, $hc/k = 1.43242$.

	δ	π	σ		δ	π	σ
$w = \omega/kT$	1.5613	3.5715	3.6613	$\bar{v}$	0.287	0.033	0.028
χ	0.01223	0.01872	0.01017	s_1	0.859	0.153	0.134
$\ln Q_V + \epsilon_0/kT$	0.2356	0.0285	0.0260	c_1	1.398	0.446	0.403
	+0.0136	+0.0044	+0.0021				
S_V/R	0.6504	0.1318	0.1226	$\overline{v^2}$	0.46	—	—
	+0.0327	+0.0161	+0.0080				
C_V/R	0.8194	0.3797	0.3629	s_2	1.73	—	—
	+0.0374	+0.0317	+0.0164				
				c_2	4.6	—	—

THE FREE ENERGY, ENTROPY AND HEAT CAPACITY OF STEAM FOR TEMPERATURES UP TO 1500°K

From the data of Freudenberg and Mecke,[2] the vibrational constants in cm^{-1} are: $\omega_\delta = 1635$, $\omega_\pi = 3740$, $\omega_\sigma = 3834$, $\omega_\delta\chi_\delta = 20$, $\omega_\pi\chi_\pi = 70$, $\omega_\sigma\chi_\sigma = 39$, $y_{\delta\pi} = 20$, $y_{\pi\sigma} = 109$, $y_{\sigma\delta} = 20$. The moments of inertia are

$$10^{40} \times A = 0.996 + 0.045v_\sigma + 0.026v_\pi - 0.098v_\delta,$$

$$10^{40} \times B = 1.908 + 0.014v_\sigma + 0.033v_\pi - 0.034v_\delta, \quad (26)$$

$$10^{40} \times C = 2.981 + 0.047v_\sigma + 0.062v_\pi + 0.062v_\delta.$$

While there may be some doubt as to the accuracy of Freudenberg and Mecke's expressions for the moments of inertia in the higher vibrational states, their equations seem reasonably accurate for the states which are of importance in calculations for temperatures below 1500°K. From Eqs. (26)

$$M_v = 2.3801 \times 10^{-60}(1 + 0.0342v_\sigma + 0.0321v_\pi - 0.0477v_\delta - 0.00147v_\delta^2), \quad (27)$$

the other quadratic terms in the expression for M_v making negligible contributions to the calculated thermodynamic quantities for the temperature range considered.

Table I gives (for $T = 1500°K$) the values[5] of ω/kT and χ for the three fundamental frequencies and also the values of the functions necessary for the calculation; these latter were obtained by interpolation in Gordon and Barnes' tables.

For this temperature, $\ln q_0/2 = 6.19597$, $\sigma_{BC}/3 = 0.00369$, $\sigma_B\sigma_C/12\sigma_A = 0.00039$. Hence, excluding the nuclear spin contributions to the free energy and entropy, the approximate values of $\ln Q_{RV} + E_0/RT$, S_{RV}/R and C_{RV}/R from Eqs. (13), (24) and (25) are 6.4975, 8.6261 and 3.113, respectively; the "exact" values[6] from Eq. (6) are 6.9474, 8.6258 and 3.112.

The contributions of the vibrational interaction terms involving $y_{\delta\pi}$, $y_{\pi\sigma}$ and $y_{\sigma\delta}$ to $\ln Q_{RV} + E_0/RT$ are only 0.00018, 0.00009 and 0.00015 for this temperature; the corresponding items for S_{RV}/R are 0.00102, 0.00071 and 0.00089, while for C_{RV}/R they are 0.0039, 0.0039 and 0.0035, respectively. The y-terms are thus of much less importance than the rotational-vibrational interaction terms, i.e., those involving a_δ, a_π, a_σ and b_δ, which contribute -0.01236, -0.03403 and -0.0453 to $\ln Q_{RV} + E_0/RT$, S_{RV}/R and C_{RV}/R, respectively.

Table II gives the numerical values[5] of $-(F° - E_0°)/T$, $S°$ and $C_P°$ for steam for the temperature range 298.1–1500°K, the rotational-vibrational contributions being computed by means of Eqs. (13), (24) and (25). None of the values of $-(F° - E_0°)/T$ and $S°$ includes the nuclear spin contribution of the two hydrogen atoms, $2R \ln 2 = 2.754$ cal./deg.; this must be added to the entries if the table is to be used in conjunction with Giauque's table for hydrogen.[7] The third decimal place has been retained in the table merely for convenience in interpolation.

From Table II and the data for hydrogen[7] and

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[5] The universal constants used in computing Tables I and II were those given in *International Critical Tables*, Vol. I: $h = 6.554 \times 10^{-27}$, $k = 1.372 \times 10^{-16}$, $C = 2.9986 \times 10^{10}$, $R = 1.9869$; hence the additive constant for the translational free energy equation is -7.2671.

[6] These values are exact in the sense that the only error is that introduced by the use of Eq. (1); in the note at the end of this paper it is shown that this error is negligible for 1500°K.

[7] Giauque, J. Am. Chem. Soc. **52**, 4816 (1930).

TABLE II. *The free energy, entropy and heat capacity of steam.*

$T°K$	$-(F°-E_0°)/T$	$S°$	$C°_P$	$T°K$	$-(F°-E_0°)/T$	$S°$	$C°_P$
298.1	37.179	45.101	8.000	850	45.627	53.987	9.347
300	37.230	45.151	8.002	900	46.106	54.525	9.497
350	38.452	46.389	8.066	950	46.563	55.043	9.648
400	39.513	47.472	8.155	1000	46.999	55.542	9.799
450	40.452	48.439	8.260	1050	47.418	56.023	9.948
500	41.296	49.315	8.379	1100	47.820	56.489	10.095
550	42.062	50.119	8.504	1150	48.206	56.941	10.240
600	42.765	50.864	8.635	1200	48.579	57.380	10.382
650	43.415	51.561	8.771	1250	48.940	57.807	10.522
700	44.020	52.216	8.910	1300	49.289	58.223	10.656
750	44.587	52.836	9.053	1400	49.956	59.022	10.914
800	45.121	53.425	9.199	1500	50.586	59.783	11.153

oxygen,[8] $\Delta S°_{298.1}$ for the reaction $H_2+O_2/2$ $=H_2O(g)$ is -10.64 cal./deg.; from this in combination with Rossini's accurate value[9] of $\Delta H_{298.1}$, viz., $-57,809$ cal., $\Delta F°_{298.1}$ for steam is $-54,637$ cal. For liquid water, $S°_{298.1}$ is 16.75 cal./deg. and $\Delta F°_{298.1}$ is $-56,690$ cal.

The data of Table II can also be combined with the spectroscopic free energy data for hydrogen,[7] carbon monoxide[10] and carbon dioxide[11] and the thermal data of Rossini[9, 12] to compute the equilibrium constant for the water-gas reaction $CO+H_2O=CO_2+H_2$. $\Delta S°_{298.1}$ is here -10.09, $\Delta H_{298.1}$ is -9814; hence $\Delta F°_{298.1}$ is -6806 cal. and $\Delta E_0°$ is -9646 cal. Table III gives the resulting values of $R \ln K=R \ln (p_{CO}\cdot p_{H_2O}/p_{CO_2}\cdot p_{H_2})$ for the range 600–1500°. The numbers in Table III are on the average about 0.07 cal./deg. less than those previously computed[11] and for the range 900–1259° agree even more closely with the results of Neumann and Koehler's experiments;[13] for example, Neu-

TABLE III. *The equilibrium constant for the water-gas reaction.*

$T°K$	600	700	800	900	1000
$R \ln K$	-6.57	-4.40	-2.81	-1.62	-0.69
$T°K$	1100	1200	1300	1400	1500
$R \ln K$	$+0.04$	$+0.63$	$+1.12$	$+1.53$	$+1.88$

[8] Johnston and Walker, J. Am. Chem. Soc. **55**, 172 (1933).

[9] Rossini, Bur. Standards J. Research **6**, 1 (1931).

[10] Clayton and Giauque, J. Am. Chem. Soc. **54**, 2610 (1932).

[11] Gordon, J. Chem. Phys. **1**, 308 (1933).

[12] Rossini, Bur. Standards J. Research **6**, 37 (1931).

[13] Neumann and Koehler, Zeits. f. Elektrochemie **34**, 218 (1928).

mann and Koehler found $K=1.61$ for 1259°K, while from Table III, $R \ln K$ for this temperature is 0.93, i.e., $K=1.60$. Their results for 15 temperatures in this range show a mean deviation from the numbers obtained by interpolation in Table III of less than $+0.02$ cal./deg. in $R \ln K$; for the range 700°–900°, however, the mean deviation is somewhat larger—about $+0.14$ in $R \ln K$. The indirect measurements of this equilibrium by Emmett and Schultz[14] also agrees satisfactorily with Table III; with three exceptions (773°, 823°, 923°) their results for 8 temperatures between 723° and 1073° agree with the data of the table within ±0.04 cal./deg. in $R \ln K$.

EVALUATION OF THE ROTATIONAL STATE SUM FOR A RIGID UNSYMMETRICAL ROTATOR

The procedure that has been adopted almost universally in the past when it has been necessary to evaluate the rotational state sum for a rotator with three different moments of inertia has been to replace the sum by its limiting value for high temperatures

$$Q_R \approx (\pi/\sigma_A\sigma_B\sigma_C)^{\frac{1}{2}}, \qquad (28)$$

where σ_A, σ_B and σ_C are as defined under Eq. (1) and suitable symmetry and nuclear spin factors are to be applied when necessary. While Eq. (28) is a valid approximation at very high temperatures, there is no general rule for estimating its error in any actual case. In the special case that two of the three moments of inertia are

[14] Emmett and Schultz, J. Am. Chem. Soc. **51**, 3249 (1929); **52**, 892 (1930); **55**, 1376 (1933).

equal, Viney[15] and Kassel[1] have deduced a relation which serves to evaluate Q_R to a higher degree of accuracy than the uncorrected Eq. (28). If the moments of inertia are A, C and C, their equation may be written, to a first order of approximation

$$Q_R = \exp\,(\sigma_C/4)\cdot(\pi/\sigma_A\sigma^2_C)^{\frac{1}{2}}$$
$$\cdot\{1+\sigma_C/12-\sigma^2_C/12\sigma_A+\cdots\}. \quad (29)$$

In the general case, however, where $A \neq B \neq C$, their method cannot be applied, since the energy is not an explicit function of the moments of inertia. It is apparent, however, that the expression on the right of (29) for a rotator with moments of inertia A, $(BC)^{\frac{1}{2}}$ and $(BC)^{\frac{1}{2}}$, should be a better approximation to the value of the actual rotational state sum than the uncorrected expression on the right of (28). On this plausible assumption the rotational state sum is replaced by the expression on the right of Eq. (1).

To obtain an estimate of the error actually introduced by the use of Eq. (1), the energy levels were calculated for the special case $A = 1 \times 10^{-40}$, $B = 2 \times 10^{-40}$, $C = 3 \times 10^{-40}$, and the state sum and its derivatives were computed. These constants are roughly those for steam and, since they correspond to a molecule as unsymmetrical and with as small moments of inertia as is likely to be met with in practice, they provide a particularly good test of Eq. (1).

The algebraic equations from whose roots the eigenvalues for the rotator can be obtained, have been tabulated by Dennison[16] and by Nielsen.[17] For values of J, the rotational quantum number, $\leqslant 8$, the energy levels were found by solving their equations (see Table IV); for $J \geqslant 9$, the asymptotic formulae of Kramers and Ittman[18]

were used. While the latter are not particularly accurate as far as the calculation of individual levels is concerned, it was found by actual computation for $J = 7$ and $J = 8$ that they give the contributions to Q_R and its derivatives with an accuracy of about 1/5 of a percent. Since even for $T = 330°$K (the highest temperature for which the calculation was made), the levels with $J > 8$ contribute less than 3 percent of Q_R, 10 percent of Q_R' (see Eq. (33)) and 22 percent of Q_R'' (Eq. (34)), the error introduced by using the asymptotic formulae is, at most, a unit or two in the fourth decimal place of $\ln Q_R$ and S_R/R and in the third decimal place of C_R/R. For lower temperatures for which the relative contribution of the high J states is less, the uncertainty will be still smaller.

For a rigid rotator with three different moments of inertia, there are $2J+1$ distinct levels,[16] each $(2J+1)$-fold degenerate, for each value of the rotational quantum number J; these $2J+1$ levels are distinguished by a quantity τ which takes the $2J+1$ values $-J$, $J+1$, $\cdots$ $J-1$, J, the lowest level (for the given J) being assigned $\tau = -J$ the next lowest $\tau = -J+1$ and so on. The rotational state sum thus becomes

$$Q_R = \sum_{J=0}^{\infty} \sum_{\tau=-J}^{+J} (2J+1)\cdot e^{-\epsilon_{J\tau}/kT} \quad (30)$$

and the rotational entropy and heat capacity are given by

TABLE IV. Values of $(8\pi^2\epsilon_{J\tau}/h^2)\times 10^{-40}$.

$A = 1 \times 10^{-40}$, $B = 2 \times 10^{-40}$, $C = 3 \times 10^{-40}$.

$J=0$: 0.

$J=1$: 5/6, 4/3, 3/2.

$J=2$: 2.24267, 2.83333, 3.33333, 4.83333, 5.09067.

$J=3$: 4.83333, 5.06325, 6.05848, 7.33333, 7.50000, 10.27008, 10.27485.

$J=4$: 7.88133, 8.00491, 9.63908, 10.63900, 11.09047, 13.66176, 13.69425, 17.69433, 17.69487.

$J=5$: 11.5824, 11.6417, 14.0188, 14.7278, 15.6406, 17.9080, 18.0308, 21.9389, 21.9436, 27.1170, 27.1172.

$J=6$: 15.934, 15.961, 19.126, 19.574, 21.118, 22.999, 23.333, 27.053, 27.075, 32.207, 32.207, 38.540, 38.540.

$J=7$: 20.945, 20.955, 24.900, 25.153, 27.460, 28.916, 29.635, 33.041, 33.122, 38.166, 38.170, 44.473, 44.473, 51.962, 51.962.

$J=8$: 26.616, 26.620, 31.310, 31.441, 34.603, 35.634, 36.930, 39.899, 40.120, 45.003, 45.020, 51.276, 51.276, 58.743, 58.743, 67.385, 67.385.

[15] Viney, Proc. Camb. Phil. Soc. 29, 142 (1933).

[16] Dennison, Rev. Mod. Phys. 3, 280 (1931). There are two misprints in Dennison's cubic for $J = 7$; he gives

$$x^3-56\alpha x^2+(784\alpha^2+776\beta)x-2304\alpha^3-10584\alpha\beta=0. \quad (A)$$

By a change of variable, Nielsen's[17] corresponding cubic can be written in Dennison's notation

$$x^3-56\alpha x^2+(784\alpha^2+784\beta)x-2304\alpha^3-11584\alpha\beta=0. \quad (B)$$

Eq. (B) fulfills the condition that the energy levels should be the same whether α and β are replaced by $\alpha_1\beta_1$, $\alpha_2\beta_2$ or $\alpha_3\beta_3$.

[17] Nielsen, Phys. Rev. 38, 1432 (1931).

[18] Kramers and Ittman, Zeits. f. Physik 58, 217 (1929).

$$S_R/R = Q_R'/Q_R + \ln Q_R, \qquad (31)$$

$$C_R/R = Q_R''/Q_R - (Q_R'/Q_R)^2, \qquad (32)$$

$$Q_R' = \Sigma\Sigma(2J+1)\cdot(\epsilon_{J\tau}/kT)\cdot\exp[-\epsilon_{J\tau}/kT], \quad (33)$$

$$Q_R'' = \Sigma\Sigma(2J+1)\cdot(\epsilon_{J\tau}/kT)^2\cdot\exp[-\epsilon_{J\tau}/kT]. \quad (34)$$

Table IV gives the numerical values of Q_R, Q'_R and Q_R'' as computed from Eqs. (30), (33) and (34) together with the resulting $\ln Q_R + E_0/RT$, S_R/R and C_R/R for $T = 330.44°$, $198.26°$, $132.17°$ and $99.13°$K, i.e., for $10^{40}\cdot h^2/8\pi^2 kT = 0.12$, 0.2, 0.3 and 0.4; the table also gives the values obtained by using the approximate expression (1) instead of the exact expressions (30), (33) and (34). It should be noted that if the uncorrected Eq. (28) had been used in place of Eq. (30), the resulting value of $\ln Q_R$ would have been 4.6486 for 330.46° and 2.8427 for 99.13°. It is evident from the table that with the assumed moments of inertia and for room temperature and up, the use of Eq. (1) will not introduce an error of more than 0.001 cal./deg. in $F°/T$ or $S°$, or of more than 0.002 cal./deg. in $C_P°$. Since the case chosen for illustration is a particularly unfavorable one, it seems safe to conclude that Eq. (1) may be used with confidence in similar calculations for other unsymmetrical rotators. For low temperatures, however, the calculated thermodynamic quantities deviate widely from those predicted by Eq. (1); for example, curve a of Fig. 1 shows the low temperature rotational heat capacity curve for the rotator of Table IV.
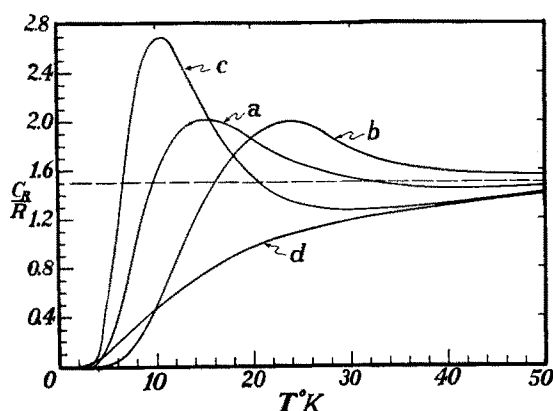
In the previous discussion, all questions of symmetry and of nuclear spin have been ignored. If the rotator possesses two equivalent atoms with non-spinning nuclei and if, as in the case of steam, the symmetry axis of the molecule coincides with the intermediate moment of inertia, Dennison[16] has shown that the rotational levels for a given J are alternately symmetric and antisymmetric in the rotational part of the wave function; for $J = 0$, 2, 4, $\cdots$, the lowest level is symmetric and for $J = 1$, 3, $\cdots$, antisymmetric, i.e., for either odd or even J, the levels with $\tau = 0$, ± 2, ± 4, $\cdots$ are symmetric and those $\tau = \pm 1$, ± 3, $\cdots$, antisymmetric. In carrying out the summations of Eqs. (30), (33) and (34) only those rotational levels are to be counted which are of the required symmetry character and, for any temperature so high that the summations over the symmetric and antisymmetric states are the same, this is obviously equivalent to adding the usual Ehrenfest "symmetry term" $-R \ln 2$ to $-F°/T$ and to $S°$ and leaving $C_P°$ unaltered. For the rotator of Table IV at the highest temperature of Table V, this condition is fulfilled, e.g., the sums over the symmetric and antisymmetric levels in Q_R are 52.963 and 52.957, respectively, but for low temperatures this is not the case. For example, if the electronic and vibrational parts of the wave function are such that only symmetric rotational states are to be counted, C_R/R for 198.26°, 132.17° and 99.13° is 1.508, 1.516 and 1.513, respectively; for still lower temperatures, the C_R/R-temperature curve for such a symmetrical molecule is shown in curve b of Fig. 1.

If the equivalent atoms, as in steam, each possess one-half unit of nuclear spin (the ex-

Fig. 1. C_R/R as a function of temperature for an unsymmetrical rotator $A = 1\times 10^{-40}$, $B = 2\times 10^{-40}$, $C = 3 \times 10^{-40}$.

TABLE V. $A = 1\times 10^{-40}$, $B = 2\times 10^{-40}$, $C = 3\times 10^{-40}$.

$T°$K	330.44	198.26	132.17	99.13
Q_R, Eq. (30)	105.92	49.700	27.4189	18.0677
Q_R', Eq. (33)	157.34	73.290	39.9757	26.0384
Q_R'', Eq. (34)	392.76	182.894	99.6460	64.7483
$\ln Q_R + E_0/RT$ Eq. (30)	4.6627	3.9060	3.3112	2.8941
$\ln Q_R + E_0/RT$, Eq. (1)	4.6633	3.9068	3.3109	2.8916
S_R/R, Eq. (30), (33)	6.1482	5.3807	4.7692	4.3353
S_R/R, Eq. (1)	6.1486	5.3824	4.7742	4.3427
C_R/R, Eq. (30), (33), (34)	1.501	1.505	1.509	1.507
C_R/R, Eq. (1)	1.500	1.500	1.500	1.500

tension to other j_S values is obvious) and if the symmetry requirement of the molecule as a whole is such that states symmetric in the rotation are to be combined with states antisymmetric in the spin and *vice versa*, the weight factors will be $2J+1$ for the "para" levels, i.e., those with $\tau=0$, ±2, $\cdots$, and $3(2J+1)$ for the "ortho" levels, those with $\tau=\pm1$, ±3, $\cdots$. For high temperatures this is equivalent to multiplying Q_R, Q_R' and Q_R'', computed in the absence of symmetry and spin, by $(1/2+3/2)$, that is, to adding the usual symmetry and spin terms $-R\ln 2+2R\ln 2$ to $-F°/T$ and S_0, cf. Eq. (2). This method of allowing for symmetry and spin is thus justified for the rotator of Table IV at the highest temperature of Table V but is not valid for any temperature so low that the high temperature 3 : 1 ratio of ortho to para molecules does not hold (see Table VI

TABLE VI. *Percentage para molecules in the equilibrium mixture.*

$T°K$	330.44	132.17	66.09	39.65	26.44
Percent	25.00	25.12	25.51	26.52	30.04
$T°K$	15.86	11.33	7.93	5.66	4.96
Percent	45.58	65.82	87.42	97.41	98.86

which gives the equilibrium percentage of para molecules at various temperatures for the rotator of Table IV). The rotational heat capacity curve of such an equilibrium mixture is shown in c of Fig. 1; for higher temperatures, C_R/R approaches the limiting value 3/2 as in the case of curves a and b; for example, $C_R/R=1.503$, 1.505, 1.503 and 1.501 for 99.13°, 132.17°, 198.26° and 330.44°, respectively.

Since the ortho and para states are non-combining, it is probable that a mixture cooled from high temperatures would retain at low temperature the 3 : 1 ortho-para ratio in a state of "frozen" equilibrium. The rotational heat capacity curve for such a metastable mixture is shown in curve d of Fig. 1; for $T>50°K$ in the case chosen for illustration, curves c and d become practically identical.

The possibility of a frozen equilibrium of this kind is of interest in connection with the "Third Law" entropy of steam, which is nearly 0.9 cal./deg. less than the spectroscopic value. If ice consists of such a 3 : 1 mixture and it is assumed that the rotational states of steam carry over into the crystal, the ortho molecules will be trapped at low temperatures in the lowest state antisymmetric in the rotation i.e., $J=1$, $\tau=-1$; this state has a multiplicity of 9 (3 from rotation and 3 from spin) and as a consequence the "zero-point" entropy over and above the high temperature spin entropy $2R\ln 2$ will be $3R/4\cdot\ln 3=1.64$ cal./deg. just as in the case of hydrogen. Giauque and Ashley[19] have pointed out, however, that at temperatures as low as 10°K the only rotations possible in ice are about the symmetry axis of the molecule. Under these conditions the wave functions and eigenvalues are no longer those for a spacial rotator with three moments of inertia, but correspond more nearly to those for a plane (two-dimensional) rotator.[20] The lowest antisymmetric rotational state has $J=1$ and is doubly, not triply, degenerate in the rotation, corresponding to their value $3R/4\cdot\ln 2=1.03$ cal./deg. for the zero-point entropy which is to be added to the third law value.

[19] Giauque and Ashley, Phys. Rev. 43, 81 (1933).
[20] Pauling, Phys. Rev. 36, 430 (1930).